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Occurrence, Fate and Impact of Atmospheric Pollutants on Environmental and Human Health

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Occurrence, Fate and Impact of Atmospheric Pollutants on Environmental and Human Health

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Foreword

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Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

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Preface

Throughout the world, urban and agricultural communities have become more spatially intertwined resulting in blurred land use boundaries. Thousands of persistent and non-persistent organic pollutants are emitted to the atmosphere from primary and secondary sources. Emissions from urban, agricultural, and natural areas, such as particulate matter (PM_{10}, $PM_{2.5}$), volatile organic compounds (VOCs), and semi-volatile organic pollutants, can decrease overall air quality and negatively affect human health. These atmospheric pollutants can also be transported an deposited to proximate and remote ecosystems leading to adverse effects. After being emitted to the atmosphere, pollutants are subject to a variety of processes, such as diffusive air-water, air-soil and air-vegetation exchanges, gas-particle partitioning, dry/wet deposition, photochemical degradation, etc. All of these processes may influence their atmospheric occurrence, transport, deposition, and impact on the environment.

This publication, developed after a symposium at the 2012 Society of Environmental Toxicology and Chemistry World Congress in Berlin Germany, examines emerging trends in research related to the role of the atmosphere in facilitating the global transport of pollutants and as an exposure pathway for humans and wildlife. Major topics include the examination of atmospheric processes controlling the fate and transport of persistent organic pollutants; modeling and assessment of human and wildlife exposure; and novel approaches for utilizing the atmosphere as a tool to assess sources of contamination.

Transport processes controlling atmospheric transport and deposition of persistent organic pollutants (POPs) like air-water and air-soil exchange have been examined in numerous research publications. In the present work, Gioia *et al.* (Chapter 1) take a fresh look at recent findings in the cycling of PCBs and processes that control their transport from source regions to remote oceanic environments. High PCBs concentrations off the Western coast of Africa indicate new source regions in the Southern Hemisphere which has been relatively uncontaminated in the past. Cabrerizo *et al.* (Chapter 2) extend the discussion of POPs transport to include air-soil exchange and additional compound classes: polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides. Their findings indicate that annual cycles of volatilization from soils in lower latitudes have become important secondary sources of POPs which are available for transport to cooler areas at higher latitudes.

In recent years, scientists have also utilized their understanding of air-water and air-soil partitioning to make new discoveries regarding unknown global sources of POPs and other contaminants. Work by Bidleman *et al.* (Chapter 8) focuses on the question of whether there are sources of “new” DDT in North

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America. Utilizing knowledge regarding the technical formulation components, the physical and molecular properties of the compounds, and archived samples from long term monitoring networks, this group has been able to distinguish a number of DDT sources to remote monitoring stations in the Arctic.

Other contributors to this book have demonstrated the need for and the utility of large-scale atmospheric contaminant monitoring networks. Miglioranza *et al.* (Chapter 9) describe results of the Latin American Atmospheric Passive Sampling Network which utilizes XAD-2 resin samplers at over 50 sites in 12 countries. This long-term project is designed to generate critical information on sources and occurrence of POPs in South America and to examine the effectiveness of the Stockholm Convention at reducing overall concentrations of POPs in the Southern Hemisphere. In a region where monitoring networks are lacking, Castro-Jiminez *et al.* (Chapter 11) conducted a critical review of available over-water contaminant measurements in the Mediterranean Sea. PAHs were found to be the most abundant compound class of POPs entering the Sea from the atmosphere; however, the Mediterranean may also serve as a source of some compounds to the atmosphere in open sea regions where air concentrations are lower.

Emissions of pesticides to the atmosphere from areas of heavy agricultural production has been a concern in many regions of the world. Research by Raina *et al.* (Chapter 10) has provided insights into changes in crop production and pesticide use in the Canadian Praries. Temporal variability in atmospheric pesticide concentrations were consistent with differences in weather and agricultural activity, and newly introduced pre-emergent herbicides were identified as having the potiential for long-range transport. In another agricultural region of North America, wetlands in California serving as habitat for amphibians were examined for agricultural pesticides and for correlations with population status in Fellers *et al.* (Chapter 7). Transects of sites from the Pacific coast to the Sierra Nevada Mountains were established to investigate potential exposure from atmospherically transported residues.

Air pollution in the form of particulate matter has typically been associated with industrial processes and urban environments, but long range atmospheric transport of particulate matter from natural sources has become a concern from an environmental and human health perpective. Morman *et al.* (Chapter 3) have investigated the transport of particulate matter from dust storms in Mali, West Afica to areas downwind in the Cariibbean and measured trace metal concentrations. They also utilized *in vitro* bioaccessibility extraction methods to assess the potential for human exposure to Pb via inhalation and ingestion of particles collected at the source and at downwind sites. Results suggest that changes in trace metal bioaccessibility may be occurring during atmospheric transport and warranting further research. Delving further into the human exposure realm, Hertel *et al.* (Chapter 6) provide an overview of recent efforts in Denmark which combine air quality monitoring data with advanced spatial analysis tools and health registry data to examine human health risks associated with exposure to various urban air pollutants and to pollen. Results indicate that populations are exposed to regional sources and additional sources emitted within the city. Of particular concern are contributions from emission sources from less than 10 m above the ground such as those from high traffic areas.

Of particular concern for human exposure is the presence of PAHs in ambient air. This class of compounds and their metabolites are known carcinogens, and exposure can occur in both urban and rural environments. van Drooge (Chapter 4) provides a critical review of recent findings regarding the fate of PAHs in different types of environments and examines the potential risks to human health from exposure to PAHs via the atmosphere. In addition, Fleming and Ashley (Chapter 5) explore the potential for humans who smoke tobacco to serve as vectors for PAH residues and reveal a previously unexplored exposure route (third-hand smoke) for non-smokers. Scientists contributing to this book cross the boundaries of environmental science, atmospheric chemistry, and toxicology. Increased interaction among scientists from different disciplines will be required achieve a greater understand of the role the atmosphere plays in transporting contaminants to remote regions and contributing to the exposure of humans and wildlife to a variety of pollutants.

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Laura L. McConnell

Dr. McConnell is a Research Chemist with the US Department of Agriculture, Agricultural Research Service in Beltsville, Maryland. She has worked in environmental science research for more than 20 years. She specializes in the investigation of chemical and physical processes controlling the environmental fate of agriculturally-relevant pollutants with an emphasis on atmospheric transport and deposition. She has served as Chair of the Division of Agrochemicals of the American Chemical Society, and currently serves as the President of the Chemistry and the Environment Division of the International Union of Pure and Applied Chemistry. Dr. McConnell has authored 80 peer-reviewed journal articles and has mentored numerous graduate and undergraduate students. She has received awards for her research from within and outside her agency including the Presidential Early Career Award for Scientists and Engineers.

Jordi Dachs

Dr. Dachs is a Research Scientist at the Department of Environmental Chemistry of the Institute for Environmental Assessment and Water Research (IDAEA-CSIC) in Barcelona. His research interests are the transport, impact and environmental fate of semi-volatile organic pollutants and organic matter in Oceanic and Continental ecosystems. The study of oceans and the oceanic atmosphere has played an important role in his scientific career, and he has participated in numerous sampling cruises, sometimes serving as chief scientist, in all the world oceans and the Mediterranean and Black Seas. He has made important contributions on the role that biogeochemical controls play on the atmospheric deposition and cycling of organic pollutants between the atmosphere and aquatic ecosystems. He has published more than 110 papers in SCI international journals and is among the most cited authors in the field of "Environment/Ecology". He teaches graduate courses on" Environmental Organic Chemistry" and "Marine Pollution", and has mentored numerous Master and PhD students.

Cathleen J. Hapeman

Dr. Cathleen J. Hapeman is a Research Chemist for the US Department of Agriculture, Agricultural Research Service in Beltsville, Maryland. She received her Ph.D. in 1986 from the University of Maryland, College Park in mechanistic organic photochemistry and has been with USDA-ARS ever since.

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She has been involved in basic and applied research concerning pollutant fate, blending chemical and environmental process expertise with practical experience of agricultural practices and acquired regulatory knowledge. For eight years, she served as Research Leader of the Environmental Quality Lab for eight years where she and her colleagues were awarded the Secretary of Agriculture's Team Honor Award (2000) for their work on mitigating the effects of vegetable production on surrounding ecosystems. Dr. Hapeman is currently the Program Chair of the AGRO Division of the American Chemical Society and is editor of the PICOGRAM. The focus of Dr. Hapeman's current is discerning pollutant fate and transport at the ag-urban interface and as a function of land-use changes.

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Chapter 1

Atmospheric Transport, Cycling and Dynamics of Polychlorinated Biphenyls (PCBs) from Source Regions to Remote Oceanic Areas

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Polychlorinated biphenyls (PCBs) are ubiquitous in the environment. Their persistence coupled with their potential toxicity has prompted international regulations and increased effort to understand their regional and global scale presence, and the processes that influence their fate and transport. PCBs can travel in the atmosphere away from source regions through long-range atmospheric transport and be deposited to water and terrestrial surfaces. This chapter focuses on the atmospheric concentrations of PCBs and factors controlling their spatial and temporal variability from source regions to oceanic remote areas. Air data show a strong latitudinal trend with the highest PCB concentrations in Europe and the lowest in the Arctic and in the tropical and subtropical southern hemisphere. High PCB levels were observed off the west coast of Africa and Asia, and possible factors controlling these high levels and

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their implications for the global cycling of PCBs are discussed. Furthermore, air-water interactions are disussed in remote areas of the open ocean. Of particular importance is the evidence for near steady-state air-water equilibrium or net volatilization in the tropical and subtropical regions, while advective inputs still dominate in the Northern hemisphere. Net deposition dominates over volatilization in the Arctic region. This chapter seeks o examine recent findings in the global transport of PCBs and to identify areas of uncertainty in the understanding of the factors controlling the residence time of PCBs in different areas of the globe.

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Introduction

PCBs were first synthesized in 1881 by Schmidt and Schulz but their commercial production only began in 1929 in USA (*1*). They were marked as mixed products under various trade names depending on the country where they were produced such as Aroclor (Monosanto, USA), Phenochlor and Clophen (Bayer, EU). Because of high chemical and thermal stability, electrical resistance, low or no flammability, PCBs had extensive applications. They have been used as dielectric fluids in capacitors and transformers, in plasticizers, adhesives, inks, sealants and surface coatings (*2–4*). Their basic structure is a biphenyl with one to ten chlorine substituents and a general structure of $C_{12}H_{10-n}Cl_n$ (n=1-10, m=1-10) (Figure 1).

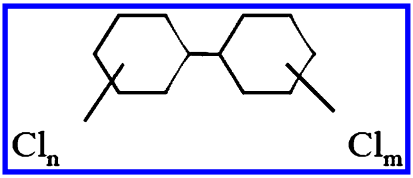

Figure 1. Molecular structure of PCBs.

There are 209 different congeners with one to ten chlorines atoms attached. The International Council for the Exploration of the Seas (ICES) has reported that 7 PCB congeners are frequently reported reported in environmental samples are PCB 28 (2,4,4′-triPCB), PCB 52 (2,2′,5,5′-tetraCB), PCB 101 (2,2′,4,5,5′-pentaCB), PCB 118 (2,3′,4,4′,5-heptaCB), PCB 138 (2,2′,3,4,4′,5-heptaCB), PCB 153 (2,2′,4,4′,5,5′-heptaCB), PCB 180 (2,2′,3,4,4′,5,5′-heptaCB). The seven ICES PCBs were recommended for monitoring by the European Union Community Bureau of Reference; these PCBs were selected as indicators due to their relatively high concentrations in technical mixtures and their wide chlorination range (3–7 chlorine atoms per molecule).

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Production of PCBs peaked in the 1960s in Europe and USA and terminated in the mid 1970s, when they where ultimately banned in the late 1970s/early 1980s (*3*). The most recent inventory of PCB production estimates the cumulative global production of PCBs at 1.3 million tonnes (*5*). Approximately 97% of this has been used in the Northern Hemisphere, mostly between 30 °N and 60 °N (*5*). Before the ban, PCBs entered the environment through both point and diffusive sources such as landfill sites, accidental releases/spillages via leaking during commercial use of electrical equipment and transformer and capacitor fires, incineration of PCB waste (*1*, *3*). Current atmospheric levels of PCBs in the environment are due to primary anthropogenic emissions (e.g. accidental release of products or materials containing PCBs), volatilization from environmental reservoirs which have previously received PCBs (e.g. oceans, large lakes and soil), incidental formation of some congeners during combustion processes (*5*) or PCB containing e-waste transported to developing countries (*6–8*)

PCBs are also classified as persistent organic pollutants (POP) by the UN-ECE (United Nations Economic Commission for Europe) Convention on Long-Range Transboundary Air Pollution (CLRTAP), because they: a) possess toxic characteristics; b) are persistent in the environment; c) tend to bioaccumulate in higher trophic levels; d) undergo long-range atmospheric transport; and e) can result in adverse environmental and human health effects at locations near and far from sources. POPs represent a very small percentage of chemicals in commerce, and many of them are already strictly regulated or banned from production and use. Due to their persistence and their tendency to undergo long-range atmospheric transport, they have been detected in all the environmental compartments, even in remote areas like open ocean and polar regions, where POPs have never been manufactured or used (*9–12*). As a result, their regulation has become an international policy issue based upon their possible effects on human health and potential environmental risks (*13*).

Atmospheric transport has been regarded as the main route for dispersing PCBs away from industrialized and densely populated areas and depositing to water and terrestrial surfaces (*9*, *14–16*). Once in the environment they degrade only very slowly and recycle and partition between the major environmental media depending on their physical-chemical properties. Persistence is an important environmental concern since toxic effects do not dissipate significantly over time and their risk assessment is difficult (*17*). In addition, they have low aqueous but high lipid/organic solubilities which results in their bioaccumulation in lipid-rich tissues and in their biomagnification through food chains (*18*, *19*).

Equilibrium Partition coefficients such as the octanol-water (K_{OW}) partition coefficient and the bioconcentration factor (BCF) refer to their hydrophobic and lipophilic nature and their tendency to bioaccumulate in the food-web. Conversely, the half-life gives insight into the time required for a contaminant to degrade in an environmental compartment. Partitioning is not just related to the properties of the chemical, it also depends on the conditions of the surrounding media, the presence of other reactive compounds or the mode of entry of the compound into the compartment (*20*).

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Primary and Secondary Sources

In order to regulate and control the release of PCBs into the environment it is important to know how the chemical has been released. The fate and transport of PCBs are dependent on their physical-chemical properties and the geographical position and distribution of their sources. Generally, they are directly emitted into the environment from primary and diffusive sources, accidental releases and disposal. After they have been released, they can be trapped in environmental reservoir (e.g. soil and oceans) and volatilize from these back into the atmosphere (secondary sources).

A major question is the extent to which current ambient levels are controlled by primary sources or re-emission/re-cycling of secondary sources (*21–24*). Figure 2 is a conceptual diagram, showing how ‘a primary source controlled world’ (scenario 1) compared with a ‘secondary source controlled world’ (scenario 2). In scenario 1, PCBs emissions would be continuing from diffusive primary sources in areas of past use (i.e. urban/industrial locations) and reaching background locations via LRAT/advection. Over long time intervals, site-by-site differences in the rates of PCBs loss would not be expected, provided primary emissions are dominating and they continue to emit the compound mixture over time (*7*). In scenario 2, however, site-by-site differences in rates of loss may be apparent, because the rates of re-emission and reaction would be dependent on air-surface characteristics and environmental variables (e.g. temperature).

Long-Range Atmospheric Transport

The atmosphere is the major pathway for the delivery of PCBs to water and terrestrial surfaces; therefore, in this sense it represents a critical compartment for the global distribution and cycling of PCBs. As mentioned earlier, first emissions and then atmospheric long-range transport are major mechanisms to distribute PCBs widely through the global environment.

Persistence and long-range atmospheric transport (LRAT) are two essential properties for defining POPs. First, in source regions the chemical must be emitted in the atmosphere in significant quantities either by primary or secondary emissions. Second, the chemical must be sufficiently persistent to be transported through the atmosphere to remote regions. The *residence time* gives an indication of the average life expectancy of a pollutant in an environmental compartment; indeed it is an indicator of persistence and is best calculated at steady state.

Under unsteady-state or dynamic conditions, a *characteristic time* is often calculated similarly as the mass divided by the output rate. It is the average time that the chemical spends in the compartment. *Half-life* ($t_{1/2}$) is defined as the time span within which the chemical decays by 50% of the initial concentration.

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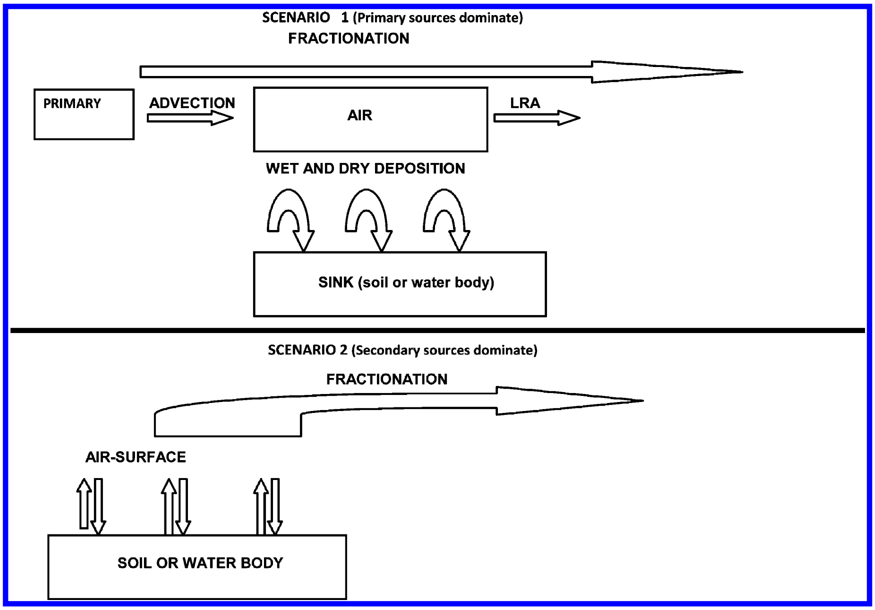

Figure 2. Conceptual diagram of a 'primary sources controlled world' (scenario 1) and a 'secondary sources controlled world' (scenario 2). (adapted from Gioia et al. (23))

Spatial and long-term trends have been monitored by many multinational and national air sampling networks of selected POPs, such as the joint Canada-US, Integrated Atmospheric Deposition Network (IADN), the New Jersey Atmospheric Deposition Network (NJADN) in the US and the Toxic Organic Micro Pollutants Survey (TOMPS) in the UK, operated on behalf of the UK Department of the Environment, Food and Rural Affairs (DEFRA), or the European EMEP database from ground stations (http://www.nilu.no/projects/ccc/emepdata.html). Recently, studies that have used passive samplers (PAS), have been useful in our understanding of the spatial and temporal distribution of POPs (*21–27*).

Many of these studies have shown that half-lives of PCBs are typically of 4-5 years (*23*, *24*, *28–30*). The IADN and EMEP monitoring networks have noted negative gradients of air concentrations away from the emission source that supports the findings of lower reported concentrations over the open-ocean than at the coast (*6*, *8*, *30–33*). Additionally, samples from North-South latitudinal transects in the Atlantic indicate higher concentrations in the Northern Hemisphere than in the Southern Hemisphere (*6*, *8*, *30–37*). This finding broadly reflects the ongoing emissions of PCBs. from populated/industrialized regions of the Northern Hemisphere . Finally, it should be noted again that monitoring networks in remote oceans are lacking. They are mostly found in land or coastal sites. However, long-term studies over the open ocean and other remote locations are scarce. Since they involve large financial costs and it is unrealistic to assume that monitoring studies can cover the large number of POPs (and newly emerginf contaminants) and geographic areas that are needed to assess the risks posed by these chemicals to the overall ecosystem health.

Condensation and Global Fractionation

As mentioned earlier, PCBs have been found in pristine environments like the Arctic and the Antarctic regions (*9–11*, *33*, *34*). This behaviour was explained in the formulation of the "Global Fractionation" hypothesis, which has influenced both the regulatory and scientific communities. Because PCBs are semivolatile, they have the tendency to volatilise at higher ambient temperatures and be deposited as temperatures decline. Wania and Mackay (*38*) proposed the idea that POPs can potentially migrate from warmer regions and become fractionated on latitudinal and altitudinal gradients during LRAT on a regional and global scale. This concept embodies ideas about "Global Distillation", "Cold Condensation", (i.e. that compounds could become enriched in colder environments), and "Global Fractionation" (i.e. that the compound mixture changes with travel distance) (*38*). The extent of global fractionation will depend on the physical-chemical properties of compounds such as vapour pressure (P_L) and octanol-air partitioning coefficients (K_{OA}). P_L describes the tendency for liquids and solids volatilize. K_{OA} expresses the partitioning of a chemical to between air and organic matter (*38*), assuming that octanol is a good surrogate for organic matter.

According to the global fractionation theory, the more volatile PCB congeners will be transported and condensed in colder regions and less volatile congeners will be deposited in warmer regions close to sources. The effect of this would be a relative enrichment of the more volatile compounds in colder (polar) areas over time. Two major scenarios can lead to global fractionation; 1) after being released by primary sources, a chemical is deposited near or far from sources depending on its physical chemical properties. In this case the environmental reservoir will act as a sink and absolute amounts will be expected to decrease with distance from sources areas (primary sources dominate); 2) re-emission from environmental reservoir will control the air concentration. In this case the fractionation will become more important over time and the concentration of some chemicals can increase with latitude (secondary sources dominate) (see Figure 2)

Over the last 20 years there has been a significant interest in studying and testing these concepts (*21–24*, *33*, *34*). However, to summarize several studies, it is clear that many factors (other than temperature) also exert an influence over the regional and global scale distribution of PCBs. These includes: proximity to sources, properties of the receiving environment (e.g. soil organic matter contents; water body particulate and biological properties; atmospheric reaction rates) (*39*). Other factors that influence PCB transport are sinking particles in the water column, wet and dry deposition, degradation processes, burial in sediments, etc. Indeed, a range of biogeophysical variables not considered traditionally such as the phytoplankton biomass, the extent of the ocean Mixed Layer Depth (MDL), spatial and temporal differences in aerosol concentrations, ocean stratification,

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and the turbulent diffusion coefficient, could also play an important role in the fate of POPs in the oceans.

Uncertainties remain whether environmental reservoirs act as sources or sinks and whether primary or secondary sources are controlling the levels of PCBs in the environment (*22*, *25*, *40*, *41*). Gioia et al. (*33*) found decreasing concentrations at higher latitudes and evidence of fractionation processes with increasing concentrations of less chlorinated PCBs at high latitudes, which are less prone to cold trapping and being sequestered by organic matter in the ocean. Nevertheless, the cold condensation effect of substances at high latitudes is generally accepted, especially for terrestrial ecosystems. Therefore, POPs in the Northern polar environment is considered as “priority issue” by the Arctic Monitoring and Assessment Programme (*42*).

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Deposition and Other Atmospheric Removal Processes

The oceans play an important role in controlling the environmental transport, fate and sinks of POPs at regional and global scales (*38*, *43*). Although PCB concentrations in the open ocean have been shown to be lower than those observed in coastal areas (*9*, *10*, *44*) the large oceanic volume implies that they may represent an important inventory of PCBs. Furthermore, the pathway air – deposition – water – phytoplankton – food web transfer – wildlife/human exposure is of key importance for these bioaccumulating compounds. Many studies including modelling work have shown that terrestrial organic matter (soil and forested surfaces) has an important influence on the dynamics and inventory of POPs (*45–47*). Therefore, it is logical to think that high productivity regions of the ocean may exert an important influence on the global distribution of PCBs. Jurado et al. (*39*), assessed the spatial and seasonal variability of the maximum reservoir capacity of the ocean compartment to act as a sink of PCBs and showed that temperature, phytoplankton biomass and mixed layer depth (MLD) can influence the reservoir capacity of the ocean (i.e. air-ocean equilibrium/storage issues). However, kinetically controlled processes such as particle settling, reactions and metabolism also need to be considered.

In the water column, PCBs can be found truly-dissolved, sorbed to colloids or sorbed to particles. Hydrodynamics of the water masses, such as turbulence and marine currents, influence the spatial distribution of PCBs in the ocean (*48*). Dissolved PCBs can volatilize back to the atmosphere or can sorb to particles and organisms such as phytoplankton, and they can be removed from the surface waters and delivered to the deep ocean by sinking of particles and by zooplankton vertical migration. This will depend on the physical-chemical properties of the congeners. The Henry’s Law constant (HLC) is the ratio between the compound saturated liquid vapour pressure and its solubility in water. Therefore, a compound with higher K_{OW} and lower HLC will tend to partition to particles in the water column and sink to the deep ocean, while those with lower K_{OW} and higher HLC values will volatilise back to the atmosphere more easily. Depending on several environmental factors, the oceans can act as a source of PCBs to the atmosphere, as a storage compartment or as a sink. However, there is a lack of open ocean

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seawater data due to the difficulties associated with the sampling procedures for PCBs (e.g. large volume, partition to colloids, etc), shipboard and laboratory contamination and the costs associated with the use of ships in the open ocean.

In the atmosphere, PCBs partition between gas and aerosol phases and may then be removed by five major mechanisms: dry deposition of particle bound pollutants, diffusive gas exchange between the atmosphere and the surface ocean, scavenging by precipitation (wet deposition) and $OH^{\cdot}$radical degradation. Figure 3 is a conceptual diagram of the major processes affecting PCBs in the oceanic atmosphere. Many studies have acknowledged the importance of air-water exchange in understanding the environmental fate of PCBs at local, regional and global scales (*39*, *49–52*). Gaseous exchange of contaminants between the atmosphere and the ocean is driven by a concentration difference and transport by molecular and turbulent motion. Knowledge of whether surface ocean waters/lakes are in dynamic equilibrium with the atmosphere, or the net direction of flux (i.e. whether absorption or volatilization dominates), is therefore crucial for our understanding of the global cycling and fate of PCBs. Air-water exchange is the most dominant depositional process at the global scale compared to wet and dry deposition (*39*). Available measurements of PCB air-water exchange fluxes in remote oceanic regions are very scarce because of the lack of simultaneous measurements of air and seawater, even though they are needed because of the key role of oceanic controls on regional and global dynamics and sinks of these chemicals.

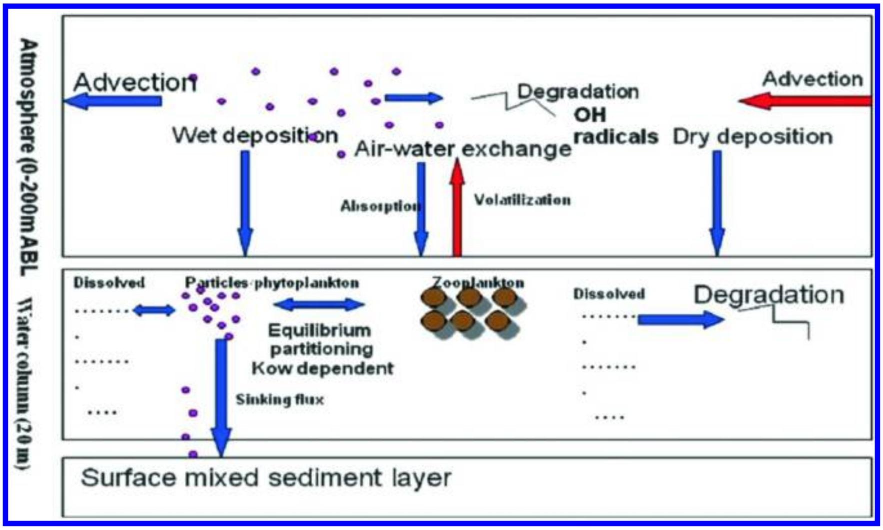

Figure 3. Major processes affecting POPs in the atmosphere and the ocean. (from Gioia et al. (53))

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Jurado et al. (*54*) estimated that wet deposition shows a high spatial and seasonal variability, with maxima located in the Intertropical Convergence Zone (ITCZ) and in low temperature regions. Seasonal variability reflects the northward shift of the ITCZ in the Northern Hemisphere in July. Average wet deposition fluxes estimated for the Atlantic Ocean in this study are 110 ng m^{-2} yr^{-1}. However, when raining events and non-raining time periods are integrated, air-water diffusive exchange fluxes acquire an important role, which can be dominant in some regions and for some POPs. The contribution of dry depositional fluxes to total deposition has been estimated by Jurado et al. (*39*) over the Atlantic Ocean. The results of the study show that for all the PCB congeners, air-water exchange dominates the dry deposition mechanisms with the exception of mid-high latitude where low temperature and high wind speed can enhance dry depositional fluxes for the less volatile PCB congeners.

Anderson and Hites (*55*) suggest that reactions with OH-radicals are the major removal pathway for PCBs in the atmosphere. Mandalakis et al. (*56*) showed that gas phase concentrations of PCBs were depleted significantly due to the oxidative attack of OH radicals at remote sites of Eastern Mediterranean. However, other studies have shown diurnal cycles over the pristine ocean atmosphere[57], with daytime concentrations higher than night time, suggesting that other processes, not just atmospheric reactions, play a role. Jaward et al. (*57*) suggested that there were a number of water column biogeophysical processes controlling the gas phase concentrations in the atmospheric boundary layer. This raises important questions about air-water exchange and within-ocean processing of POPs.

Equilibrium Partitioning

Partition coefficients have been widely used to describe the distribution and partitioning of PCBs into the environment. The concept of partition coefficients indicates equilibration between two phases due to diffusion. When there is no net transfer of mass of chemical between the phases and the concentrations of chemical in each phase is constant equilibrium is reached, and the resulting ratio is called the equilibrium partition coefficient. In the real world there are many situations where equilibrium partitioning is not reached. However, these coefficients are useful to characterize how long it would take for a compartment to reach equilibrium or to determine the tendency of a chemical to accumulate in one compartment. On the other hand, equilibrium partition constants are needed to calculate the rate of transfer of a compound across interfaces, as shown earlier.

From an environmental standpoint, the HLC is a key parameter used to model the diffusive exchange of semivolatile chemicals such as PCBs between surface waters and the atmosphere (*49*, *50*, *58*, *59*). Accurate knowledge of a chemical's HLC and how it changes with environmental conditions, including temperature and ionic strength, is essential to predict the environmental behaviour, transport, and fate of many classes of organic chemicals.

HLC has been determined in laboratory studies using different methodologies and its determination is subject to a heated debate (*60*, *61*). Furthermore, various sensitivity studies have noted that HLC can constitute an important source of uncertainty in the estimation of the net direction of the fluxes (*62*). Laboratory experimental determinations of HLC are performed with pure water, while natural waters contain varying levels of DOC, colloids, suspended particles and salts. These constituents can modify the partitioning of hydrophobic compounds into the dissolved phase and in turn the HLC. However, there is little systematic understanding of the role of these factors.

Gioia et al. (*53*) estimated field-derived air-water partition values for PCBs and found that they were a factor of 2-3 higher than those reported previously from standard measurement procedures made in the laboratory using pure water and much higher PCBs concentrations. It is interesting to speculate that if the field data give the 'right' values for HLC, there are important implications for how laboratory measurements are made and used in PCBs modelling. This highlights that significance of non-ideal solutions in environmental systems will need to receive more research attention in the future, since it could influence not only laboratory determination of Henry's Law constants, but the determination of other physical-chemical properties.

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Temporal Trends of PCBs

On average PCBs are declining in the atmosphere of Europe and North America, typically with an average half life of 4–5 years (*23*, *24*, *28*). In the Arctic atmosphere, temporal trends comparisons with earlier measurements from the NCP and the AMAP datasets shows that PCBs are slowly declining in the European Arctic atmosphere (*33*, *34*).

In contrast, little change is observed in air concentrations over the remote open ocean over the past 19 years (1990-2009) (*6*, *8*, *32*, *37*). Of particular importance is also the evidence in this study for close air-water coupling in the southern hemisphere (i.e. close to steady state conditions), while advective inputs still dominate in the northern hemisphere (*6*, *32*). If a half life of 4–5 years is assumed to also apply to the open Atlantic Ocean, the concentration between the 1990 and 2005 should differ by about a factor of 8–10 –presumably sufficiently different to be detectable.

The lack of a measured difference perhaps implies that air concentrations in these remote oceanic environments are undergoing little change, compared to the declines observed at the land-based locations close to sources. Interestingly, Panshin and Hites (*63*) compared PCB in oceanic air over Bermuda in 1992/1993 with those of several studies in 1970s at the same location, and found no statistically significant difference. Hillery et al. (*29*) also concluded that the atmospheric concentrations of PCBs near Lake Superior, the most remote of the Great Lakes, remained unchanged over a period of 6 years. Axelman and Broman (*64*) argued that these observations indicate PCBs may be removed slowly from the environment, when viewed from a global or hemispheric perspective, with PCBs being diluted into the remote areas of the earth rather than being permanently removed from global cycling. This implies that source-region gradients would decline over time as PCBs become more uniformly distributed (*65*). The comparison of results with those of land-based and other oceanic studies should give insights into changing levels and distributions of organichlorine pesticides (OCPs) and PCBs over the different geographical regions. This comparison must be done cautiously, because they only reflect short sampling periods and therefore specific conditions such as atmospheric circulation and also the exact route of the sampling vessel and different sampling techniques which influence sampling in the ocean.

Spatial Trends

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Source inventories of PCBs show that the ratio of emissions between the northern and the southern hemisphere (NH:SH) is ~20:1. However, ambient levels show a smaller difference. Inaccuracies with the source inventories and/or NH "dilution" to the SH over time may explain these observations. Relatively high levels of PCBs have been reported for the West African coast during different cruises on board two different vessels, *RV Pelagia* and *RV Polarstern*, in 2001, 2005 and 2007 respectively (*6*, *8*, *25*, *26*). The sources were unknown although strong land-based emissions are suspected. Source inventories have not identified Africa as important for PCB usage raising interesting questions about unaccounted for sources/processes. A strong latitudinal trend over the oceans is also observed within the Northern hemisphere with the highest PCB concentrations near the coasts of Europe, North America and Asia and the lowest in the Arctic and tropical and subtropical remote regions of the Pacific, the Atlantic and the Indian ocean, suggesting that the underlying levels in the remote marine atmosphere are controlled by LRAT (*32–34*, *36*, *37*).

Gas-phase concentrations have also been reported to increase near the ice-margin zone, presumably due to enhanced volatilization induced by ice melting, which could be currently enhanced due to climate change (*33*, *34*). Gioia et al. (*33*) raises questions about the role of ice as a compartment/buffer/source/sink for POPs in the Arctic, both in the short-term and as global climate changes occur to affect the properties and the extent of the ice sheets.

Zhang et al. (*36*) reported PCB concentrations in the remote Pacific ocean and found that, in general, average NH air concentrations were about 4 times higher than in the SH. The range of atmospheric Σ_{ICES}PCBs reported is similar to measurements by Jaward et al. (*25*) (4.5-120 pgm^{-3}) and Gioia et al. (*32*, *33*) (3.7-220 pg m^{-3}) for the Atlantic and the Arctic Ocean (0.8-100 pg m^{-3}).

In a more recent study on a cruise East to West cruise transect, from Shanghai, China to Cape Verde in the Central Atlantic Ocean, Gioia et al. (*8*) reported the mean concentration of Σ_7PCBs in the present study is in the same range as those measured in European background sites (2-121 pg m^{-3}) (*66*). Breivik et al. (*7*) reported that potential sources in the African and Asian regions of relatively high levels of PCBs may include illegal dumping of PCB-containing wastes with release via volatilization and uncontrolled burning, and the storage and breakup of old ships. Therefore, emissions of some industrial organic contaminants may be decreasing faster in former use regions (due to emission reductions combined with uncontrolled export), at the expense of regions receiving these substances as obsolete products and wastes.

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Air-Water Exchange of PCBs and Oceanic Sinks

Gaseous exchange of contaminants between the atmosphere and the ocean is driven by a concentration difference and transport by molecular and turbulent motion. Air–water gas exchange is the most dominant depositional process at the global scale compared to wet and dry deposition (*39*) for those PCBs which atmospheric occurrence is mainly in the gas phase.

In general, Gioia et al. (*33*) reported a net deposition of PCBs in the Arctic region especially near the marginal ice zone due to an increase in atmospheric concentrations of PCBs, but there were uncertainties whether the ice was a source of POPs to the atmosphere or whether it is due to ice-water-atmosphere interactions. Knowledge of contaminant levels in sea ice remains one of the weakest and more controversial areas of the Arctic research. The biological pump plays also an important role by removing PCBs from the water column, modifying the air–water gradient in concentrations which leads to enhanced net deposition of PCBs. Dachs et al. (*43*) assessed the role of the biological pump at the global scale. They reached the conclusion that increased atmospheric deposition fluxes were found at high latitudes and in other regions with high primary productivity such as upwelling regions. Jurado and Dachs (*67*) have also shown that the biological pump can considerably reduce the atmospheric residence times of hydrophobic PCBs by sequestering PCBs from the atmosphere. Malagón-Galbán et al. (*34*) provided the first field evidence of the role that the biological pump plays in productive oceanic Arctic regions, and confirms that the biological pump reduces and minimizes the transport of PCBs to the Arctic during the summer.

Several studies have shown that air and water concentrations of PCBs are close to equilibrium conditions in more oligotrophic areas of the tropical and subtropical regions of the remote ocean because of the lack of the biological pump (*24*, *32*). More recent studies have reported net volatilization of PCBs in subtropical and tropical regions of the Pacific, Atlantic and Indian Oceans (*8*, *36*, *37*). Zhang et al. (*36*) suggested that ceased production and usage of PCBs as well as degradation have led to lower environmental concentrations. The relatively low atmospheric concentrations combined with the relatively low sinking of particulate matter can result in a reduced air-water gradient and an increase in net volatilization.

What is clear is that increased net deposition occurs in high productivity areas like the Arctic regions, while net volatilization is observed in the tropican and subtropical regions of the oceans. What is unclear from the present and previous studies (*8*, *36*, *37*) is whether the revolatilization observed in the subtropical ocean is due to a temporary or to a permanent condition of the ocean and to what extent potential new sources of PCBs (*6*–*8*) in Asia and Africa for example can eventually affect the reservoir capacity of POPs in the remote or adjacent ocean.

Conclusions

Primary emissions and then LRAT are major mechanisms to distribute PCBs widely through the global environment. Once in the atmosphere they can be distributed in the pristine remote oceanic environment far from sources and trapped in cold regions such as the Arctic. Generally, higher atmospheric PCBs concentrations are measured in the northern hemisphere than in the southern hemisphere, which is in agreement with historical global production. Sources inventories show that the ratio of emissions between the northern and the southern hemisphere (NH:SH) is ~20:1. Inaccuracies with the source inventories and/or NH 'dilution' to the SH over time may explain these observations. High PCB levels found off the west coast of Africa and Asia raise interesting questions about unaccounted for sources/processes. A strong latitudinal trend over the oceans, with the highest PCB concentrations in Europe and the lowest in the Arctic and the remote tropic and subtropical ocean, suggests that the underlying levels in the remote atmosphere are controlled by LRAT, with deposition dominating over volatilization for PCBs.

Air-water exchange has been regarded as the most important depositional process of PCBs to the ocean waters. The direction of the air-water fluxes give insight on the role of ocean as source or sink of PCBs. There is the evidence for near steady-state conditions or net volatilization in the southern hemisphere, while net deposition still dominate ambient levels in the northern hemisphere including the Arctic region. This raises questions about the role of ice as a compartment/ buffer/ source/ sink for POPs in the Arctic, both in the short-term and as global climate changes occur to affect the properties and the extent of the ice sheets.

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Chapter 2

Soil-Air Exchange Controls on Background Atmospheric Concentrations of Polychlorinated Biphenyls (PCBs), Organochlorine Pesticides (OCPs), and Polycyclic Aromatic Hydrocarbons (PAHs): A Case Study from Temperate Regions

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The environmental fate of persistent organic pollutants (POPs) depends on their behavior and transport at local and global scale, and soil-air exchanges processes are believed to play a major role controlling POPs reservoirs and global distribution. Measurements of POPs fugacity gradients suggest that soils from lower latitudes and temperate regions, as those studied in the Ebro river watershed (Spain), are starting to be important secondary sources of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) to the atmosphere and that atmospheric background concentrations of PCBs, OCPs and polycyclic aromatic hydrocarbons (PAHs) are now controlled by temperature dependent re-emissions from soils. In contrast, regions where the soil-air partition coefficient (KSA) values are elevated due to higher soil organic matter content (SOM) or lower temperatures, as is the case of UK sampling sites, soils will act as important traps and accumulate more PCBs and OCPs. These regions will need more time to reach equilibrium and become significant secondary sources. The close coupling of POPs fugacities in soil and air suggest a strong control of

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the atmospheric occurrence of POPs in the lower atmosphere in rural regions.

Introduction

Over the last 50 years and due to the economic development, humans have manufactured and consumed thousands of synthetic chemicals in industry and agriculture, some of them classified as persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) (e.g dichlorodiphenyltrichloroetane (DDTs), hexachlorocyclohexane (HCHs) or hexachlorobenzene (HCB). As a result, some environmental compartments, such as soils, have become important reservoirs of POPs (*1*), with a historical net accumulation of POPs while primary emissions were important. In background regions with no historical direct inputs to soils, the occurrence of these chemicals in the atmosphere and soils is influenced by their volatilization from soils and atmospheric deposition events as the main vector for their spatial re-distribution from secondary and potential primary regional sources. In addition to man-made POPs, the presence of polycyclic aromatic hydrocarbons (PAHs) in soils has received much attention since the 60's (*2*). Combustion of fossil fuels, such as coal and petroleum in domestic and industrial applications, and biomass combustion are the major anthropogenic sources of PAHs to the environment. In addition to combustion processes, there is some evidence for biogenic PAH formation in the environment (*3–6*).

Soil-air partitioning is a key process driving the environmental fate of POPs and PAHs in the environment, and determining the extent of soils as a reservoir of organic pollutants. Indeed, due to POP's physico-chemical properties, especially their strong affinity with soil organic matter (SOM), soils have become the largest terrestrial reservoirs for POPs (*7*). Due to POPs partitioning with SOM, the availability of POPs to undergo biological degradation, remobilization, burial and toxic effect have been suggested to be linked to the carbon cycle thus suggesting that POPs are part and are interrelated with the carbon cycle (*8*). Beside the soil properties, the flux and direction of air-soil exchange of POPs have been reported to be influenced by climatic factors and also chemical emission (*9–13*). It is clear that primary sources dictated levels in the past, especially during the initial period of increasing production, use, and emissions. However, as restricted measured in the use of PCBs and OCPs were adopted decades ago, it is believe that secondary sources will dominate the future presence of these chemicals in the atmosphere. Despite the great interest that the soil-air exchange of POPs between the atmosphere and the soil has raised over the last years, soil fugacity is usually estimated from models of the soil-air partition coefficient (K_{SA}) with the associated unavoidable uncertainties associated with these parameterizations (*14*, *15*). The pioneering work from Hippelein and McLachlan (*16*) allowed to determine the fugacity in soil in laboratory conditions by stripping soil with air, showing than both temperature and humidity were important parameters affecting the soil fugacity. However, it is difficult to extrapolate these determinations of fugacity in soil to field conditions. The few previous attempts to measure soil-air

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partitioning and fluxes in field conditions are the studies performed by Jones, Bidleman and co-workers (*17–19*). While they were appropriated to measured fluxes and gradients providing the concurrent meteorological parameters, it is not clear that the air-soil partitioning can be assessed because the gas phase concentration determined close to the soil may not have been equilibrated with the soil surface. The development and application of an operational soil fugacity sampler (*20*) opened the door, for first time, to field studies that accurately determine the variables driving the soil-air partitioning and fluxes of POPs in the field. Thus, the objectives of this chapter are to synthesize the work performed during several sampling campaigns using the soil fugacity sampler (*20*) in N-NE Spain and NW England with the aim i) to elucidate to which extent current atmospheric levels of PCBs, HCB, HCH and PAHs are controlled by volatilization from soils, and ii) provide a direct comparison of the different families of organic pollutants.

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Experimental Approach

Case Studies of PCBs, OCPs and PAHs in Background Soils of Temperate Areas

Nine background sites in temperate areas of Northern Spain (along the Ebro river watershed) and Northwest UK were selected for the study of the influence of soil-air partitioning and exchange on the atmospheric occurrence of POPs (Figure 1). In total, four sampling campaigns were performed and distributed as followed: three sampling campaigns were carried out in June 2006, November 2006, and September 2007 in locations along the Ebro river basin (Spain), while the sampling in the UK sites was performed during August-September 2008. All the selected sites were non-agricultural rural or semirural sites with no direct sources of pollutants, so we assumed that all pollutants found there may have introduced by diffuse atmospheric processes. In order to measure the soil-air partition coefficient (K_{SA}) under field conditions, soil surface samples at each sampling site were taken by gently collecting the soil surface layer (approximately top 0.5-1 cm) and analyzed for POPs concentration after sampling the air equilibrated with the soil. K_{SA} describes the equilibrium partitioning of a chemical between the air and the soil and was calculated as follows:

$$K_{SA} = C_S / C_{SA} \qquad [1]$$

where C_S is the POPs concentration in the soil surface (ng g dw^{-1}) and C_{SA} (ng m^{-3}) is the gas phase concentration that has been equilibrated with the soil surface. The air equilibrated with the soil surface was sampled by deploying the soil fugacity sampler (*20*) above the surface soil at each sampling site. Briefly, in this sampler, the air that has been equilibrated in terms of POPs fugacity with the soil surface passes through a glass fiber filter to remove dust particles and a polyurethane foam plug, in which the compounds from the gas phase were retained. Basically, the main advantage of this sampler in comparison to high volume samplers, is that allows for accurately determining the air equilibrated with the soil (thereafter defined as POPs fugacity in soil) by reducing the flow rate (8-10 l min^{-1}) and thus

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allowing for air that passes below the sampler to equilibrate in terms of POPs concentrations with the soil surface. The POPs fugacity in soil (f_s) (in Pa) was therefore directly determined directly under field conditions by:

$$f_s = 10^{-9}\, C_{SA}\, RT / MW \qquad [2]$$

where R is the gas constant (8.314 Pa m^3 mol^{-1} K^{-1}), MW is the chemical molecular weight (g mol^{-1}), and T is the temperature (K).

Each sample was an integration of 24 h of sampling with a total air volume of 10-14 m^3. In parallel to the soil fugacity sampler, an ambient air sampler located at 1.5 m height was also deployed operating with the same flow rate/conditions than the soil fugacity sampler in order to determine ambient air concentrations of POPs or ambient air fugacities (f_a) (in Pa):

$$f_a = 10^{-9}\, C_a\, RT / MW \qquad [3]$$

where C_a is the measured ambient air concentration in ng m^{-3}.

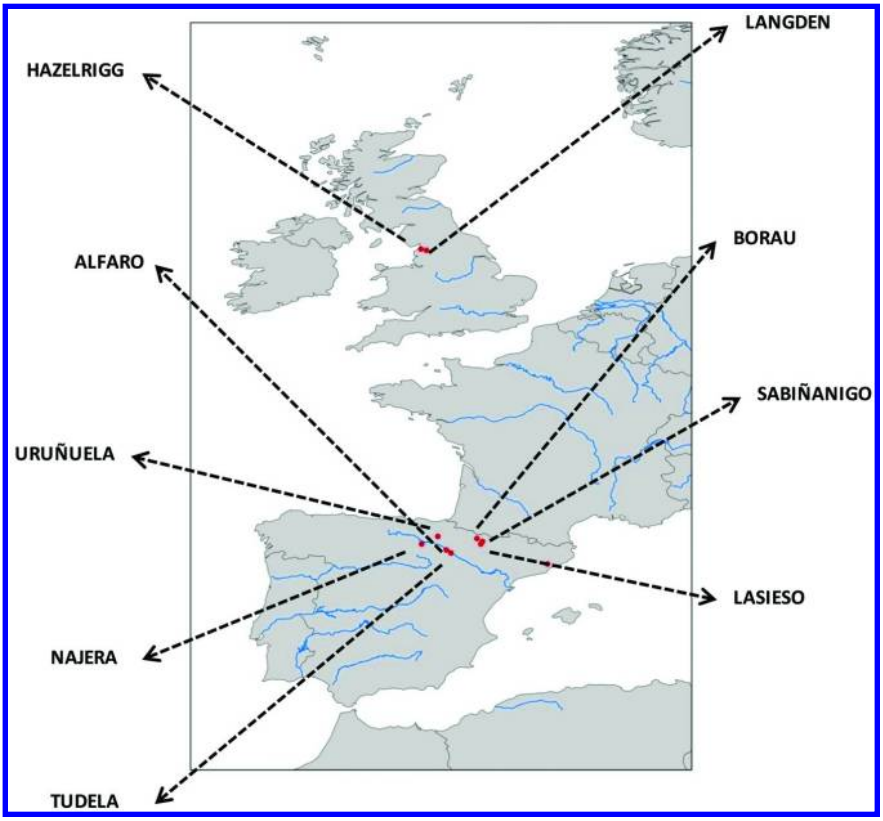

Figure 1. Map of selected sampling sites along the Ebro river basin (Spain) and in NW UK

In Occurrence, Fate and Impact of Atmospheric Pollutants on Environmental and Human Health; McConnell, L., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

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Analytical Methodology

Briefly, soil samples and samples used to determine soil and ambient air fugacities were soxhlet extracted for 24 h in dichlorometane:methanol (2:1v/v) and acetone:hexane (3:1v/v) respectively and spiked with PCB 65, PCBs 200, phenanthrene-d10, crysene-d12 and perylene-d12. Extracts were then cleaned and fractionated using 3 g and 1.5 g alumina deactivated 3% respectively. Soil extracts were eluted in a first fraction (containing PCBs and OCPs) with 5 ml of hexane and with 12 ml dichlorometane: hexane (2:1 v/v) for the PAHs fraction. PCBs, OCPs and PAHs from soil and ambient air fugacity extracts were eluted in one single fraction using 12 ml dichloromethane:hexane (2:1 v/v). All samples were analyzed for the following PCB congeners, OCPs and PAHs: tri-PCB 18, 17, 31, 28, 33; tetra-PCB 52, 49, 44, 74, 70; penta-PCB 95, 99/101, 87, 118; hexa-PCB 110, 151, 149, 153, 132/105, 138, 158, 128, 169; hepta-PCB 187, 183, 177, 171/156, 180, 191, 170; octa-PCB 201/199, 195, 194, 205; nona-PCB 206, 208, 209. Regarding OCPs, the following compounds were analyzed: HCB, HCH isomers (α-HCH, β-HCH, γ-HCH, δ-HCH) and DDT and its metabolites (p,p′-DDT, o,p′-DDT, p,p′-DDD, o,p′-DDD, p,p′-DDE, o,p′-DDE) and for PAHs the following parent PAHs and alkyl homologues were analysed: phenanthrene (Phe), anthracene (Ant), fluoranthrene (Flu), pyrene (Pyr), benzo(a)anthracene (B(a)ant), chrysene (Cry), benzo(b&k)fluoranthene (B(b&k)f), benzo(e)pyrene (B(e)pyr), benzo(a)pyrene (B(a)pyr), perylene (Pery), dibenzo(a,h)anthracene (Dib(a,h)ant), benzo(g,h,i)perylene (B(g,h,i)pery), indeno(1,2,3-cd)pyrene (In(1,2,3-cd)pyr, dibenzonthiophene (DBT), methyldibenzonthiophenes (ΣMDBT), methylphenanthrenes (ΣMP), dimethylphenanthrenes (ΣDMPD). Quality assurance and control parameters have been provided elsewhere (*6*, *12*, *13*). The detected compounds in blanks were PCB 52, 70, 118, 149, 152, δ-HCH, p,p′-DDE, p,p′-DDT, Phe, Ant, Flu and their abundance were in the range of 2-10% of the levels found in samples, thus indicating minimum contamination during storage, sampling, transport and processing. Therefore, samples were not blank corrected.

A gas chromatograph equipped with an electron detector capture (GC/EDC) (Agilent Technologies, model 6890N and 7890N) were used for PCBs and OCPs analysis using the method described elsewhere (*12*, *13*). The quantitative analyses for PAHs were carried out by gas chromatography coupled to mass spectrometry (GC/MS). Samples were injected in an Agilent 6890 Series GC System coupled with a 30 m capillary column (HP-5MS, 0.25mm x 0.25um film thickness) (see method in Cabrerizo et al. (*6*)).

Results and Discussion

Parameters Affecting Ambient Air Concentration (and Ambient Air Fugacities)

Temperature (*T*) was observed to be the most important parameter influencing the atmospheric concentration of PCBs, PAHs and OCPs in temperate regions, with higher concentrations during the warmer sampling periods (June 2006 and

September 2007). The influence of temperature is usually viewed as evidence that local or proximate sources, either primary or secondary, have a strong influence on the atmospheric levels of organic pollutants (*21*). This is consistent with the fugacity gradients observed, since they had a volatilization component for all chemical families (*6*, *12*, *13*). Figure 2 shows the influence of *T* on atmospheric concentrations for the POPs families studied. Overall, we observed that ambient air temperature affected ambient air concentrations of PCBs and OCPs, which higher concentrations in warm periods, in agreement with an enhance released of POPs from soils during warm seasons. This temperature influence on ambient concentrations was not observed for PAHs (e.g. phenanthrene and anthracene), which show a lack of dependence on temperature (e.g phenanthrene) or higher ambient air concentrations at lower temperatures (e.g anthracene). Different reasons may account for this behavior, i) the fact that PAHs are not persistent, especially in the atmosphere, with atmospheric half lives of hours due to reaction with OH radical. These degradation processes are more effective during warm periods, ii) the presence of higher emissions of PAHs due to heating, wood burning or other combustion sources during winter time, iii) the presence of potential biogenic sources in soils and other environmental compartments that may not be temperature dependent (*6*, *22*). The lack of an influence of *T* for PAHs cannot be viewed as a sign of lack of local sources, but of varying sources at different seasons (biogenic and pyrolitic sources) and different extend of atmospheric degradation processes. Other studies have also reported a weak or lack of *T* dependence of atmospheric concentrations of PAHs (*23*), while the key role of temperature as a control of atmospheric concentrations of PCBs and OCPs has been described in numerous studies (*21*, *24*, *25*). If local sources control the atmospheric occurrence of POPs and PAHs in rural areas, it is important an assessment of the factors driving the air-soil partitioning and exchange of POPs.

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Parameters Affecting the POPs Concentration and Fugacity in Soils

Soil Properties

The nature of the surface matrices in direct contact with the atmosphere are very important for the partitioning of POPs between the air and soil surfaces. This is particularly true if these surfaces are covered by lipophilic organic substances which offer a high capacity to store POPs. Soils contain these kinds of substances such as humic acids, which are able to retain POPs due to the high affinity of these pollutants to non-polar phases. Soil organic matter quantity is generally considered as the main descriptor of the sorption of hydrophobic pollutants (*26*) and has been recognized as an important variable that influences the concentration of POPs at local, regional and global scale (*1*, *27*). Soils having the higher soil organic matter content in these studies have shown higher concentrations of all the chemicals considered: PCBs, OCPs and PAHs (Figure 3). This trend has been observed previously in other studies (*1*, *27*) thus soil organic matter is a major reservoir of POPs at regional and global scales (*1*, *7*) and its capacity to immobilize

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POPs, preventing them from re-volatilization back into the atmosphere, was also evidenced for banned PCBs, α-HCH, γ-HCH and o,p′-DDT and p,p′-DDT metabolites as their soil fugacities (*fs*) are lower for those soils having the highest SOM content (Figure 4). This scenario contrast with the observation of PAHs and HCB fugacity in soil for which high variability was observed and it is not possible to elucidate significant differences due to soil organic matter content. In the case of phenanthrene, and consistent with the discussion done above on its potential biogenic sources, the lack of trend observed would be consistent with phenanthrene and methyl-phenanthrenes originating from degradation of organic matter (triterpenes), which would lead a higher fugacity at higher SOM content, but this trend could be masked by the role that higher SOM has as increasing the soil fugacity capacity, thus decreasing the tendency to escape from soil (fugacity).

The common role of organic matter content as a descriptor of the burden of hydrophobic pollutants, and in agreement with previous studies in European soils (*28*), were observed between the different POPs families' concentrations for ΣPCBs, ΣPAHs, HCB, ΣHCH and ΣDDT, across the whole set of soils (Figure 3). The common role of soil organic matter as a sorbing phase, induce that the concentrations of the different families of POPs are correlated among them with statistically significant correlation (p-level<0.001 or p-level<0.05) (Table 1). This is an important observation, because these POPs account for chemicals with diverse sources, and these significant correlations among them imply that regardless of sources, once they enter the environment they behave in a similar way which depends on their physical-chemical properties and environmental characteristics, therefore, POPs are part and are interrelated with the different biogeochemical cycles of the biosphere, especially that of organic matter.

Parameters Affecting Soil-Air Partitioning of POPs

Temperature and soil organic matter quantity have been identified as the most important parameters controlling the soil-air partition coefficient (K_{SA}) of PCBs, OCPs and PAHs together with their physicochemical properties (K_{OA}). Higher K_{SA} were obtained at lower temperatures and higher soil organic matter content (Figure 5 and 6). The influence of temperature and soil organic matter is observed to be significant for all POPs, except for HCBs. In this study, soil redox potential, soil *pH*, altitude, nitrogen fraction (f_N) or organic carbon/nitrogen ratio (f_{OC}/f_N) were used as indirect parameters of soil organic matter type since not direct measurements of humin and fulvic acids or humins were performed. Soil-air partition coefficient normalized by soil organic carbon content (K_{OCA}) was correlated with soil redox potential, f_N and altitude for PAHs. K_{OCA} for PCBs were correlated with f_{OC}/f_N and altitude but not with redox potential, in the same way that DDTs, while non statistically relationships were observed when considering HCHs (*6*, *12*, *13*). However, the influence of soil type is small in comparison to temperature and amount of soil organic matter.

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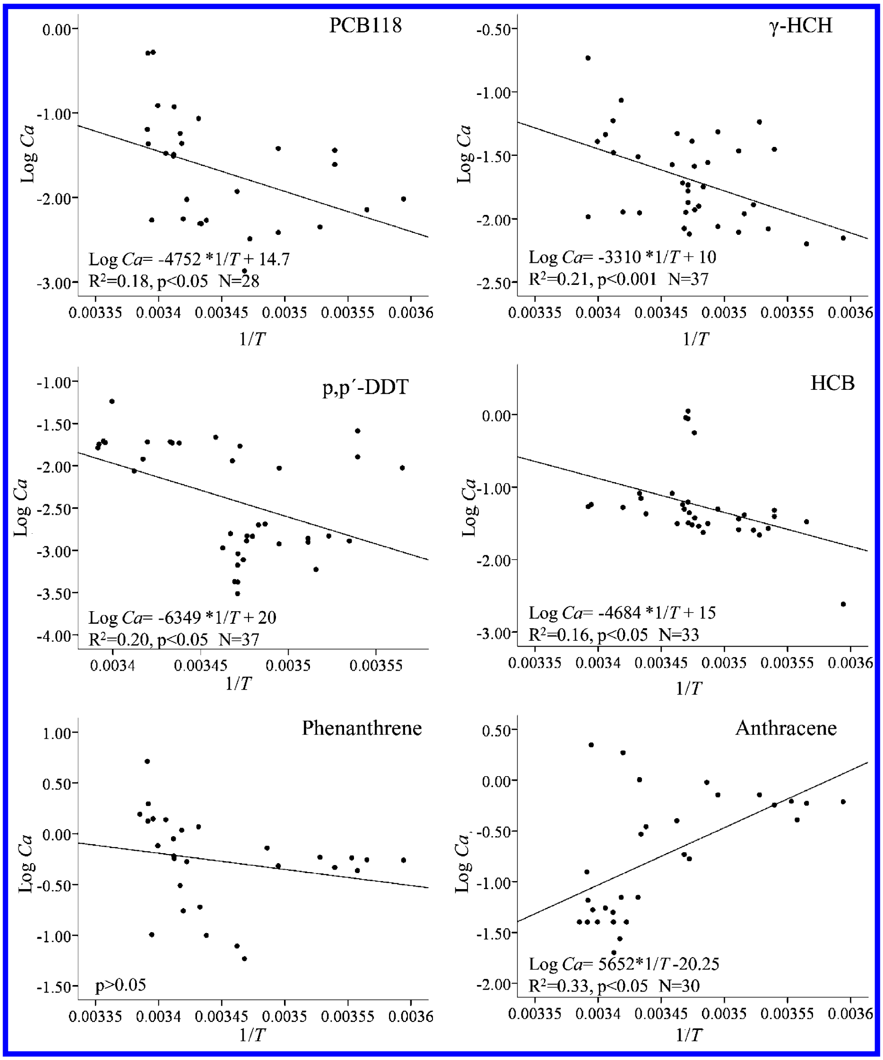

Figure 2. Comparison of ambient air concentrations (Log Ca in ng m^{-3}) regressed against 1/T for selected PCBs, OCPs and PAHs.

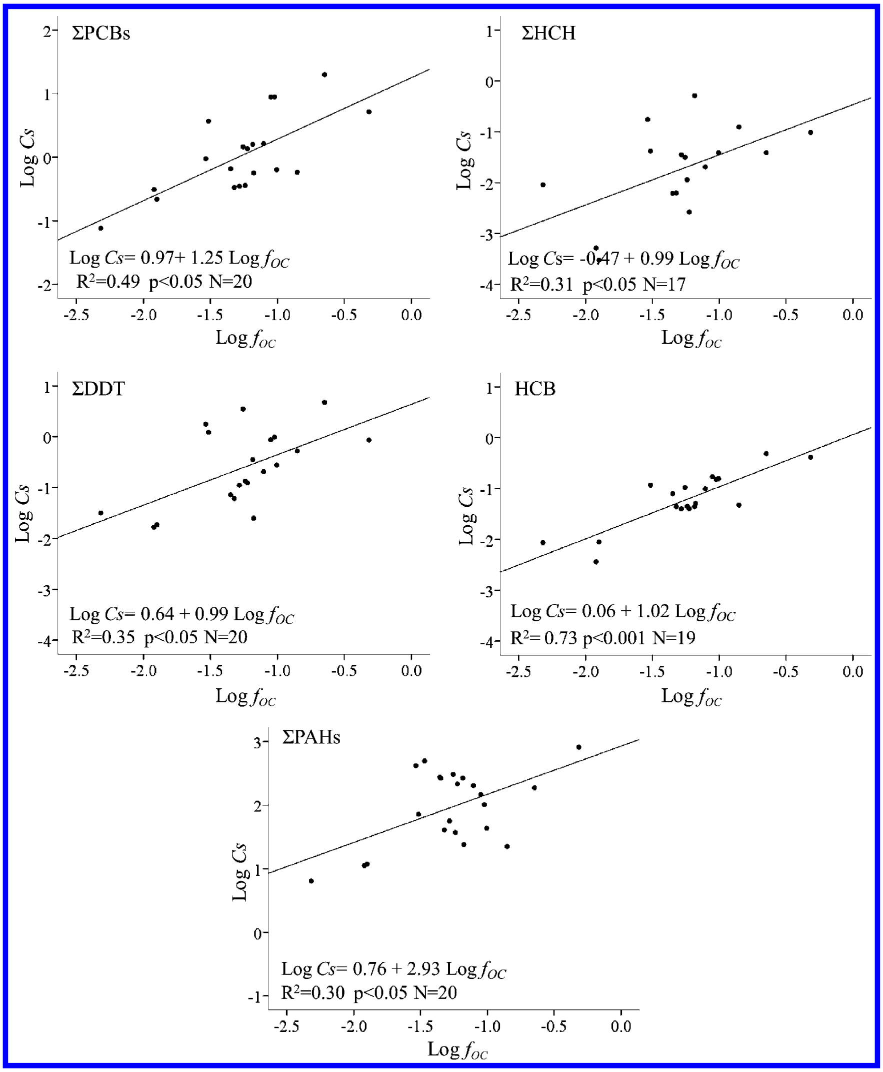

Figure 3. Soil concentration of POPs in soil (Log Cs in ng gdw^{-1}) regressed against soil organic carbon (Log f_{OC}) for selected POPs families

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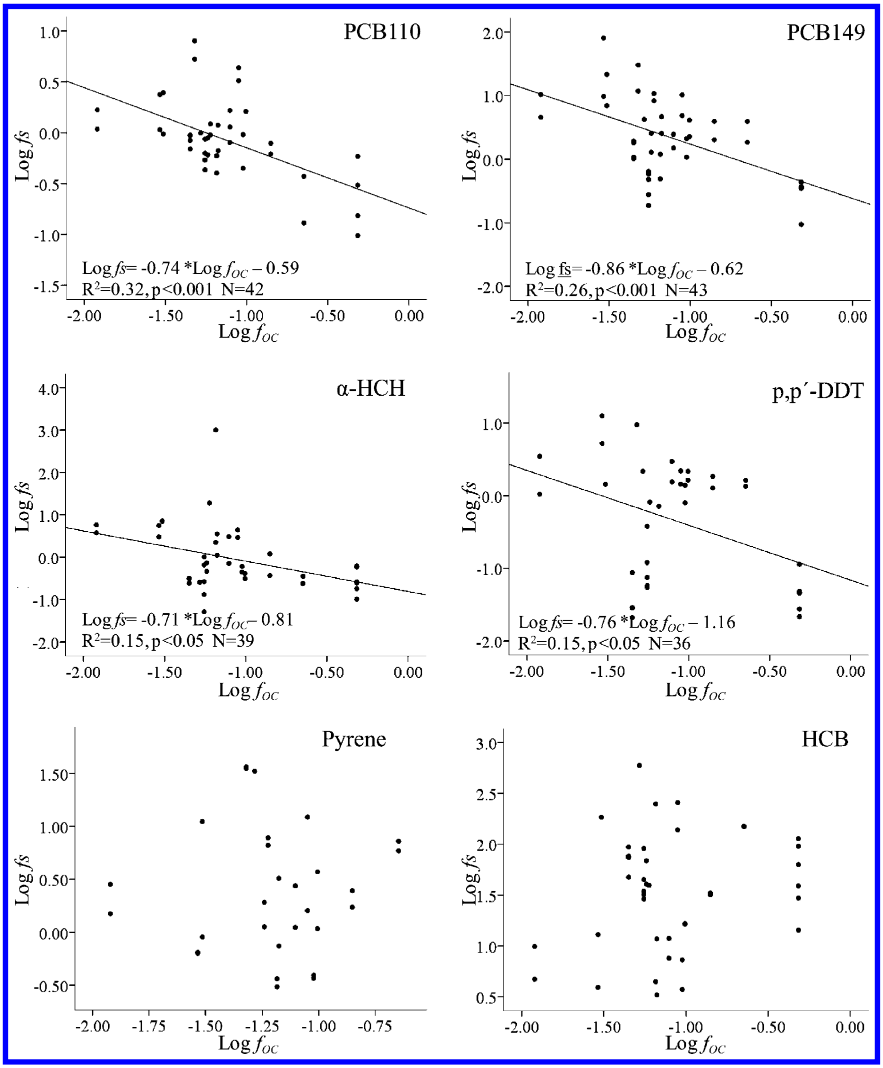

Figure 4. Soil fugacities of selected PCBs, OCPs and PAHs regressed against Log f_{OC}

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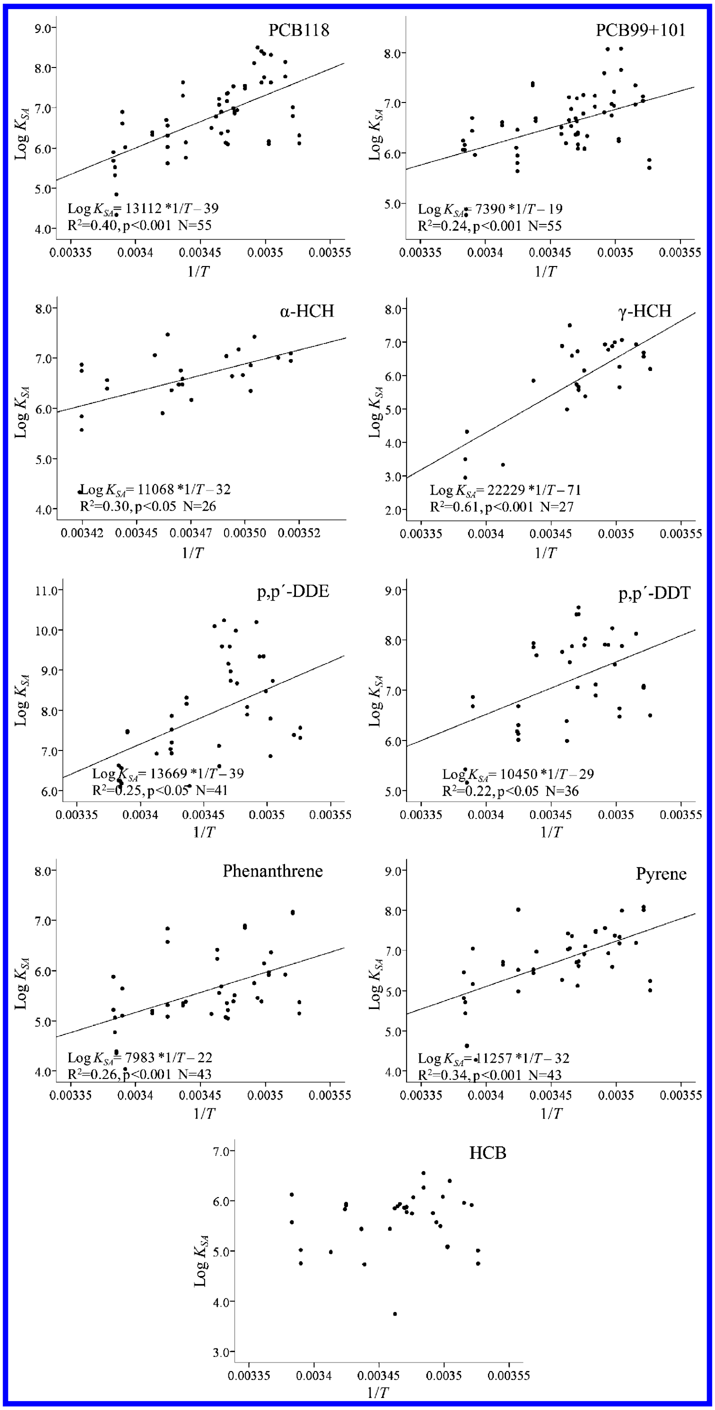

Figure 5. Influence of 1/T on the soil-air partition coefficient (Log K_{SA})

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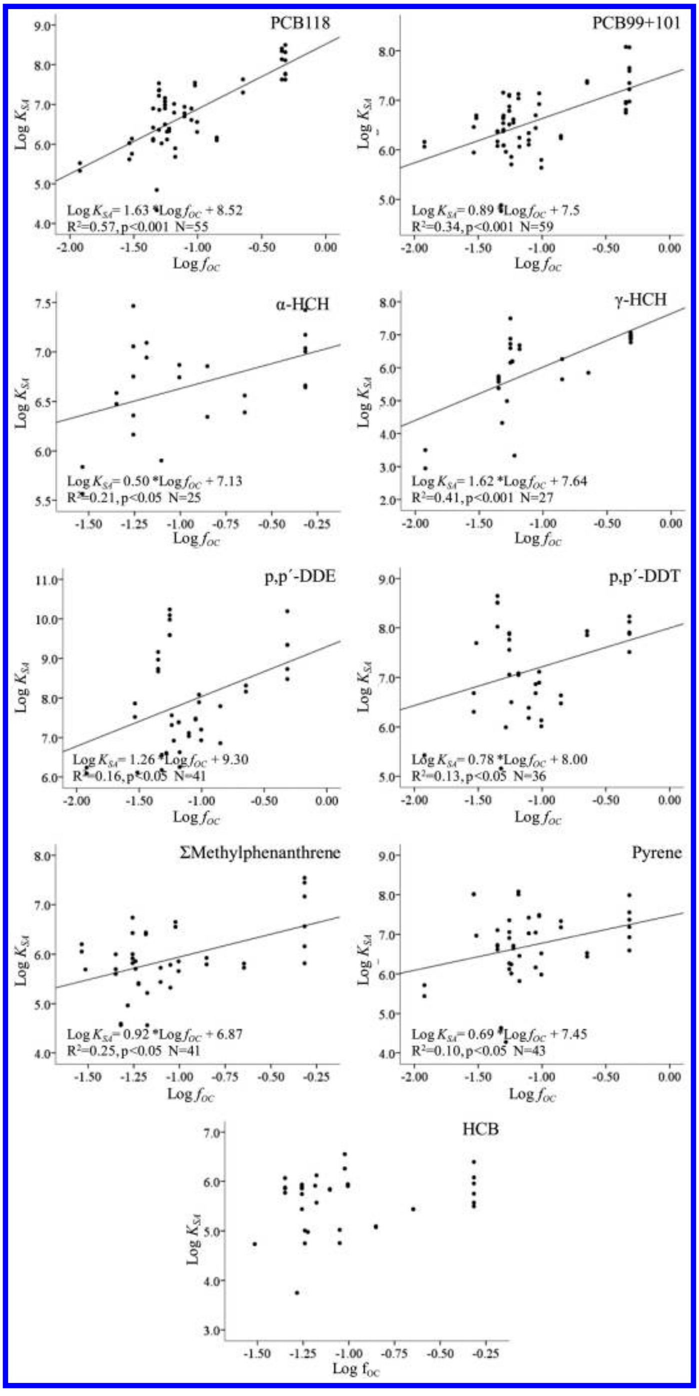

Figure 6. Influence of OC (Log f_{OC}) on the soil-air partition coefficient (Log K_{SA})

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Table 1. Correlation coefficients among the different families of POPs for all soils

	HCB	*ΣDDT*	*ΣHCH*	*ΣPCBs*	*ΣPAHs*
HCB	1.00				
ΣDDT	0.67[b]	1.00			
ΣHCH	0.42[a]	0.54[a]	1.00		
ΣPCBs	0.71[b]	0.64[b]	0.24[a]	1.00	
ΣPAHs	0.57[b]	0.48[a]	0.30[a]	0.49[b]	1.00

[a] $p<0.05$, [b] $p<0.001$, the data were log-transformed before analysis.

Soil-Air fugacity Gradients: An Assessment of Soils as Secondary Sources of POPs to the Atmosphere in Temperate Regions

The comparison of fugacities in soil and ambient air makes it possible to infer the direction of air-soil exchange. When fugacity in soil is higher than fugacity in ambient air, there is a net volatilization of the chemical. In contrast, if fugacity in ambient air is higher than fugacity in the soil, there is net deposition of the chemical.

The comparison of POPs fugacity in soil with the fugacity in ambient air (Figure 7) shows that for PCBs and OCPs the soil and the atmosphere are close to equilibrium but with a tendency of soils to be a net source to the atmosphere during warmer periods (early and late summer campaigns) at Ebro's river watershed sites. While for OCPs there was a net volatilization during warmer periods and net deposition during colder periods. For PCBs, the air is equilibrated with soil for colder periods with also a net volatilization at warmer periods. Therefore, secondary sources are more important for PCBs than for OCPs in the Ebro river watershed. Under this scenario dominated by secondary sources, the measured POPs fugacities in soil allow for assessing, for the first time, whether the ambient air POPs fugacities are correlated with the soil fugacities, which would support that secondary emissions are controlling the atmospheric concentrations of PCBs and OCPs, which in addition, would further support that the measured temperature dependence of ambient concentrations are a consequence of the local/regional secondary sources from soils. For the Ebro's river watershed sites, there is indeed a close coupling between air and soil fugacities, suggesting that the atmospheric levels of banned PCBs and OCPs are temperature dependent and controlled by re-emission from soils (see Figure 8).

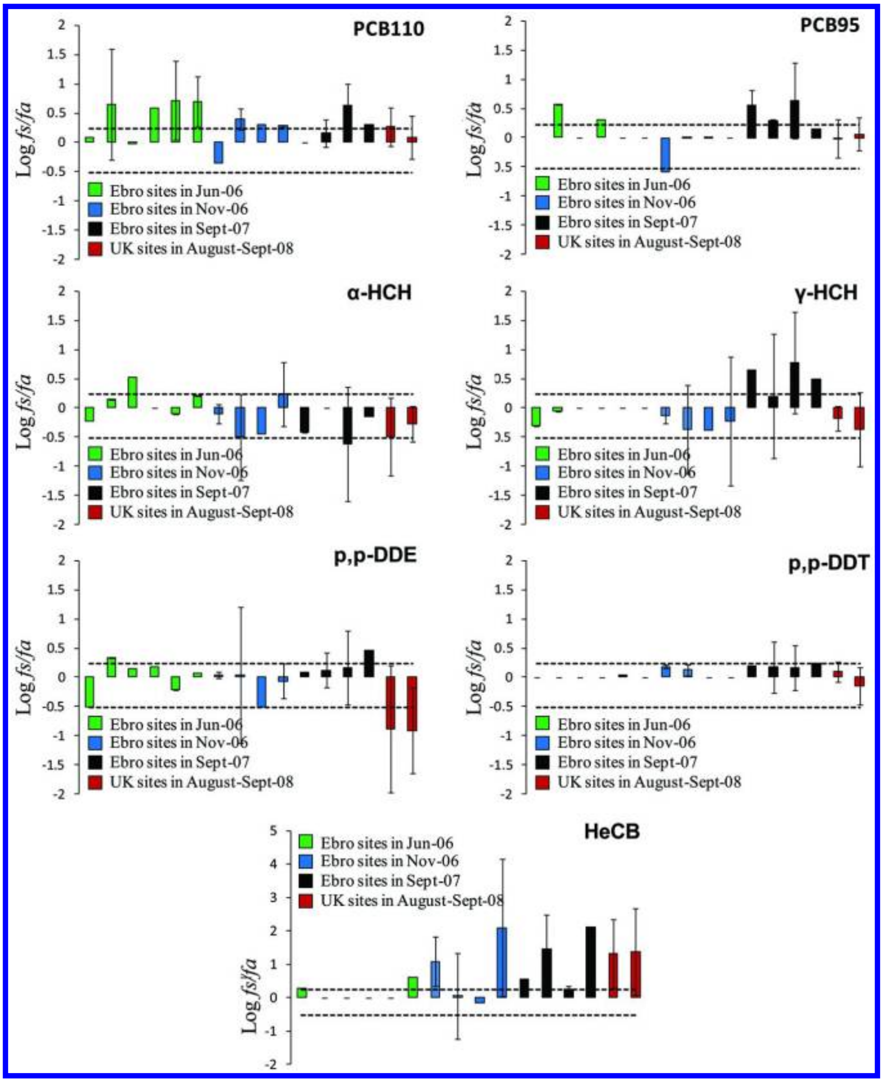

Figure 7. Soil/Air fugacity ratio (fs/fa) in logarithmic scale for the different sampling campaigns in Ebro (Spain) and UK for selected PCBs and OCPs. Dash lines indicates equilibrium (range +0.23, -0.52)

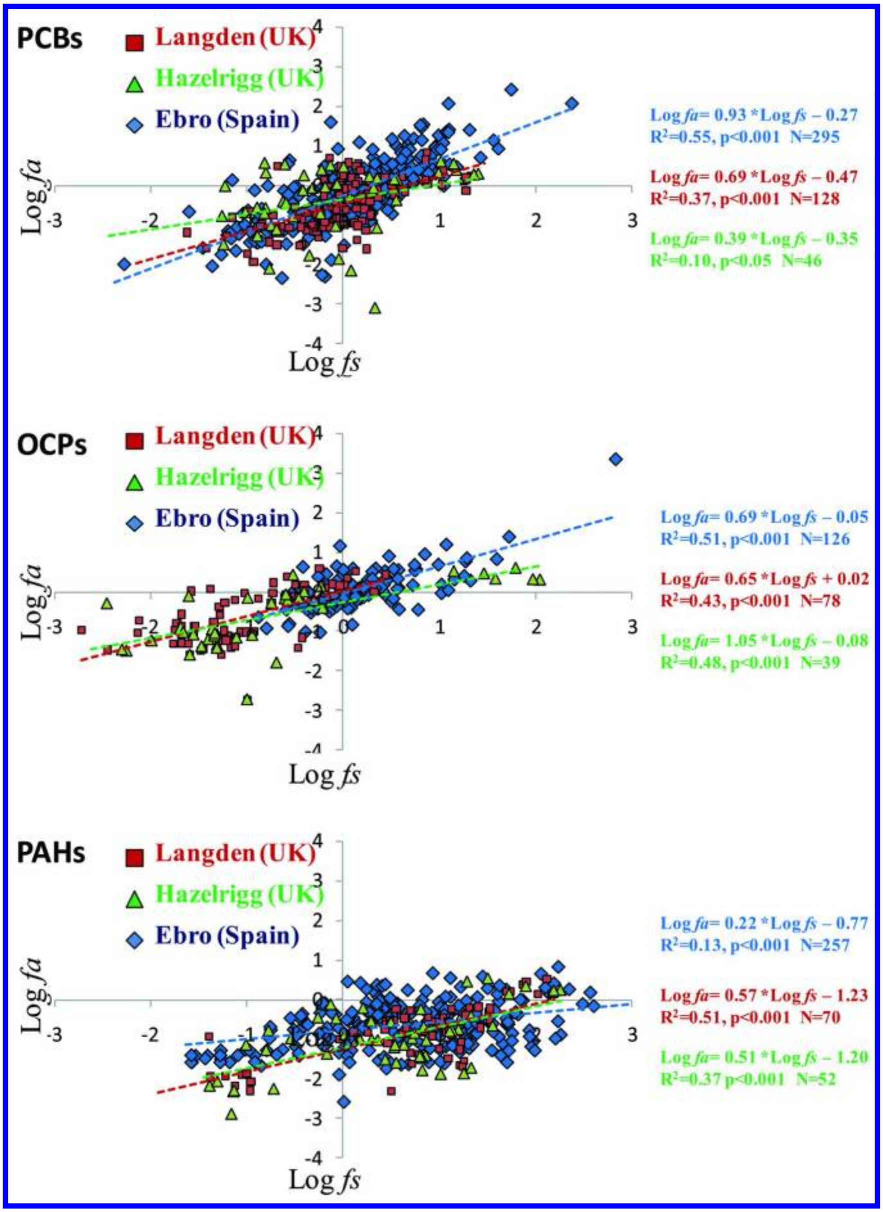

Figure 8. Log soil fugacity (fs) versus ambient air fugacity (fa) for PCBs, OCPs and PAHs at Ebro's (Spain) and UK's sampling sites in all sampling campaigns

Conversely, for soils at the UK sites the scenario was different. At the UK sites, the POPs fugacities in soil indicated that soils during summer were rather a net sink than a net source (PCB52, 95, 110, 118, γ-HCH and p,p′-DDE). Thus, the scenario observed for Ebro soils is different than that observed in the NW England, where even in the late summer soils are a net sink for some POPs. If soils are not a significant secondary source to the atmosphere, or even are a net sink, then POPs fugacities in the atmosphere and soil may not be correlated, because the soil fugacity capacity of soils is orders of magnitude higher than that of the atmosphere (*7*) and soil concentrations and fugacities do not respond fast to atmospheric inputs of POPs. Indeed, there was a lower correlation between fugacities in soil and fugacities in ambient air in the NW England sites in comparison to Ebro's river watershed sites (Figure 8). The correlations for the two UK sites and all PCBs or organochlorine compounds are still significant, because air and soil are close to equilibrium for many compounds. These observations suggest that soils in this region are still under-saturated or close to equilibrium with respect to the atmospheric PCBs and OCPs levels. There is a smaller control of atmospheric concentrations due to emissions from soil, and it is possible that there are still significant primary sources to the regional environment (*29*).

The ambient air fugacities PAHs are also correlated with their fugacity in soils (Figure 8). Thus, the atmospheric occurrence of lighter PAHs such as phenanthrene and methylated phenanthrenes is strongly dependent on the volatilization fluxes from soil. The soil-air gradients of these PAHs are high and ubiquitous, and it is difficult to explain them without considering a biogenic source for these compounds (*6*). It may also indicates, that the high concentrations of phenanthrene described in rural regions may be due to volatilization from soils.

The comparison of sites in N-NE Spain and NW England, which are regions with different soil characteristics and climatic regimes, show that currently there is a transport, presumably due to grasshopping, of PCBs from mid latitudes (Spain) to higher latitudes (UK). Other assessments of soil-air exchange at global scale (*30*) suggest that soils with lower fugacity capacity may represent higher fluxes of POPs to the atmosphere, even though this statement could not be proved due to a lack of realistic measurements of POPs fugacity in soil. The present work allows to evaluate this working hypothesis by comparing the measured K_{SA} with the measured fugacity gradients (Figure 9). Indeed, for some low MW PCBs and OCPs, fugacity gradients are inversely correlated with K_{SA}, thus soils are more important secondary sources in regions with soils containing lower amounts of organic carbon and higher temperatures (Ebro's river watershed) than in colder environments such as NW England where soils also have higher organic carbon content. However, this was not observed for the more hydrophobic congeners. For phenanthrene, there is also a significant correlation of K_{SA} with the fugacity ratio, but this is not observed for heavier PAHs as chrysene which may be of pyrolitic origin, and for which there is not a ubiquitous volatilization flux.

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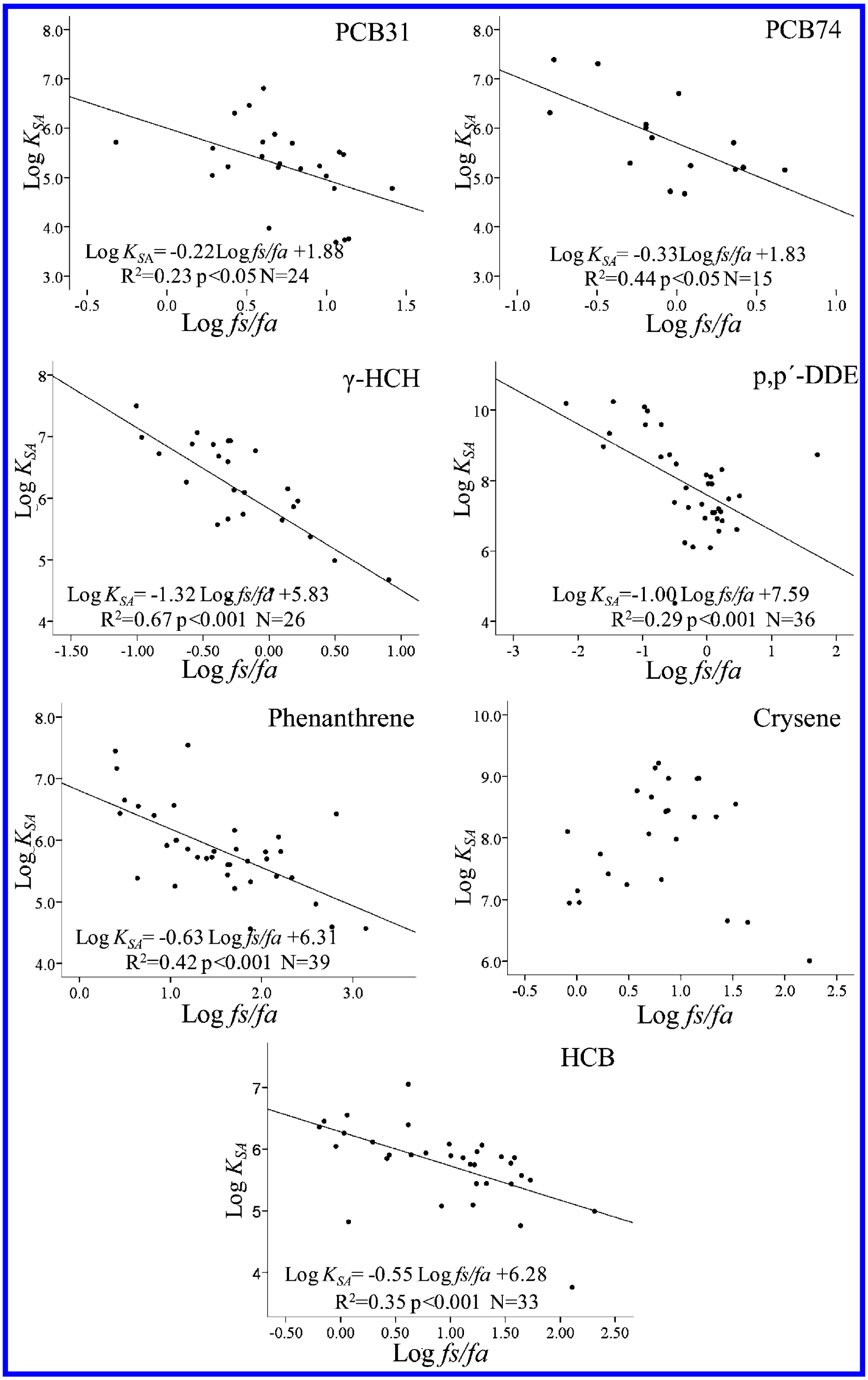

Figure 9. Soil-air partition coefficient (Log K_{SA}) regressed against soil-air fugacity ratio (Log fs/fa) for selected PCBs, OCPs and PAHs.

After decades of legislative control on some legacy POPs, primary sources may have been reduced significantly, and the low capacity soils in Spain (Mediterranean Soils) are becoming secondary sources to the atmosphere. Conversely, in the UK, the primary sources may have also being reduced, but soils had never reached their total reservoir capacity and they are still a net sink of some PCBs. Primary sources should reduce further for high capacity soils to become secondary sources of PCBs to the atmosphere, but the time scale for this to happen cannot be discerned with the available data set. For non-persistent POPs such as PAHs: no differences between sampling regions were observed. We observed a ubiquitous behavior of PAHs in both temperate areas, with soils being important sources of lighter PAHs to the atmosphere, as *fs/fa* decreased as increasing the K_{OA}. The volatilization gradients of fugacities were especially high for phenanthrene and its alkyl homologues. The magnitude of re-emission of PAHs by volatilization was also temperature dependent with higher emission measured at higher temperatures.

Apart from temperature, soil organic matter type also influenced the magnitude of re-emission, which may be related to soil microbiology. Since half life's of phenanthrene in the atmosphere is short, in order of minutes to hours, it is difficult to justify the high levels of PAHs described here and elsewhere in background environments. In addition, such large fugacity gradients would be difficult to maintain in the time without a local source. Therefore, it is suggested that potentially biogenic sources should be considered to maintain the huge fugacity gradients of phenanthrene and its alkyl homologues as observed in all sites. A coupling of soil-air fugacities of PAHs was also observed (see Figure 8) suggesting, as in the case of PCBs and OCPs, that atmospheric concentration of PAHs are affected by PAHs re-emission from soil surface. According to the behavior observed for more volatile PCBs and OCPs, fugacity ratios for more volatile PAHs were inversely correlated with K_{SA}, while this trend was not observed for higher molecular weight PAHs, in agreement with behavior observed for most chlorinated PCBs.

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Conclusions

An extensive sampling effort for studying the processes controlling the soil-air exchange and atmospheric concentrations of POPs show that temperature and amount of organic matter in soil are the two most important factors. POP fugacities in soil are higher at higher temperatures and at lower amounts of soil organic matter. In northern Spain, where soils are poor in organic matter and the climate is warm, there is a generalized net volatilization of organic pollutants with a seasonal variability. Conversely, at northern England, with soils with high organic matter content and lower temperatures, soils become a net sink or are close to equilibrium with the atmosphere even during summer. Generally, the temperature influence on the atmospheric concentrations of POPs, the net volatilization discerned from fugacity gradients, and the correlation between fugacity in soils and the atmosphere suggest that currently the atmospheric occurrence of legacy POPs in many regions is dominated by secondary sources.

Acknowledgments

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Chapter 3

Trace Metals in Saharan Dust: The Use of in Vitro Bioaccessibility Extractions To Assess Potential Health Risks in a Dustier World

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Exposure to fine particulate matter (PM) is acknowledged as a risk factor for human morbidity and mortality. Epidemiology and toxicology studies have focused on anthropogenic sources of PM and few consider contributions produced by natural processes (geogenic), or PM produced from natural sources as a result of human activities (geoanthropogenic PM). The focus of this study was to elucidate relationships between human/ecosystem health and dusts produced by a system transitioning from a dominantly natural to a geoanthropogenic PM source. As part of a larger study investigating the relationship between atmospheric transportation of African dust, human health, and coral reef declines, we examined dust samples sourced in Mali, Africa, collected using high-volume samplers from three sites (Mali, Tobago and U.S. Virgin Islands). Inhalation and ingestion exposure pathways were explored by filter extractions using simulated lung and gastric fluids. Bioaccessibility varied by metal and extraction fluid. Although too few samples were analyzed for robust statistics, concentrations for several metals decreased slightly while bioaccessibility increased at downwind sites.

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Introduction

It is generally accepted that exposure to air pollution may increase risk for human morbidity and mortality particularly for susceptible individuals (e.g. preexisting conditions, age). One component of air pollution, particulate matter (PM), affects more people than any other according to the World Health Organization (*1*). The WHO identifies PM components as sulfates, nitrates, ammonia, sodium chloride, carbon, mineral dust and water (*2*). Sources of particulate matter may be natural (e.g., forest fires, mineral dusts and volcanic ash) or anthropogenic (e.g. fossil fuel combustion, industrial emissions). Until recently, research on the effects of PM on human health generally examined anthropogenic (industry and combustion by-products) sources with few studies considering contributions from geogenic PM (produced from the Earth by natural processes, e.g., volcanic ash, windborne ash from wildfires, and mineral dusts) or geoanthropogenic PM (produced from natural sources by processes that are modified or enhanced by human activities, (e.g., dusts from lakebeds dried by human removal of water, dusts produced from areas that have undergone desertification as a result of human practices). However, a growing concern related to a changing climate, increasing desertification and the long range as well as local related health effects is evident in the media. Epidemiological studies have identified associations between far-traveled dusts and increased morbidity and mortality in Europe and Asia (*3*, *4*).

Although dust storms occur frequently worldwide, there is increasing concern that desertification and the frequency and volume of emitted dusts will increase with climate change (*5*). Researchers are examining the potential health effects of these ‘far-traveled dusts’ from large primary sources such as the Sahel/Sahara and Asia. In Europe, Perez et al (*4*) examined the effects of Saharan dust coarse particles (< 10 μm, PM10) and daily mortality in Barcelona, Spain and found an increase in daily mortality (8.4% per increase of 10 $\mu g/m^3$) on Saharan dust days as compared to non- dust days (1.4%). Similar results were observed in studies that followed in other areas of Europe (*3*, *6*). Closer to the source, there is a paucity of information (*7*) but two studies found similar trends. In the Canary Islands, Lopez-Villarrubia et al (*8*) found rates of respiratory mortality increased 4.9% for each PM10 increase of 10 $\mu g/m^3$ and Gyan et al (*9*) identified increased rates of pediatric asthma exacerbation in a retrospective study in Trinidad.

Of additional concern, a combination of factors such as regional geomorphology, socioeconomic, and synthetic organic chemical use may be altering the quality of transported dusts (*10*). Traditionally, all forms of garbage were burned for fuel and to add nutrients to the soil in the Sahara and Sahel of West Africa. Prior to the 1980s, mainly animal and plant waste was burned, but today, plastic products, tires and manufactured goods also are burned (*10*). Has this predominately geogenic system which has transported dust for millennia shifted to a geoanthropogenic system?

Although many studies have demonstrated an association between increased morbidity and mortality and PM, there is little agreement regarding which component(s) (e.g. metals, organic components such as endotoxins) or size fraction is responsible for these effects. Some of the general factors known

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to influence health related effects are: intensity and duration of the exposure; physical and chemical characteristics of the material; microbial or other pathogens present in the material; and the bioaccessibility, biodurability and bioreactivity of the material in the body fluids; and individual physiological factors such as immune response, age, gender and personal habits (i.e. smoking) (*11*).

Trace metal concentrations alone do not predict potential toxicity or activity in organisms, as solubility in fluid(s) encountered following inhalation or ingestion is a primary factor controlling accessibility of the trace metal in the organism. Bioaccessibility as defined by Ruby et al (*12*) is the fraction of a potential toxicant that becomes soluble and is then available for absorption. Often confused with bioavailability, bioaccessibility is a measure of the physiological solubility at the portal of entry into the body whereas bioavailability is the fraction of an ingested dose that crosses the gastrointestinal epithelium and becomes available for distribution to internal target tissues and organs (*13*). *In Vitro* bioaccessibility (IVBA) extractions are a quick and inexpensive method designed to estimate the solubility, or bioaccessibility, of metal (loid)s in dusts, soils and other environmental materials using simulated body fluids.

As part of a larger study investigating the relation between long-distance atmospheric transport of Saharan dust and human and ecosystem health (i.e. coral reef declines), we examined bioaccessibility of metal and metalloid toxicants in atmospheric mineral dust from the dust source region (Mali, West Africa; ML) and at two downwind sites in the eastern Caribbean [Tobago (TT) and the U.S. Virgin Islands (VI)] (Figure 1). We conducted IVBA extractions using simulated gastric and lung fluids compositionally similar to those in the human body to explore ingestion and inhalation exposure pathways of these far traveled dusts.

Methods

Sample Collection

Dust samples were collected using high volume samplers. In Mali brushless electric blower motors (Mercury Northland BBA14 222HMB-00, 240v, 50/60hz) in custom aluminum tripod enclosures were used. In the Virgin Islands and Tobago, a permanent magnetized motor (MAX-SE 3 Phase, TECO- Westinghouse, Round Rock, TEXAS, USA, 230/460 v, 11.8/5.9 amp, 5 HP) powered a high volume HAUCK turbo fan and a computer (ABB, Zurich Switzerland,TYPE: ACH401601112) controlled motor speed and recorded elapsed time. Quartz microfibre filters (QFFs; numbered 8”x10” Whatman Grade QM-A Sheets, #1851-865; preconditioned at 600°C for 8 hrs, weighed (Mettler Toledo AB204-S analytical balance), and stored individually (in Ziploc™ bags) were used as the sampling medium at all sites for metals bioaccessibility studies. Due to logistical constraints, weather and sporadic electrical outages (all sites), sampling times varied (range 23-63 hrs. most often 44-48 hr.). Following sample collection, each filter was folded in half using Teflon forceps, placed in the original plastic bag, frozen until transferred to a desiccator, and weighed to constant weight. Sample and control filters were handled identically except no air was drawn through controls. Sample volumes varied with sampling time, flow rate, and vagaries of the electrical system. Because of the wide range of ambient conditions during which samples were collected, sample volumes were corrected to standard ambient temperature (298K) and pressure (100kPa). Due to uncontrollable factors, sampling dates at the three sites did not overlap nor was the same dust mass sampled at both source and downwind sites.

Figure 1. Generalized sample location map. ML refers to sample collection location, Emetteur Kali, Bamako, Mali; FT refers to the collection site at Flagstaff Hill, Tobago; VI refers to the collection site on St Croix, US Virgin Islands.

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Particle Size

A scanning electron microscope (SEM) was used in an attempt to determine particle size and mineralogy; however, this proved difficult as the particles were embedded within the quartz filter and extraction was incomplete. Because downwind site (TT and VI) samples had sample weights below that needed for mineralogical evaluation and the particles had embedded in the filter, only one filter (ML) was analyzed to obtain mineralogy and estimates of particle size.

In Vitro Bioaccessibility

For this study, we used a gastric extraction based on the U.S. Environmental Protection Agency (USEPA) method (*14*) for estimating lead bioaccessibility (*15*). Gastric bioaccessibility is relevant to this study as particles that fail to traverse the nasopharyngeal region may become trapped in the mucous lining and would be ingested. This test has also been evaluated for use in measuring arsenic bioaccessibility (*16*, *17*) but its use has not been validated for other metals by animal studies although it is frequently used in this manner. Our IVBA methodology for other media (e.g. soil) extractions employs a soil-to-liquid ratio of 1:100 based on previous studies (*18*, *19*). Because particulate mass varied among filters and because several tests were to be performed on each filter, the filters were quartered. Subsequently, the solid: solution ratio varied but is approximately 1:1000. A subset of 12 filters were selected based on sufficient sample mass to ensure the filters could be quartered and still produce an analytical signal above the method detection limit for most elements.

Filters were quartered using ceramic scissors in a clean environment while wearing nitril gloves. Each filter was weighed, quartered and then each quarter weighed and recorded. Two of the quarters were placed in separate clean, acid washed 120 mL HDPE bottles for extraction. One quarter was submitted for analysis of 30 elements using a four acid digestion method (*20*). Prior to beginning the four acid digestions, the filter sections were dissolved by adding 4 mL of concentrated hydrofluoric acid. The sample analytical results were filter-blank subtracted prior to any calculation. Due to the small mass of sample on the filter and the need to quarter the filters, errors in estimation of absolute particle mass on each quarter filter are likely. The filter quarters were rolled with the sample collection side out prior to placing them in the bottle to ensure leachate solution contact with the entire collection surface. In addition to the samples, a procedural blank and a control blank (filter) were added to each analytical batch for quality control.

The simulated gastric fluid (SGF) was produced by adding about 60 mL of concentrated (12.1 N) HCl to 2 L of 0.4 M glycine solution (*14*, *18*). A preheated water bath was used to warm the solution until it reached 37°C and the pH was then adjusted by drop-wise addition of concentrated HCl until a value of 1.50 ± 0.05 was reached. The simulated gastric fluid was added to each bottle and the bottles were placed on a wrist-action shaker within a preheated (37° C) Environ-Shaker 3597/2 (Lab Line Instruments, Inc.). After one hour, approximately 20 mL of solution was removed, filtered through a 0.45-μm nitrocellulose syringe

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filter into a new acid-washed bottle and stabilized with HNO_3 until analysis could be completed. The extraction solutions were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (*20*). The ICP-MS system was calibrated with multi-element standard solutions prepared from commercially available stock solutions. U.S. Geological Survey standard reference water samples (*21*) were analyzed as quality control samples.

A neutral pH (7.4) simulated lung fluid (SLF) such as dust particles would encounter through an inhalation exposure was also used as an extraction fluid. The simulated lung fluid was developed to examine solubility in a variety of materials (*22–24*). This fluid, produced by dissolving analytical grade chemicals in ultrapure 18-ohm water (Table I), was adapted from Bauer et al (*22*) but a batch method was used instead of the flow-through design they utilized. We also did not use the formaldehyde and methanol used in the Bauer et al. (*22*) method due to concerns that these chemicals could introduce excessive metal contaminants. The simulated lung fluid was warmed to 37° using a preheated water bath and the pH of the solution was titrated to 7.4 by the drop-wise addition of HCl. The SLF was added to the bottles containing the filter section and placed on a wrist-action shaker within a preheated (37° C) Environ-Shaker 3597/2 (Lab Line Instruments, Inc.) to provide both constant temperature and agitation for 24 hours. The samples were removed, centrifuged at 2000 rpm for two minutes and filtered into new acid-washed bottles using a 0.45µm nitrocellulose syringe filter. A 3 mL aliquot was collected and refrigerated for speciation of arsenic (As), chromium (Cr) and selenium (Se) utilizing an high performance liquid Chromatography (HPLC) method developed by Wolf (*25*). The remaining solution was preserved with concentrated HNO_3 until analyses could be completed. The extraction solutions were analyzed by ICP-MS in the manner described in the previous section.

Table I. Simulated lung fluid composition.

Compound	***Concentration***
NaCl	6780 mg/L
NH_4Cl	535 mg/L
$NaHCO_3$	1770 mg/L
NaH_2PO_4 • H2O	166 mg/L
Na_2CO_3	630 mg/L
glycine	450 mg/L
H_2SO_4	51 mg/L
Na_3-citrate •2 H_2O	59 mg/L
$CaCl_2$ • 2 H_2O	29 mg/L

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Results

Particle Size and Mineralogy

Because the particles were embedded within the quartz filter, attempts at extraction were incomplete and no trends in grain size were discernible. Further complicating the analysis, quartz fibers from the filter were released during the removal process that interfered with the analysis. The backscattered electron brightness of the quartz made automated size analysis of the particles difficult using scanning electron microscopy (SEM). In general, the majority of particles observed in the Mali sample were less than 3 µm (Figure 2). Analysis completed on one filter, ML-2, indicates that the majority of particles identified are clay phases (*26*). Energy Dispersive Spectroscopy (EDS) and morphology analyses suggest smectite, kaolinite and illite may be present but could not be confirmed without X-Ray diffraction (*26*). Other phases identified in decreasing order of abundance include quartz, iron oxide, feldspar, dolomite, sodium sulfate, gypsum, calcite, titanium dioxide and an unidentified zinc particle.

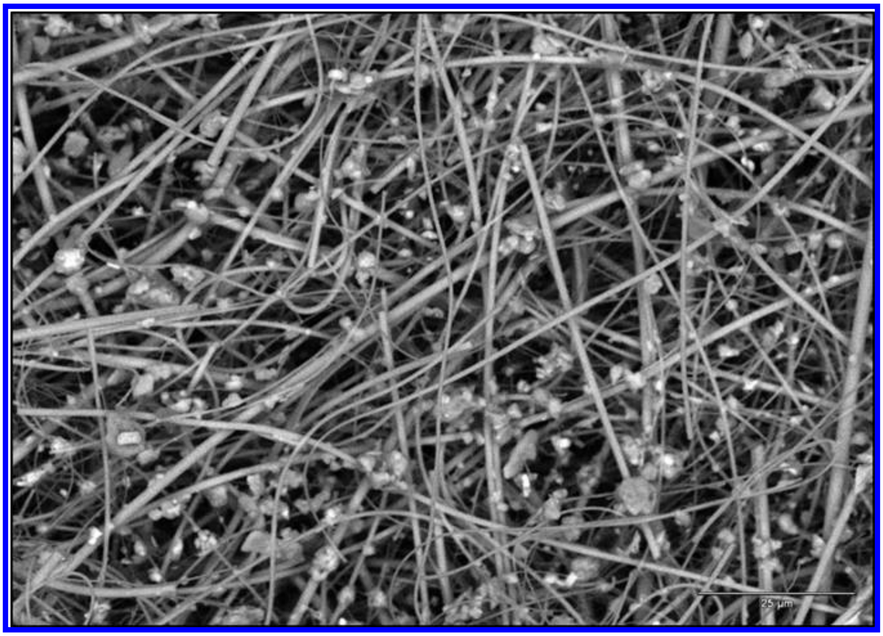

Figure 2. Backscattered electron image of dust collected on filter at Emetteur Kali, Bamako, Mali. Note 25 micrometer size bar in lower right corner.

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In Vitro Bioaccessibility and Total Metal Concentration

Bioaccessibility varied by extraction fluid and metal with several exceeding 50% (Tables II, III, IV). There is some indication of trends, i.e. decreasing total concentration and increasing bioaccessibility in several metals discussed below. Robust statistics are not possible based on the small sample size analyzed. For perspective, the total chemistry results from the collected air filters are compared to the U.S. soil mean concentration (*27*), USEPA human health screening levels for residential soils (RSL) (*28*) and the USEPA ecological soil screening (ECO SSL) guidelines (*29*). In general, total concentrations of metals in the dusts were not excessively high though many exceeded the U.S. soil mean concentration (the average concentration of elements in soil samples from the conterminous United States) (US soil mean, Tables II, III, IV). Only arsenic exceeded the USEPA's human health screening levels for residential soils (RSL) (0.39 mg/kg) (*28*). The RSLs are concentrations of individual contaminants in soil that may necessitate further study (*28*) and are not intended to represent action levels or cleanup standards. Also, the 0.39 mg/kg RSL for arsenic is for a cancer endpoint, and is a concentration lower than found in nearly all natural US soils. Total concentrations for several metals, cadmium (Cd,) copper (Cu), chromium (Cr) (if all is Cr III), lead (Pb), vanadium (V) and zinc (Zn), exceeded the avian and mammal ECO-SSL's (Table V) (*29*). These guidelines, developed by the U.S. EPA, identify contaminants of potential concern commonly found at superfund sites for plants, birds, soil invertebrates, and mammals (*29*). They are designed to be protective of ecological receptors that commonly come into contact with or consume biota that live in the soil and are used during the screening stage of an ecological risk assessment.

Arsenic

Several samples exceed the US soil mean for total concentration of As. These samples range from 3.8 to 7.5 mg/kg total As, with a median of 6.3 mg/kg and mean of 6.0 mg/kg. All samples exceed the EPA RSL for inorganic As (0.39 mg/kg, cancer endpoint) (*28*). Total concentrations do not exceed the ECO SSL's for arsenic. Gastric bioaccessibility is greater than 40% for several samples. Lung fluid bioaccessibility ranged from 12% to over 100%. Total As concentration decreased slightly from the source location to the downwind site (Figure 3) while bioaccessibility in both the GSF and LSF tended to increase following long-distance transport. Speciation of As in the SLF was determined to be As (V) in six of the twelve samples, the remaining samples registered less than the instrument reporting limit (Table II).

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Table II. Filter trace metal concentration presented as total in mg/kg, and simulated lung fluid (SLF) and simulated gastric fluid (SGF) extractions presented as the per cent of the solid soluble in the extraction fluid (% bioaccessible) [a].

SAMPLE NAME	As (total, mg/kg)	As, SLF (% bioaccessible)	As, SGF (% bioaccessible)	Cd (total, mg/kg)	Cd, SLF (% bioaccessible)	Cd, SGF (% bioaccessible)
ML627	7.5	*	38	0.3	*	50
ML623	7.1	*	*	0.3	16	63
ML001	6.6	*	83	0.5	31	71
ML005	6.3	12	25	0.3	12	88
ML009	6.3	40	19	0.5	21	86
ML016	6.9	<1	43	0.7	15	69
ML605	5.6	15	68	0.3	22	80
FT629	3.8	*	100	0.2	*	100
FT634	6.2	188	118	0.4	*	73
FT646	4.7	293	143	0.4	*	62
VI690	4.7	*	45	0.4	78	100
VI001	*	*	*	0.3	70	90
US soil mean**	5.2			n/a***		

SAMPLE NAME	Cu (total, mg/kg)	Cu, SLF (% bioaccessible)	Cu, SGF (% bioaccessible)	Cr (total, mg/kg)	Cr, SLF (% bioaccessible)	Cr, SGF (% bioaccessible)
ML627	35	11	30	109	0	13
ML623	31	17	30	115	0	8
ML001	34	26	49	135	*	5
ML005	40	11	*	115	*	7
ML009	36	24	11	147	0	5
ML016	37	21	8	150	0	6
ML605	30	23	*	123	3	8
FT629	4	80	*	68	23	89
FT634	7	80	*	70	28	63
FT646	7	50	*	69	40	*
VI690	11	68	70	50	0	21
VI001	*	4	11	47	*	70
US soil mean**	17			37		

[a] Sample locations are indicated as follows: ML – Emetteur Kati,Bamako, Mali; FT – Flagstaff Hill, Tobago; VI- St Croix, US Virgin Islands. Bioaccessibility is calculated as leachate concentration in mg/kg divided by total concentration in mg/kg multiplied by one hundred. All values were blank corrected prior to calculations. * indicates values less than method reporting limit or blank correction resulted in a negative number and no value could be calculated. ** US soil mean concentration in mg/kg is presented for reference (27); ***no value available for Cd). A median Cd value of 0.2 mg/kg in surface soils has been reported (30).

Cadmium

Total Cd concentrations do not exceed ECO SSL for soil invertebrate or avian species but some samples do exceed the mammal SSL value. The range for Cd total concentrations was 0.2 to 0.7 mg/kg with a median and mean of 0.4 mg/kg. Cadmium bioaccessibility is high in both SLF (12 to 78%) and SGF (50 to 100%). Total concentration values remain fairly consistent (Figure 3) but show some increase in bioaccessibility as they move from the source to the Caribbean sites.

Copper

Most sample total concentrations exceed the US soil mean for copper (*27*), but do not exceed the ECO SSL for soil invertebrates or mammal species. Several samples do exceed the avian ECO SSL recommendation for Cu. Total Cu concentrations range from less than the method reporting limit (after blank correction) to 40 mg/kg, with a median of 30 mg/kg and a mean of 22 mg/kg. Several gastric leachate samples resulted in negative number after blank correction, possibly the result of co-precipitation and subsequent filtering. Cu appears to be more soluble in the near neutral pH SLF than the acidic SGF. The range for Cu bioaccessibility in the SLF is 4 to 80% and in the SGF 8 to 70%. Values tend to be lower in total concentration and higher in bioaccessibility in downwind sites in most samples.

Chromium

Total Cr concentrations ranged from 47-150 mg/kg (median 112 mg/kg, mean 100 mg/kg). All values exceed the ECO SSL's for avian and mammalian species with the assumption that all Cr present is Cr III. All samples were less than the method reporting limit for Cr speciation in the SLF. In the low pH of the simulated gastric fluid, any hexavalent Cr will be reduced to form Cr III. Bioaccessibility was low in most of the SLF extractions, and varied in the SGF (range 5-89%).

Iron

Most iron (Fe) concentrations are less than US soil means and ranged from 7222 to 45634 mg/kg (mean 32097 mg/kg; median 39336 mg/kg). Total Fe concentrations do not exceed EPA SSL levels and decrease with distance from the source location (Figure 3). Bioaccessibility was low in both the SLF (less than the reporting limit – 6.1 %) and SGF (2-9 %) (Table III). However, given the high total concentrations this does represent a considerable extractable amount available for uptake.

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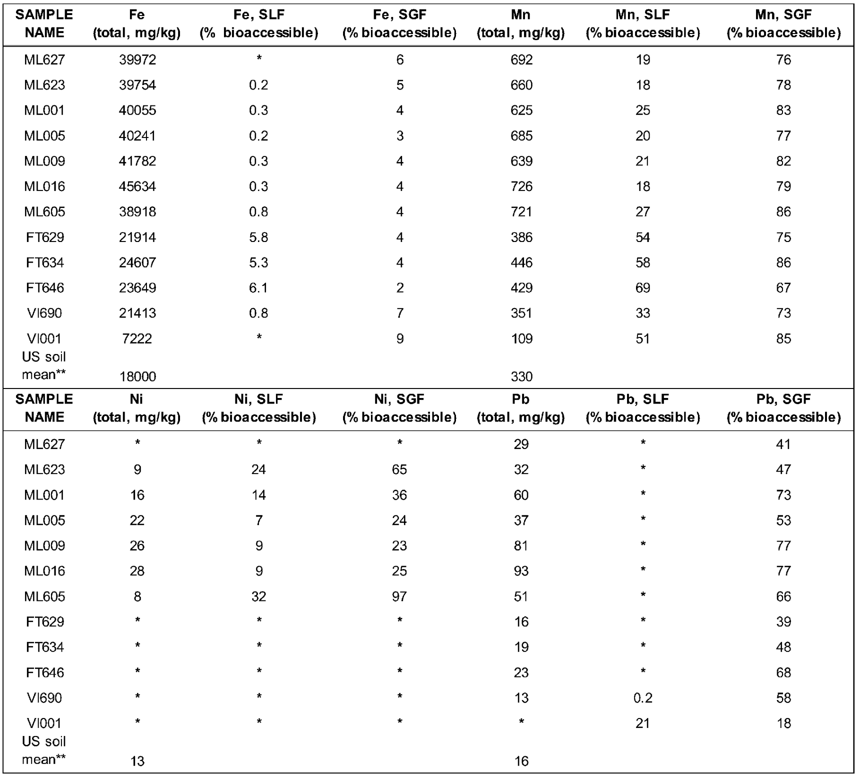
Table III. Filter trace metal concentration presented as total in mg/kg, and simulated lung fluid (SLF) and simulated gastric fluid (SGF) extractions presented as the per cent of the solid soluble in the extraction fluid (% bioaccessible) [a].



SAMPLE NAME	Fe (total, mg/kg)	Fe, SLF (% bioaccessible)	Fe, SGF (% bioaccessible)	Mn (total, mg/kg)	Mn, SLF (% bioaccessible)	Mn, SGF (% bioaccessible)
ML627	39972	*	6	692	19	76
ML623	39754	0.2	5	660	18	78
ML001	40055	0.3	4	625	25	83
ML005	40241	0.2	3	685	20	77
ML009	41782	0.3	4	639	21	82
ML016	45634	0.3	4	726	18	79
ML605	38918	0.8	4	721	27	86
FT629	21914	5.8	4	386	54	75
FT634	24607	5.3	4	446	58	86
FT646	23649	6.1	2	429	69	67
VI690	21413	0.8	7	351	33	73
VI001	7222	*	9	109	51	85
US soil mean**	18000			330		

SAMPLE NAME	Ni (total, mg/kg)	Ni, SLF (% bioaccessible)	Ni, SGF (% bioaccessible)	Pb (total, mg/kg)	Pb, SLF (% bioaccessible)	Pb, SGF (% bioaccessible)
ML627	*	*	*	29	*	41
ML623	9	24	65	32	*	47
ML001	16	14	36	60	*	73
ML005	22	7	24	37	*	53
ML009	26	9	23	81	*	77
ML016	28	9	25	93	*	77
ML605	8	32	97	51	*	66
FT629	*	*	*	16	*	39
FT634	*	*	*	19	*	48
FT646	*	*	*	23	*	68
VI690	*	*	*	13	0.2	58
VI001	*	*	*	*	21	18
US soil mean**	13			16		

[a] Sample locations are indicated as follows: ML – Emetteur Kati,Bamako, Mali; FT – Flagstaff Hill, Tobago; VI- St Croix, US Virgin Islands Bioaccessibility is calculated as leachate concentration in mg/kg divided by total concentration in mg/kg multiplied by one hundred. All values were blank corrected prior to calculations. * indicates values less than method reporting limit or blank correction resulted in a negative number and no value could be calculated. ** US soil mean concentration in mg/kg is presented for reference (27).

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Table IV. Filter trace metal concentration presented as total in mg/kg, and simulated lung fluid (SLF) and simulated gastric fluid (SGF) extractions presented as the per cent of the solid soluble in the extraction fluid (% bioaccessible) [a].

SAMPLE NAME	U (total, mg/kg)	U, SLF (% bioaccessible)	U, SGF (% bioaccessible)	V (total, mg/kg)	V, SLF (% bioaccessible)	V, SGF (% bioaccessible)
ML627	3.7	10	22	105	2	16
ML623	3.7	13	22	108	4	14
ML001	3.6	15	21	101	4	14
ML005	4.6	15	21	101	3	10
ML009	3.8	17	19	99	4	11
ML016	4.5	14	21	106	4	11
ML605	4.6	16	24	94	5	11
FT629	4.1	13	12	69	*	21
FT634	4.8	11	14	75	*	18
FT646	5.1	13	18	72	*	*
VI690	1.7	16	25	74	23	41
VI001	0.7	*	*	36	12	79
US soil mean**	2.3			58		

SAMPLE NAME	Zn (total, mg/kg)	Zn, SLF (% bioaccessible)	Zn, SGF (% bioaccessible)
ML627	94	*	69
ML623	89	*	42
ML001	142	100	78
ML005	110	*	25
ML009	164	3	75
ML016	169	6	65
ML605	118	*	46
FT629	41	*	*
FT634	55	23	*
FT646	105	27	*
VI690	72	*	75
VI001	10	*	147
US soil mean**	48		

[a] Sample locations are indicated as follows :ML – Emetteur Kati,Bamako, Mali; FT – Flagstaff Hill, Tobago; VI- St Croix, US Virgin Islands. Bioaccessibility is calculated as leachate concentration in mg/kg divided by total concentration in mg/kg multiplied by one hundred. All values were blank corrected prior to calculations. * indicates values less than method reporting limit or blank correction resulted in a negative number and no value could be calculated. ** US soil mean concentration in mg/kg is presented for reference (27).

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Manganese

Manganese total concentrations range from 109 to 726 mg/kg. Total concentrations for some samples do exceed the ECO SSL levels for plants and soil invertebrates. Bioaccessibility values range from 18 to 69% in the SLF and 67 to 86% in the SGF.

Nickel

Both total and bioaccessible concentrations of nickel (Ni) are low and many values are less than the reporting limit. While some source values exceed the US soil mean, they do not exceed the ECO SSL values.

Lead

For these samples, total Pb concentrations do not exceed the residential soil RSL (400 mg/kg) but most do exceed ECO SSL's for avian species and several samples exceed the mammalian guidelines. Total concentrations ranged from less than the reporting limit (after blank correction) to 93 mg/kg Pb (mean 41mg/kg, median 32 mg/kg). Concentrations were higher in the source region, due most likely to continued use of Pb compounds in the fuel through 2006 (*31*), and possible occurrence in the plastics and other man-made materials that are being combusted as fuel. Lead is very soluble in the SGF and much less so in the SLF. The low observed solubility in the SLF may indicate the lack of lead dissolution at the less aggressive pH, coupled with the reaction of any lead that had been solubilized with phosphate in the SLF to form insoluble lead phosphate phases.

Uranium

Most total uranium concentrations are slightly above the US soil mean and range from about 1 to 5 mg/kg (Table IV). They are slightly more bioaccessible in the SGF (mean 20%) than the SLF (14%).

Vanadium

Most vanadium total concentrations exceed the US soil mean as well as the avian ECO SSL. Total concentrations for V range from 36 – 108 mg/kg, with a mean of 87 and a median of 96. The ECO SSL is exceeded for avian guidelines only. Vanadium is bioaccessible in both the SGF and the SLF, but clearly more soluble in the acidic SGF. The data reflect lower concentrations at downwind sites (Figure 3) yet higher bioaccessibility in both SGF and SLF.

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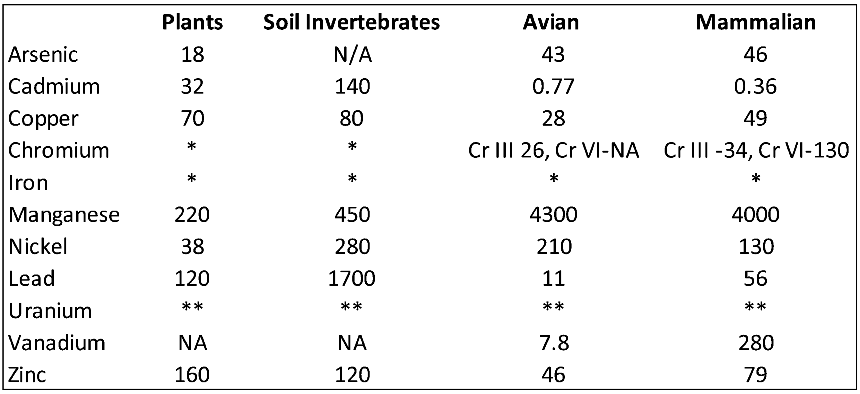
Table V. Ecological soil screening level values in mg/kg dry weight [a] (*29*).



	Plants	Soil Invertebrates	Avian	Mammalian
Arsenic	18	N/A	43	46
Cadmium	32	140	0.77	0.36
Copper	70	80	28	49
Chromium	*	*	Cr III 26, Cr VI-NA	Cr III -34, Cr VI-130
Iron	*	*	*	*
Manganese	220	450	4300	4000
Nickel	38	280	210	130
Lead	120	1700	11	56
Uranium	**	**	**	**
Vanadium	NA	NA	7.8	280
Zinc	160	120	46	79

[a] * Not enough data to derive. **Not published at time of this publication. NA not available.

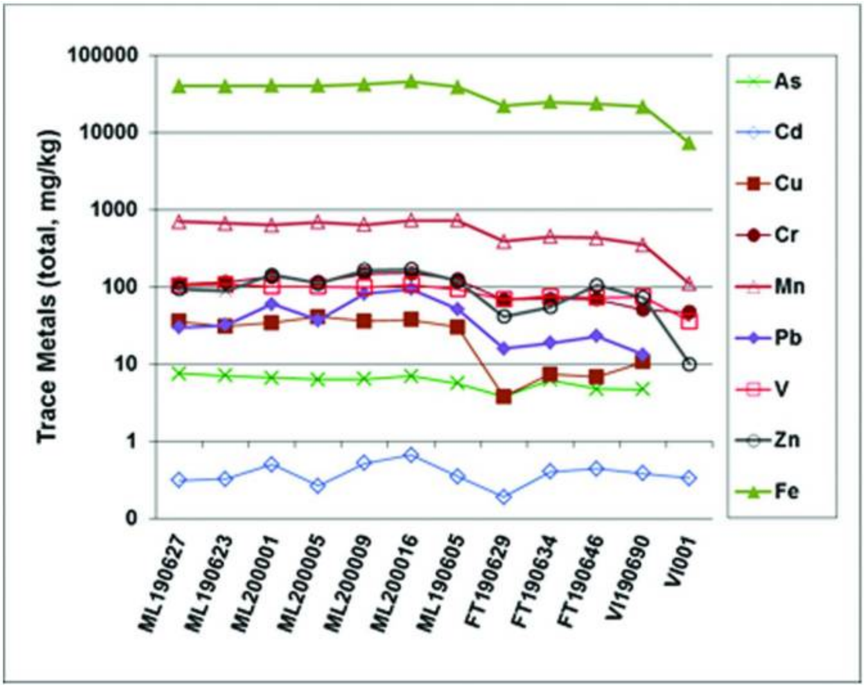


Figure 3. Trace metal concentration, as mg/kg, in dusts from filters. ML = Emetteur Kali, Bamako, Mali; FT = Flagstaff Hill, Tobago ; VI = St Croix, US Virgin Islands.

Zinc

Most zinc total concentrations exceed the US soil mean value and several values exceed both the avian and mammal ECO SSL. The range for total Zn for these samples is 10 – 169 mg/kg with a mean of 97mg/kg (median 99 mg/kg). Zinc is soluble and bioaccessible in the SGF (25 to >100%) but much less so in the SLF.

Discussion and Conclusion

Although a significant amount of research has been conducted to clarify which factors (e.g. composition, particle size) are responsible for the health-related effects of what is commonly referred to as air pollution there is little consensus. Inconsistencies may be related to a number of factors including: sample and source characterization, model parameters, and population susceptibility. Variation in the number of components and their concentrations in and on the surface of particles in the air and the complexity of surface chemistry on small volume-to-high surface area particles presents a difficult challenge to determining the etiological mechanisms responsible. Far traveled dusts, including our samples, can be transported along with biologic components such as bacteria, fungi, and endotoxins (*10*) and carry on their surface organic contaminants and metals with known toxicities from both natural and anthropogenic sources. Gyan et al (*9*) cites potential allergens and irritants in Saharan dust including plant-derived constituents such as pollens and the high iron content in the form of surface-complexed iron as probable factors for the increased rates of asthma exacerbation in their study. Additionally, not much is known about the particle surface chemistry occurring during atmospheric transport in chemically and physically extreme conditions [e.g. exposed to high levels of solar radiation, multiple freeze-thaw cycles, and relatively acidic conditions (*10*)]. These variables may affect a variety of properties and, as is evident in our results, the solubility of some metals.

Health related effects of low-level chronic exposures for some trace metals have not been well defined as early research and regulatory guidelines focused on occupational health. Arsenic, for example, has recently been implicated in cardiovascular disease (arrhythmias and cerebrovascular accidents (CVA) or strokes), and diabetes at low levels of exposure (*32*). Exposure pathways for inorganic arsenic include inhalation, as well as ingestion, and arsenic is well absorbed (80-90%) from the gastrointestinal tract (*33*). Some of the metals examined here are classified as essential nutrients at low concentrations (i.e. Cr III) whereas others are typically considered toxicants (i.e. As, Pb). Some trace metals may have different toxic thresholds depending on species (i.e. Cu).

Release of ferrous iron from a wide range of respirable PM types (e.g., asbestos, coal fly ash, iron sulfides, iron-rich volcanic ash) has been implicated as a substantial contributor to oxidative stress and toxicity in the lungs (*34–36*). Our results indicating high levels of SLF-extractable iron raise the possibility that these intercontinental dusts pose risks for chronic, low–level oxidative stress related to bioaccessible iron. However, further work is needed to confirm whether the extractable iron is colloidal and/or dominated by ferrous rather than ferric

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iron. High SLF-bioaccessible levels of other variable oxidation state metals or metalloids (e.g., Mn, As, Cu, V) warrant further examination for their possible contribution to oxidative stress, as well as their other toxicity effects.

Although IVBA extractions do not provide a direct measure of human or ecosystem health risk they enhance sample characterization by providing insight into what and how much is soluble in a physiologically based fluid. Our results may also provide some insight into atmospheric transport-related effects on particle chemistry. For example for some metals, total concentration decreases slightly (Figure 3), and bioaccessibility increases at downwind sites (As, Cd, Cu in SLF) (Table II). The increased solubility may be partially related to decreasing particle size downwind resulting in a larger particle surface area. Other chemical reactions occurring during transport may also play a significant role. Trends for some metals vary by the fluid type and may reflect the difference in fluid pH. For example Cu bioaccessibility was greater following long-distance atmospheric transport only in the neutral pH SLF. No strong interpretations may be inferred, as few samples were analyzed and sample number varied among sites.

Thorough characterization of sample and source materials is essential as elucidating causal factors using a simple mass or particle-size based system that does not consider the composition of the sample is unrealistic. This study expands the use of IVBA methodology by analyzing PM samples collected by active air filtering, a method which has not to our knowledge been explored in the past. In addition we utilize two physiologically based fluids to infer different exposure pathways, inhalation and ingestion. Our results indicate the use of filters to collect and assess sample bioaccessibility may be a practical alternative to assist in sample characterization. Results from this pilot study indicate changes in bioaccessibility of some bioactive and potentially toxic metal (loid)s in mineral dusts occur during long-distance atmospheric transport.

Disclaimer

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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Chapter 4

Human Exposure to Polycyclic Aromatic Hydrocarbons in Urban and Rural Ambient Air

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic compounds in the ambient air. They are composed of two or more fused benzene rings and emitted into the atmosphere after incomplete combustion of organic material and evaporation of PAH containing fossil fuels. Due to their physico-chemical properties and ambient environmental conditions they partitioning between vapor and particle phase in the atmosphere and undergo atmospheric transport. Some PAHs, and their metabolites are carcinogenic, which makes their presence in the ambient air of concern. Humans can be exposed to substantial doses due to the vicinity of important combustion sources, such as vehicle emissions and biomass burning emissions, during daily activities. In urban areas traffic is a dominant source, while in rural area wood burning can be dominant. The composition of PAHs in these emissions depends on many factors, such as the type of fuel as well as combustion efficiencies. Moreover, once emitted into the atmosphere, the atmospheric lifetime of PAHs is influenced by many factors, such as photo-chemical oxidation and meteorological conditions. PAH concentrations are normally higher near potential emission sources and their levels can be determined using different sampling devices. The exposure to atmospheric PAHs and consequent risk assessment on human health is not trivial and many variables should be taken in account. The following chapter gives an update on the occurrence, distribution and fate of PAHs in ambient air and it

In Occurrence, Fate and Impact of Atmospheric Pollutants on Environmental and Human Health; McConnell, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

gives estimates on the actual human health risks related to the exposure of PAHs in ambient air.

1. Physico-Chemical Properties of PAHs

Polycyclic aromatic hydrocarbons, or PAHs, form a ‘group’ of compounds that consist of C and H atoms, grouped in the form of fused benzene rings (Figure 1). There are many PAHs that consist of alkyl-, nitro-, amino-, hydroxyl-substitutions. However, in the context of this chapter, the discussion is restricted to the unsubstituted PAHs. PAHs can contain two- to six-membered rings. In general, PAHs are lipophylic and this charateristic increases with increasing complexity of the compound (higher molecular weight). This property can be expressed by the partition coefficient between octanol and water (K_{ow}), where the lipophylic compounds have relatively high values (Table 1) (*1–3*) since they have low solubility in water. PAHs range from compounds that are semi-volatile to the more complex compounds that are essentially non-volatile and therefore associated with atmospheric particulate matter. This volatility can be expressed as the sub-cooled liquid vapour-pressure (P_L), where the vapour-pressure decreases with increasing complexity of the compound (Table 1). The ratio between the vapour pressure of the PAHs and their solubility (in water) is reflected in the Henry’s Law constant (H) (Table 1), where H decreases with increasing complexity of the PAHs. These aforementioned properties are important for the understanding of the occurrence and fate of PAHs in the environment as well as for the absorption capacity of PAH in lung membranes. As a rule of thumb, one could consider the two- and three-ring PAHs are 95% in the gas phase of the atmosphere; whereas four-ring PAH are 50% in the gas phase and 50% adsorbed to atmospheric particulate matter. The five- and six-ring PAHs are 95% in the particulate phase.

2. Emission Sources of PAHs

PAHs are the products of any combustion involving fossil fuels, or any other organic material, like vegetation. PAHs are also substances in fossil fuel, and therefore evaporation to the atmosphere after environmental exposure is another emission source. Diagenetic processes, in soils or sediment, may also produce PAHs but their significance as sources to the atmosphere is small. Fuel combustion is considered to be most important emission source of PAHs to the atmosphere (*4*). Combustion sources are numerous and the composition of PAHs depends on the organic material as well as on the temperature under which the combustion takes place (*5*). At low combustion temperatures larger molecules of high molecular weight are easily generated due to lower combustion efficiencies. There are therefore large uncertainties in the emissions factors from the different combustion sources. Nevertheless, there are indications that gasoline fuelled engines emit relatively more high molecular weight PAHs (more complex) than diesel vehicles (*6*). In comparison to these vehicle emissions, also wood combustion emits relatively more high molecular weight PAHs (Table 2)

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(*5–7*). The relative composition of isomers, such as fluoranthene versus pyrene or indeno[123cd]pyrene versus benzo[ghi]perylene, can add useful information upon the emission source, since the ratio between these compounds differ in the different sources ((*8*) and references therein; Table 3). However, the variation within a source often overlaps the variation among the different sources, due to combustion efficiencies. Moreover, after emission PAHs are subject to oxidation which may change the original composition (*9*). Therefore, caution should be taken with the use of the isomeric ratios for source apportionment purposes (*8*).

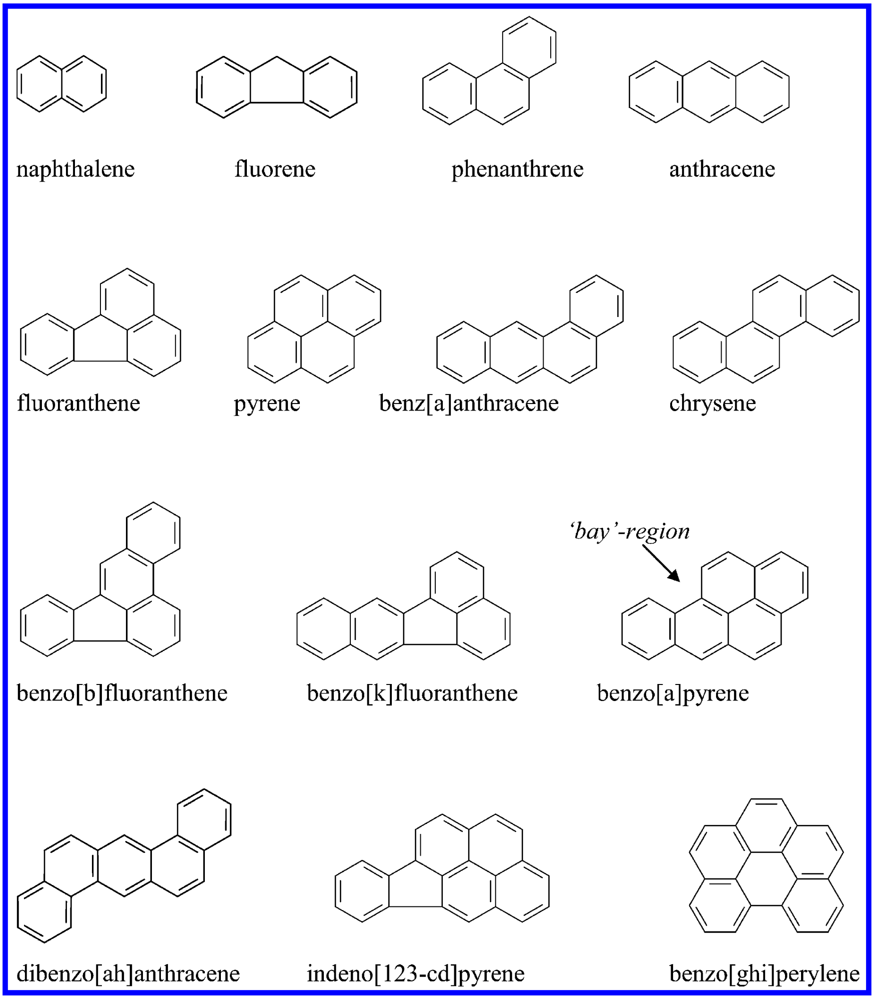

Figure 1. Molecule structures of some PAHs

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Table 1. Selected physico-chemical properties of PAHs at 278 K (*1–3*)

	Mol Wt.[a]	P_L[b]	*Log* K_{ow}[c]	*H*[d]
Fluorene	166	0.72	4.2	7.9
Phenanthrene	178	0.11	4.6	3.2
Anthracene	178	7.8×10^{-2}	4.5	4.0
Fluoranthene	202	8.7×10^{-3}	5.2	0.6
Pyrene	202	1.2×10^{-2}	5.2	0.9
Benz[a]anthracene	228	6.1×10^{-4}	5.9	0.6
Chrysene	228	1.1×10^{-4}	5.9	0.2
Benzo[b j]fluoranthene	252		5.8	0.15
Benzo[k]fluoranthene	252	4.1×10^{-6}	6.0	0.11
Benzo[a]pyrene	252	2.1×10^{-5}	6.0	0.045
Indeno[123-cd]pyrene	276			
Dibenz[ah]anthracene	278	9.2×10^{-8}	6.8	0.069
Benzo[ghi]perylene	276	1.4×10^{-8}	6.5	0.076

[a] molecuar weight (a.m.u.); [b] sub-cooled liquid vapour pressure (Pa); [c] logarithm of the octanol – water partition coefficients; [d] Henry's Law Constants (Pa m^3 mol^{-1})

Besides application of the relative composition of PAHs, based on the emission factors from the different combustion sources, some PAHs are exclusively related to the sources and therefore serve as organic tracers for these sources. In the case of (pine) wood burning, retene is directly related to this source, since it is not formed during fossil fuel combustion (*10*), whereas coronene is typically observed in fossil fuel combustion (Table 2). But also in this case, the combustion efficiencies and the type of fuel determine the emission rates.

Historical data on PAH emissions are often not available; however, evidence of increased fuel combustion in order to generate energy for anthropogenic activities is documented and related to the 'Industrial Revolution'. This has lead to an increase of environmental PAH concentrations since the 19th century in industrialized areas, such as the European continent. Although in the early years wood and charcoal from wood was often used as fuel. In the late 19th century and early 20th century low temperature coal combustion was the major source of PAHs. In the course of the 20th century other fuels, such as petroleum derived fossil fuels and gasoline, gained importance. PAH emissions from wood combustion (i.e. biomass burning), either for domestic heating or provoked by wildfires is an important source, although natural occurrence of wildfire does not appear to contribute significantly to the induced PAH emissions seen in the 20th century.

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Table 2. Examples of emission factors for PAHs from different combustion sources.

	Two-stroke mopeds (µg/km)	*Gasoline vehicle (µg/km)*	*Diesel truck (µg/km)*	*Wood pine (mg/kg)*
phenanthrene		0.9	12.2	0.7
anthracene		0.1	1.6	0.2
fluoranthene		2.0	13.0	4.0
pyrene		2.5	22.6	3.8
benz[a]anthracene	2.4	1.9	3.6	1.2
chrysene	1.7	3.8	9.9	1.1
benzo[b/k]fluoranthene	4.7	4.9	5.6	1.5
benzo[e]pyrene	1.8	2.0	2.6	0.5
benzo[a]pyrene	3.1	1.9	1.3	0.7
indeno[123cd]pyrene	2.3	0.5		0.5
benzo[ghi]perylene	4.3	4.7	1.6	0.4
coronene	4.8	1.1		
reference	(*5*)	(*6*)	(*6*)	(*7*)

The increase of atmospheric PAH emissions is reflected in remote Alpine lakes on the European continent. These lake ecosystems can be used as sentinel ecosystems to reconstruct the atmospheric pollution load (*11*, *12*) since these lakes essentially receive pollutant inputs from regional or long-range atmospheric transport and undergo little perturbation, either biologic or anthropogenic.

As shown in Figure 2, PAHs show different downcore profiles in the Alpine sediment samples from Eastern Europe and in the peat samples from northwestern United Kingdom (UK). In the former case, the concentrations increased after 1950 and started to decrease after 1990; whereas, these compounds started to increase in the 19th century. These differences may reflect the later industrial development in Eastern as compared to Western Europe. Thus, in the UK, the PAH concentration increased after 1820 with a peak concentration around 1925. This onset corresponds to the start of the Industrial Revolution in the UK. After 1960 the concentration decreased to low concentrations in the 1980s, which could reflect lower inputs from heavy industry and changes in combustion fuels for domestic heating as consequence of air quality legislation (*13*).

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Table 3. Example of isomer ratios of selected PAHs.[a] Source: (*8*)

		COMBUSTION SOURCE						
		Coal	*Diesel vehcle*	*Gasoline vehicle*	*Natural gas*	*Oil*	*Vegetation*	*Wood*
FL/FL+PY	*mean*	0.57	0.40	0.52	0.49	0.52	0.49	0.50
	sd	0.21	0.05	0.13	0.18	0.20	0.07	0.16
IP/IP+BGP	*mean*	0.48	0.19	0.32	0.32	0.36	0.35	0.42
	sd	0.29	0.13	0.11	0.17	0.14	0.04	0.18

[a] FL= fluoranthene; PY= pyrene; IP= indeno[123cd]pyrene; BGP= benzo[ghi]perylene.

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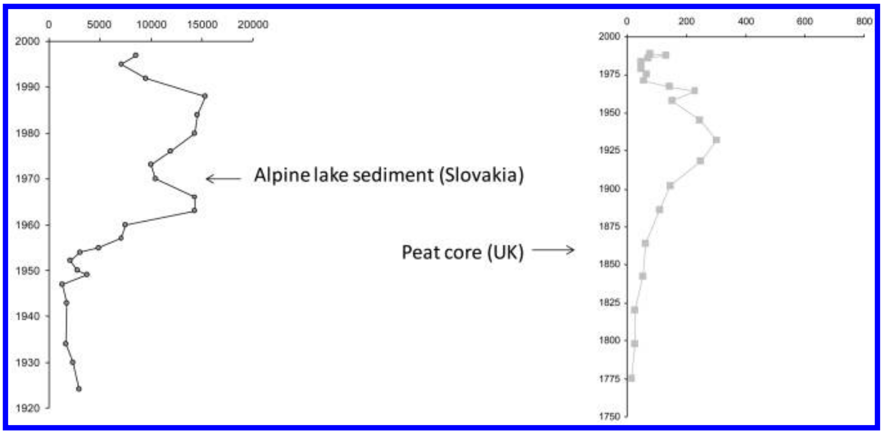

Figure 2. Downcore ΣPAH concentrations in a sediment core (ng/g) from the High Tatras, Slovakian Republic (46.163°N; 20.106°E) (12) and from a peat core (mg/g) in the flaxmere bog in northwestern UK (13)

The exact amount of PAHs emitted to the atmosphere is highly uncertain, due to variable emission factors, and incomplete inventories. Nevertheless, the European Environmental Agency (*4*) reports several national emission inventories and show that the total PAH emissions in 1990 were around 4,000 Mg while they were 1,500 Mg in 2005, which implies a decrease of 61% for the PAH emissions in about 15 years. This decrease was explained by 1) the decrease of coal combustion for domestic heating, 2) the improvement in the technologies for metal refining and smelting, and 3) the regulations on emissions in road transport (*4*). On the European continent, the major emission source of PAH is ‘residential’ (50%; Figure 3) which mainly means combustion of fuels for domestic heating. The other main sources: energy production, waste, agriculture, industrial processes, and road transport, have an almost even share of the other 50%.

Two of these emission sources, ‘residential’ and ‘road transport’, are the most relevant ones concerning human exposure. In areas were wood is readily available and the winters are cold, such as northern countries and rural areas, biomass burning for domestic heating is more practiced than in urban areas or in areas with a milder climate. On the other hand, road transport and industrial activities are denser in large urban areas. Therefore the population living in these urban areas is more exposed to PAHs that are emitted from traffic or industrial sources, while the population in rural areas is more exposed to emissions from biomass combustion.

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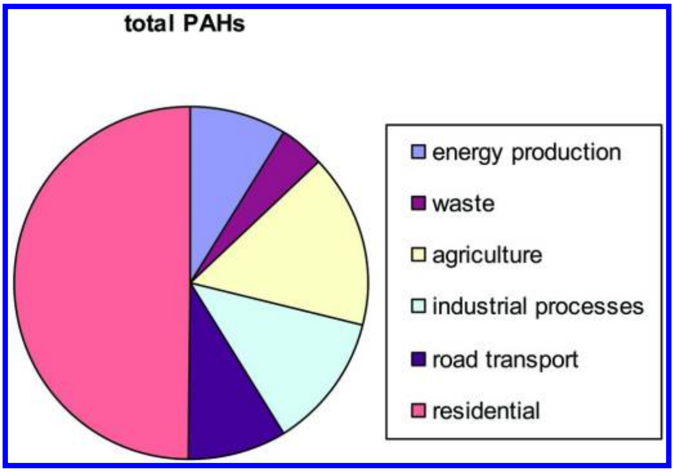

Figure 3. European emissions of PAHs in 2009 by sector group (4).

3. Atmospheric Distribution and Fate of PAHs

3.1. Atmospheric Lifetime

Most PAHs enter into the environment by combustion emission to the atmosphere. These combustion processes generally produce particles with aerodynamic diameter less than 1 µm (*14*). As temperatures decrease rapidly in small distances from the combustion source the gas-phase compounds polymerize and condense to form polycyclic aromatic compounds and eventually soot particles. The peak concentrations of PAHs in aerosols are typically between 0.01 µm and 0.5 µm in diameter. They may therefore be atmospherically transported over long distances. In this way they have become ubiquitous contaminants reaching remote areas; however, emission inventories indicate that atmospheric concentrations may have decreased in the recent decades due to estimated emission decreases.

In general, fluoranthene and higher molecular weight PAHs tend to bind to atmospheric particles while the lower molecular weight PAHs are present in the gas phase (*15*, *16*). As a consequence of partitioning, some PAHs are removed from the atmosphere by particle deposition, either dry particles or *via* precipitation, or by gas exchange. On the other hand, lower molecular weight PAHs are more susceptible to direct or indirect photodegradation than the particle bound higher molecular weight PAH (*9*, *17*). OH radical attack is the most important photodegradation pathway for PAHs in the atmospheric gas phase, but also the reaction with NO_2 is a substantial degradation pathway (*9*, *17*). During atmospheric transport these oxidation processes modify the levels and the composition of PAHs in an air mass. The atmospheric lifetimes for fluorene, phenanthrene, anthracene, and pyrene are estimated to be 22, 11, 1.5 and 26 days, respectively, while atmospheric half-lives using different molecular structure descriptors in a regression QSAR (Quantitative Structure-Activity Relationships) model were estimated to range between 1.5 day and less than one hour (Table

4, (*18*)). These calculations used the molecular structures and physico-chemical properties of the compound and environmental conditions, in combination with statistical tests. However, the protective properties of atmospheric particles, including soot particles, substantially extends the real atmospheric lifetime of particle bound PAHs (*9*).

Table 4. Atmospheric half lives of some PAHs (adapted from (*18*))

	Atmospheric half life values (h)	
Name	*Average*	*maximum*
Fluorene	37.2	67.6
Anthracene	1.1	1.7
Phenanthrene	11.0	20.0
Fluoranthene	11.2	20.4
Pyrene	1.3	2.0
Chrysene	4.4	7.9
Benz[a]anthracene	2.0	3.0
Benzo[b]fluoranthene	7.9	14.5
Benzo[a]pyrene	0.7	1.1
Benzo[ghi]perylene	1.8	3.2
Dibenz[ah]anthracene	2.3	4.3

3.2. Gas and Particle Partitioning of PAHs

Since most of the atmospheric PAHs are related to incomplete combustion, there is a direct relationship between PAHs and soot particles. Soot is also produced by incomplete combustion in fossil fuel and biomass burning. Like PAHs, soot occurs ubiquitously and can account for about half of the carbonaceous particles in the atmosphere. Structurally, soot, or sometimes referred to as black carbon (BC), may be differentiated between soot-carbon (small particle size; SC) and char/charcoal. The former originate during the condensation of hot combustion gases involving free radical reactions of acetylene species leading into PAH, macro PAH, and SC. Conversely, charcoal originates from incomplete combustion of plant tissue and diagenesis (*19*) and always contains a core of unburned biomass material. During the past decades, studies of SC as a strong sorption matrix has received increasing attention (*19–21*). Adsorption onto SC has been shown to be significant for the overall atmospheric transport of PAH to European alpine areas (*22–24*).

The exchange of PAHs from the gas phase to a surface, *e.g.* atmospheric particles, soil, water, vegetation or other surfaces, is controlled by the affinity of the compound to this surface. The ratio of vapour pressure to water solubility can

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be used as a prediction of partitioning between the atmosphere and water surface (Henry's Law; H constant). In many model calculations, the ratio between PAH levels in octanol and water, the octanol-water partition coefficient (K_{ow}), is used as a reference for the distribution of PAH in organic material (*2*). Consequently, the expression H/RT (C_{air})/C_{water}) and K_{ow} ($C_{octanol}/C_{water}$) provide the octanol-air partition coefficient (K_{oa}),

$$K_{oa} = K_{ow} RT / H$$

which can be used as the indicator for the distribution of PAH between the atmosphere and particle surfaces. Since H is temperature dependent, K_{oa} is temperature dependent as well.

The significance of soot carbon for atmospheric transport and particulate-gas partitioning of PAH has been assessed in several studies (*19–25*). This exchange is based on the particulate-gas partition coefficient K_p

$$K_p = C_p / (C_g \text{ x TSP})$$

where C_p and C_g are the concentrations in the particulate and gas phase, and TSP is the concentration of total suspended particulate matter in the atmosphere, respectively.

Usually there is a significant linear fit between K_p and the subcooled liquid vapor pressure (P_L; (*25*)) of PAHs. Organic matter plays an important role in the particle/gas partitioning of these compounds ((*25*) and references therein), which can be described by the following equation:

$$\text{Log } Kp = \log Koa + \log f_{OM} - 11.91 \qquad [1]$$

where K_{oa} is the temperature corrected octanol-air partitioning coefficient. Log K_oa = log K_{ow} x RT/H, where K_{ow} is the octanol-water coefficient, R is the gas constant, T the mean air temperature and H the temperature-corrected Henry's law constant.

However, when applying the fraction of organic matter (f_{OM}) to the model calculations there is often an underestimation of the predicted K_p, especially in remote areas. This underestimation can only be corrected by using unrealistically high, f_{OM} values. Notwithstanding, a general agreement between predicted and measured K_p is observed when both organic matter absorption and soot-carbon adsorption are included in the model (see equation below).

$$K_P = \frac{f_{OM}\, MW_{OCT}\, \gamma_{OCT}}{\rho_{OCT} MW_{om} \gamma_{OCT} x10^{12}} \cdot K_{oa} + f_{EC} \frac{a_{ec}}{a_{ac} \text{ x } 10^{12}} K_{sa}$$

where the expression

$$\boxed{\frac{f_{OM}\, MW_{OCT}\, \gamma_{OCT}}{\rho_{OCT} MW_{om} \gamma_{OCT}\, x10^{12}} \cdot K_{oa}}$$

is the relationship between K_p and K_{oa} as described in its simplified form in equation [1], assuming γ_{OCT}/γ_{OM}, MW_{OCT} /MW_{OM} to be equal to 1 and ρ_{OCT} to be 0.820 kg L^{-1}. f_{EC} is the fraction of elemental carbon in atmospheric particles, which was estimated to be less than 5% in rural and remote sites (*14*), a_{ac} is the surface area of active carbon, a_{ec} is the specific surface of elemental carbon and 10^{-12} is a factor for unit correction. Assuming that the ratios γ_{OCT}/γ_{OM}, MW_{OCT}/MW_{OM} and a_{ec}/a_{ac} are equal to 1, it is possible to predict K_p values from f_{OM} and f_{EC} (Figure 4).

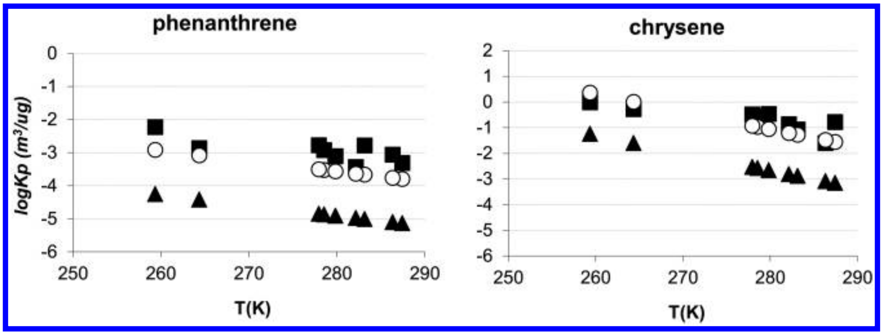

Figure 4. Measured and predicted Kp values (m³/µg) in the atmosphere in the remote Alpine station Skalnate Pleso (High Tatras): measures (squares); predicted from K_{oa} (triangles); predicted from K_{oa} and K_{sa} model (circles). Source: (24).

3.3. Occurrence of PAHs in the Ambient Air in Rural and Urban Areas

As mentioned earlier, PAHs occur both in the gas and particulate phase of the atmosphere, which depends on the physico-chemical properties of the compounds, the composition of the particle matrix and the meteorological conditions. Besides this partitioning, the emission source, its emission strength (both in terms of quantity of 'sources' as well as combustion efficiency), and meteorological conditions determine the atmospheric PAH concentrations. Generally, the atmospheric concentrations decrease exponentially with distance from the emission source, due to dispersion and dilution with ambient air (*26*), to more homogeneous background concentrations. It is obvious that wind speed and direction affects this dilution of ambient concentrations (*27*). However, generally, remote areas show the lowest PAH concentrations, followed by rural areas and urban areas (Figure 5) (*24*, *28*), due to the larger distance from potential emission sources. The difference can be one or two orders of magnitude, which also suggests differences in human exposure to these compounds in different areas. In certain areas, after initial PAH emissions, the landscape and high frequency of anti-cyclonic weather conditions decrease the dilution effect, resulting in high ambient air background concentrations. This is the case in many mountain valleys and other areas with stagnant conditions. Especially in winter and during the night, when thermal inversions are more frequent and the combustion of fuel (fossil and/or non-fossil) is generally more intense. Under these conditions, the air pollution is concentrated in a thin air layer at ground level. An example of such an area is the Po valley in Northern Italy (Figure 6). Strong thermal inversions in winter in combination with an increase of biomass burning results in

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much higher PAH background concentrations in the rural areas than observed in urbans area such as the densely populated area of Barcelona (Figure 7 and Figure 8) where sea-breezes can disperse the local contamination. In rural areas the PAH concentrations are low in summer ($\sum$PAH$_{part.}$~0.2 ng/m^3), but high in winter ($\sum$PAH$_{part.}$~13 ng/m^3. It was estimated that biomass burning contributes 30% to 70% of the ambient air PAHs in winter, while this contribution was insignificant in summer (*29*). This example illustrates that in addition to knowledge of emission sources, adequate monitoring of ambient air concentrations and information on meteorological conditions are necessary for an accurate risk assessment of PAH exposure to humans.

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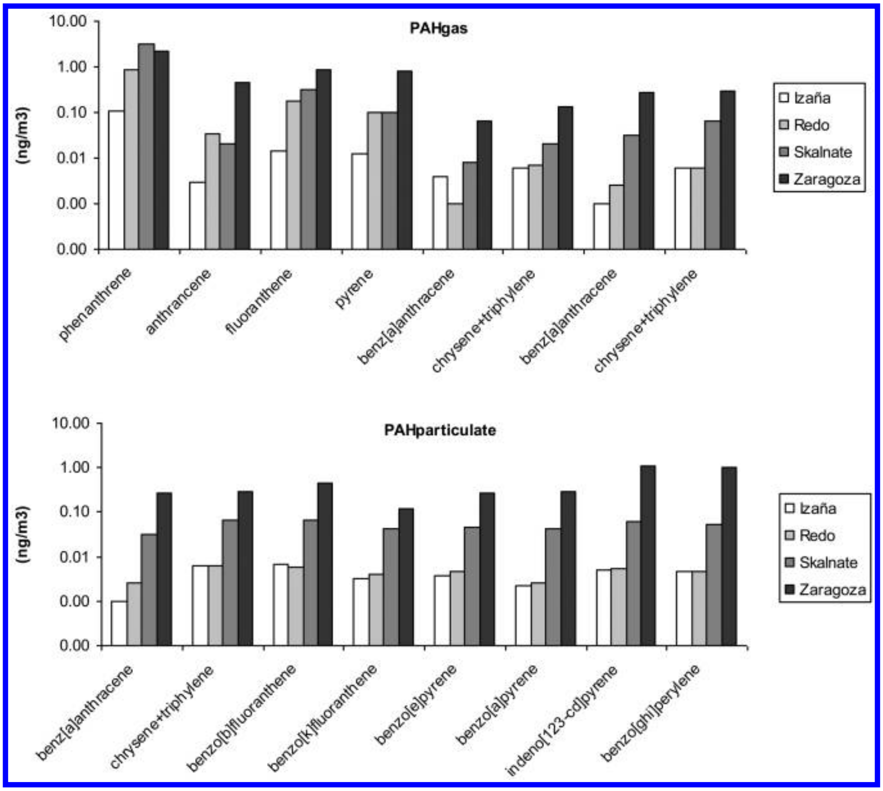

Figure 5. Ambient air PAH concentrations (ng/m³) in the gas and particulate phase in Izaña (remote; Canary Islands), Redo (remote southern Europe), Skalnate (remote, central Europe) and Zaragoza (urban, southern Europe). (Sources: (24, 28)).

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Figure 6. Thermal inversion in the semi-rural area of Northern Italy and the accumulation of air pollution in a thin layer, especially in the cold period when biomass burning for domestic heating and litter removal from fields and gardens is practiced (foto: November 2008).

Figure 7. Thermal inversion in the urban area of Barcelona and the accumulation of air pollution in a thin layer during the colder periods in the year (Foto: November 2009).

Conventional collection of gas and particle-bound PAH in ambient air is performed by passing an air through an adsorbent and collecting the aerosols on filters after low or high volume sampling (normally 12 or 24 hours). Samples are extracted in by organic solvents and analyzed on sensitive instruments, such as a gas chromatograph coupled to a mass spectrometer (GC-MS). Figure 8B (*30*) shows that the upper cut-off of the collected particles on the filter is of minor importance for the analysis of PAHs, since almost all PAHs are related to the smallest cut-off (PM_1; all particles with an aerodynamic diameter less than 1 µm). In fact, in areas close to an emission source PAHs are normally distributed in the particle range between 0.04 – 0.14 µm, while this particle size range increase slightly to 0.14 – 1.72 µm at larger distance from the source (*31*). These values are in agreement with the peak concentrations of PAHs observed in urban areas of Barcelona which were found to be predominantly in the particle size of < 0.5 µm (*32*).

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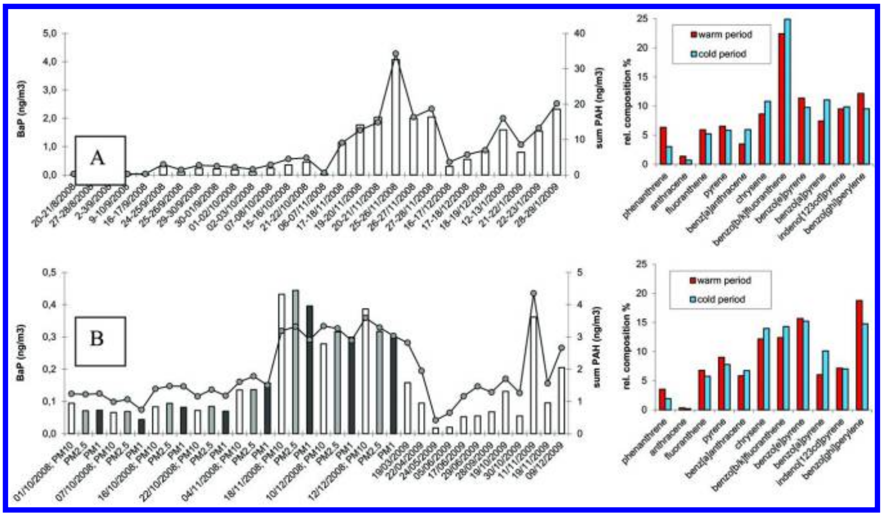

Figure 8. A. ΣPAH particle phase concentrations (ng/m^3; grey dots connected with lines) and benzo[a]pyrene (BaP) concentrations (ng/m^3; bars) in PM$_{10}$ from summer 2008 to winter 2009 (left) in a semi-rural background site in Northern Italy. On the right the relative composition of PAHs is shown (29). B. ΣPAH particle phase concentrations (ng/m^3; grey dots connected with lines) and benzo[a]pyrene (BaP) concentrations (ng/m^3) in PM$_{10}$ (white) PM$_{2.5}$ (grey) and PM$_1$ (black) in 2008 and 2009 in an urban background site in Barcelona, Spain. On the right the relative composition of PAHs is shown (30).

Although the conventional method offers accurate PAH concentrations, they often do not allow observation of the processes that influence the ambient air concentrations, such as changes in meteorological conditions or source emissions. Alternative analytical methods, such as direct filter introduction-thermal desorption (Figure 9; (*33*)), allow the sampling and analytical time to be reduced to a few hours, but still offer retrospective evaluations of the air quality concerning these toxic compounds. Nevertheless, the strong relationship between PAHs and soot carbons can be used as a first approach to evaluate the levels of PAH contamination. Relatively fast methodological procedures exist for the quantification of soot carbon (or black carbon; BC equivalents) in aerosols. These methods are based on optical techniques, where the light transmission and reflectance with respect to the aerosols on a filter are measured. The measured absorbance of light is related to the BC mass. The optical methods, such as the multi-angle absorption photometer (MAAP) and the Aethalometer, offers the analysis of BC in almost real-time (minutes). The determination of the optical determination of BC should be in agreement with other, more conventional measurements, such as those from thermal-optical methods. Although conflicting results have been reported in the past (*34*) related to method conditions, sites, and particle properties, the results are within acceptable uncertainties near the emission sources. An example of the comparison between BC and PAH in the ambient air PM is shown in Figure 9. A two-day sampling campaign with 3 hour

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sample resolution under contrasting meteorological conditions show that BC and particle bounded benzo[a]pyrene (r^2 = 0.94) have very similar temporal trends (*35*). It also illustrates that the concentrations of both parameters can change within a factor of five in 3 hours, due to the increase of emissions in the afternoon and calm wind conditions.

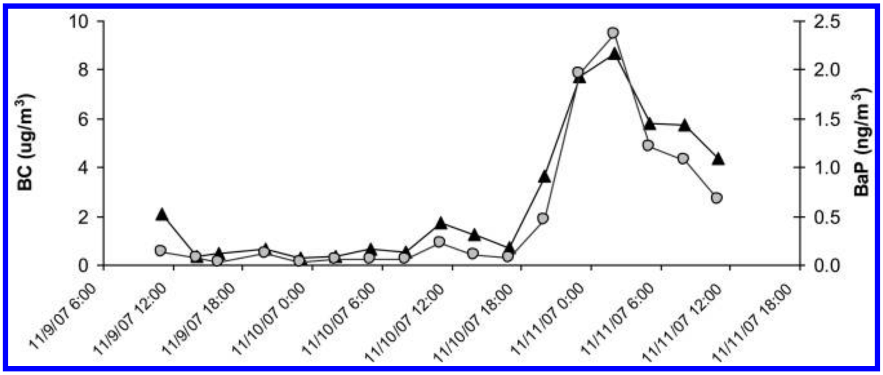

Figure 9. BaP (black trangles) and BC (grey dots) concentrations at 3 hour sample resolution in a rural area in Northern Italy during a North-Föhn event that finished in the morning of 10 November. After that the air pollution is build up again. (Source: (34))

In large urban areas, where vehicle emissions are a major emission source, the PAH concentration decrease with distance from busy streets. This decrease is in the same range as those observed for ultra-fine particles (<0.1 µm) (*26*) and illustrates the strong relationship near sources between these type of particle and related contaminants, such as PAHs and soot carbon. Hourly BC analyses that have been performed since 2009 in the urban background atmosphere in Barcelona show a daily cycle with peak levels around 7:00h and 19:00h due to traffic rush hours. Interestingly, these peaks are in contrast with the general particulate matter (PM_{10}) fraction concentrations that have their peak levels around midday (*36*). This difference between BC and PM is important, since it indicates that PM does not automatically reflect the BC, and thus probably PAH exposure loads in the urban area.

Recent development of micro Aethalometers that operate with small air fluxes and at minute-scale temporal resolution has increased insights into BC source apportionment and its temporal trends, especially in complex urban areas, where the sources can be multiple and the source strength can vary from site to site. A micro Aethalometer was used with a 5-minute sampling resolution to observe the spatial and temporal BC variation (and presumable particle-bound PAHs) on sidewalks along traffic intensive streets and nearby public outdoor areas, such as a park, a schoolyard and exhibition area in Barcelona. Very calm wind condition (wind speed <0.5 m/s) minimized the influence of wind speed on the results. Figure 10 shows the BC concentrations and the track of the sampling during this exercise. The highest concentrations (BC ~10 μg/m^3) corresponded to the sidewalks in the busy streets (~ 2500 vehicles per hour), while the lowest concentrations (~ 3 μg/m^3) corresponded to the sites farthest away from the traffic, *i.e.* measurements done at the playground, schoolyard, exhibition area, and at altitude. These BC concentrations correspond to estimated benzo[a]pyrene concentrations of ~ 3 ng/m^3 on the sidewalks in busy streets and ~ 0.3 ng/m^3 in the urban background sites. From this exercise one can observe that the exposure to BC, and presumably particle-bounded PAHs, vary significantly with distance from the potential emission sources. These differences are very important when evaluating the human health effects after exposure to the ambient air.

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4. Biological Activity

Continuous exposure to airborne pollution represents a risk of cardiovascular and respiratory diseases and lung cancer (*37*). Mortality in cities with high pollution load exceeds that observed in relatively clean areas, and improvements in urban air quality results in reduction of mortality by respiratory and cardiovascular illnesses (*38*). Moreover, chronic exposure to ambient air pollutants has been adversely associated to birth outcomes and infant health and development (*39*, *40*). There is increasing evidence that the ambient air particle-bound PAHs are relevant to evaluating health risks of poor health quality (*41*). In fact, emitted pollutants do not have borders in the outdoor air and their presence is only controlled by emission sources.

Inhalation is the major exposure pathway for air pollution to humans. However, the penetration in the respiratory system and the deposition in the lungs depend for example on the respiration frequency, the pause between inhalation and exhalation, size (diameter) of the particle, as well as the physico-chemical property of the contaminant. Larger particles (5- 10 μm) will more easily impact the walls of the upper track, while the smaller particles (0.5 – 1 μm) penetrate into the bronchioli and alveoli (Figure 11). Only a small part of the inhaled particles will eventually deposit in the lung, while the majority of the particles (and pollutants) are exhaled again. The efficiency of particles deposited in the deepest parts of the lung is highest for the particle around 0.02 and 2 μm diameter, while the efficiency is much lower for particle above and below this range, as well as the ones around 0.1 μm (*42*). The lung deposition of the small particles is of concern for the human exposure to PAHs since these pollutants are related to this particle fraction. Nevertheless, for the uptake in the blood and for the exposure to other organs, the contaminants still have to pass the lung membranes. Membranes in the lungs are like a lipid compartment between two aqueous compartments (lung liquid and blood). PAHs are lipophyllic (hydrophobic; high K_{ow}) which makes them diffuse rather easily to the membrane, but after that they leave the membrane slowly (*43*). The result is that especially the particle-bound PAHs may accumulate in the lung membranes and have long ‘residence’ times (weeks) before they are removed even when ambient air concentrations are rather low.

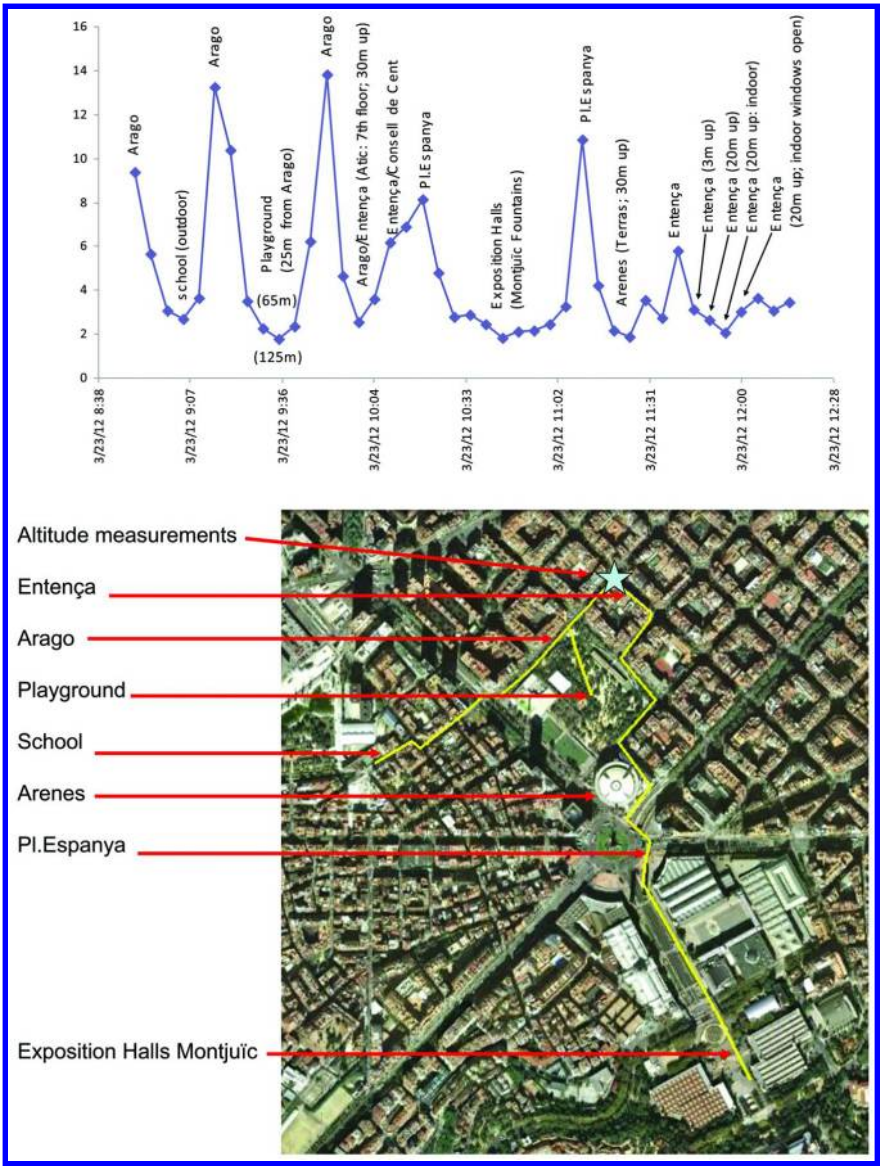

Figure 10. BC (μg/m³) concentrations at 5-minute time resolution along the sidewalks of a busy street in Barcelona and public outdoor places in Barcelona (March 2012).

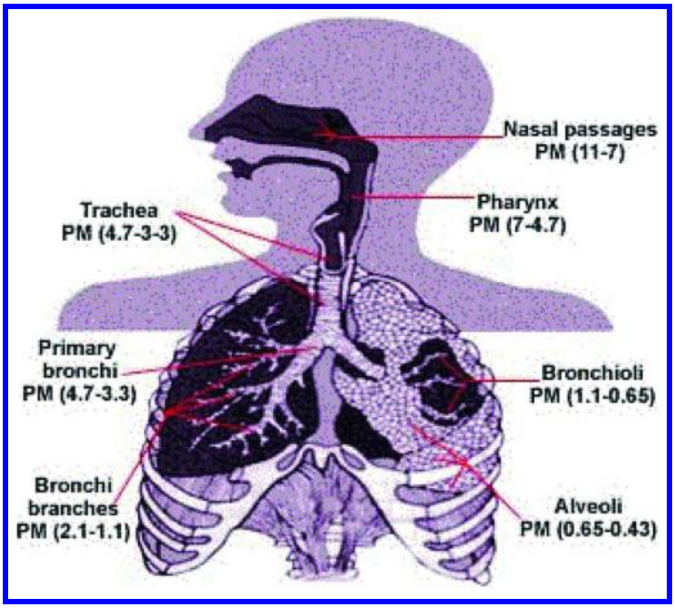

Figure 11. Schedule of human respiratory system and the size distribution of penetrated particles.

PAHs constitute a substantial fraction of the toxicity associated to particles in ambient air, due to their characteristic carcinogenic and mutagenic properties (*44*, *45*). In the late 1970s, the United States Environmental Protection Agency (U.S. EPA) listed 16 PAH as 'Priority Pollutants' (Figure 1). This list was later adopted by the European Union. Moreover, the CAFE directive of the European Union establishes an annual limit value of 1 ng/m^3 for the occurrence of benzo[a]pyrene in atmospheric particulate matter (*46*), although others have suggested setting the limit value to 0.1 ng/m^3 (*44*). These limit values do not at all guarantee that PAHs will do no harm since no 'safe' level can be recommended for benzo[a]pyrene and other PAHs due to their carcinogenicity (*38*). Moreover, complete removal of PAHs from the atmosphere is impossible, and therefore limit values should be established to control their ambient air levels and possible health risks. A first step in establishing such limits is a dose-effect relationship. Evidence for these relationships come partly from data that were extrapolated from adverse health effects of coke-oven workers in the mid-twentieth century, where an increased risk of death from cancer of the respiratory system was demonstrated (*38*). Other data was obtained from animal experiments, where cancers were observed after exposure to high doses of benzo[a]pyrene. Unit risks for benzo[a]pyrene (lifetime risk per ng/m^3 BaP) are summarized in *44* and show large variations between the values, ranging from 0.3×10^{-6} to 430×10^{-6} per ng/m^3 BaP. These values indicate that a lifetime exposure to 1 ng/m^3 BaP results in one extra cancer case in 3,000 or 3,000,000 individuals exposed. The WHO (*38*) recommended an intermediate risk unit of 0.9×10^{-6} per ng/m^3 BaP, which indicates one cancer case per 10,000

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individuals exposed for a lifetime to 1 ng/m^3 BaP. In this way, a lifetime exposure to 0.1 ng/m^3 would lead to one cancer case per 100,000 individuals exposed.

The data obtained from experimental studies on PAH is not conclusive, neither is this data ideal for a quantitative risk assessment. Moreover, for many of the PAHs the toxicity data is non-existent. Nevertheless, many PAHs are classified by the IARC (International Agency for Research on Cancer) as human carcinogens or probable and possible human carcinogens, based on their appearance in products, such as coal tar, soot and tobacco smoke, or based on the molecular structure in relation to toxicity tests. Already during the eighteenth century cancers were observed in chimney cleaners due to soot exposure, while in the early twentieth century the relationship between cancer and occupational exposure to coal tar and soot was noted. For a PAH to be carcinogenic, or have mutagenic properties, the compounds must consist of at least four rings. These rings should be configured in such a mode that the molecule contains a ‘bay’- or ‘fjord’-region (see Figure 1 for benzo[a]pyrene).

The PAHs effect in different ways the processes that are involved in carcinogenesis, *i.e.* 1) mutations by altering the gene expression (initiation phase), 2) proliferations of cells (promotion phase) and 3) tumor progression towards malignancy and autonomous cell growth (progression phase) (*43*). Many PAHs act both as initiators and promoters of cancers. The mutagenic property is linked to the metabolic conversion of PAHs to reactive intermediates, such as epoxi-PAHs, that can form adducts with the DNA and inducing mutations (*43*). Another essential step of the toxic effects of different PAHs is their binding to the aryl hydrocarbon receptor (AhR), a key regulator of phase I and II metabolic enzymes (*47*). The presence of ‘bay’- and ‘fjord’-regions in the molecular structure increases their carcinogenic potency. Therefore, it is expected that the AhR affinity could be a good indicator for carcinogenicity. The ectopic activation of the AhR controlled genes is also known as “dioxin-like activity”, since dioxins are among the most powerful known agonists (*48*). Therefore, assays to detect AhR activation and subsequent signal transduction are useful to monitor pollution loads in environmental samples (*49*). A variety of aryl hydrocarbon-responsive reporter assays based on mammalian cell lines (*50*) or genetically modified yeast strains (*48*) have become common tools to detect AhR-binding activities in a variety of samples and matrices (Figure 12). Single cell (either vertebrate or yeast) bioassays do not provide a chemical characterization of the hormone-receptor ligands, but their low cost and easiness of handling makes them a first choice when testing large numbers of samples or compounds.

Based on the molecular structure and evidence from toxicity tests the PAHs can be classified on their toxic potency. A practical tool to estimate this toxic potency of a mixture of PAHs in atmospheric samples is the application of the Toxic Equivalent Factors (TEFs) with benzo[a]pyrene as reference compound. In the past different toxic equivalent factors have been presented. As an example, the U.S. EPA (*51*) separated the PAHs in carcinogenic or non-carcinogenic PAHs, by giving a TEF value of ‘0’ to the non-carcinogenic PAHs and a TEF = 1 to benzo[a]pyrene as being most toxic. Then other PAHs were given values in the range between ‘0’ and ‘1’ (Table 5). The fact that the values are rounded in orders of magnitude illustrates the existence of the large uncertainties in the ‘real’ toxic potency, which depends on different factors, such as exposed concentration, sensitivity of the organisms, the target organ and toxic effect. However, the application of TEFs in combination with the ambient air PAH concentrations are useful to estimate the effective toxicity of PAHs in ambient air. For example, dibenzo[a]h]anthracene has the same TEF as benzo[a]pyrene, however the ambient air concentration of this later compound is easily an order of magnitude higher, which decreases the exposure risk of dibenzo[ah]anthracene with respect to benzo[a]pyrene. Figure 12 illustrates that the best correlations between the measured biological activity of PAH (determined in a yeast-cell assay (*52*)) and the measured ambient air PAH concentrations are obtained after the application of the toxic equivalent factor. The figure also demonstrated that at ambient air concentrations ranging from a few pg/m3 to a few ng/m3 the response of the Ah-Receptor is almost linear. There is no threshold in dose-response for PAH which is in accordance with carcinogenic 'character' of these compounds. Even at low ambient air concentrations the PAHs have effects on biological systems, including humans. Therefore it is important to minimize the emissions of these compounds in order to reduce human health risks.

Table 5. Toxic Equivalent Factors for PAHs (*51*).

	EPA 1993
Benzo[a]pyrene	1
Benzo[a]anthracene	0.1
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.01
Chrysene	0.001
Dibenz[a,h]anthracene	1
Indeno[1,2,3-c,d]pyrene	0.1

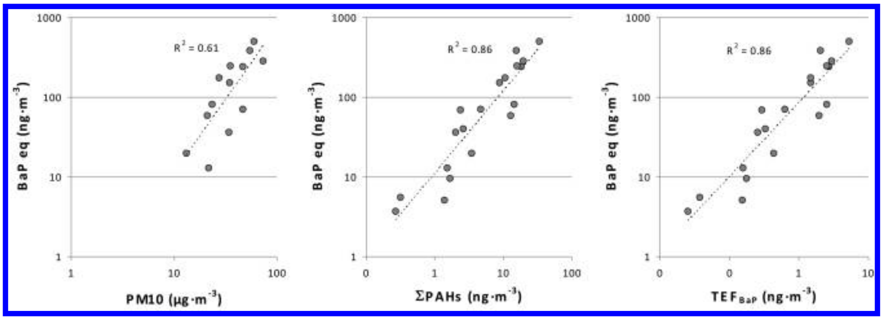

Figure 12. Correlations of measured PM10 (µg/m3), ΣPAH (ng/m3) and Toxic Equivalent (EPA) (ng/m3) versus the 'dioxine-like' activity (BaPeq ng/m3) determined by the RYA bioassay in the PM_{10} samples collected in Northern Italy (see Figure 8A).

5. Conclusions

PAHs range from semi-volatile to almost entirely particle bound. This adsorption to atmospheric particulate matter extends the atmospheric lifetime of PAHs. This allows them to be transported via the atmosphere to remote areas. However, the important emission sources for PAHs are situated relatively close to human settlements; and the atmospheric lifetime is therefore less relevant. Many humans are exposed to relatively fresh emissions from fuel combustion sources. The PAH concentrations are generally higher in winter time due to increased emissions (energy demand) and stable atmospheric conditions (in certain areas). These circumstances increase the overall background concentrations of PAH and can result into background concentrations that exceed the annual limit value of 1 ng/m^3 for benzo[a]pyrene. Meteorological conditions, such as wind speed and wind direction, have large influences on PAH exposure levels. Especially in urban areas, the concentrations decrease rapidly with distance from the emission source, such as busy streets. Nevertheless, large part of the population is constantly exposed to substantial PAH levels.

It has been recognized for many years now that PAHs and PAH-related products, such as soot and coal tar, are carcinogenic environmental pollutants. Models and assays exist to evaluate their biological activity. Nevertheless, there is still a lack of knowledge on the toxicological mechanisms behind the exposure in humans under environmental conditions, and in specific for inhalation of ambient air PAHs.

The tools to safe-guard air quality for these compounds is not sufficient. To date, the legislation on the ambient air quality control focuses only on the level of benz[a]pyrene, while other compounds that also demonstrate biological activity are not measured. The sampling strategies and analytical procedures are cost- and time-consuming, which results in few monitoring stations and an often incomplete sampling-time coverage. Therefore in many areas there are large uncertainties on the ambient air concentrations and the source apportionment of these pollutants. PAH concentrations are normally higher near the combustion sources. The presence of these sources, *e.g.* combustion engine vehicles in a busy street, is indicative of higher PAH concentrations. Alternative methods exist to quantify PAHs in ambient air at higher time resolution. The abundance of PAHs in ambient air could estibmated using on-line analysis of black carbon, since PAHs correlate with this more easily measured pollutant.

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Chapter 5

Polycyclic Aromatic Hydrocarbon (PAH) Residues on Tobacco Smokers' Hands: Potential Vector for Exposure to Non-Smokers

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Polycyclic aromatic hydrocarbons (PAHs) have previously been quantified in mainstream and sidestream environmental tobacco smoke (ETS) yet there is a paucity of data quantifying these contaminants in third-hand smoke (THS), the residue adhering to the smoker and smoking environment after smoking. The purpose of this study was to evaluate concentrations of 19 individual PAHs in THS adsorbed to smokers' hands and to assess the potential for exposure to nonsmokers. Smokers' hands were wiped with alcohol-soaked cotton balls and compared to non-smokers' hands wiped the same manner. Smokers' hands had significantly higher PAH levels ($p<0.05$) than non-smokers for eleven of the 19 PAH compounds. After smoking one cigarette, up to 4% of some PAHs emitted in sidestream smoke may adsorb onto a single hand as THS residue. PAHs adsorbed to smokers' bodies as THS residues may represent a potential source of exposure to non-smokers.

Introduction

The burning of tobacco products produces environmental tobacco smoke (ETS) comprised of both gaseous and particulate phases containing over 4000 known chemicals (*1*). The term ETS refers to both the smoke exhaled by the smoker, referred to as mainstream smoke, and that released passively in the

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burning process, termed sidestream smoke. Passive exposure to ETS, commonly referred to as second hand smoke, has conclusively been linked to a myriad of deleterious human health effects including respiratory issues in children [e.g., (*2–4*)]. An additional concern arising from ETS, third hand smoke (THS), has recently attracted scientific scrutiny. The term THS, or residual secondhand smoke, is defined as the gaseous and particulate residue adsorbed onto smokers' clothing and/or skin, as well as any other surfaces, such as walls, carpets and furniture of indoors environments (*5*).

In the past decade, a handful of researchers have begun to evaluate THS with the aims of characterizing the chemical composition of the residue, assessing exposure risks and evaluating potential health implications. Much of this recent research has focused on either using nicotine as an indicator for THS in enclosed environments such as houses and cars [e.g., (*6–8*)], or has investigated the role of nicotine residues in THS as precursor in the formation of carcinogenic compounds such as nitroamines within indoor environments [e.g., (*9*, *10*)]. For example, Matt et al. (*6*) found significantly higher nicotine levels in dust, surfaces, and air from cars where smoking was permitted compared to levels in cars in which smoking was not permitted. Using nicotine residues from fingertips as tracers of THS exposure, Matt et al. (*7*) also found that non-smokers living in homes where smoking was allowed were exposed to nicotine from THS that lingered months after smokers vacated the homes.

These recent data support the notion that THS impairs indoor air and surface quality even long after active smoking has ceased. In the United States, toughening indoor smoking laws has undoubtedly led to reductions in exposure of these and other chemicals to non-smokers. However, Matt et al. (*8*) concluded that even limiting smoking to the outdoors contaminated indoor settings 5 - 7 times more than not smoking at all. In that study, parents who smoked outside were able to lower ETS contamination and exposure to their infants yet their efforts were insufficient to achieve levels of nicotine found in non-smokers' homes and exposures found in infants of non-smoking parents. They suggested that ETS may make its way into the home through windows and doors if cigarettes are smoked outside and through contaminated clothes, skin and dust carried into the home when cigarettes were smoked elsewhere. They suggested that skin, among other vectors such as air, surfaces and dust, should be considered in a comprehensive assessment of secondhand smoke residue.

Although quantifying nicotine levels is a relatively inexpensive and accurate method to identify THS residues within cars and other indoor environments (*6*), there are very few research studies characterizing the levels of other potentially harmful chemicals in THS, such as polycyclic aromatic hydrocarbon (PAHs). Studies over the past two decades have concluded that PAHs, a suite of chemicals produced from the incomplete combustion of carbon-containing materials, are present in mainstream and sidestream smoke [e.g., (*11–13*)] at concentrations as high as 2.9 and 6.8 μg/cigarette, respectively (*14*). Recently, by analysis of settled household dust, Hoh et al. (*15*) concluded that tobacco smoke-generated PAHs are a component of THS.

To date, assessment of PAHs levels adsorbed to smokers' skin and clothing as THS have not been studied. It is these THS residues that may represent a vector for

PAH exposure, especially to high-risk individuals such as infants who may come into contact with a smoker's skin or clothing. Because of this, we conducted this preliminary study quantifying PAH concentrations in third-hand smoke residues remaining on smokers' hands with the aim of assessing the significance of these contaminants to act as an exposure route to non-smokers.

Methods and Materials

Sample Collection

We employed dermal hand wipes, a simple method for the collection of adsorbed compounds from surfaces [e.g., (*16*)]. Participants were given an instruction sheet briefly outlining the steps to follow for the collection of samples, a vial of 5% isopropanol, a plastic bag of sterilized cotton balls, and a pre-cleaned glass jar. Participants were asked to wash their hands with soap and water and to dry their hands thoroughly prior to collection of a wipe.

For the control group (non-smokers, denoted NS), participants were asked to wipe a single hand, both front and back, using an isopropanol-soaked cotton ball. The cotton ball was placed in a sealed jar. For the treatment group (smokers, denoted S), following washing and drying of hands, one cigarette was smoked as per the smoker's personal preferences except that they were asked to hold the cigarette in one hand for the entire duration of the smoking process. After smoking, each smoker collected an isopropanol-soaked cotton ball wipe of the hand used. Smoking was performed outdoors under ambient conditions where factors such as wind speed, humidity, and air temperature were not controlled or recorded. In all, 170 cottons balls were collected from the treatment group and 160 cotton balls were collected from the control group.

Sample Extraction and Clean-Up

In a prior pilot study, analysis of single cotton balls used to wipe residues from a smoker's hand after one cigarette yielded individual PAH masses below instrumental detection. In this study, to increase our ability to detect PAHs at detectable levels, composite samples containing 10 cotton ball wipes were employed. Therefore, 17 samples from smoker's hands and 16 samples from non-smoker's hands were analyzed. In addition to the composited samples, three blanks, each containing 10 alcohol-soaked cotton balls, were extracted and analyzed.

Prior to sample extraction, a known volume of a d12-perylene solution was added to samples and blanks to act as a surrogate to assess analyte loss in the extraction and preparation processes. Samples and blanks were extracted with hexane using a Soxhlet extractor for 18 hours. After extraction, the solvent was reduced in volume using roto-evaporation and further concentrated to 2 mL under a purified N_2 stream. Extracts were cleaned-up using liquid-solid chromatography with alumina as the stationary phase and hexane as the mobile phase. The collected eluent was concentrated to 1 mL by evaporation under a N_2 stream. Prior to instrumental analysis, extracts received d10-fluoranthene as an internal standard.

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Instrumental Analysis

Nineteen individual PAHs (Table 1) were identified and quantified using a gas capillary chromatograph (Perkin Elmer Autosystem XL) and a mass spectrometer (Perkin Elmer TurboMass Gold) operated in the selected ion-monitoring mode. A 30 meter (0.25 mm internal diameter, 0.25 μm film thickness) 5% phenylmethyl silicon capillary column (DB-5; J&W Scientific, Santa Clara, CA, USA) was used to separate PAHs. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The injector and the capillary interface temperatures were 280 and 300 °C, respectively. Ten microliters of each sample was injected in a splitless mode. Each PAH was identified by its retention time relative to the retention time of mixed standard (Supelco Separation Techologies, Bellefonte, PA, USA) and confirmed by the abundance of the secondary mass fragment relative to the molecular ion. Quantification of individual PAHs was performed through the internal standard method using a five-point calibration curve. The mean surrogate recovery was 67% (standard error 6%; n=33). Concentrations were not corrected for surrogate loss. Blank based detection limits for most individual PAHs, defined as the mean concentrations plus three times the standard deviation of the mean, were 0.05 ng/sample.

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Results

Samples for both treatment (S) and control (NS) groups were analyzed to determine the mass of each PAH (ng) contained in a sample. Individual PAH compound masses were then divided by 10, the total number of wipes constituting a sample. Because each wipe represented the THS residue collected from a single hand, these values were expressed in concentration units of the mass of PAH per hand (ng/hand). Means, standard deviations, standard errors, medians, minimums and maximums for S and NS groups, expressed as ng/hand, were summarized (Table 1).

Mean concentrations of all nineteen PAHs were present above instrumental detection limits on S and NS hands (Figure 1). For each PAH, hands of smokers had higher mean concentrations (ng/hand) compared to concentrations on non-smokers' hands. For t-PAHs, the sum of all quantified PAHs in this study, values were 37 ng/hand for S compared to 11 ng/hand for NS (Table 1). The PAH profile of mean PAH residues on smokers' hands (Figure 1) was dominated by anthracene, phenanthrene, and pyrene. The PAH profiles between the S and NS groups were highly correlated ($r^2=0.69$; $p<0.05$).

Concentrations (ng/hand) of most PAHs were significantly higher for the S compared to NS groups. At a 90% confidence interval (those having p values <0.10), 16 of the 19 PAHs (except acenaphthene and 1-methylanthracene) were significantly elevated on smokers' hands compared to hands of non-smokers (Table 1). Eleven of the 19 PAHs (except acenaphthylene, acenaphthene, phenanthrene, 1-methylanthracene, pyrene, benzo[e]pyrene, benzo[b]fluoranthene) were significantly different at the 95% confidence interval (those having $p<0.05$; Table 1).

Table 1. Summary of PAH concentrations (ng/hand) from smokers (S) and non-smokers (NS).

	Mean		*Std Dev*		*Std Error*		*Median*		*Min*		*Max*			*Enrich-ment*
PAH Compound	*S*	*NS*	*S*	*NS*	*S*	*NS*	*S*	*NS*	*S*	*NS*	*S*	*NS*	*p-Value*	*Ratio*
acenaphthylene	0.80	0.19	1.78	0.16	0.20	0.05	0.35	0.29	ND	ND	7.60	0.37	0.09	4.3
acenaphthene	2.03	0.20	5.85	0.17	0.49	0.05	0.38	0.28	ND	ND	24.45	0.50	0.11	10.1
fluorene	0.66	0.19	0.71	0.19	0.16	0.05	0.32	0.17	ND	ND	2.51	0.67	0.01	3.4
phenanthrene	7.07	1.83	15.80	2.30	1.71	0.46	0.97	1.09	0.41	0.44	63.31	9.52	0.10	3.9
anthracene	9.95	1.58	19.49	1.16	2.41	0.40	1.74	1.38	0.42	0.48	77.45	4.97	0.05	6.3
1-methylanthracene	1.18	0.62	2.85	0.84	0.29	0.16	0.34	0.32	0.23	0.22	12.16	2.98	0.23	1.9
1-methylphenanthrene	1.20	0.51	1.95	0.33	0.29	0.13	0.36	0.42	0.25	0.23	8.26	1.54	0.09	2.3
fluoranthene	0.52	0.15	0.47	0.16	0.13	0.04	0.43	0.18	ND	ND	1.87	0.55	0.003	3.5
pyrene	3.41	0.38	8.47	0.21	0.83	0.09	0.75	0.34	0.14	ND	35.59	0.87	0.08	9.1
benzo[a]fluorene	0.34	0.23	0.12	0.12	0.08	0.06	0.34	0.31	0.15	ND	0.63	0.35	0.01	1.5
benzo[b]fluorene	0.36	0.22	0.34	0.06	0.09	0.06	0.25	0.24	0.20	ND	1.67	0.28	0.05	1.7
benzo[g,h,i]perylene	0.68	0.32	0.52	0.06	0.17	0.08	0.52	0.29	0.32	0.26	2.25	0.44	0.01	2.2
dibenzo[a,h+a,c]anthracene	0.63	0.38	0.31	0.13	0.15	0.10	0.55	0.32	0.35	0.28	1.53	0.66	0.004	1.6
indeno[1,2,3-cd]pyrene	0.82	0.33	0.65	0.07	0.20	0.08	0.52	0.29	0.35	0.27	2.67	0.48	0.004	2.5
perylene	1.57	0.71	1.58	0.50	0.38	0.18	1.07	0.49	0.47	0.30	7.10	1.75	0.02	2.2
benzo[a]pyrene	1.49	0.66	1.30	0.44	0.36	0.17	1.11	0.43	0.36	0.31	5.44	1.68	0.01	2.3
benzo[e]pyrene	2.16	1.29	1.89	1.49	0.52	0.32	1.26	0.44	0.30	0.20	6.29	5.09	0.08	1.7

Continued on next page.

Table 1. (Continued). Summary of PAH concentrations (ng/hand) from smokers (S) and non-smokers (NS).

	Mean		*Std Dev*		*Std Error*		*Median*		*Min*		*Max*			*Enrichment*
PAH Compound	*S*	*NS*	*S*	*NS*	*S*	*NS*	*S*	*NS*	*S*	*NS*	*S*	*NS*	*p-Value*	*Ratio*
benzo[k]fluoranthene	1.23	0.51	1.65	0.52	0.30	0.13	0.67	0.25	0.28	0.10	7.08	1.73	0.05	2.4
benzo[b]fluoranthene	0.98	0.51	1.69	0.43	0.24	0.13	0.50	0.30	0.29	0.27	7.18	1.76	0.14	1.9
t-PAHs	*37.06*	*10.81*	*52.30*	*5.88*	*8.99*	*2.70*								*3.4*

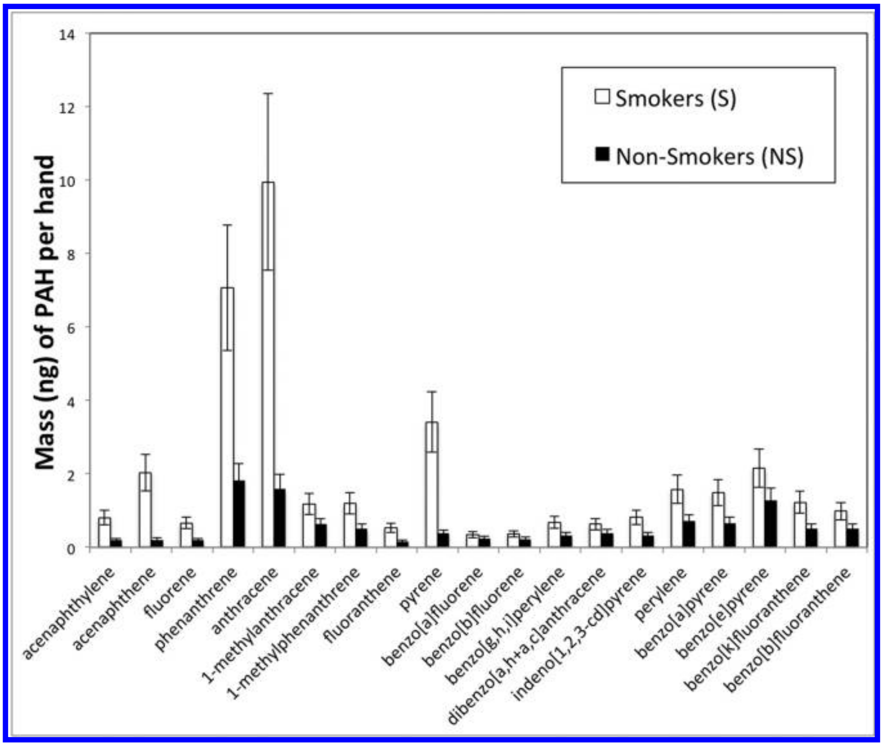

Figure 1. Mean masses of PAHs on smokers (after smoking one cigarette) compared to non-smokers hands. Error bars represent ± standard error (n=17 for S; n=16 for NS).

Discussion

Most PAH compounds were detected on the hands of both smokers (S) and non-smokers (NS). Detectable levels of PAHs for NS, although surprising, likely resulted from ineffective or no washing of hands prior to samples collection. For both S and NS, concentrations of PAHs (ng/hand) were highly variable, as denoted by the minimum and maximum values (Table 1). Moreover, standard deviations of the mean were extremely high, reflecting enormous variability in the concentrations of PAH residues on hands of both groups. This high variability (e.g., in such factors as wind, temperature, and humidity) was expected as smoking was performed under natural outdoor conditions. Because smokers were not asked to change their smoking habits, except to continuously hold the cigarette in one hand during the duration of the cigarette's burning, smoker-dependent variables including hand size (adsorptive surface area), duration of smoking, and rate and depth of inhalation (*14*) may influence PAH concentrations and ultimately be reflected in absorbed residues. Also, sidestream smoke has been shown to have significantly higher levels of PAHs than mainstream environmental tobacco smoke (*11*). If the smoker favors fewer, shallower drags as opposed to longer, deeper drags, more sidestream smoke may be emitted and lead to higher dermal PAH concentrations. Lastly, brand of cigarette may have an influence on adsorbed residues because PAHs concentrations and profiles vary with tobacco blends and processing (*13*, *14*, *17*).

An "enrichment ratio" for each PAH was calculated by dividing the mean concentration (ng/hand) of S by the mean concentration for NS. The ratio represents the additional loading of PAHs on the hands of smokers following the use of a cigarette (Table 1). Values ranged from 1.5 for benzo[a]fluorene to 10 for acenaphthene. When considering t-PAHs, smokers had 3.4 times more PAHs on their hands than non-smokers. Lower molecular weight PAHs (defined here as acenaphthylene to pyrene) had, on average, higher enrichment ratios (5±3) compared to higher molecular weight PAHs (define as benzo[a]pyrene to benzo[b]fluoranthene) having, on average, lower enrichment ratios (2.0±0.4). Preferential adsorption of lower molecular weights PAHs (having higher vapor pressures) onto hands of S versus NS may have implications for exposure and toxicity assessments.

NS are representative of only the ambient environment while S includes the additional contamination from smoking. The difference between the residues on S and NS hands can be solely attributed to the PAHs emitted from the consumed cigarette. The concentration of PAHs adsorbed to a smoker's hand from a cigarette was calculated (Table 2) using the mean concentration of PAH per hand of non-smokers subtracted from the mean concentration on the smoker's hand (Table 1). For significantly different PAHs ($p<0.05$), adsorbed residues ranged from 0.10 ng/cigarette for benzo[a]fluorene to 8.37 ng/cigarette for anthracene. Additionally, the sum all hand-adsorbed PAHs that were significantly ($p<0.05$) different from non-smokers hands, was 12.95 ng/cigarette.

Using a commercially available fine-cut tobacco product for their study, Moir et al. (*14*) analyzed thirty individual PAHs released from sidestream smoke using highly standardized, International Organization for Standardization (ISO) conditions and employing smoking machines. These data were coupled with our concentrations of PAH residues per cigarette to calculate the percentage of sidestream ETS that becomes THS on hands (Table 2). Percentages ranged from 0.03% for fluorene to 3.7% for perylene. While this does suggest THS residues may be a potential source for PAH exposure to non-smokers, its contribution is small in comparison to sidestream smoke. Additionally, one must consider that these values, though based on experimental data, are estimates due to the numerous factors that influence THS adsorption. However, considering these THS PAH residue data were based on samples collected under outdoor smoking conditions where some variables were not controlled, they may be underestimating the residues on smokers' hands. Also, THS PAH residues on a smoker's hand represent only a fraction of the total PAH reservoir of a smoker, compared to the total residue on all exposed skin (e.g., face and neck), hair and clothing. The smoker's hand may be the area of highest residues due to proximity to the burning cigarette, but other locations such as exposed skin and clothing may have significant THS PAH residue.

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Table 2. Concentrations of PAHs adsorbed onto smokers' hands from one cigarette (this study) compared to sidestream ETS.

	Concentration Adsorbed onto Hand (ng/cigarette) (This Study)	*Concentration in Sidestream ETS (ng/cigarette) (Data from Moir et al. (14))*	*Percent of Sidestream Smoke Adsorbed to Hand from One Cigarette*
fluorene	0.46	1429	0.03
anthracene	8.37	755	1.11
fluoranthene	0.37	699	0.05
benzo[a]fluorene	0.10	not analyzed	
benzo[b]fluorene	0.14	not analyzed	
benzo[g,h,i]perylene	0.37	44.7	0.82
dibenzo[a,h+a,c]anthracene	0.24	not analyzed	
indeno[1,2,3-cd]pyrene	0.49	41.7	1.17
perylene	0.86	23.6	3.66
benzo[a]pyrene	0.83	91.7	0.90
benzo[k]fluoranthene	0.71	25.8	2.76
t-PAHs (above)	*12.95*		

The values presented in this study represent the PAH residues after smoking one cigarette in outdoor settings. Smokers may compound their THS PAH residues through repeated smoking of cigarettes. Washing hands or changing clothes may diminish or remove this burden. However, even after smoking just one cigarette, the smoker may be a vector for contaminant exposure to non-smokers, especially children. Further studies need to address the degree to which these PAHs are available to non-smokers (e.g., infants, toddlers) in close contact with THS residues of smokers (e.g., nursing mothers, babysitters, parents/guardians, childcare workers).

Conclusions

By smoking only one cigarette under natural outdoor conditions, a significant THS residue of PAHs is adsorbed onto smoker's hands. While smoking outdoors may reduce THS PAH exposure to non-smokers, this study reveals the potential for smokers to act as potential vectors for exposure to non-smokers and environments where smoking is banned. To completely capture the health risk posed by THS, further studies need to address such issues as the off-gasing or desorption potential of these compounds. At that point, a thorough ranking of the importance of THS residues as exposure route compared to other exposures modes (e.g., release of PAHs from such cooking methods as open fires, THS in dust and carpet/furniture/wall, incense burning, indoor tobacco smoking, etc.) may be undertaken.

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Chapter 6

Utilizing Monitoring Data and Spatial Analysis Tools for Exposure Assessment of Atmospheric Pollutants in Denmark

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Air pollutant levels in Denmark are generally moderate due to a windy climate and moderate local emissions. Despite this, a series of epidemiological studies point to air pollution as a cause of severe adverse health effects in the Danish population. Significant relationships between air pollutant

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levels and negative health outcomes in the Danish population have thus been found for end points like: stroke, lung cancer, chronic obstructive pulmonary disease, asthma in adults, wheeze in infants, asthma hospital admissions in children, diabetes, and vascular function in the elderly. These findings have been possible as a result of combining the unique Danish health registry data with detailed exposure assessments based on routine monitoring data and/or high resolution exposure modelling. In the following we will have focus on exposure assessment methodologies. Some of the airborne pollutants that are not all well described, and for some pollutants the population based assessments are mainly indicative and incomplete. This especially counts for all airborne allergens. Today about 21% of the Danish population suffer from allergenic rhinitis and a proportion of these are affected by aeroallergens that are associated to specific pollen. There are many different species of airborne pollen in our ambient environment and a fraction of these negatively affects human health. However, this information on the exposure of allergenic pollen is either limited or not available. Initiatives have been taken that aim to bring pollen monitoring up to the same level as general air pollution monitoring programmes have today, including new observational methods for exposure estimates and the use of atmospheric models. As already stated the following chapter describes and discusses the applied methodologies and some of the main findings of the Danish studies on air pollution and pollen exposure assessment, and the associated negative health impact in the Danish population.

Introduction

It is well established that both exposure to short-term episodes of elevated air pollution levels and long-term exposure to generally increased air pollution levels is responsible for negative health effects in the population. Particulate air pollution is generally considered to be the most hazardous of the ambient air pollutants. Atmospheric particles are highly heterogeneous, and the mechanisms behind the health effects are not fully understood. In addition to other adverse health effects, air pollution is estimated to cause more than three million annual premature deaths worldwide (*1*). Seventy five percent of the European population, expected to rise to 80% by 2020, reside in cities (*2*) where generally the highest air pollution exposures and associated health effects take place (*3*), and the world's urban population is still increasing.

The wide spectrum of atmospheric phenomena governing air pollution concentrations take place on various temporal (from seconds to months and

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years) as well as spatial scales (from a few meters to thousands of km). When modelling human exposure, we are often mainly interested in obtaining a good description of the pollutant conditions in the urban areas. Within cities, buildings represent physical obstacles that play a crucial role in causing generally elevated pollutant levels in the urban environment. This is particularly evident inside street canyons where the canyon vortex flow governs the pollution dispersion (*4*). The local contribution to urban air pollution depend on a series of parameters: the extent of the urban area, and the density of temporal pattern in local emissions. Meteorological conditions however also heavily affect the actual pollutant levels, as they govern dispersion conditions as well as transport in and out of the city area (*5*).

The local air pollution level is the result of a competition between emission processes, which increase concentrations, and dispersion, advection, transformation and deposition processes that reduce or nulify them. Those pollutants for which local contributions dominate, such as *e.g.* nitrogen oxides which will usually have a significant signal from local traffic, pollutant levels will naturally follow the temporal variations in the emissions. However, for some pollutants, and this especially concerns particulate pollutants, the contribution from long-range transport will often dominate (see the sketch in Figure 1). For mass based fine fraction particles like $PM_{2.5}$ (mass of particles with an aerodynamic diameter of less than 2.5 μm), the contribution from pollutant sources outside the city will often contribute more than 50%, even inside trafficked urban streets with intense traffic emissions. The contribution from local sources to local pollutant levels close to the ground, where the highest exposure takes place, is highly dependent on release height. Air pollution emitted from a high release height will in many cases be transported out of the urban area before being dispersed down to ground level. For urban industries, power plants and other sources for which regulations enforce release from tall chimneys, the contribution to the local ground level air pollution is therefore usually marginal. These sources primarily contribute to air pollution in the regional context. In contrast, pollutant emissions related to road traffic, domestic heating and smaller industries typically take place at low heights, and therefore contribute significantly to local pollutant levels. Contributions from "low" sources (less than 10 m above ground level) therefore often dominate ground level pollution levels inside urban areas.

Denmark has a coastal climate with generally windy conditions. With an area of 43,000 km^2 and 5.6 million inhabitants, Denmark is located in Northern Europe in the region between the relatively polluted central European areas and the much less polluted Scandinavia (*7*). For those pollutants that have a significant long-range transport component, levels are therefore generally at the low end of the range. However, at local hot spots (*e.g.* urban streets with intense traffic), levels may still be significant near high emission sources, especially as dispersion in the urban environment will be constrained by building obstacles. In the following section we will look at available information concerning pollution levels, trends, and temporal and spatial variation for Danish conditions. We will also discuss how this information is used in assessing exposure, for specific cohorts as well as for the population as a whole.

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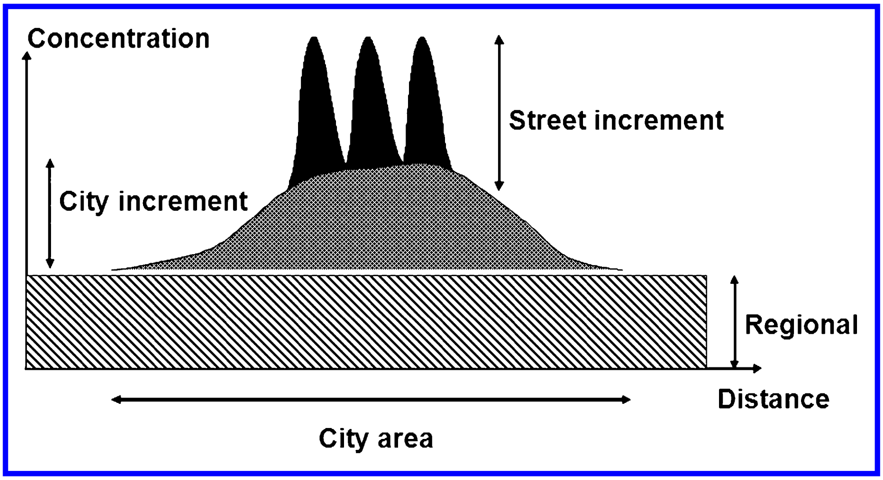

Figure 1. A schematic illustration of the air pollutant contribution from regional transport, the city area and the street. The relative magnitude of the various contributions depends both on the pollutant in question, and on the actual dispersion conditions (governed by the meteorology). Modifed with permission from Hertel et al., 2007 (6).

Air Pollution Exposure Assessment

Human exposure refers to an individual's contact with a pollutant concentration, and may be determined by the application of direct as well as indirect methods (*8*). Direct methods concern studies on the single individual using portable monitor measurements or performing measurements of biological markers *e.g.* pollen. The personal monitors are carried by the study subject during a campaign period. Biomarkers can be measurements of pollutant concentrations or degradation products in blood, urine etc., but may also be parameters expressing health effects like *e.g.* oxidative damage of DNA in white blood cells. Generally, direct methods are only feasible for smaller cohorts during shorter campaign periods as the measurements are resource intensive. Such data is, however, crucial in the evaluation of exposure modelling as well as for testing the usefulness of fixed site measurements as proxies for personal exposure. The personal exposure monitors may be integrated samplers that collect pollutants over some period of time and are subsequently analysed in the laboratory, but they can also be continuous monitors that utilise a self-contained analytical system for online measurements on location. In both cases the instrument may be either passive or active monitors. Active monitors use a pump to bring air through a collector or sensor, whereas passive monitors rely on diffusion to bring the pollutants into contact with a sensor or collector. In recent years, a number of new lightweight online personal exposure monitors that send output to a mobile phone via a Bluetooth connection have become available. This technology is still fairly new, and the devices are in many cases not yet fully validated, but results seem promising and these instruments present many new possibilities in exposure assessment studies.

Indirect methods are based on combining information about pollutant concentrations and time spent in specific environments. The pollutant concentrations may be determined from measurements, from model calculations, or from combinations of measurements and calculations. It is common to apply the concept of a microenvironment, defined as 3-dimensional space within which the pollutant concentration at a specific time is spatially homogeneous or has well-known statistical properties. Microenvironments may for example be the interior of a car, the interior of a house, or simply an urban, suburban or rural area. Most models can consider a number of different microenvironments and a subset of the models can also consider transport and transformation of pollutants from one to another microenvironment (*e.g.* from urban to suburban). They are called chemistry transport models (CTMs). CTMs usually operate on a fixed grid that covers a particular geographical region (a town, a country or a continent), where each grid point in the region corresponds to a specific microenvironment. The concept of micro-environments is particularly useful when assessing the exposure of cohorts for which time-activity patterns may be obtained. A time-activity pattern describes a person's path and associated activities as they move betwen different micro-environments. A very crude indirect method is categorical classification based on indicators such as type of residence (*e.g.* urban, rural or industrial), job classification (occupational exposure), or the presence of indoor sources like tobacco smoke, gas stoves etc. The categorical classification is however generally considered crude, and inadequate for application in air pollution epidemiology. Measurements from fixed site routine monitoring stations are widely used as indicators of population exposure, but calculations from air quality models are becoming more and more common in exposure assessment. Most of the epidemiological studies that determine dose-response relationships use urban background levels as exposure proxies. Dose is the amount of pollution inhaled or taken up in the body. In fact the term "dose-response" is misleading as it is usually "concentration-response" that is being determined. In Danish studies fixed site measurements from the routine monitoring network, but also modelled urban background and front door street pollution levels have been used as exposure proxies. This is described in more detail in the following.

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Air Pollution Levels and Trends in Denmark

The Danish air quality monitoring program consists of a rural and an urban sub-networks. Rural monitoring is performed at eight measurement stations located in the countryside and distributed over the country to represent the different regions. Monitoring sites have been carefully selected to avoid influence from local air pollutant sources. The urban program includes measurements in the four largest Danish cities (Copenhagen, Aarhus, Aalborg, and Odense). Measurements are performed at one urban background and one street site in each city (except for the capital Copenhagen, where there are two street sites).

Since the 1970's there has been significant focus within Europe on sulphur emissions, due to the acidification of forests and other natural areas but also due to the impact of sulphur compounds on human health. Emission reductions in Denmark as well as accross the EU has lead to a decrease in SO_2 concentrations by a factor of 5 to 10 since the 1980's. Levels are far below EU limit values. Carbon monoxide (CO) can be hazardous to health, but limit values have never been exceeded in Denmark, and levels have furthermore decreased by a factor of 3 to 5 since the early 1990's. Easily measurerable indicator components may, however, serve as indicators for or even be used for estimation of concentrations of other compounds for which monitoring is less straightforward or highly resource-intensive. Compounds that are not harmful at the observed concentration level may thus serve as useful indicators of harmful compounds at critical levels, and CO is an example of a compound that has sometimes been used as an indicator of traffic pollution from petrol-driven vehicles.

Nitrogen oxides from traffic are mainly emitted as nitrogen monoxide (NO). Inside the urban street the retension time is relatively short (minutes) and only very fast reactions have time to take place. The distribution between harmless NO and the airway irritant nitrogen dioxide (NO_2) is therefore to a great extent determined by the fast reaction between NO and ozone (O_3) that forms NO_2, and the similarly fast photodissociation of NO_2 back to NO and O_3 (in reality an O radical is formed, but this radical almost instantly react with O_2 to reform O_3).

$$\boxed{\begin{array}{ll} NO + O_3 \rightarrow NO_2 + O_2 & \\ NO_2 + h\nu \rightarrow NO + O & \qquad\qquad (1) \\ O + O_2 \rightarrow O_3 & \end{array}}$$

The concentration of NO_2 is thus strongly governed by O_3 from distant sources. This and the increasing fraction of directly emitted NO_2 (especially from diesel engines) is the reason for the limited reduction in NO_2 levels that has been observed despite significant NO_x reductions in recent years. This also holds for Denmark as described in the previous section (and reflected in the data shown in Figure 2). The reason is the increasing fraction directly emitted as NO_2, but also the chemical conversion of NO to NO_2 in the reaction with ozone (O_3). For the latter, the O_3 concentration is usually the limiting factor for the conversion.

The trend in NO_x concentrations has followed the trend in Danish NO_x emissions; a decrease of similar magnitude as that for the transport sector, as well as other sectors (Figure 3). This emission reduction is the reason for similar decreasing trends (of about 60%) at street, urban background and rural sites. Also NO_2 levels have also decreased but not to the same extent as NO_x. The smallest decrease is found for the street stations (about 25%) whereas urban background and rural sites have experienced considerably larger decreases (about 60%).

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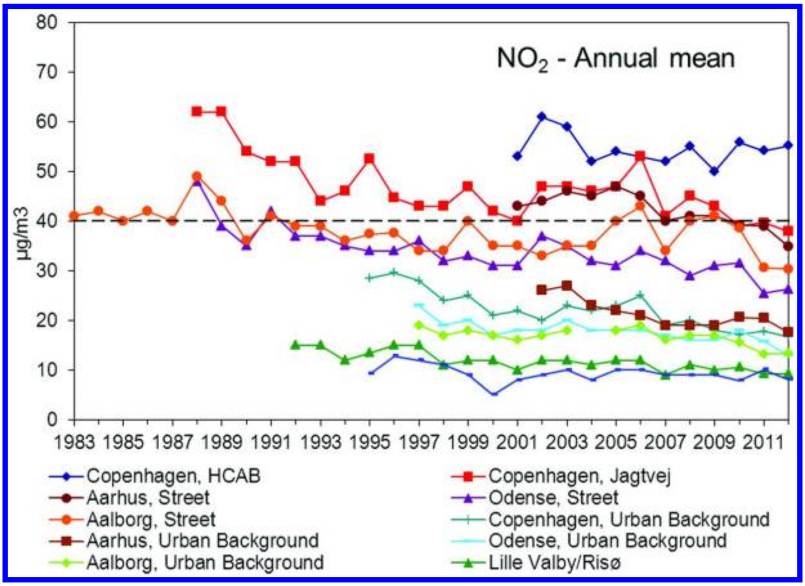

Figure 2. Trends in annual mean nitrogen dioxide (NO_2) concentrations at Danish air quality monitoring stations from 1983 to 2012. The dotted line indicates the limit value of 40 µg/m^3 enforced by the EU Directive on Air Quality and Cleaner Air for Europe. Levels have decreased, though only marginally in recent years. Source: Danish Center for Environment and Energy, Aarhus University.

Ozone is not directly emitted to the atmosphere, but instead formed through reactions involving VOCs, NO_x and sunlight. The location at Northern latitude means that the solar radiation is not strong enough to lead to high ozone production in the troposphere over Denmark. Health related limit values for O_3 on annual and hourly means are not exceeded in Denmark, but every few years the hourly mean values exceed the 180 µg/m^3 at which the EU directive demands that the population is informed.

Particle size and most likely also chemical composition play a central role for the negative health effects associated with human exposure, and ambient air always contains a complexe mixture of particles of different size and chemical make-up. Size governs the atmospheric processes of the particles as well as their deposition in the human respiratory system. Particles in ambient air typically appear in three rather distinct size classes (or modes); these classes are usually termed ultrafine (diamteter 0.01 - 0.1 µm or 10 - 100 nm), fine (diameter 0.1 – 2.5 µm) and coarse (diameter 2.5 – 10 µm).

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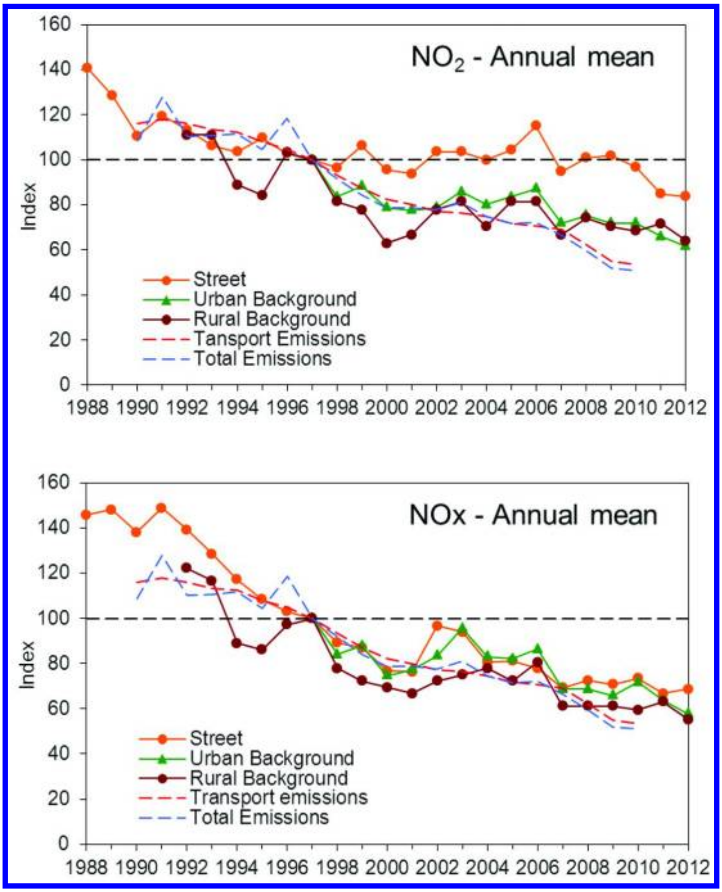

Figure 3. The relative trend in NO_2 (upper) & NO_x (lower). Values are been indexed to 100 for the year 1997, the were urban background measurements started. The decrease in annual mean values of NO_2 on street, urban background and rural levels correspond to the decrease in Danish emissions of NO_x from the transport sector and in total. Note that two stations (H.C. Andersens Boulevard in Copenhagen & Banegårdsgade in Aarhus) are not included in the averages for street stations, since the measurements at these two stations started later than at the other stations.

Only the two measures of the mass concentrations of particles with aerodynamic diameter < 10 µm and < 2.5 µm (PM_{10} and $PM_{2.5}$) are regulated in European directives, and therefore routinely measured in urban monitoring programmes, including the Danish programme. Although ultrafine particles represent a minor contribution to mass concentrations, particles in this particle range constitute most of the particles in terms of number concentrations (Figure 4). Examples of harmful constituents of ambient atmospheric particles are polycyclic aromatic hydrocarbons (PAHs), but also heavy metals (*e.g.* lead, cadmium and arsenic) that are known to be toxic.

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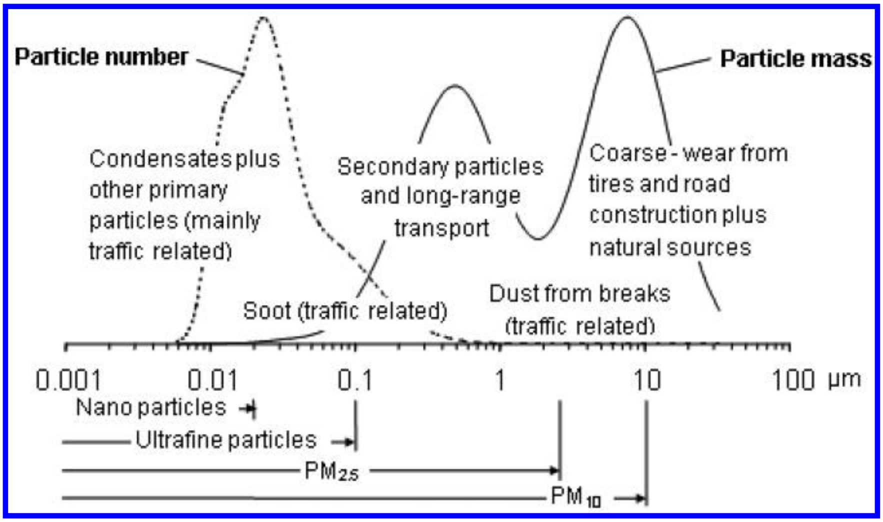

Figure 4. Typical size distribution of particles in busy urban street air, both as mass and number concentration. The horizontal axis is the particle diameter in µm. The black line is mass distribution, dominated by the coarse and secondary particles. The dashed line is the number distribution, dominated by ultrafine particles. Note that one particle with a diameter of 10 µm has the same weight as 1 billion particles with a diameter of 0.01 µm.

In Denmark, particle number concentrations in the range 6 to 700 nm have been measured on a routine basis since 2002. These particle counts are often (incorrectly) called ultrafine particles, although they actually also include particles in the range 100 to 700 nm, a fraction that in a typical urban street constitutes about 10% of the total ultrafine fraction. The fine fraction $PM_{2.5}$ has been measured at the street station H.C. Andersens Boulevard (HCAB) in Copenhagen since 2007, and at the other stations in the urban air quality monitoring programme since 2008. Since 2011, the chemical composition of $PM_{2.5}$ has been routinely monitored. The chemical analyses show that about 5% of $PM_{2.5}$ originates from natural sources (sodium (Na), chlorine (Cl), magnesium (Mg), Potassium (K), and calcium (Ca)). Between 35 and 42% consists of secondary inorganic material (sulphate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+)), of which the first two are related to combustion and the latter to agricultural animal production. In rural background, $PM_{2.5}$ contains 3% elemental carbon whereas this fraction is 13% at HCAB, clearly demonstrating the contribution to elemental carbon from local road traffic in the street environment (these figures are derived from data published in (*9*)). Organic material consists of hundreds of compounds that have sufficiently low vapour pressure to stick fully or partially to ambient atmospheric particles. Many of these compounds, which constitute 20 to 22% of $PM_{2.5}$, are secondary particulate material that is formed from both biogenically (substantially rural) and anthropogenically (substantially urban) emitted organic gasses. The relative contributions of these two sources are in the same range: in mass they are 3.3 and 3.8 µg/m^3 in the rural background and street, respectively. This group includes a range of potent hazardous compounds like carcinogenic PAHs whilst about 28% consists of non-identified compounds, which includes water-bound to hygroscopic salts (sea salt & ammonium sulphate). Other contributions to this group come from heavy metals and soil dust.

PM_{10} has been measured on a routine basis in Denmark since 2000 (except for HCAB where PM_{10} has been measured since 2006). Before that, measurements of total suspended particulate matter (TSP) were made going back as far as 1980. The cut off for TSP is not well defined, but it falls in the range 15 to 20 µm (meaning that TSP is PM_{15} – PM_{20}). Despite the differences in the two measurement methods, it is clear that concentrations have decreased since the 1980's. In 2000 when the TSP measurements were replaced by PM_{10}, concentrations had been halfed compared with observations in 1980. Since 2000, PM_{10} levels have decreased by 20 to 30%. PAH levels have been measured in Denmark since 1990, and have shown that emissions of PAH and benzo[a]pyrene increased from the onset of monitoring up to 2007. This increase is due to a significant rise in the use of wood stoves for domestic heating in Denmark, a source that contributed 90% of the emissions of these pollutants in 2010 (*10*). Negative health effects are well established for particulate heavy metals, and these have thus been measured in Denmark for the past 30 years. For most of the heavy metals concentrations have as a results of regulation of emissions decreased substantially over the period they have been measured. The most pronounced decrease is for lead, which has decreased by two orders of magnitude due to the removal of lead from gasoline. Copper concentrations have increased due to emissions from brakes that have contained large amounts of copper since the phaseout of asbestos.

Measurements of elementary carbon in $PM_{2.5}$ have been performed since 2010 at the street station HCAB and the rural background station at Risø. Data series are currently not sufficiently long to analyse trends. At street stations elementary carbon is mainly related to traffic, and since PM emissions from traffic have decreased over the last 10 years this is also considered to be the case for elementary carbon (*10*). For the rural background the main source is domestic heating, and levels are believed to have increased as a result of increasing use of wood stoves. Releases from wood stoves are increasing; whereas, emissions from road traffic are decreasing. Time series are too short to evaluate trends in organic carbon contents of $PM_{2.5}$ and PM_{10}.

Exposure Modelling

Models designed for exposure assessment include CTMs based on the micro-environment approach and statistical models relating exposure to selected and easily determined parameters. Stocastic components may be added to the CTMs in order to reflect variability in pollutant concentrations at specific micro-environments. In Danish exposure assessments, only CTMs have been applied to the calculation of pollutant concentrations at urban background and at the street address level; whereas, statistical models have been applied in source apportionment analyses.

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As previously stated, it is common to apply urban background concentrations as proxies for personal exposure. Our health assessment studies have shown that assessment of street address level air pollution may also be useful, and in some cases provide stronger relationships to health effect endpoints than urban background measurements. The sketch in Figure 1 illustrates that the pollutant level in an urban street may be considered as consisting of three components: a regional contribution, the city increment, and the street increment. In order to model street pollutant levels, it is necessary to handle all three contributions. A wide range of different types of models based on different principles and operating on different scales, are available for describing air pollutant concentrations. These models use different mathematical expressions to describe the governing physical and chemical processes (emission, dispersion, advection, transformation, and dry & wet deposition), but they all require proper input data such as meteorology, emissions and land use for the applied model domain in order to produce realistic pollutant concentrations. The quality of the input data determines to a very large extent the quality of the modelling: “garbage in means garbage out” – poor quality input data will always lead to poor quality model results. Integrated model systems, where a hierarchy of models describing different scales is combined, are currently being developed at various institutes. In Denmark, the socalled THOR system is covering all scales from hemispheric transport, over regional and urban scale, down to single streets (*11*).

Various models have been developed for describing urban background pollution levels. The dispersion conditions in the city are strongly affected by the city structure, which may degenerate movements at scales as large as the whole city area itself. In the Danish exposure studies, measured urban background levels have been applied when available, but in cases when this is not possible, the Urban Background Model (UBM) (*12*) has been applied. In the UBM, the urban area is sub-divided into a grid net with a resolution of 1 km x 1 km. Contributions from individual area sources are integrated along wind direction paths. It is assumed that the dispersion increases linearly with distance from the source. Horizontal dispersion is accounted for by averaging the calculated concentrations over a certain wind direction dependent sector, centered on the average wind direction.

In Denmark and many other Western countries, traffic pollution contributes a significant part of the population exposure to air pollution. Urban streets with high motorized traffic congestion are thus the pollutant hot spots, where the population experiences the heighest exposures. In Denmark, the Operational Street Pollution Model (OSPM) (*13*) is applied for assessment of street pollution levels in the urban areas. The OSPM represents state-of-the-art in operational models and is currently applied in more than 17 countries around the world (*14*). In OSPM, the concentrations are calculated hour-by-hour, using a combination of a plume model for describing the direct pollutant contribution from vehicle emissions in the street and a box model for describing recirculation within the street by the vortex flow (Figure 5). OSPM makes use of a simplified description of the flow and dispersion conditions inside an urban street, but it has been found to work very well for regular street canyons that dominate in the city centres. OSPM has since the year 2000 been extended to handle several street configurations like streets with holes in the building façade along the street, buildings on only one side or streets without buildings etc. Monitoring sites in urban streets are often placed in regular street canyons. Therefore only few observational data are available for model validation with different street configurations than street canyons.

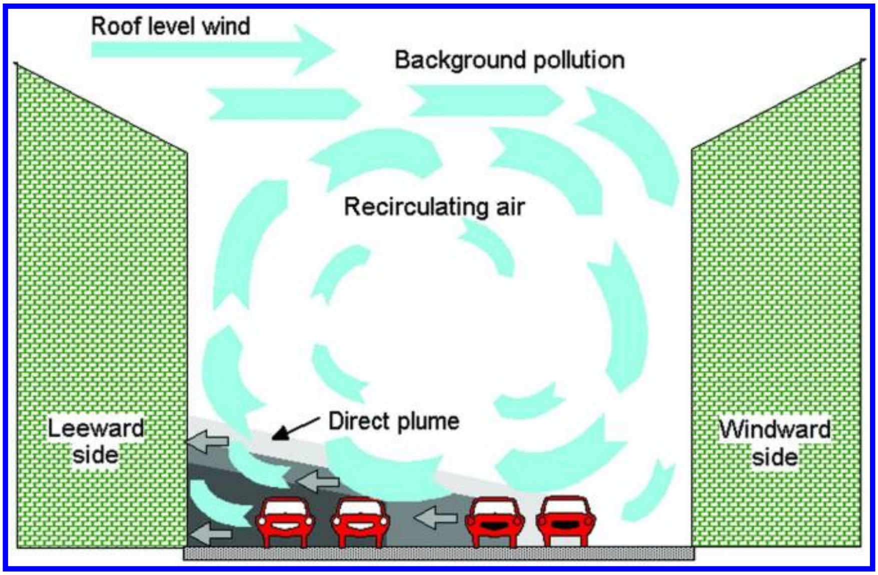

Figure 5. Illustration of the flow and dispersion inside a regular street canyon. The wind above roof level blows perpendicular to the street in the above figure, thus creating a vortex inside the street canyon with the wind direction at street level opposite to the wind direction above roof level. Pronounced differences of up to a factor of 10 in air pollution concentrations on the kerbsides are the result of these flows. Air quality on one side of the street might thus be poorer than on the opposite side of the street, if there are prevailing winds.

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It appears from the description of the NO_x chemistry that this chemistry could be simplified to only two reactions: the reaction between NO and O_3 leading to the formation of NO_2, and the photodissociation of NO_2 reforming NO and O_3 (assuming instant formation of O_3 from the O radical in the photodissociation. For implementation in operational models, a simple and easily applicable parameterisation has been derived (*15*). Tests have shown that model calculations using this simple parameterisation are in good agreement with observations. In the modelling within the Danish exposure assessment, this simple parameterisation is used in both the UBM and OSPM.

The basic requirements for calculating air pollution concentrations at the street address level is access to input data on traffic, meteorology, background pollutant levels and street configuration. The information on street configuration

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may be obtained from manual observations, but this is not feasible when calculations are needed for large cohorts. The feasible solution is to apply Geographical Information Systems (GIS), and this is what has been done in the Danish AirGIS system (*16*, *17*). AirGIS is based on air quality models, available technical and cadastral maps (buildings, roads, address points, property limits) and available Danish administrative databases on buildings, property limits and population.

A part of AirGIS is a 2½-dimensional landscape model applied for generating the street configuration data for large numbers of addresses (Figure 6). The landscape model interprets the digital maps and the available registry data. The approach in most of the Danish long-term exposure studies has been to use present and historial addresses in the Danish Central Population Register (CPR). These addresses have been geocoded, and the coordinates of the addresses have then been used in the 2½ dimensional GIS based model in AirGIS to indentify relevant roads, buildings, street widths, building heights etc. that are necessary input data for the air quality model in the AirGIS system. Traffic loads, vehicle types and driving speeds have been determined for all streets in the country using information obtained in either digital form or in manually filled in schemes combined with information about the street type and countrywise road traffic statistics. Air pollutant concentrations are computed by combining the regional scale model DEHM with the UBM and the OSPM. This approach allows generation of street configuration data for thousands of addresses, and has been applied e.g. for 200,000 addresses for the Danish Diet, Cancer, Health cohort of 57,000 people (each having on average lived at 4 addresses). Thereby AirGIS provides the opportunity to perform uniquely detailed exposure assessment on the street address level, which as we will see in the following sections has been shown to give stronger relationships to health endpoints compared with assessments based on fixed site routine monitoring stations. In addition to address level exposure assessment, AirGIS has a facility for tracing people (Figure 7). This facility has been used in a number of studies where personal monitoring has been performed as a supplement to the exposure assessment, but also as a test of the model system.

Results from Health Assessment Studies

Exposure to short-term episodes of elevated air pollution concentrations may lead to negative health effects within hours to days after the exposure.This was i.e. evident after the episodes in the Meuves Valley in 1930 and in London in 1952. These episodes lead to elevated concentrations of sulphate-rich particles as a result of intense local emissions of sulhur dioxide related to domestic heating and cooking. The elevated levels were ten fold typical levels of that time, which were again ten fold present levels. New epidemiological methods in the past two decades have made it possible to detect negative health effects on a range of health outcomes, including hospital admissions, illnesses, premature death, changes in lung function etc., even at relatively low pollution levels observed in large cities in Europe and USA.

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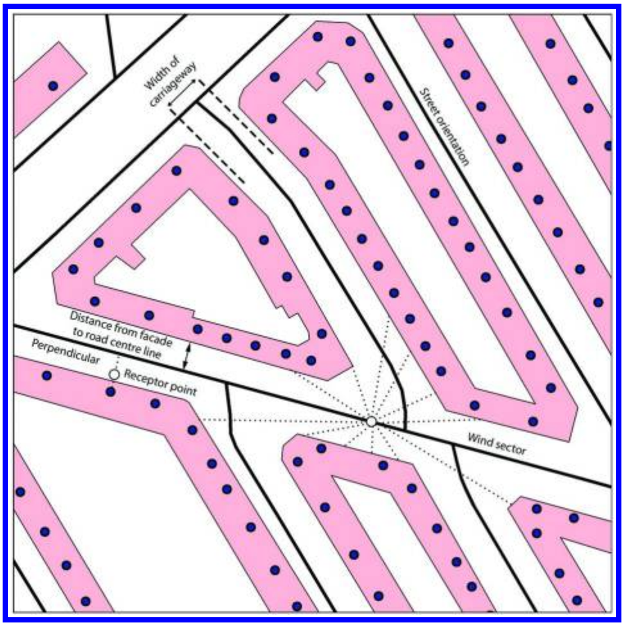

Figure 6. Illustration of the 2½ dimensional model applied for generation of street configuration data in the AirGIS. The calculation procedure is built on digital maps and data from Danish national registries. The parameters that are determined include; general building height in the area, building height in wind sectors, width and orientation of the street and distances to street intersections.

Short-term effects are usually studied in time-series studies where health endpoints in short time windows are related to daily variations in pollutant or allergen loads. Typically, short-term effects are observed with hours to few days from an episode, but there are examples of studies that have determined effects up to 40 days after an episode. These studies are in principle free of confounders from individual factors such as lifestyle, since within the short time frame, the conditions for the population are the same without changes in these factors. Factors that may change and can affect the results are factors that vary during the study period, such as season, temperature, weekday or *e.g.* influenza epidemics. Most studies are based on the classical timeseries design where the number of negative health incidenses are modelled for the pollutant level in the days before an event using Generalised Additive Modelling based on Poisson regression. This approach demands a sufficient number of events every day in order to ensure reliable calculations and relatively long (several years) time series of data are needed. In recent years, the case-crossover design with logistic regression has become more common since this methodology has less drawbacks. In case-crossover studies, theair pollution levels on a day just before an event

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(hospitalization, death etc.) are compared with the air pollution levels on control days, that is typically on the days same weekdays within the same calendar month when the event has not occured. Panel studies are another common type of short-term effect study where disease or disease biomarkers are monitored and linked to exposure levels in a relatively small well characterized group of people. Contrast in exposure may be used to force more pronounced effect signals *e.g.* by making study subjects exercise in highly polluted air etc. Another method for evaluating short-term health effects of exposure to an air pollutant or aeroallergen, is in a challenge chamber, also known as exposure or climate chamber. The chamber allows for a small group of study subjects to be exposed to the chosen pollutant in a controlled environment. The air in the chamber is filtered to exclude any other contamination than the examined substance. Care is taken to insure that all study subjects are exposed to the same levels, and continuous measurements are performed. The advantage to the challenge chamber is that precise data on exposure can be acquired, and and as study subjects serve as their own controls, confounding is minimized and less subjects are required to obtain statistical power (*18*). In Denmark chamber studies has been performed on *e.g.* sulphur dioxide (*19*) ozone and particulate matter (*20*, *21*) and on wood smoke (*22*). Chamber studies on aeroallergens and pollen are currently being performed in the Danish chambers.

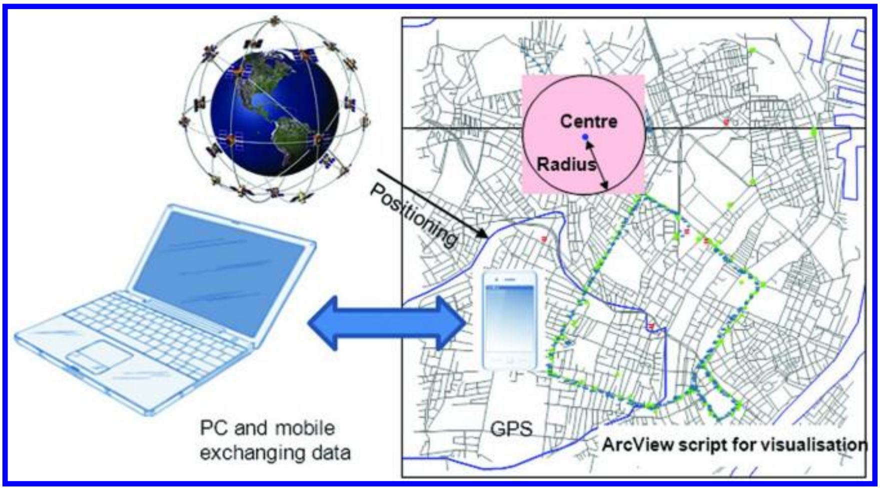

Figure 7. System for tracking people by a Global Positioning System (GPS). The GPS is build into a mobile telephone and SMS's are used for transferring positions of a study subject every 20s to a computer. A tracking program collects the GPS data. A dynamic area-tracking feature ensures that SMS's are only sent when the subject is moving (settings may be changed on-line by the phone). The movement of a study subject can be traced on digital maps in real time.

Long-term effects of air pollution have mostly been studied in cohort studies in which cohorts of study subjects are created, characterized regarding address, socioeconomic status, health and lifestyle and followed for a number of years. Mean annual levels of pollutants at the home addresses are assigned to each subject based on either area sampling methods or modeled exposures. The relationships between pollutant levels and adverse health outcomes, commonly mortality, are analyzed with the Cox proportional hazards model and other statistical models. Cohort studies have provided the strongest associations between air pollution and health effects but are prone to confounding from individual and other factors unless very well characterized prospectively.

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Copenhagen Health Endpoint Studies

Nine published studies have related health endpoints in Danish registries to air pollutant measures in Copenhagen. All studies are based on NO_2, NO_x, CO, PM_{10}, $PM_{2.5}$ and particle number concentration measurements during 1999 - 2010 from the urban background station on the roof of the H.C. Ørsted Institute (refered HCØ in the following) in Copenhagen as exposure proxy for the Copenhagen population. One study used hourly mean, whereas the rest have diurnal mean pollutant levels as exposure proxies. Studies included hospitals within a 15 km radius of HCØ, or similar or smaller radius for the address of the event or residence. Health endpoints include cardiovascular and respiratory disease especially amongst elderly people (>65 years), myocardial infarction, asthma among children from the Danish national patient registry, strokes from a national indicator project in Danish hospitals, death caused by cardiovascular and respiratory disease from the Danish cause of death registry, cardiac arrest outside hospital from ambulance data, and a panel survey of 400 children predisposed to develop asthma and followed up on their third birthday. For all studies a lag of up to 6 days from exposure to health effect measure is applied, and the effect is estimated in percentage of incidence relative to a interquartile change (IQR) in the pollutant component. The latter means a change from the level that 25% of measurements are below to the level that 75% of the measurements are below. This will often be close to a 50% change from the average value. In the following we describe shortly the studies and their findings (Table I).

1: Death caused by respiratory and cardiovascular illness during summer and winter was studied by case-crossover design (*23*). The study included death from stroke, cardiovascular and respiratory illness among residents >18 years old within 15 km from the monitoring station at the HCØ during 1999 to 2006. Focus was on the impact of temperature changes, the relation to PM_{10}, NO_2 and CO was also investigated within a 5 days lag period for winter and summer separately. No robust relationships were found between deaths and 6-days averaged pollutant levels, but a significant 3 – 4% increased risk of cardiovascular death was found within the same day and 2 days after a IQR increase in PM_{10} in summer, and a similar result was found for day 1 – 3 in winter. The study showed, however, also a decreased risk of respiratory death within 3 - 5 days after increase in NO_2 for both

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6-month periods, and decreased risk of death from stroke 3 days after an increase in PM_{10} during winter. It is possible that there are uncertainties in the death cause register, and also that there may be delay in deaths related to medical treatment.

2: A time series design was used to study hospital admissions from 1999 to 2004 within 15 km of HCØ for respiratory and cardiovascular illness among elderly, and asthma among elementary school children (*24*). For all endpoints, the study showed significant relationships to PM_{10}. Results showed shorter lag time for cardiovascular illness (1 - 3 days) with an effect estimate of 3% per IQR, compared with respiratory illness (2 - 4 days) with an effect estimate of 4% for elderly and 8% for children per IQR. Significant relationships were also found for NO_2 and CO, but these were significantly reduced when PM_{10} was included. For source allocations of PM_{10}, there was strongest relationship to soil dust and secondary particle in the case of cardiovascular illness, for biomass in the case of respiratory illness, and for traffic in the case of asthma in children.

3: This was a time series study on daily hospital admission 2001 to 2004 within 15 km of HCØ for respiratory and cardiovascular illness among elderly and asthma among children in relation to particle size and number that were analysed with respect to sources and potential effect (*25*). Significant relationship was found between hospital admission of elderly and primary PM_{10} with effect estimate of 3% for cardiovascular and 5% for respiratory illness per IQR. Similar relationship was found for particle number with diameter around 212 nm; whereas, no significant relation was found for ultrafine particle number after adjustment for other components. For hospital admission of children for asthma a significant relationship was found for particle number with a diameter of 212 nm, and less strong relationship to ultrafine particles and NO_2; whereas, no relationship was found for PM_{10}.

4: A case-crossover design was used to study hospital admissions during the time period 2002 to 2006 of people >18 years old living within 15km of HCØ for respiratory illness, and for brain and cardiovascular illness (*26*). The study had focus on effects of daily temperature changes but also the relation to PM_{10}, NO_2 and CO was investigated within a five days lag period separately for winter and summer 6-monht periods. For both half years significant relations were found between PM_{10} and hospital admission for respiratory illness with effect estimates of 4% and 2% per IQR in summer and winter, respectively. For the summer half a significant 2.6% increase per IQR was found between PM_{10} and NO_2 and hospital admission for cardiovascular illness and for NO_2 and hospital admission for stroke. No significant relationships were found for the winter.

5: Case-crossover and time series analysis were compared for the time period 1999 to 2006 of hospital admissions for myocardial infaction among people >18 years old and with residence within 15km HCØ (*27*). The study focused on daily temperature changes but also the relation to PM_{10}, NO_2 and CO was investigated within a 4 days lag period separately for winter and summer. For the winter a just significant increase of about 4% in hospital admissions per IQR was found for 6 days average PM_{10}, and only a moderate relation for the day four after similar increase in summer. However, significant increases of respectively 4% and 8% after an IQR in 3-4 days average of NO_2 and CO linked to traffic in summer, but no relationships for winter.

Table I. Total exposure-response estimates found in relation to air pollution components in short-term studies in Copenhagen. Central estimate of risk is given in % for an interquartile (IQR) change for each component. Bold indicate statistically significant. An interval is given when several datasets are used.

Health endpoint	*PM_{10}*	*$PM_{2.5}$*	*Particle #*	*NO_2 / NO_x*	*CO*
Interquartile range, IQR	*(7)[b] 13-14 $\mu g/m^3$*	*5 $\mu g/m^3$*	*3800-3900*	*6-7/9 pbb*	*120 ppb*
Cardiovascular death, lag 0-5 days	3%			0 to 1%	0 til 1%
Deaths of stroke	0%			0 to 2%	-2 til 2%
Deaths of respiratory disease all ages, summer & winter, 0-5 d lag	-3 to 1%			-2%	-5%
Cardiovascular hospital admission >65 years old lag 0-3 d, or all ages summer & winter 0-5 d lag	**3%**[a] **2%**	**3%**[a]	0%	0 to 2% 2 % & 3%	1 to 2% 1%
Myocardial infarction summer & winter, 0-5 d lag	0 & 4%			2 % & 4%	2 & **7%**
Cardiac arrest outside hospital, 3-4 d lag	**5%**[a] (IQR 7)	**4%**[a]	3%	2 to 3%	2 to 4%
Mild ischemic (clot) stroke, 0-4 d lag	8%		**21%**[a]	11%	10%
Respiratory admission >65 years old, 0-4 d lag, and for all ages summer & winter 0-5 d lag	**4 to 6%**[a] **4%**	0%	4%	**4 to 6%** 0% & 4%	2 to 4% 1 & 3%
Asthma hospital admission 0-18 years old, 0-4/5 d lag	**2 to 8%** [a]	**9 to 15%**[a]	6-7%	**4 to 13%**[a]	0 to 10%
Wheezing among susceptible 0-1 year old & 0-3 year old, lag 2-4 d	21% & 4%		92% & -15%	**45%/30%** **19%/14%**	33% & 7%

[a] Dominant in model with other air pollutants. [b] The value in the branket refers to study on cardiac arrest outside hospital.

6: Cardiac arrest outside hospital and within a radius of 5 km of HCØ was studied by case-crossover design for the time period 2000 to 2010 (*28*). In the study the components PM_{10}, $PM_{2.5}$, $PM_{10-2.5}$, NO_2, NO_x, CO, O_3 and particle number, area and surface area were investigated with a time lag of 1 to 24 hours and within five days lag period. Significant relationship was found between cardiac arrest and PM_{10} / $PM_{2.5}$ concentrations 3 to 4 days before, and with effect estimates of respectively 5% and 4% for an IQR increase. Whereas no relation was found for any of the other components. Similarly no other relationships were found within 24 hours for all components.

7: This was a case-crossover study for the time period 2003 - 2006 within 15km of HCØ of number and severeness of daily acute hospital admission for brain stroke and myocardiac arrest (*29*). Relations were investigated for PM_{10}, particle number, NO_x and CO within 4-day lag periods. The study showed a borderline significant increased risk of 7- 8 % for ischemic stroke within 4 days after an IQR increase in particle number concentration, NO_x and CO, but non-significant increase of only 2% for PM_{10}. There was no association for hemorrhagic stroke. Subdividing and limiting to those that are formed locally and are less severe (about 40% of cases), there was strongest association for particle number concentration, leading to 21% increased risk at IQR increase.

8: Hospital admissions in a radius of 15km of HCØ during 2001 - 2008 of children for asthma were studied by case-crossover design (*30*). Daily hospital admissions were linked to air pollutant components. For more than half of the period particle number concentrations and size distributions were available. Significant associations were found for PM_{10} and NO_x with effect estimates of 7-11% per IQR, mainly among small children, and there was no association for total particle number concentration. Association was found for $PM_{2.5}$ but not robust when correcting for PM_{10}.

9: This was a cohort study of 205 children within 15km of HCØ born of women with asthma were followed from birth and until 3 years of age during 1998 to 2004 (*31*). Parents noted daily wheezing and other symptoms, and this was linked to air pollution components. A significant relationship was found between symptoms and PM_{10}, NO_2, NO_x and CO in first year of life, while for the three years totally this was only found for NO_2/NO_x. Relation to CO disappeared when PM_{10} or NO_x/NO_2 was included. Particle number concentrations were only measured for 1/3 of the period, but a just significant 2-fold increased risk of symptoms 2-4 days after IQR increase was found in first year of life; a result similar to the risk of other components. Limiting to children living within 5km of HCØ increased the relationship between symptoms and particle number concentration to 2.46 per IQR. No relationship between particle number concentration and symptoms for second and third year of life. Measurements of $PM_{2.5}$, soot, NO_x and NO_2 were performed in bedroom at the address three times within the first 18 month of life, but this was not linked to symptoms (*32*). These pollutant levels were mainly determined by indoor sources like tobacco smoking, while traffic outside the home had less importance.

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Denmark Cohort Long Term Air Pollution Studies

Eleven published studies have investigated long-term effects of exposure to air pollution in Denmark. The exposure proxy has typically been the time-weighted average pollutant level at the addresses at which the study subject has lived. In most case NO_2 or NO_x has been used as an indicator of traffic pollution, and it should be noted that NO_x and particles are strongly correlated in Danish streets (*33*). The following studies are, when nothing else is noted, based on the Danish Diet, Cancer and Health cohort (*34*) (Table II). The cohort consists of 57,053 residents of Copenhagen or Aarhus aged 50 – 64 years without a history of cancer at enrolment between 1993 and 1997. Each participant completed questionnaires covering food intake, lifestyle habits, health status and social factors, etc. at enrolment. Address history from 1971-2012 was collected for all cohort participants by linkage with the Danish civil registration system (*35*). Exposure was determined using AirGIS (for the two oldest studies OSPM before AirGIS was developed) calculations from 1971 and forward. All results were corrected for other risk factors related to the relevant illness.

1: Cohort study on 5,534 deaths of which 1,285 were related to cardiovascular disease. The results showed that risk of death increased by 8% per 10 $\mu g/m^3$ NO_2 (95% CI: 1-14%), and by death related to cardiovascular mortality, the increase risk was 16%. NO_2 was also related to ischemic heart disease and stroke, but these results were not significant. The study showed no lower effect limit for NO_2 concerning death and death related to cardiovascular illness. The effect was strongest among those who had intake of <200 g fruit and vegetables per day and lowest among those that had intake of >400 g fruit and vegetables per day.

2: Cohort study on 1,984 first time strokes and among these 142 were fatal (*36*). The results showed that a 43% increase in NO_2 was associated with 5% (95% CI: 1-11%) increased risk of stroke and 22% increased risk (95% CI:0-50%) for fatal stroke.

3: Cohort study on 122 incidenses of mortality related to diabetes. The results showed that death related to diabetis increased by 31% (95 CI: -2 to 76%) per 10 $\mu g/m^3$ NO_2. Other time periods and measures for traffic at residence at the time of inclusion showed also relationship to dealth from diabetis.

4: Cohort study investigating 2,877 first time incidenses of diabetes (*37*). The results showed a 4% increase (95% CI: 0.8%) in risk of diabetis per 5 $\mu g/m^3$ increase in NO_2 at the address. Also measures of traffic at time of inclusion showed relation to diabetis.

5: Cohort study on 1,786 incidenses of Chronic Obstructive Pulmonary Disease (COPD) (*38*). The results showed an 8% (95% CI: 2-14%) increase risk of COPD per 6 $\mu g/m^3$ NO_2 and a 5% (95% CI: 1-10%) increased risk per 12 $\mu g/m^3$ NO_x (IQR).

6: Cohort study on 977 insidences of asthma (*39*). The results showed a 12% (95% CI: 4-22%) increased risk of asthma per 6 $\mu g/m^3$ NO_2 and the categorical analysis showed that concentrations > 19 $\mu g/m^3$ were associated with 38% (95% CI:14-66%) increased risk of asthma compared with exposures < 13 $\mu g/m^3$.

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Table II. Results from Danish cohort studies of long-term health effects of air pollution; percentage increased risk per increase in pollution (CI: 95 % confidence intervals). Per 10 µg/m³ (unless else otherwise noted).

	NO_2	*NO_x*
Mortality		
Total	8 % (CI: 1 - 14 %)	
Cardiovascular illness	16 % (CI: 3 - 31 %)	
Ischemic	8 % (CI: -11 - 30 %)	
Stroke	9 % (CI: -17 - 42 %)	
Incidents/hospital admission		
Cardiovascular illness		
Stroke, all	5 % (CI: -1 - 11 %) per 43 % increase in NO_2	
Stroke, fatal	22 % (CI: 0 - 50 %) per 43 % increase in NO_2	
Airways disease		
COPD	8 % (CI: 2 - 14 %) per 6 µg/m³	5 % (CI: 1 - 10 %) per 12 µg/m³
Asthma (elderly)	12 % (CI: 4 - 22 %) per 6 µg/m³	
Lung cancer		9 % (CI: -21-51 %) & 37% (CI: 6-76 %) per 100 µg/m³

7: Two studies on incidence of lung cancer. The first study included 679 incidences of lung cancer and a comparison group of 3,481 people collected from three Danish cohorts: Diet, Cancer, Health cohort (established 1993-97), Østerbro study (established 1976-79), and Copenhagen Male Study established 1970-71) (*40*). The results showed that a 100 µg/m³ increase in NO_x was associated with a 37% (95% CI:12-88%) increased risk of lung cancer, and the categorical analysis showed that at concentrations above 72 µg/m³ NO_x was associated with 45% (95% CI:12-88%) increased risk in comparison with concentrations below 30 µg/m³ NO_x. The second study was based solely on the Diet, Cancer, Health cohort and followed the subjects over long timeperiod, and thus included 592 insidences of lung cancer (*41*). The results showed a 9% (95% CI:-21-51%) increased risk of lung cancer per 100 µg/m³ NO_x, while the categorical analysis showed that NO_x concentrations above 30 µg/m³ were associated with 30% (95% CI: 5-61%) compared with concentrations below 17 µg/m³.

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8: Cohort study on the incidence of other types of cancer. Results showed association to lever cancer (IRR=1.7; 95% CI: 0.7-3.9), cervical cancer (IRR=2.5; 95% CI:1,0-5.9) and brain cancer (IRR=2.1; 95% CI:1.3-4.2). All results, however, were based on few data. Cervical cancer may be related to more frequent infections to Human Papillomavirus in urban areas were pollutant levels are also high.

9: Case-control study on the incidence of childhood cancer in the entire Danish population (children in age 0-14 years) (*42*). Study included 1,969 cases of the most common childhood cancer (leuchemia, hart tumour and lymphoma) and 5378 controls selected as best possible match. The results showed no connection between NO_2 at residence and risk of childhood cancer. A positive association was, however, found for a rare Hodgkins and the low number of incidences makes this finding highly uncertain.

10: Case-control study on the risk of developing schizophrenia from 15 years of age and forward and whether this was linked to air pollution at the address. The study followed the 7,455 children from the study above (*43*). 29 cases of schizophrenia were indentified in the Danish Central Psychiatry Registry. The results showed an increased risk at high concentrations of CO, benzene and much traffic at the residence after adjusting for age, sex and urbanization degree at residence.

Aeroallergen Exposure Assessment

Many substances can invoke a health response, including substances of biological origin such as allergenic pollen. Individuals exposed to allergenic pollen may develop rhinitis, conjunctivitis, asthma or a combination of the three (*44*). Today about 21% of the Danish population suffer from allergenic rhinitis (*45*) whilst atopic asthma affects about 6% of the Danish population (*45*). The sensitization of individuals to an allergen and subsequent development of symptoms is dependent on the magnitude and frequency of exposure.

Allergenic pollen is not classified as a pollutant, which has caused exposure studies to pollen to receive less attention than exposure studies to tradititional air pollutants such as chemicals and gasses. Furthermore, there are no international agreements that require monitoring of pollen concentrations in the air. This stands in contrast to the national and international agreements on air quality monitoring that states the obligations with respect to monitoring. As such national observation programmes tend to be less extensive than their air quality counterparts. The Danish monitoring programme consists of two permanent monitoring stations. The Copenhagen station has been running since 1977, and a second station in Viborg began has been running since 1979 (*46*). In Denmark pollen counts have been reported since 1979, and today a pollen forecast is issued on a daily basis during the pollen season. In Europe, the monitoring is organized within the voluntary programme the European Aeroallergen Network (EAN), that during the period 2000-2009 included 521 pollen monitoring stations (*47*). Chemical air pollutants have the potential to affect allergic subjects directly by stressing the respiratory system (*48*) but also indirectly *e.g.* by affecting the allergenic potency of the pollen through protein nitration by the polluted air (*49*). The aggravating effects of air pollutants on pollen allergy have been studied as the link between allergic rhinitis (*50*) and atopic asthma symptoms (*51*) and the fluctuations in ambient NO_2, PM_{10}, SO_2 and O_3 concentrations. It has also been shown that allergen can adhere to particulate matter, and be inhaled with this (*52*). Studies on exposure to O_3 and NO_2 have shown an increased airway response to pollen allergen (*53*, *54*) , and it has been shown that the sensitising potential of allergen may increase following binding to diesel exhaust particles (*55*).

Pollen monitoring networks consist almost exclusively of urban background stations situated at roof level, in order to avoid influence from nearby pollen sources. Data from these sites are often used as proxy for exposure. However, this means that there is little information on concentrations on the actual exposure near the surface. Surface concentrations of grass pollen have been reported to much higher than roof top concentration (*56*, *57*) which may be explained by nearby sources to grass pollen and a general redcution in concentration from the surface to roof top locations (*58*). A series of experiments is therefore currently being performed in Denmark's second largest city of Aarhus on grass pollen. The main idea is to combine observations and models (*58*) in a similar approach as for air quality in order to assess the surface concentrations of grass pollen and corresponding exposure of sensitive individuals. Ths includes new experiements that combine data from the three temporary background monitoring stations set up in Aarhus 2009-2011 (*58*). with dedicated exposure campaigns (*59*). This research initiative is on-going and by the time of writing two studies within a PhD study are under review for subsequent publication in international journals:

1: A comparison of background grass pollen monitoring stations with those at street level in an urban canyon. The street canyon microenvironment is a key urban exposure environment, and aerosol dispersion within the canyon environment is controlled by within-canyon airflow patterns, which includes some degree of air recirculation (see previous section). In this study grass pollen concentrations measured at street level within a canyon in central Aarhus tended to be smaller than concurrent pollen concentrations measured at a nearby background monitoring station. This pattern appears to be the result of the recirculating air becoming gradually depleted of pollen as it settles out of the air. The important implication is that data from monitoring stations tends to over-estimate exposure in the street canyon environment (*60*).

2: A direct personal exposure study was performed in an area of Aarhus where grasses were known to grow. Inhaled pollen grain dose was measured using a novel Nasal Air Sampler whilst walking a set route, with measurements made at regular time intervals between 12:00 – 20:00, and dose data compared with background concentrations from a monitoring station. Dose measurements and background concentrations were found to show an opposite trend over the period: the greatest dose rates occurred at midday and lowest at 20:00, whilst the opposite trend was found for background concentrations. The ratio between dose rate and background concentration was calculated for times of day when grass sources in the study area were thought not to be active, for use in estimating grass pollen dose from background concentration data (*59*).

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These and other studies on the effects of pollen exposure and the dynamics of pollen concentrations are in progress with the aim of developing an integrated monitoring and assessment strategy for pollen, similar to that used in air pollution. This will require the development and validation of an exposure model for use in extending monitoring capacity and estimating exposure at specific locations on large scales for use in e.g. epidemiological studies. Such a system may eventually become part of an overall air quality monitoring system where both air quality and aeroallergen forecasts are available in a location specific manner,and could for example be disseminated to the public on a personal basis via a smart phone platform.

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Conclusions and Perspectives

The Danish air pollution exposure and health studies demonstrate the strength of having access to the unique Danish health registries in combination with methodologies for performing detailed exposure assessments. Despite the relatively low pollution levels in Denmark, statistically significant associations between air pollution levels and a large variety of adverse health outcomes with great public health importance have been documented. Planning is underway to apply the same methodology on assessment of the health impact of various airborne allergens including pollen and various agriculturally related pollutants. At the same time the applied methodologies in exposure assessments and epidemiological analyses are being further refined and will be applicable to health impact assessment as well as targeting mitigation strategies. More results will thus be produced in the years to come.

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Chapter 7

Pesticides in Amphibian Habitats of Central and Northern California, USA

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Previous studies have indicated that toxicity from pesticide exposure may be contributing to amphibian declines in California and that atmospheric deposition could be a primary pathway for pesticides to enter amphibian habitats. We report on a survey of California wetlands sampled along transects associated with Lassen Volcanic National Park, Lake Tahoe, Yosemite National Park, and Sequoia National Park. Each transect ran from the Pacific coast to the Cascades or Sierra Nevada mountains. Pacific chorus frogs (*Pseudacris regilla*), water, and sediment were collected from wetlands in 2001 and 2002. Twenty-three pesticides were found in frog, water, or sediment samples. Six contaminants including trifluralin, α-endosulfan, chlordanes, and *trans*-nonachlor were found in adult *P. regilla*. Seventeen contaminants were found in sediments, including endosulfan sulfate, chlordanes, 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene (4,4′-DDE), and chlorpyrifos. The mean number of chemicals detected per pond in sediments was 2.4 (2.5, standard deviation).

In Occurrence, Fate and Impact of Atmospheric Pollutants on Environmental and Human Health; McConnell, L., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

In water, 17 chemicals were detected, with β-endosulfan being present in almost all samples. Trifluralin, chlordanes, and chlorpyrifos were the next most common. The mean number of chemicals in water per pond was 7.8 (2.9). With the possible exception of chlorpyrifos oxon in sediments and total endosulfans, none of the contaminants exceeded known lethal or sublethal concentrations in *P. regilla* tissue. Endosulfans, chlorpyrifos, and trifluralin were associated with historic and present day population status of amphibians. Cholinesterase, an essential neurological enzyme that can be depressed by certain pesticides, was reduced in tadpoles from areas with the greatest population declines.

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Introduction

Global declines of amphibian populations have been well documented, and many causes have been suggested for these declines including habitat loss and degradation, diseases such as chytridiomycosis, climate change, ultraviolet radiation, introduced predators, and contaminants (*1*).

The Central Valley of California, USA, is an extremely productive agricultural area. Each year hundreds of thousands of kg of active ingredient pesticides are applied to crops. These chemicals can volatilize and be carried by wind currents for long distances (*2*) where they are deposited in some of our largest parks and wilderness areas (*3*). There they can come into contact with aquatic organisms including amphibians. Several studies have found measurable concentrations of pesticides and other organic contaminants in air, snow, water, and sediments of wetlands inhabited by California amphibians (*3–6*), as well as in frog tissues (*7–10*). Some of these pesticides can be lethal at a few parts per billion, within the range of environmentally realistic concentrations (*11*, *12*). In addition, sublethal concentrations can reduce rates of growth and development, and thus affect tadpole survival (*13*). Other pesticides induce endocrine effects that may alter reproductive success (*14*).

The purpose of our study was to describe pesticide concentrations in water, sediment, and Pacific chorus frog (*Pseudacris regilla*) tissue over a two year period, and a broad geographic area extending from the Pacific coast through the Central Valley to the Cascades or Sierra Nevada mountains. The null hypotheses we tested were: 1) there are no apparent north-south or west-east trends in pesticide concentrations within central and northern California; 2) historic and present day status of amphibian populations are not related to pesticide concentrations, and 3) cholinesterase concentrations in adult and larval treefrogs do not differ geographically, or between populations showing declines or not.

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Material and Methods

Frog, Tadpole, Water, and Sediment Samples

Pseudacris regilla adults and tadpoles, sediment, and water were collected in 2001 and 2002 along four transects that began at the Pacific coast and extended east to montane sites in the southern Cascades and the Sierra Nevada: *Lassen*, *Tahoe*, *Yosemite*, and *Sequoia* (Figure 1). From north to south the transects were: Fort Bragg to Lassen Volcanic National Park; Point Arena to Lake Tahoe; Point Reyes National Seashore to Yosemite National Park; and Piedras Blancas to Sequoia National Park. Sampling occurred at five locations along each transect: *Coast* (3 – 66 m elevation), Coast Range mountains (*Range*; 131 – 691 m), eastern edge of the Central Valley (*Valley*; 61–150 m.), Cascades/Sierra Nevada foothills (*Foothill*; 265– 858 m), and mid-elevation of the Cascades/Sierra Nevada (*Montane*; 1887 – 2359 m). The Point Reyes to Yosemite transect had an additional high-elevation location near Tioga Pass in Yosemite (*Alpine*; 2605 – 3019 m).

Quality Assurance/Quality Control

All solvents utilized in this study were reagent grade or chromatographic grade from Fisher Scientific (Springfield, NJ, USA). All solid reagents such as drying agents and laboratory sand or other chemicals used in sample processing were high purity/analytical grade and were also purchased from Fisher Scientific. Organic carbon-free de-ionized water was produced using an in-house system by Hydro Service and Supplies, Inc. (Durham, NC, USA).

After collection, samples were kept on dry ice in the field and shipped by overnight delivery to USDA in Beltsville, MD. All glass jars and other glassware used in sample collection and processing were cleaned with laboratory detergent, rinsed with copious quantities of tap water, followed by organic-carbon-free de-ionized water, chromatographic grade acetone, followed by baking in a large muffle furnace at 300 °C for at least 4 h.

High purity standards ($\geq$ 98% purity) were used for all analytes (Table I) from Chem Service, Inc. (West Chester, PA, USA), Sigma Aldrich (St. Louis, MO, USA), or Cambridge Isotopes (Tewksbury, MA, USA). The compound PCB 204 (2,2′,3,4,4′,5,6,6′-octachlorobiphenyl, CAS Number 2051-24-3) was used as the internal standard. A five-point calibration curve spanning the range of sample response was established for each compound and instrument response was linear over the calibration standards range ($r^2 \geq 0.99$).

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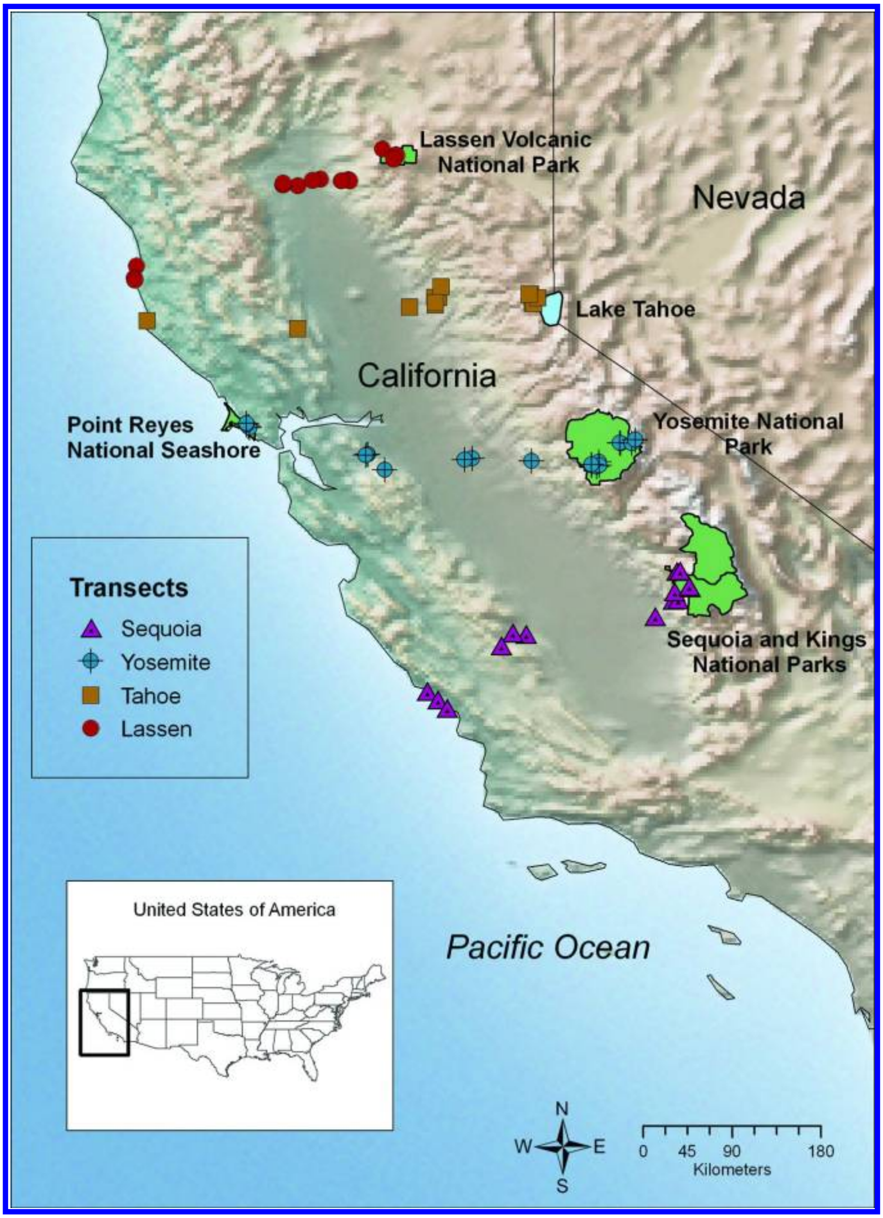

Figure 1. Map of California, USA showing the four transects and locations of the wetlands sampled along with National Parks of interest.

Table I. Target analytes with method detection limits (MDLs) and average percent spike recovery values for sample matrices.

	Method Detection Limit[a]			*Mean Percent Spike Recovery*		
	Water	*Sediment*	*Amphibian*	*Water*	*Sediment*	*Amphibian*
Common Name	*ng/L*	*ng/g d.w.*	*ng/g fr.wt.*	*Percent ± standard deviation*		
aldrin	na[b]	0.37	0.22	na	100±19	75±5
α-chlordane	0.7	0.52	0.21	58±15	116±21	79±6
γ-chlordane	0.2	0.37	0.16	85±11	115±20	79±6
chlorothalonil	0.2	0.08	0.08	95±12	26±8	98±17
chlorpyrifos	0.2	0.32	0.24	97±11	94±19	78±6
chlorpyrifos oxon	2.0	3.0	1.9	111±4	114±22	96±31
4,4′-DDD[c]	na	0.64	0.23	na	91±66	79±7
4,4′-DDE[d]	0.3	0.57	0.23	78±6	107±43	73±5
2,4′-DDT[e]	0.3	na	na	120±13	na	na
4,4′-DDT[f]	0.7	2.0	na	81±9	14±63	na
diazinon	1.2	4.6	0.93	74±36	80±87	94±29
dieldrin	na	0.89	0.16	na	103±20	95±5
α-endosulfan	0.1	0.32	0.17	99±4	93±21	79±6
β-endosulfan	0.2	0.15	0.20	98±1	95±21	79±6
endosulfan sulfate	0.3	0.28	0.26	87±2	89±21	92±16

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Table I. (Continued). Target analytes with method detection limits (MDLs) and average percent spike recovery values for sample matrices.

	Method Detection Limit[a]			*Mean Percent Spike Recovery*		
	Water	*Sediment*	*Amphibian*	*Water*	*Sediment*	*Amphibian*
Common Name	*ng/L*	*ng/g d.w.*	*ng/g fr.wt.*	*Percent ± standard deviation*		
fipronil	na	0.25	1.8	na	50±20	62±15
heptachlor	na	0.31	0.29	na	118±24	109±6
heptachlor epoxide	na	0.25	na	na	110±21	na
α-HCH[g]	0.1	0.53	0.21	78±7	86±17	76±6
γ-HCH[h]	0.2	0.16	0.20	95±8	91±17	78±5
malathion	1.6	1.8	0.80	109±12	49±106	115±6
mirex	na	0.35	0.28	na	112±21	60±8
cis-nonachlor	na	0.67	0.23	na	137±23	82±6
trans-nonachlor	0.4	0.66	0.22	59±7	136±24	81±6
oxychlordane	na	0.39	na	na	101±21	na
trifluralin	0.2	0.33	0.17	87±6	63±18	87±5

[a] Method detection limits provided assume a water sample volume of 10 L, a sediment sample dry weight (d.w.) of 10g, and an amphibian sample mass of 10g. Actual sample volumes and masses varied. Sediment MDL in ng/g dry weight, and amphibian MDL in ng/g fresh weight. [b] na = not analyzed. [c] 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene. [d] 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene. [e] 1-chloro-2-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene. [f] 1-chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene. [g] (1α,2α,3β,4α,5β,6β)-1,2,3,4,5,6-hexachlorocyclohexane. [h] (1α,2α,3β,4α,5α,6β)-1,2,3,4,5,6-hexachlorocyclohexane, also known as lindane.

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The mass spectrometer was tuned prior to each sequence of samples to evaluate the instrument performance, and chromatographic conditions were monitored closely to maintain consistent response factors and peak shape. The mass spectrometer was recalibrated every 20 to 25 sample injections. Quantification of each compound was calculated based on the area of the ion with the largest abundance. Confirmation of a particular compound in a sample was determined by the presence of at least one of the two qualifying ions in the proper ratio to the quantifying ion (± 20%). The requirement for only one qualifying ion in the proper ratio is due to the use of the ECNI mode where the number of ions in the mass spectra is often dominated by one or two ions, with very small contributions from other ions.

Method detection limits (MDLs) were determined for each analyte (*16*) (Table I). MDLs for water were <1 ng/L for all analytes except the organophosphate pesticides which ranged from 1.2 to 2.0 ng/L for a 10-L sample. MDLs for sediments and amphibians were all ≤ 2.0 ng/g based on a 10-g sample size. The limit of quantitation was defined as three times the MDL value. Mean spike recovery values for water were all ≥74% except for α-chlordane and *trans*-nonachlor, which averaged 58 to 59%. Measured concentrations of these two compounds in water were probably lower than actual values. Mean spike recovery values for sediments were all ≥ 80% except for chlorothalonil, 4,4′-DDT, fipronil, malathion, and trifluralin which were all <63%. Of these five compounds, only trifluralin was found in two sediment samples. Mean spike recovery values for amphibians were all ≥ 73% except for fipronil and mirex which were < 62%, again indicating that reported concentrations were lower than actual values. Only one amphibian sample contained detectable levels of mirex and none contained fipronil. Concentrations were not adjusted for recovery. Blank sample extracts did not exhibit any interfering peaks at levels above the MDLs.

Sediments

We used a Wildco model 2424 sediment corer (Wildlife Supply Company, Buffalo, NY) to collect 3-5 sediment cores from different areas within each wetland or site. The top 2.5 cm of each core was mixed in a clean, stainless steel bowl before transfer to a pre-cleaned, wide-mouth amber glass jar. Sampling equipment was cleaned between sites using reagent grade acetone and immersion in a 10% bleach solution to prevent the spread of infectious diseases. Samples were kept frozen until processed.

Just prior to extraction, sediment samples were thawed at 4 °C for two d. Each sample was well mixed prior to removing duplicate aliquots of approximately 15 g. The first aliquot was used to determine percent moisture, and the second aliquot was used for contaminant analysis.

The wet sediment sample was mixed with approximately 3 g of anhydrous $MgSO_4$ to dry the sample and grind it into a fine powder. The dried sample was transferred to a 22 mL, stainless steel extraction cell containing a 1.98-cm diameter cellulose filter (Dionex, Inc. Sunnyvale, CA, USA) at its bottom. The remaining space in the extraction cell was filled with clean, granular Na_2SO_4 that had been pre-baked at 500 °C for 24 h. Samples were extracted in batches of 20 samples

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with appropriate blank sample and spiked samples. Blank and spiked samples contained laboratory sand that had been baked at 430 °C for 24 h and mixed with $MgSO_4$.

Dried sediment samples were extracted using a Dionex Accelerated Solvent Extractor 200 (Dionex, Inc. Sunnyvale, CA, USA) The extraction conditions used were: oven temperature, 125 °C; pressure 1.4×10^4 kPa; heat, 6 min; static, 5 min; flush, 90%; purge, 180 seconds; solvent 1: ethyl acetate 20%; solvent 2: dichloromethane 80%; cycles, 3.

An alumina column clean-up procedure was used prior to analysis similar to methods outlined by the U.S. Environmental Protection Agency (*15*). Alumina (80-200 mesh, Fisher Scientific) was baked prior to use at 550 °C for at least 4 h. Just prior to use, 4 g of alumina was vigorously shaken with 240 µL (6% by mass) of organic-carbon-free water for approximately 10 min. The activated alumina was added to a low-pressure chromatography column followed by a 1-cm layer of clean Na_2SO_4. The clean-up column was prepared by rinsing with 25 mL of 3:1 dichloromethane:acetone. The 5 mL sample extract was transferred to the column before adding a total of 40 mL of the solvent mixture. All of the column eluant was collected. One gram of copper turnings (≥99% purity, Fisher Scientific) was added to the cleaned extract to remove elemental sulfur, and the extracts were exchanged into hexane and concentrated to a final volume of 1 mL.

Amphibian Tissue

Up to six adult male *P. regilla* and up to 10 tadpoles were collected from each site. Adult treefrogs were located at night in breeding ponds. Specimens were collected by hand or with a dip net, placed in 30 mL Teflon vials (Savillex Corp., Minnetonka, MN, USA), and stored in liquid nitrogen until shipping. Tadpoles were also collected from each site, but were only analyzed for cholinesterase activity.

Composite tissue samples (~5-10 g) were ground under liquid N_2 with 4 g of $MgSO_4$ prior to extraction using a SPEX Certiprep 6750 Freezer Mill (SPEX Certiprep, Inc., Metuchen, NJ, USA) using 2, 1-min pulverization cycles with a 1 min cooling time between cycles. Prepared samples were stored at -40 °C until extraction. Lipid content of the tissues was not determined due to the limited mass of available samples and the very low concentrations expected.

Ground tissue samples with drying agent were extracted using a slightly modified version of that used by Lehotay *et al.* (*17*). Samples were transferred to 30-mL Nalgene Teflon™ FEP tubes (Fisher Scientific). To each sample, 1.6 g of sodium acetate•$3H_2O$ was added followed by 10 mL of 1% acetic acid in acetonitrile. The tube was sealed and shaken vigorously for approximately 1 min. The tubes were then centrifuged at 1500 rpm for 1 min.

Extracts of tissue underwent a clean-up process using primary secondary amine solid phase extraction (SPE) cartridges (Varian SPEC® PSA, 10 mL reservoir, 35 mg sorbent; Varian, Inc. Palo Alto, CA, USA) to which 1.0 g of anhydrous $MgSO_4$ was added to further dry the extract. The extract was decanted from the centrifuge tube to the cartridge reservoir and allowed to pass through the bedding at approximately 3 drops/sec. The eluant was exchanged into toluene and reduced to a 0.5 mL final volume for analysis using a gentle stream of N_2. Tissue samples were extracted in batches of 20 with appropriate blank and spike samples included.

Water

Water samples were collected in 18-L stainless steel containers with airtight seals. All water samples were filtered prior to extraction using two in-line stainless steel filter holders housing a 142-mm diameter, 1-µm pore size multi-grade GMF glass fiber filter (Whatman, Inc. Florham Park, New Jersey, USA) and a 90-mm diameter 0.7-µm pore size GF/F filter (Whatman, Inc.), respectively. Approximately 10-L samples of filtered water were extracted using SPE via a method described by Liu *et al.* (*18*). Eluants were reduced to a final volume of 1.0ml in acetonitrile. Some water samples contained very fine particulates and colloidal material that were not removed by filtration. These particles clogged the SPE cartridge, hence the volume of some samples was <10 L.

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Analytical Methods

Water and sediment sample extracts were analyzed for 18 and 25 pesticides, respectively, using a Hewlett Packard (Palo Alto, CA, USA) model 5890 gas chromatograph coupled to a 5989A mass spectrometer in the electron capture negative ion (ECNI) mode with selected-ion monitoring. Methane was the ionization gas at a pressure of 213 Pa. The source and quadrapole temperatures were 150 °C and 100 °C, respectively. Chromatographic conditions were as follows: 30-m DB-17 MS capillary column (Agilent Technologies, Inc., Palo Alto, CA, USA), 0.25-mm inner diameter, 0.25-µm film thickness, ultra high purity helium carrier gas was used at a constant flow rate of at 1.42 mL/min. The temperature program was: injector port temperature 290 °C, initial oven temperature 130 °C, hold 1.0 min, 6°/min to 205 °C, hold 4.5 min, 6°/min to 300 °C, hold 5.50 min. The detector interface on each method was 300 °C.

Extracts of the amphibian tissue samples were analyzed for 22 pesticides (Table I) in pulsed-splitless mode using an Agilent Model 6890 (Santa Clara, CA, USA) gas chromatograph coupled to a Model 5973 inert mass spectrometer in the electron capture negative ion chemical ionization and selected-ion monitoring mode. Methane was the ionization gas at a pressure of 40 Pa. The source and quadrapole temperatures were 150 °C. Gas chromatography parameters for monitored compounds were as follows: 30-m DB-17 MS capillary column (J&W Scientific Corporation, Folsom, CA), 0.25-mm inner diameter, 0.25-µm film thickness, helium carrier gas, constant flow at 1.0 mL/min; temperature program: injector port temperature 230 °C, initial temperature 130 °C, hold 1.0 min, 6°/min to 205 °C, hold 4.5 min, 6°/min to 300 °C, hold 6.17 min. The injection port pressure was 82 kPa with a pulse pressure of 345 kPa for 1 min. The detector interface was 300 °C.

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Other Analyses

Total cholinesterase activity was analyzed using the spectrophotometric method developed by Ellman *et al.* (*19*) modified to accomodate the reduced volumes of reagents and substrate required by the SpectroMax 250 (Molecular Devices, Sunnyvale, CA, USA) multi-plate reader. The weights of intact tadpoles were recorded, and the tadpoles were reweighed after their gut coils were removed. Samples were diluted 1:50 w:v in pH 7.0 Tris buffer and homogenized. A 20 uml aliquot was transferred to a well and mixed with pH 7.8 Tris, 5,5′-dithiobis-(2-nitrobenzoic acid (DTNB), and acetylthiocholine. Rate of reaction was determined over 3 min at 28 °C. Rates were converted to ug/min/g of tissue and analyzed with analysis of variance.

Statistical Analysis

All concentration data were examined for the assumptions of parametric statistics including normality and homoscedasticity. Because of numerous non-detects, we employed non-parametric analyses for most of the comparisons. Although the initial sampling design followed a complete block design, the absence of water or amphibians at a few sites created missing blocks in both years. Therefore, we could not test the interaction of transects and locations, and resorted to one-way analyses using Kruskal-Wallis tests. *A posteriori* differences were determined with Tukey's tests. Because of repeated analyses of the same data set, we employed Bonferroni corrections so that $\alpha = 0.008$ for water and either 0.0021 (2001) or 0.0015 (2002) for sediments. Although this marks statistical significance, we believe that the correction may underestimate ecological significance. Therefore we show statistical at $p < 0.05$. All means are arithmetic with standard errors.

Each site was scored on current population status based on data collected over >15 years of monitoring. Population status values ranged from 1 to 4 where: 1 = zero to low decline in population sizes or in number of populations; 2 = notable declines in population sizes or in number of sites occupied; 3 = some species nearly extirpated from region, significant loss of populations; and 4 = extirpation of at least one species and typically significant declines in others.

Results

Residues in *Pseudacris regilla*

Eleven contaminants were found in adult *P. regilla* tissues during 2001, 6 of which were common and at high enough concentrations to report (Table II). Of these, trifluralin was by far the most commonly occurring, with detections at 15 of 37 sites; no other contaminant was detected in tissue at more than three sites. Except for the *Lassen* transect, sites located in the *Foothills* had the greatest number of contaminants detected in adults. In 2002, only six chemicals were found in *P. regilla*, but trifluralin was found in *P. regilla* from every wetland that supported frogs that year.

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Table II. Occurrence of contaminants in adult *Pseudacris regilla* from 37 wetlands in central and northern California in 2001, and 50 wetlands in 2002[a]. Only chemicals that occurred in both years are reported; other chemicals found in 2001 were below quantitative limits.

Chemical	*Year*	*Total Hits*	*Mean*	*Median (ng/g fr. wt.)*	*Maximum*
α-endosulfan	2001	1	0.27	0.27	0.27
	2002	1	0.28	0.28	0.28
α-chlordane	2001	3	0.59	0.68	25.11
	2002	1	1.34	1.34	1.34
γ-chlordane	2001	1	1.52	1.52	1.52
	2002	0			
mirex	2001	1	0.12	0.12	0.12
	2002	0			
trans-nonachlor	2001	2	1.11		1.61
	2002	1	0.37	0.37	0.37
trifluralin	2001	15	1.01	0.085	4.69
	2002	50	0.16	0.12	0.56

[a] Total hits = number of wetlands with a least a trace of the compound. Mean, median, and maximum in ng/g fresh weight are based on animals that had at least a trace of that chemical. If a chemical was detected, but its concentration was < MDL, a random value between 0 and MDL was used to calculate the concentration. Concentrations are not lipid normalized, but based on fresh weight. Mean and median values reported may be lower than reported MDLs due to the use of fractions of MDL values in calculations.

Contaminants in Water

Of the 49 wetlands investigated in 2001, 48 included water samples. Seventeen chemical contaminants were found in the water (Table III). α-endosulfan and β-endosulfan were nearly ubiquitous among the sampled wetlands, and were often present in combination with endosulfan sulfate. α-chlordane, chlorpyrifos, and trifluralin were also found in at least 40 of the wetlands. γ-chlordane was the only other chemical found in at least half of the sites. Wetlands had a mean of 7.8 ± 2.9 chemicals detected in water (range 0 to 13).

Concentrations for some of the most commonly detected water contaminants across locations are provided in Figure 2A to 2C and across transects in Figure 2D to 2F. During 2001, the following chemicals differed significantly among west-east locations: diazinon, α-HCH, total endosulfans, chlorpyrifos, trifluralin, and endosulfan sulfate (Table IV); endosulfan sulfate and α-HCH were significant even after the Bonferroni's correction. Concentrations of diazinon were highest at *Coast* locations than in more eastern sites except for *Alpine*, and α-HCH concentrations were highest at *Foothills* locations. With total endosulfans and chlorpyrifos, *Coast* and *Range* sites had lower concentrations than the *Foothills* or *Montane*. When comparing transects, mean concentration of γ-chlordane was high along the *Lassen* transect compared to the other transects, but that was primarily due to one site, and the variance was quite high for this chemical. Chlorpyrifos and diazinon were similar among transects but diazinon was not detected in the *Yosemite* transect samples.

Table III. Frequency of occurrence, mean, median and maximum concentrations (ng/L) in water of organic contaminants found in 47 wetlands in central and northern California during 2001[a].

Chemical	*Total Hits*	*Mean*	*Median*	*Maximum*
α-chlordane	41	1.32	1.20	3.34
γ-chlordane	34	0.17	0.02	5.09
oxy-chlordane	3	0.13	0.12	0.20
chlorothalonil	10	0.92	0.42	4.81
chlorpyrifos	40	0.34	0.24	1.13
chlorpyrifos oxon	2	0.99	0.99	1.48
diazinon	7	7.45	2.55	21.85
4,4′-DDE	2	0.41	0.41	0.66
2,4′-DDT	6	13.86	1.28	72.24
α-endosulfan	41	0.06	0.05	0.11
β-endosulfan	42	0.08	0.07	0.17
endosulfan sulfate	38	0.08	0.06	0.61
α-HCH	5	0.07	0.06	0.11
γ-HCH	15	0.59	0.09	5.0
malathion	12	0.37	0.34	0.65
trans-nonachlor	18	0.03	0.02	0.07
trifluralin	41	0.09	0.07	0.61

[a] Total hits = number of wetlands with at least a trace of the chemical. If the measured concentration was < MDL, a value of 0.5* MDL was used to calculate the concentration. This approach sometimes led to mean and median concentration values less than reported MDLs.

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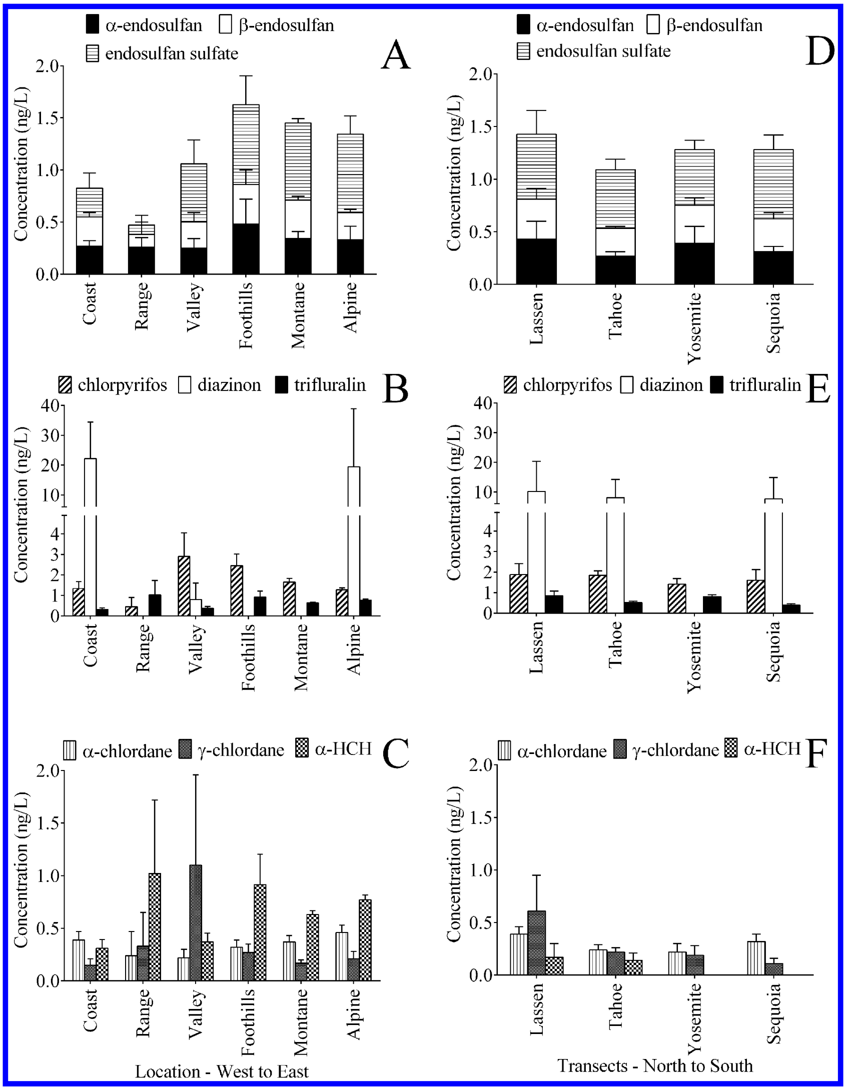

Figure 2. Distribution of contaminants (ng/L) in wetland water by location and transect for 2001. Plots A – C are mean concentrations ± standard error across location type including all sites; Plots D – F are mean concentrations ± standard error across transects.

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Table IV. Results of Kruskal-Wallis tests on ranked values of chemical concentrations by location and transect along transects that ran from the Pacific Coast to the Cascades and Sierra Nevada mountains, 2001 and 2002.

Year	*Matrix*	*Chemical*	*Comparison*[a]	*df*	*F*	*P*[b]
2001	Water	chlorpyrifos	Location	5,36	2.91	0.0262
2001	Water	diazinon	Location	5,36	3.9	0.0063
2001	Water	endosulfan sulfate	Location	5,36	4.95	**0.0015**
2001	Water	total endosulfans	Location	5,36	4.24	0.0039
2001	Water	α-HCH	Location	5,36	4.87	**0.0017**
2001	Water	trifluralin	Location	5,36	4.18	0.0043
2001	Water	γ-HCH	Transect	3,36	3.26	0.0317
2001	Water	trifluralin	Transect	3,36	3.64	0.0212
2001	Sediment	endosulfan sulfate	Location	5,40	7.04	**<0.0001**
2001	Sediment	total endosulfans	Location	5,40	6.75	**0.0001**
2001	Sediment	α-chlordane	Transect	3,40	3.32	0.029
2001	Sediment	α-endosulfan	Transect	3,40	3.56	0.022
2002	Sediment	endosulfan sulfate	Location	5,49	9.46	**<0.0001**
2002	Sediment	total endosulfans	Location	5,49	6.54	<0.0001
2002	Sediment	β-endosulfan	Transect	3,49	3.44	0.023

[a] Differences in transects reflect a north/south trend whereas difference in locations reflect west-east trends. [b] P values in bold are significantly different based on Bonferroni's correction of α=0.0020.

Contaminants in Sediments

In 2001, 16 chemicals were found in sediments, but only 12 were above the MDL (Table V, Figures 3 and 4). The most commonly occurring chemicals in sediments during 2001 were endosulfan sulfate, γ-chlordane, α-HCH, and 4,4′-DDE. The mean number of chemical detections in sediment was 2.4 ± 2.5 (range 0 to 12) per site. Only endosulfan sulfate differed significantly among locations; its concentrations were higher in the *Montane* sites than in *Coast*, *Valley* or *Foothills*, and *Alpine* had higher concentrations than *Coast*. α-endosulfan was not among the most commonly detected chemicals in sediment, but we did detect a significant difference among transects using Kruskal-Wallis with *Sequoia* having greater concentrations than *Lassen*.

Table V. Frequency of occurrence (hits) and mean, median and maximum concentrations (ng/g d.w.) of organic contaminants in sediments of wetlands in Northern and Central California during 2001 and 2002.

	2001 (n = 41)				*2002 (n = 50)*			
Chemical	*Hits*	*Mean*	*Median*	*Max*	*Hits*	*Mean*	*Median*	*Max*
α-chlordane	4	0.85	0.55	2.0	5	0.53	0.42	1.3
γ-chlordane	15	0.62	0.43	1.7	27	0.32	0.3	0.97
chlorpyrifos	6	0.63	0.64	0.91	12	0.77	0.22	6.44
chlorpyrifos oxon	3	26	30	35	2	22	22	37
4,4′-DDE	11	2.02	1.25	9.2	11	1.84	0.8	6.66
α-endosulfan	4	0.42	0.35	0.78	3	0.8	0.26	1.87
β-endosulfan	4	0.21	0.17	0.4	8	0.48	0.21	1.87
endosulfan sulfate	19	1	0.28	5.28	21	0.3	0.18	1.56
α-HCH	13	21.74	17.98	58.43	8	5.27	6.11	8.71
heptachlor epoxide	4	0.35	0.19	0.94	3	0.13	0.16	0.17
cis-nonachlor	3	0.8	0.87	0.98	3	0.92	0.75	1.64
trans-nonachlor	3	0.78	0.53	1.6	6	0.5	0.35	1.7
trifluralin	0				2	0.49	0.49	0.84

In 2002, 17 compounds were found in the sediments of the 55 wetlands with 13 above the MDL. Of these, γ-chlordane, endosulfan sulfate, chlorpyrifos, and 4,4′-DDE were most common (Table V, Fig. 3 and 4). Wetlands had a mean of 2.04 ± 2.4 contaminant detections in the sediment (range 0 to 12). Endosulfan sulfate differed among locations with *Montane* having higher concentrations than other sites and *Alpine* had greater concentrations than *Coast* or *Foothill*. The degradation product 4.4′-DDE appeared to be higher in *Alpine* locations, but large variance negated statistical significance.

The occurrence of specific sediment contaminants in one year did not reliably predict the presence of the same chemical in the other year (Table VI). In 2001, 7 (15%) of the wetlands had no detectable contaminants in sediment, though all of these had at least some contaminants in the water. In 2002, 11 (20%) of the wetlands had no detectable contaminants in the sediments. Among the 37 ponds analyzed in both years, the mean probability that a pond having a specific chemical in one year would have the same chemical in both years was 14%, and ranged from zero, for infrequently occurring chemicals, to 50% for endosulfan sulfate.

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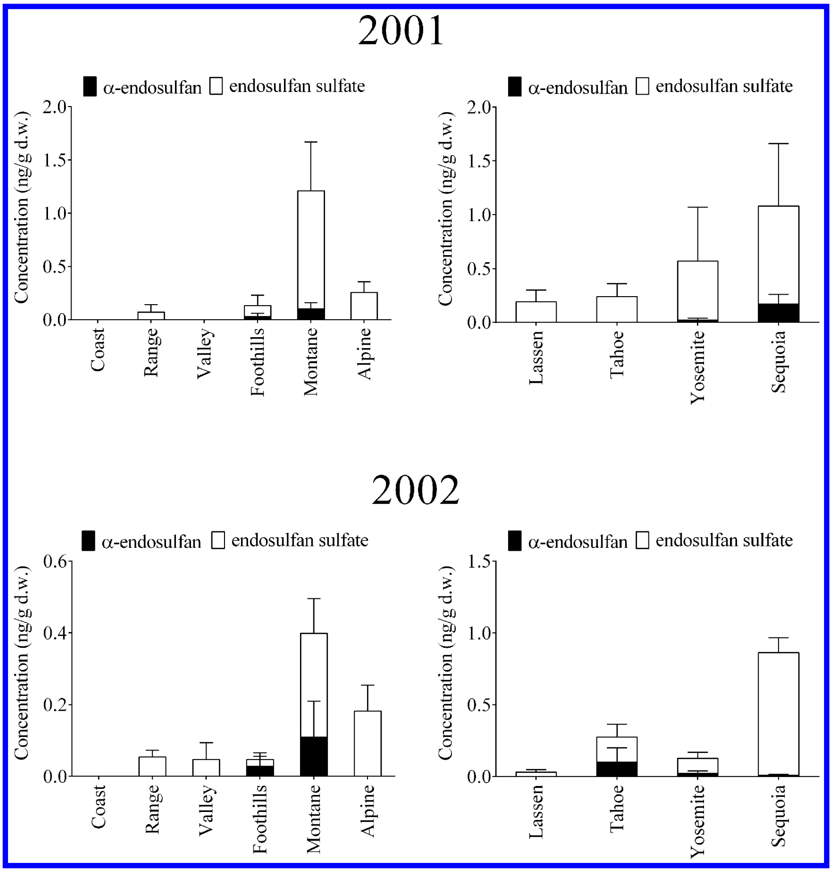

Figure 3. Distribution of α-endosulfan and endosulfan sulfate in wetland sediments by location including all sites and by transect for 2001 and 2002.

Relationship between Contaminant Residues and Amphibian Populations

Concentrations of the most common organic contaminants in water varied among amphibian population status in 2001 as did sediment concentrations in 2001 and 2002 (Figure 5). In 2001, three contaminants in water and three in sediments differed significantly among population status categories (Table VII). Aqueous diazinon concentrations were higher among status 1 wetlands (zero to low amphibian population declines) than in other population status categories. Trifluralin was significantly lower in status 1 and 4 (at least one species extirpated and substantial declines in others) wetlands than in status 3 (some species nearly extirpated) wetlands. Among sediment contaminants in 2001, α-endosulfan and α-chlordane were greater in status 4 than in 3 or 1, and endosulfan sulfate was greater in 3 and 4 than in 1. During 2002, endosulfan sulfate, γ-chlordane and chlorpyrifos were significantly different among status categories (Table VII). Chlorpyrifos and endosulfan sulfate were greater in category 3 than in 1, and γ-chlordane was higher in 3 than in 4.

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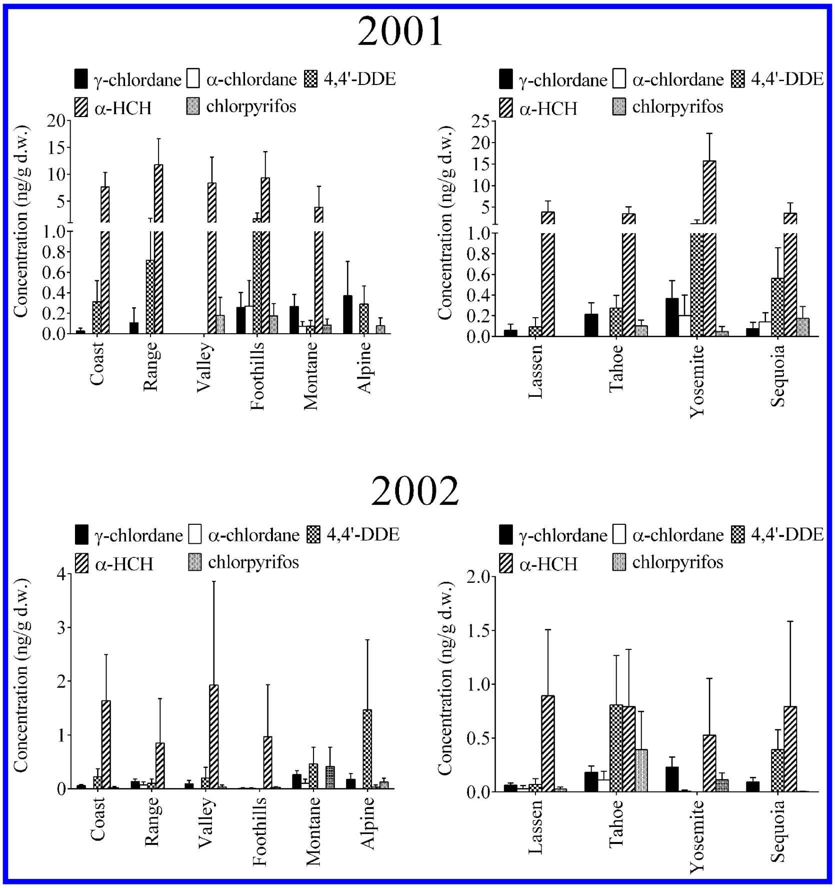

Figure 4. Distribution of pesticides and p,p'-DDE in wetland sediments by location including all sites and by transect for 2001 and 2002.

Cholinesterase (ChE) in Tadpoles

In both years, ChE activity increased significantly with developmental stage of tadpoles (2001: $F_{4,364}=50.97$, $p<0.0001$; 2002: $F_{4,408}=6.80$, $p<0.0001$). In a posteriori comparisons for 2001, late hind limb [Gosner (*20*) stage 40-41, > mid hind limb (37-39) = early hind limb (35-36) > limb bud (27-34) > pre limb (24-26)]. In 2002, the sequence was a little different: late hind limb > early hind limb = limb bud = middle hind limb > pre-limb.

In 2001, there was a significant difference among population status groups and ChE ($F_{3,34}=6.34$, $p=0.0018$), with tadpoles coming from populations with status 1 (no or slight decline in population sizes or in number of populations) having higher ChE values than those from status groups 3 and 4 (Figure 6A). In 2002, there was a similar relationship ($F_{3,38}=10.09$, $p<0.0001$) except that the status groups 1 and 2 differed only from group 3 (Figure 6C).

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Table VI. Yearly variation in the occurrence of specific contaminants in sediments of the Cascades and Sierra Nevada mountains, California, 2001-2002[a].

Chemical	*Neither Year*	*Both Years*	*2001 Only*	*2002 Only*	*Prob (%)*[b]
α-chlordane	32	1	3	1	20
α-HCH	23	3	7	4	21
γ-chlordane	13	5	9	10	21
2,4′-DDD	36	0	1	0	0
2,4′-DDE	28	2	4	3	22
chlorothalonil	36	0	0	1	0
chlorpyrifos	26	2	2	7	18
chlorpyrifos oxon	33	0	2	2	0
cis-nonachlor	33	0	3	1	0
endosulfan sulfate	15	11	6	16	50
α-endosulfan	32	1	2	2	20
β-endosulfan	30	2	2	3	28
fipronil	36	0	0	1	0
heptachlor epoxide	33	0	4	0	0
trans-nonachlor	31	1	3	2	17
trifluralin	35	0	0	2	0

[a] Values are the number of wetlands with detectable amounts of each chemical. [b] Prob is the probability that if a wetland had a chemical in one year it had it in both years. Total number of wetlands sampled in both years = 37.

In an ANOVA over transects and locations (west or east of the Central Valley) for 2001, there were significant differences in ChE activity among transects ($F_{3,29}$=7.31, p=0.0014) and locations ($F_{1,29}$=7.74, p=0.0109), but not in their interaction ($F_{3,29}$=0.98, p=0.4199). In 2001, ChE was highest along the *Sequoia* transect, and higher in western than in eastern locations (Figure 6B). In 2002, we detected differences among locations ($F_{1,32}$=8.25, p=0.0082), but not among transects ($F_{3,32}$=0.13, p=0.941), or in the interaction of transect and location ($F_{3,32}$=0.65, p=0.590). Western sites had higher ChE values than eastern sites (Figure 6D).

Cholinesterase (ChE) in Adult Frogs

We did not detect any difference among population status groups for adult ChE in 2001 ($F_{3,36}$=1.16, p=0.340). There were no significant relationships among concentrations of any of the organophosphorus pesticides and ChE activity in 2001. In 2002, there was a significant difference among status groups ($F_{3,46}$=14.44,

$p<0.0001$) with adults from combined status groups 1 and 2 having significantly higher ($p=0.05$) ChE values than those in other groups.

In 2001, there were no significant differences among transects ($F_{3,31}=1.70$, $p=0.193$), locations ($F_{1,31}=1.31$, $p=0.263$), or their interaction ($F_{3,31}=0.16$, $p=0.925$) for adult ChE (Table IV). However, in 2002, we did find significant differences in ChE activity among transects ($F_{3,43}=3.72$, $p=0.0198$) and locations ($F_{1,43}=23.64$, $p<0.0001$), but not in the interaction of transect with location ($F_{3,43}=1.32$, $p=0.282$). Adult frogs in western sites had higher ChE values than those in eastern sites ($p=0.05$), and frogs collected along the *Sequoia* transect had significantly higher values than those along other transects. In 2002, the only cholinesterase inhibitors for which we had data were chlorpyrifos and chlorpyrifos oxon in sediments; neither chemical was significantly related to ChE activity in adult *P. regilla*.

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Discussion

Twenty-three organic contaminants were found in the water or sediment of wetlands in central and northern California during 2001 and 2002. Most of the chemicals are probably not directly causing amphibian declines because the chemicals had limited distribution, low concentrations, or low toxicity. However, two groups of chemicals are of concern. One group (Group A) includes trifluralin, endosulfans, and chlorpyrifos that were all widely detected, sometimes in frog tissues, and are highly toxic in both acute and chronic exposures. Endosulfan sulfate, α-endosulfan, and trifluralin were also correlated with amphibian population status. The other group of chemicals (Group B) includes α- and γ-chlordanes, diazinon, and α-HCH. Some of these were not as widely detected than those in Group A, but others were. Diazinon is somewhat toxic to *R. boylii* (LC_{50} = 7.49 mg/L), but the oxon breakdown product diazoxon is 10x more toxic than the parent compound (*11*). The effects of other Group B chemicals are either poorly known for amphibians, or they have low acute toxicity. However, concern about sublethal toxicity or their potential to function as an endocrine disruptor points out the need for more research.

Trifluralin is a dinitroaniline, pre-emergent herbicide with low toxicity to birds and mammals, but high toxicity to aquatic organisms with 96-h LC_{50}s in the 20 to 70 μg/L range (*21*). The 96-h median lethal toxicity of trifluralin in carp (*Cyprinus carpio*) is 45 μg/L, and plasma chemistry changes were observed after 14 d at 5 μg/L, the lowest concentration tested (*22*). In addition to acute lethality, trifluralin may be genotoxic at 1 μg/L in tilapia (*Oreochromis niloticus*; (*23*)). In an in vitro assay on cultured African clawed frog (*Xenopus laevis*) eggs, trifluralin had mild anti-androgenic properties (*24*). Sayim (*25*) found that the 120 d LC_{50} for the red-bellied toad (*Bombina bombina*) was higher than that for these fish, 11.8 mg/L. In an unpublished study Sparling found that the hatching to metamorphosis LC_{50} for *P. regilla* was 5.6 mg/L. However, both studies found severe malformations including truncated and deformed hind limbs and axial skeletons at much lower concentrations (0.8 mg/L in Sparling). In a 96 hr acute toxicity test with green frog (Lithobates clamitans) tadpoles technical grade trifluralin resulted in a LD50 of 9.76 mg/L which was significantly higher than a commercial formulation (Treflan 4D) of trifluralin (LD50=2.81 mg/kg). Both concentrations were substantially higher than the highest concentration found in this study. In a 62-day chronic exposure, tadpoles subjected to 20 µg/L trifluralin were smaller at the end of the study than controls or those exposed to 200 µg/L. No meaningful mortality occurred during the entire chronic exposure (*26*).

Trifluralin was widely used in California during our study, with more than 423,663 kg of active ingredient applied in 2001, and 495,140 kg in 2002 (*27*); by 2010, the amount had declined to 214,313 kg. Our data show that trifluralin was present in water samples and in several frog tissue samples. It was also an important factor in separating sites with healthy amphibian populations from more depauperate sites. The maximum concentration of trifluralin found in water during the current study (0.612 ng/L) is orders of magnitude below the acute LC_{50} concentrations, but long term exposure to other types of pesticides can produce substantial effects at concentrations well below reported LC_{50}s (*12*, *28*).

Chlorpyrifos is a widely used, organophosphorus (OP) pesticide that is highly toxic to aquatic organisms (*21*). The parent compound or its' degradate, chlorpyrifos oxon, was found in 40 water samples during 2001. Concentrations of chlorpyrifos differed significantly among status groups with its highest concentrations in areas with substantial losses of amphibian populations. Chlorpyrifos was the most heavily used insecticide in California during our study; 758,904 kg and 643,949 kg were applied in 2001 and 2002, respectively. It is still extensively used with 583,152 kg applied in 2010 (*27*).

Sparling and Fellers (*12*) tested chronic exposure (Gosner stage 26 to metamorphosis) to chlorpyrifos and found LC_{50} values of 365 µg/L for *P. regilla* and 66 µg/L for the foothill yellow-legged frog (*Rana boylii*). Acute, 96-h toxicity of chlorpyrifos to *R. boylii* was 3.00 mg/L. However, chlorpyrifos oxon was at least 100 times more toxic than the parent form (*11*). The maximum water concentrations of chlorpyrifos found in this study was 1.1 ng/L, and that of chlorpyrifos oxon was 1.5 ng/L, well below acutely toxic concentrations. However, a few wetlands had sediment chlorpyrifos oxon concentrations as high as 37 ng/g. The toxicity of chlorpyrifos, its oxon, or other pesticides in sediments has not been investigated in amphibians and is a complex problem. Chemicals may bind with sediment particles, or organic carbon, reducing their bioavailability to aquatic organism (*e.g.*, (*29*)). Chemicals vary in their affinity for particulates, thus toxicity cannot be directly determined from sediment concentrations without accounting for these affinities.

Chlorpyrifos occurred in snow at concentrations up to 1.4 ng/L at Lake Tahoe and 4.9 ng/L in Sequoia National Park in 1996 (*5*). They also found trifluralin, chlorothalonil, diazinon, malathion, α-HCH, and endosulfans in snow or rain, and reported maximum concentrations of chlorpyrifos of 14,200 ng/L in fog. Winter depositions of pesticides were found in air, dry deposition, and surface waters from the Central Valley up to 3,322 m in the Sierra Nevada. Maximum surface water concentrations were 122 ng/L for chlorpyrifos and 39.2 ng/L for its oxon (*4*). These authors believed that, combined with other OPs such as diazinon and malathion, the total exposure surpassed the acute LC_{50} for an amphipod species (*30*).

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Table VII. Results of Kruskal-Wallis tests on ranked values of organic contaminant concentrations across amphibian population status categories in 2001 and 2002.

Year	*Matrix*	*Chemical*	*df*	*F*	*P*[a]
2001	Water	diazinon	3,38	5.53	0.003
2001	Water	α-HCH	3,38	2.94	0.049
2001	Water	trifluralin	3,38	12.16	**<0.0001**
2001	Water	chlorpyrifos oxon	3,38	2.84	0.051
2001	Water	endosulfan sulfate	3,38	5.09	0.005
2001	Water	total endosulfans	3,38	3.99	0.015
2001	Sediment	α-endosulfan	3,40	4.3	0.014
2001	Sediment	endosulfan sulfate	3,40	4.3	0.01
2001	Sediment	total endosulfans	3,40	4.01	0.014
2001	Sediment	α-chlordane	3,40	3.66	0.022
2002	Sediment	γ-chlordane	3,51	3.46	0.023
2002	Sediment	total chlordanes	3.51	0.7	0.557
2002	Sediment	chlorpyrifos	3,51	4.42	0.008
2002	Sediment	endosulfan sulfate	3,51	5.61	**0.002**
2002	Sediment	total endosulfans	3,51	6.84	**0.001**

[a] P values in bold are significantly different based on Bonferroni's correction of α=0.002.

In 1999, mean chlorpyrifos concentrations in adult *P. regilla* were about 11 ng/g in Yosemite National Park and 7 ng/g at Sequoia National Park (*10*). Diazinon and malathion were also detected in these animals, though at lower concentrations. Sparling et al. (*10*) also found that OP concentrations were greater, and cholinesterase activity was significantly lower, in areas that had reduced amphibian populations compared to areas with healthy populations. Chlorpyrifos concentrations were as high as 12 ng/L in surface waters of four wetlands in Sequoia and Kings Canyon National Parks (*9*) and concentrations were greater at sites where amphibians had declined compared to sites with healthy populations. Cholinesterase depression was also noted in the current study.

Among seven western National Parks, Sequoia National Park had more than 30 times the concentration of chlorpyrifos in the snow pack compared with other parks; moreover, Sequoia was the only park with detectable concentrations of chlorpyrifos oxon (*31*). Recently, Bradford et al. (*32*) reported mean concentrations of chlorpyrifos of 0.677 ng/g. However, their study did not find a significant relationship between pesticide concentrations and cholinesterase activity, and it appears that the relationship between pesticides and population status is not as strong at high elevation sites as it is at lower elevations (<2500 m) (*33*).

In 2010, endosulfan was banned from further use in the USA by the U.S. EPA, and the chemical has also been banned in the European Union, Australia, and 60 other nations worldwide. Many factors affect environmental persistence; endosulfan typically has a half-life of weeks to months (*21*), longer than most OPs, but much shorter than the organochlorines which have already been discontinued. Endosulfan use in California declined by 2008. Total weight of active ingredient was 69,625 kg in 2001 and 64,647 kg in 2002; usage in 2010 was greatly reduced to 16,273 kg (*27*). However, endosulfan, in one or more of its forms (α, β, or sulfate), was found in nearly all water samples during 2001 and in a large proportion of sediment samples in both years, but it was not frequently detected in *P. regilla* tissue. Nonetheless, endosulfan sulfate and α-endosulfan were major factors in separating sites with good amphibian populations from those with reduced populations in the principal components analysis.

Endosulfan can be extremely toxic to aquatic organisms. α-Endosulfan tends to be more toxic than β-endosulfan, with endosulfan sulfate intermediate (*34*). In salmonid fish, the 96-h LC_{50} is about 1.0 µg/L or less (*21*, *34*). Berrill et al. (*35*) found delayed mortality in larval wood frogs (*R. sylvatica*), American toads (*Bufo americanus*), and green frogs (*R. clamitans*) exposed to endosulfan for 96-h at concentrations ranging from 41 to 364 µg/L. Sublethal effects included hyperactivity, paralysis, weakened avoidance responses, reduced growth post exposure, swelling, and discoloration. Even a short (96-h), pulsed exposure to 0.8 µg/L of endosulfan, coupled with variable water temperatures, led to higher mortality and reduced predator avoidance several days post exposure among Blue Mountains treefrog (*Litoria citropa*) tadpoles (*36*). The 96-h LC_{50} in common toads (*Bufo bufo*) is 430 µg/L and chronic exposure to 50 µg/L led to impaired behavior, prolonged time to metamorphosis, skeletal malformations, reduced body weight, and mortality (*37*).

At least one species of declining amphibian in California is extremely sensitive to endosulfan (*12*). Chronic exposure of *R. boylii* and *P. regilla* tadpoles to a 70:30 mixture of α-endosulfan and β-endosulfan under laboratory conditions resulted in reduced growth, and increased time to metamorphosis and mortality. *Pseudacris regilla* was less sensitive than was *R. boylii*. For *R. boylii*, 100% mortality occurred at concentrations >0.8 µg/L, and the estimated LC_{50} was between 0.2 and 0.5 µg/L. For *P. regilla*, all effects occurred at higher concentrations and the estimated LC_{50} was 15.6 µg/L (*12*).

In addition to these effects, 5 µg/L endosulfan has been associated with disruption of pheromone functioning in red-spotted newts (*Notophthalmus viridescens*) (*38*) and 10 to 100 µg/L with respiratory distress and limb deformities (*39*) in streamside salamanders (*Ambystoma barbouri*). Endosulfan also appears to have mild endocrine effects in the invertebrate *Daphnia* (*40*) and in freshwater catfish (*Clarias batrachus*; (*41*)), but we do not know what, if any, endocrine effects might be on amphibians.

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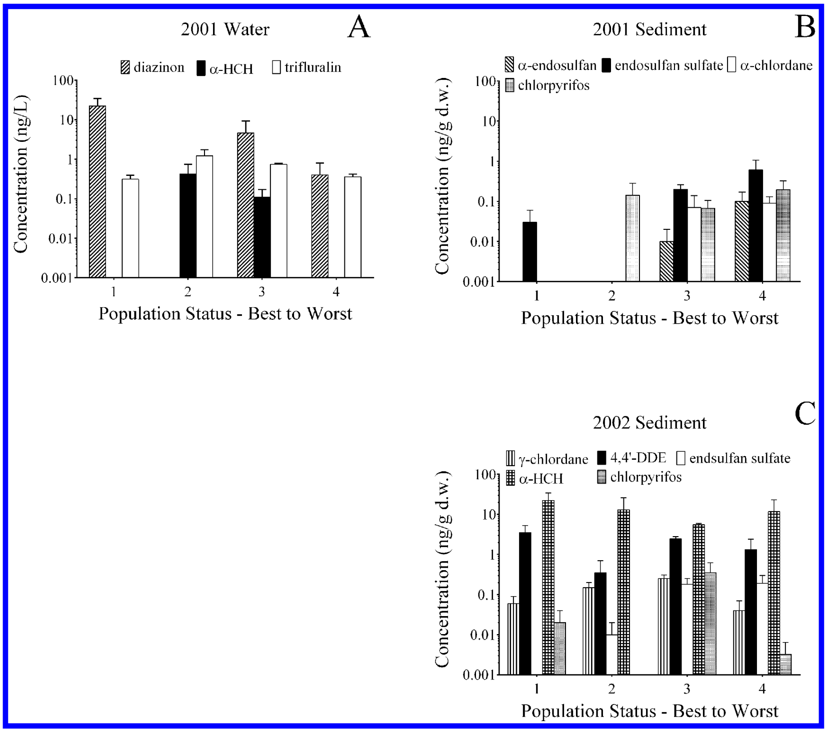

Figure 5. Distribution of most commonly detected organic contaminants in wetland water or sediments by amphibian population status for 2001 and 2002. 5A – 2001 water concentrations by population status; 5B – 2001 sediment concentrations by status; 5C – 2002 sediment concentrations by status.

The maximum concentration of endosulfan (sum of α-endosulfan, β-endosulfan, and endosulfan sulfate) found in our study was 1.2 ng/L in water and 6.2 ng/g in sediments. The concentration in water is below that thought to be toxic, but predictions of toxicity from sediment concentrations are not straightforward. However, it is possible that the endosulfan in sediments found in our study could have sublethal effects. The sum of α-endosulfan and β-endosulfan in surface waters from the Central Valley to Sequoia National Park ranged from 1.3 to 165 ng/L with a mean of 103 ng/L and a median of 108 ng/L (*4*). If endosulfan sulfate concentrations had been determined and added in, the resulting totals may have exceeded the LC50 for *R. boylii*. Other reported total endosulfan concentrations include 1.2 to 1.5 ng/L in two wetlands of Sequoia National Park (*31*); 0.94 to 4.08 ng/L in water and 0 to 1.4 ng/g (α-endosulfan only) in *R. muscosa* (now *R. sierrae*) tissues (*9*); and a range of mean values from 1 to 4 ng/g in adult *P. regilla* in California (*10*).

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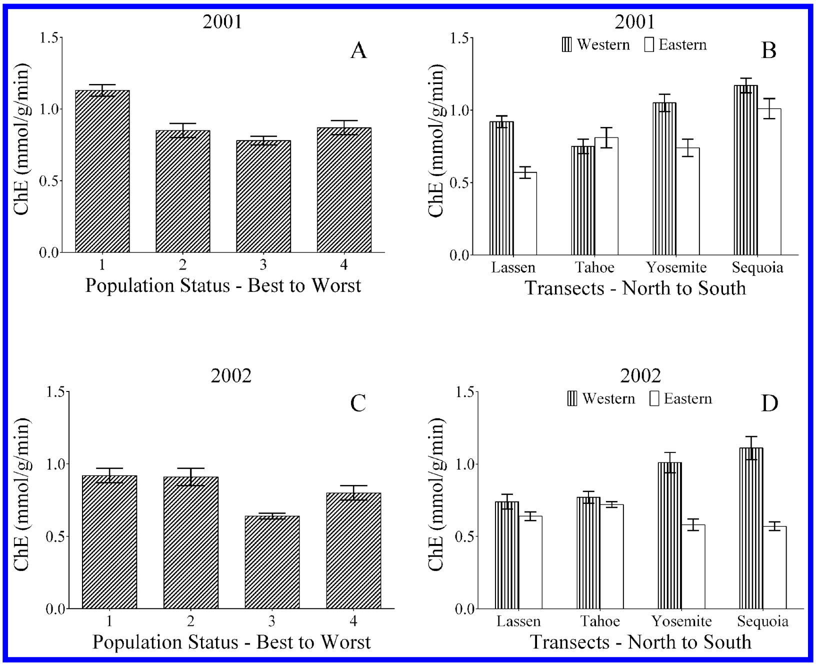

Figure 6. Cholinesterase activity for whole body Pseudacris regilla tadpoles by amphibian population status and transects for 2001 and 2002. 6A – cholinesterase values in 2001; 6B – cholinesterase values in 2002; 6C cholinesterase values across transects in 2001; 6D – cholinesterase values across transects in 2002.

Among the Group B chemicals, α- and γ-chlordane were banned for use in the USA in 1988, but they are extremely persistent organochlorine pesticides. α-HCH is an isomer of the more toxic pesticide γ-HCH (lindane) with which it is often associated. Manufacturing of lindane has also stopped in the USA and most of its use has ceased; however, it is very persistent in the environment. These chemicals are highly toxic to aquatic organisms, may bioaccumulate, and can rapidly bind with sediments (*21*). These chemicals have repeatedly been found in water and frog tissues in the Sierra Nevada (*5*, *9*), but we cannot demonstrate a causative link between their use and amphibian declines.

Diazinon differs from other Group B chemicals because it is an OP pesticide that is still being used. Its 96-h LC_{50} in *R. boylii* is relatively high, 7.49 mg/L, but the toxicity of its oxon derivative is 760 µg/L (*11*), and chronic exposures may result in lower LC_{50} values. Other studies have reported diazinon in the mountains of California (*4*, *10*). The U.S. EPA has banned many uses of diazinon including all home use and application to turf (*e.g.*, golf courses). Application of diazinon has declined from 453,401 kg active ingredient in 2001 to 57,510 kg in 2010 (*27*). However, the pesticide is still used extensively as a dormant spray on commercial orchards, and the resulting run-off was sufficient to produce toxic waters during winter in the Sacramento and San Joaquin Rivers (*42*).

Cholinesterase activity in tadpoles and in adult *P. regilla* differed significantly among locations, transects, and amphibian population status groups. These differences generally agreed with expectations based on contaminant concentrations; however, the differences weren't always consistent. For example, the Sierra Nevada transect, which tended to have the highest contaminant concentrations, had higher (=normal) ChE activities than some of the other transects, and the sites with the poorest population status (status 5) did not have the lowest ChE activities. However, sites with status 1 and amphibian populations tended to have the highest ChE activities. The disparity from what might be expected could be due to small sample sizes in some instances, or a lag between exposure and effect at the time of sampling. Johnson et al. (*43*) found that under laboratory situations, ChE activity is positively related to ambient temperature, and this may have been a factor in our study.

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Conclusions

With the possible exception of high chlorpyrifos oxon and total endosulfan concentrations in some sediments, our study did not find contaminant concentrations that were likely to produce direct mortality in amphibians. However, we found that cholinesterase in tadpoles was depressed in areas of poor population status, compared to areas with healthy populations, suggesting that exposure to toxic concentrations of organophosphate or carbamate pesticides have played a role in the decline of California amphibians. Our study consisted of snapshots of contamination over two years. Due to natural degradation and annual variation in application, volatilization, and deposition (*27*, *44*), it is unlikely that any of the measured concentrations were the highest that have occurred. Endosulfan concentrations measured by LeNoir et al. (*4*) in the Sierra Nevada Mountains of California show that values for this pesticide could be considerably higher than what we measured and surpass toxic thresholds for some amphibians. However, a recent study has shown that *P. regilla* accumulates some pesticides in their tissues at much higher concentrations than that found in the environment (*45*). Some pesticides found in frog tissue were not detected in water or sediment samples. This means that frogs are being exposed to higher concentrations of pesticides than would be expected based on analysis of environmental samples.

Another concern is that few of the wetlands were exposed to only one contaminant. In 2001, wetlands could have been exposed to 38 different combinations of chemicals, and we documented an average of 10.2 ± 3.6 chemical per environmental matrix (frog tissue, water, sediment). The effects of chemical combinations are only beginning to be understood in amphibians, but we know that pesticides can have inhibitory, additive, or synergistic effects when mixed together. For example, Relyea (*46*) found that a mixture of four pesticides, including three cholinesterase inhibitors, had additive effects. Boone and James (*47*) suggested that atrazine, nitrate fertilizers, and carbaryl did not interact in their effects on gray treefrogs (*Hyla versicolor*). However, Mazanti et al. (*48*) suggested the atrazine enhanced the toxic effects of chlorpyrifos, though atrazine was not detected in any of our wetlands, these studies show how combinations of current use chemicals affect amphibians.

In addition, there is increasing evidence that pesticides can interact with other stressors to increase amphibian mortality or cause other adverse effects. Pesticides can interact with predator effects (*49*, *50*), immune functions (*51*), population density (*52*), and habitat selection (*53*). While most of the information on chemical toxicity to amphibians comes from laboratory studies, exposures under more natural conditions have shown that interactions with the environment can be complex (*54*). Taken together, evidence from our study and other researchers suggests that pesticides may be playing a role in the decline of Sierra Nevada amphibians.

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Chapter 8

Is There Still "New" DDT in North America? An Investigation Using Proportions of DDT Compounds

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Usage of DDT ceased over four decades ago in Canada and the United States, and since 2000 in Mexico. Potential sources in the North American atmosphere today include emissions of legacy residues from soils and long-range transport from other countries where DDT is still used or recently banned. Distinction of source types is investigated here using proportions of *p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDE and *p,p′*-DDD. The relative volatilization of DDT compounds can be accurately described by their subcooled liquid vapor pressures (P_L); e.g., $(p,p'\text{-DDT}/p,p'\text{-DDE})_{AIR} = (p,p'\text{-DDT}/p,p'\text{-DDE})_{SOIL} \times P_{L,\,DDT}/P_{L,DDE}$. Using this model, the expected proportions in air due to volatilization from technical DDT and from

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soils in Canada, the U.S.A. and Mexico were estimated and expressed as the fractions F_{DDTE} = *p,p′*-DDT/(*p,p′*-DDT + *p,p′*-DDE), F_{DDTO} = *p,p′*-DDT/(*p,p′*-DDT + *o,p′*-DDT), and F_{DDTD} = *p,p′*-DDT/(*p,p′*-DDT + *p,p′*-DDD). F_{DDTE}, F_{DDTO} and F_{DDTD} predicted from soil emissions were compared to compound fractions in ambient air sampled at the Integrated Atmospheric Deposition Network (IADN) of stations on the Great Lakes between Canada and the U.S.A., and at arctic monitoring stations. F_{DDTE} in air at IADN stations on lakes Erie, Ontario, Michigan and Huron were lower than in technical DDT vapor. This is consistent with emissions of aged residues from agricultural land and urban centers near these lakes. By comparison, F_{DDTE} values were higher at stations on Lake Superior where atmospheric DDT is likely due to long-range transport rather than regional soil emissions. F_{DDTE} increased from the early 1990s to 2005 at the Lake Superior stations and at the Canadian arctic station Alert between 2002-2005, whereas a significant decline in F_{DDTE} was observed at the Norwegian arctic station Zeppelin Mountain. The mean F_{DDTO} in air at IADN stations were consistent with either soil emissions or technical DDT composition, but annual values showed significant downward trends at two Canadian stations, and also decreased with time at Zeppelin Mountain (but not at Alert). These trends might signify contribution from “dicofol-type” DDT sources, which have a lower F_{DDTO} than technical DDT or soil emissions, or preferential degradation of *p,p′*-DDT vs. *o,p′*-DDT over time. F_{DDTD} in air at IADN stations were lower than in technical DDT vapor, showing the influence of soil sources. The enantiomer proportions of the chiral compounds *o,p′*-DDT and *o,p′*-DDD were nonracemic in some soils and ambient air, but enantiospecific analysis has not been done for IADN air samples. It is suggested that isomer, parent/metabolite and enantiomer composition information be incorporated into air monitoring programs to help identify sources.

Introduction

DDT has been deregistered in Canada and the United States since the early 1970s, but parent DDT and metabolites DDE and DDD are still found in soil, air and precipitation. An open question is whether the residues found in atmospheric samples are due to long-range transport from countries where DDT is currently or formerly used, emissions from "legacy" residues in regional soils, or both. The issue was raised 28 years ago in a paper by Robert Rapaport and coworkers, "New" DDT inputs to North America -- Atmospheric Deposition (*1*). The authors collected cores in 1981-1983 from peat bogs in Minnesota, Ontario, Maine and

Nova Scotia, and analyzed them for DDT compounds to determine historical loadings and current deposition. They noted that, while total DDT (ΣDDTs) peaked in the mid- to late-1960s, deposition continued throughout the late 1970s and early 1980s at a lower level and declined more slowly. Moreover, the composition of ΣDDTs in the 1980s peat layers was marked by a high proportion of "fresh" DDT (*p,p'*-DDT and *o,p'*-DDT) in comparison to stable DDE and DDD degradation products. These observations led the authors to suggest that DDT from Mexico and Central America was being transported and deposited in the Great Lakes region a decade after its deregistration in the U.S.A.

Usage of DDT for malaria control was prevalent in Mexico until the late 1990s (*2*–*7*). Under a North American Regional Action Plan (*8*) Mexico reduced its usage of DDT from 650 tons in 1996 to 15 tons in 1999 and all DDT use was officially stopped by 2000 (*9*). Cumulatively, 69545 tons of DDT was used for malaria control programs between 1957-2000 (*7*). DDT was also used in Mexican agriculture, but discontinued by 1990 except for public health campaigns (*4*, *5*). Levels of ΣDDTs in the atmosphere of southern Mexico between 2000-2006 exceeded average ambient air concentrations in the U.S.A. and Canada by an order of magnitude or more (*3*, *10*–*13*), and ΣDDTs was similarly elevated in the air of Belize, Central America during 1995-1996 (*14*). Some portion of this DDT may be influencing air concentrations in other parts of North America, but there are other potential sources of DDT to be considered: emission of soil residues from past usage in Canada and the U.S.A., air transport across the Pacific Ocean from Asia, and the global circulation of DDT from continued usage in tropical countries and re-emissions from soil and water worldwide. Usage of the acaricide dicofol (2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol) may also lead to DDT contamination, since dicofol is manufactured from DDT and the technical product in some countries contains DDT residues elevated in *o,p'*-DDT and *o,p'*-DDE (*15*–*19*).

Air monitoring of DDTs and other persistent organic pollutants (POPs) in the Great Lakes region has been carried out continuously since the early 1990s by the Integrated Atmospheric Deposition Network (IADN) of Canada and the United States. The time series through 2004 showed that gas-phase DDT and metabolites were declining with times for 50% decrease of 5-16 years, depending on the compound and site (*20*). Regressions at all stations through 2007 gave halving times of 5.8, 8.2 and 14.9 years for ΣDDTs in the particulate phase, gas phase and precipitation, respectively (*21*, *22*). Air parcel trajectory analysis (*23*, *24*) and transport modeling (*25*, *26*) have targeted the southern U.S.A. as a major source region for DDT, toxaphene and other organochlorine pesticides. Temperature and proximity to population centers were also identified as significant factors for ΣDDTs at IADN stations (*20*, *21*).

The wealth of IADN data, together with recent measurements in Mexico, provides an opportunity to examine potential sources of DDT in the Great Lakes atmosphere based on chemical profiles of parent *p,p'*- and *o,p'*-DDT and metabolites *p,p'*-DDE and *p,p'*-DDD. Proportions of DDT compounds have been used to speciate sources in the air of China (*16*–*18*, *27*), and in other environmental media (*28*, *29*). Objectives of the present study are to: a) set bounds on proportions of DDT compounds that are expected from emission of

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legacy residues in soils, b) compare the compound proportions found in ambient air to these limits to determine if "new" DDT is present.

Experimental

Data Sources for DDTs in Soil and Air

Literature data for DDT residues in soils were collected which span 1985-2009 (Table 1) (*5*, *7*, *33*, *34*, *36*, *42*, *45*, *47–57*, *60*, *67*, *100–112*). These cover farms, orchards, urban areas and rural/background sites in Canada, the U.S.A. and Mexico. Some of the measurements were made in national parks, which comprise a variety of land uses and where DDT was formerly used.

Proportions of *p,p′*-DDT to *o,p′*-DDT, and *p,p′*-DDT to metabolites *p,p′*-DDE and *p,p′*-DDD, were expressed as fractions, which are preferred to ratios for averaging and other statistics (*30*, *31*): F_{DDTO} = *p,p′*-DDT/(*p,p′*-DDT + *o,p′*-DDT), F_{DDTE} = *p,p′*-DDT/(*p,p′*-DDT + *p,p′*-DDE), and F_{DDTD} = *p,p′*-DDT/(*p,p′*-DDT + *p,p′*-DDD). Compound fractions were calculated only when both species were quantifiable (e.g., both *p,p′*-DDT and *p,p′*-DDE in F_{DDTE}). This avoided generating artificially low or high fractions which would have been obtained by substituting detection limits for missing species.

Levels of DDTs in ambient air at IADN stations (Table 2) were obtained from the IADN database for Canada: Point Petre (PPT, Lake Ontario, 1992-2004), Burnt Island (BNT, Lake Huron, 1993-2004), Egbert (EGB, southern Ontario, 1997-2003), and the U.S.A.: Sturgeon Point (STP, Lake Erie, 1992-2005), Sleeping Bear Dunes (SBD, Lake Michigan, 1992-2005), Chicago (IIT, Illinois Institute of Technology, 1996-2005), Cleveland (CLV, 2003-2005), Brule River (BRR, Lake Superior, 1996-2002), Eagle Harbor (EGH, Lake Superior, 1990-2005). This time series covers the collection period of most soils data and air measurements in Mexico. The IADN network uses a sampling train consisting of a glass fiber filter to capture the particle-bound fraction followed by a solid adsorbent trap (Canada: polyurethane foam, U.S.A.: XAD-2 resin) for the gaseous fraction (*32*). Only the gaseous DDT compounds are considered here, since the intent is to compare chemical profiles in air to vapor emissions from soil. Other published atmospheric data for Canada, the U.S.A. and Mexico-Central America (Table 2) (*3*, *10–12*, *46*, *67–69*, *71*, *113–116*) were obtained from shorter-term high volume air sampling campaigns or deployment of passive air samplers to integrate air concentrations over several months to a full year.

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Table 1. ΣDDT in soils of Canada, U.S.A. and Mexico, ng g^{-1} dry weight.

State/ Province	Land use[b]	Sites[c]	Year	Samples	Range[d]	ΣDDT[a] Mean of positive[d]	% positive	GM	Refs.
United States									
PA,OH,IN,IL	A	40	1995-1996	40	<0.5-11800	460	85	9.6	50
AL,LA,TX	A	62	1996-2000	62	0.1-1490	140	100	31	36,100
SC,GA	A	32	1999	32	0.1-45	12	100	5.4	101
TX	S	13	not spec.	56	<0.5-70		68		102
TN,TX,WA	P	4		8	<0.5-32		88		
CA	A	95	1985	95	8-29900	1960	100	528	103
CA	A	6	2005	6	11-786	355	100	155	104
NJ	A	9	not spec.	120	ND-2040		38		47
NJ	O	5		191	10-41600		100		
NJ	R,A	80	1985-87	80	<2-7400	580	35	17	105
WA	O	3	2003	6	5500-21000	10100	100	9170	48
WA	U	1	2003	2	260-630	440	100	405	
ME	F	6	1993	60	270-1900	1007	100	848	106
Canada									
ON	A	5	2000	5	260-24000	5400	100	1200	107
ON	A	1	2004	1	19000		100		34
NB,QC,ON, SK,AB	A	8	1989-1991	8	1-950	210	100	31	49
ON	U,R	7	2002	7	1.0-18	6.8	100	4.5	108
SK	A	33	1999	39	<1-150	22	70	4.2	51
SK	P	4	1999	4	<1-150	100	75	46	
SK	P	19	2008-2009	310	<1-55300	1480	45	117	52
BC	A	7	1999-2000	7	5-4530	1310	100	186	33
BC	A	12	1989	12	<10-7160	1700	75		109
BC	A	9	2002-2003	36	<20-6000	1570	67		110
ON	O	18	1994	18	<120-7100	3260	72		45
ON	O	2	1991	2	41-70200		100		49
BC	O	4	1999-2000	4	4280-18200	11400	100	6810	33
BC	O	4	1994	4		14400	100		45
ON	P	6	2005	275	2-316000			1210	42
PE,QC,ON, SK.BC	A,U,R	5	2005	5	2-178	51	100	14	67
Mexico									
CH,CL,CP,MR NL,SI,TB,VE	A	16	2005	16	0.06-82	10	100	1.5	60
PU,MX	A		2003	50		54	100		111
PU,MX	A		2006	50	31.8-136	71	100		112
CP,VE,YU	R	4	2005	4	0.02-0.11	0.17	100		60
CL,CP,VE	U	9		9	0.11-360	45	100	4.7	
CP	U	2	2003	20	300-11740	190, 4760	100		53
CP,OA	U	2	1998-2000	9	3320-8200	4350	100	3630	56
CP	U	1	2004-2007	20	10-19000		100	70	7
CP	U	5	not spec.	92	2-27000		100	10-947	54
CH	U	3	2009	40	2-1400		100	65-423	5
TB	U	9	2009	50	2-123		100	4.0-46	55
SO	U	24	2007	183	ND- >680	46[e,f]	72		57
SO	A	24		51	ND- >120	27[e,f]			

a) ΣDDT = one or more: *p,p*'-DDT, *p,p*'-DDE, *p,p'*-DDD, *o,p*'-DDT, *o,p*'-DDE, *o,p*'-DDD.
b) Land use: A = agriculture, O = orchard, U = urban, city or small communities, S = school, F = forest (DDT sprayed), P = national park, R = rural/background.
c) Sites are single sampling points or groups of sampling points in a specific location, e.g. orchard, community, national park.
d) Ranges and means are derived from single samples, or from reported means, medians or geometric means at different sites. ND = below detection, where the limit is not specified.
e) Mean assumes zero for non-detectable (ND) samples.
f) Units of µg g^{-1} reported in the paper are incorrect and should be ng g^{-1}, confirmed by correspondence with the authors.

Table 2. ΣDDTs in air of Canada, U.S.A. and Mexico, gas phase, pg m^{-3}

		ΣDDT[a]				F_{DDTE}		F_{DDTO}		F_{DDTD}		
	Years	Range[b]	Mean[b]	S.D.	N	Mean	S.D.	Mean	S.D	Mean	S.D	Refs.
IADN [c]												
PPT	1992-2004	0.3-135	17.8	21	421	0.17	0.07	0.45	0.15	0.83	0.12	
BNT	1993-2004	0.2-25.5	4.3	3.8	347	0.22	0.11	0.40	0.17	0.76	0.15	
EGB	1997-2003	0.4-332	40.4	52	180	0.22	0.07	0.45	0.19	0.91	0.13	
STP	1992-2005	0.4-206	27.9	26	488	0.34	0.17	0.68	0.16	0.71	0.25	
SBD	1992-2005	0.1-173	13.6	18	493	0.36	0.19	0.71	0.15	0.70	0.24	
IIT	1996-2005	2.8-349	59.9	57	320	0.40	0.14	0.66	0.13	0.78	0.22	
CLV	2003-2005	2.5-118	26.1	22	82	0.47	0.15	0.65	0.15	0.79	0.21	
EGH	1990-2005	0.05-34.4	5.2	5	504	0.53	0.22	0.74	0.17	0.82	0.11	
BRR	1996-2002	0.1-22.8	4	3.3	188	0.51	0.26	0.67	0.24	0.46	0.28	
Canada												
Kensington, PE	2004-2005	ND-215	98.1		20	0.25		0.60		0.61		67
Bonavista, NL	2000-2001		13		1[d]	0.84				0.89		11
East Point, NS	2000-2001		32		1[d]	0.35				0.89		11
St. Leonard, NB	2000-2001		66		1[d]	0.28				0.98		11
Villeroy, QC	1993-1995		11		36	0.36						68
St. Anicet, QC	1994-1995		12		24	0.42						67
St. Anicet, QC	2004-2005	ND-364	87.6		14	0.35		0.56		0.71		67
Baie François, QC	2004-2005	ND-246	76.5		14	0.30		0.57		0.84		67
Mingen, QC	1994-1995		5		13	0.40						68
Toronto, ON	2000-2002	12-312	93		15	0.30		0.57				113
Toronto, ON	2000-2001		60		1[d]	0.21				0.92		11
Toronto, ON	2005	68-443	173		9	0.18		0.66		0.91		67
Big Creek, ON	2000-2001		42		1[d]	0.11				0.89		11
Egbert, ON	2004-2005	13-538	181		17	0.19		0.53		0.85		67
Vineland, ON	2004-2005	87-4380	1170		19	0.08		0.85		0.92		67
Kananaskis, AB	2000-2001		15		1[d]	0.88				0.66		11
Observation, AB	2003-2004	4.0-14	10	4	6[d]	0.25	0.16	0.58	0.28			71
Donald Stn., BC	2000-2001		29		1[d]	0.79				0.97		11
Summerland, BC	2000-2001		185		1[d]	0.14				0.97		11
Abbotsford, BC	2004-2005	17-280	114		11	0.24		0.46		0.86		67
Revelstoke, BC	2003-2004	15-71	43	26	6[d]	0.67	0.19	0.89	0.11	0.90	0.12	71
Yoho, BC	2003-2004	20-51	35	13	5[d]	0.59	0.15	0.90	0.04	0.96	0.02	71
U.S.A.												
Green Bay, WI	1988-1989	ND-40	23.7		8	0.37						114
Lakes Erie,Huron, Michigan, Ontario	1990	12-417	97		15	0.39						114
Youngstown, OH	2000-2001		29		1[d]	0.42				0.92		11
Solomons, MD	2000-2001		20		1[d]	0.31				0.85		
Musc. Sh., AL	2000-2001		76		1[d]	0.49				0.86		11
South Haven, MI	1992-1994	12-11000	1150		94	0.26		0.70		0.97		46
Pellston, MI	1992-1994	4-111	27.1		76	0.51		0.61		0.74		46
Dexter, MI	1992-1994	5-389	66.4		62	0.37		0.67		0.80		46
Deckerville, MI	1992-1994	4-402	39.3		69	0.41		0.63		0.75		46
Galveston Bay, TX	1995-1996	ND-74	31	17	24	0.40		0.55		0.78		115
Pinelands, NJ	2000-2001		31		43	0.32	0.19					69
New Brunswick, NJ	2000-2001		237		26	0.15	0.07					69
Mexico												
Tapachula	2000-2001	350-1570	997	358	18	0.51	0.15	0.77	0.04	0.94	0.03	10
Tapachula	2000-2001		737		1[d]	0.49						11
Tapachula	2002-2003	275-896	547	176	14	0.55	0.08	0.80	0.04	0.96	0.02	3
Chetumal	2000-2001		353		1[d]	0.57						11
Tabasco	2003-2004	85-940	239	245	13	0.74	0.13	0.86	0.12	0.90	0.06	3
Veracruz	2003-2004	467-2140	1200	488	20	0.45	0.07	0.76	0.04	0.92	0.04	3
Chiapas Mts.	2003-2004	1010-3600	2360	593	18	0.83	0.05	0.88	0.02	0.98	0.01	3
Celestun	2005-2006		1980		4[e]	0.32		0.76		0.90		12
Colima	2005-2006		750		4[e]	0.52		0.64		0.82		12
Cordoba	2005-2006		129		4[e]	0.53		0.64		0.82		12
Cuernavaca	2005-2006		500		4[e]	0.35		0.65		0.93		12
Mazatlan	2005-2006		76		4[e]	0.24		0.67		0.80		12
Mexico City	2006	31-160[g]	30-110		5[f]	0.71-0.80		0.79-0.87		0.93-0.95		116

a) ΣDDT comprises one or more: *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *o,p'*-DDE, *o,p'*-DDD.

b) Ranges and means may be derived from single samples, or from reported means, medians or geometric means at different sites.

c) Canada: PPT = Point Petre, BNT = Burnt Island, EGB = Egbert. U.S.A.: STP = Sturgeon Point; SBD = Sleeping Bear Dunes; IIT = Illinois Institute of Technology (Chicago); CLV = Cleveland; EGH = Eagle Harbor; BRR = Brule River.

d) Passive air samples, integrated 365 days.

e) Passive air samples, integrated 90 days.

f) Passive air samples, integrated 42-60 days.

g) Range for urban and semi-urban/rural areas.

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Distribution of DDT Compounds between Soil and Air

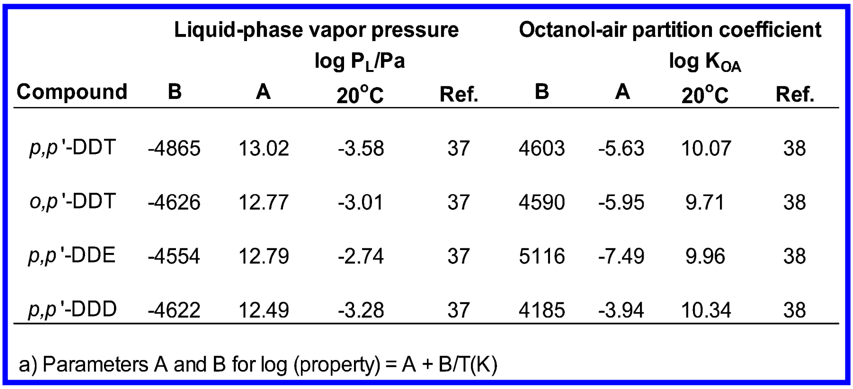
Soil-air exchange of DDT compounds having different volatilities was investigated at 4-7 farms/orchards in British Columbia (BC) with 3-39% soil organic matter (SOM) (*33*), one Ontario (ON) farm with 70% SOM (*34*, *35*), and 14 farms in the southern United States. (SUSA) with 1-4% SOM (*36*). Soil was collected from the top 5 cm and multiple air samples were taken within 5-40 cm of the soil surface using a glass fiber filter to exclude soil dust followed by a polyurethane foam plug to trap gaseous compounds. Fractionation of the DDT compounds between soil and air was predicted by assuming that compound volatility is directly related to the subcooled liquid vapor pressure (P_L) and inversely related to the octanol-air partition coefficient (K_{OA}) (*34*, *35*), e.g.:

$$(p,p'\text{-DDT}/p,p'\text{-DDE})_{air} = (p,p'\text{-DDT}/p,p'\text{-DDE})_{soil} \times P_{L,DDT}/P_{L,DDE} \quad (1)$$

$$(p,p'\text{-DDT}/p,p'\text{-DDE})_{air} = (p,p'\text{-DDT}/p,p'\text{-DDE})_{soil} \times K_{OA,DDE}/K_{OA,DDT} \quad (2)$$

and similarly for *p,p'*-DDT/*o,p'*-DDT, and *p,p'*-DDT/*p,p'*-DDD. P_L and K_{OA} values as functions of temperature were taken from (*37*, *38*) (Table 3). DDT compound ratios were then expressed as the fractions F_{DDTE}, F_{DDTO} and F_{DDTD}.

Table 3. Volatility properties of DDT compounds[a]



	Liquid-phase vapor pressure				Octanol-air partition coefficient			
			log P_L/Pa				log K_{OA}	
Compound	**B**	**A**	**20°C**	**Ref.**	**B**	**A**	**20°C**	**Ref.**
p,p'-DDT	-4865	13.02	-3.58	37	4603	-5.63	10.07	38
o,p'-DDT	-4626	12.77	-3.01	37	4590	-5.95	9.71	38
p,p'-DDE	-4554	12.79	-2.74	37	5116	-7.49	9.96	38
p,p'-DDD	-4622	12.49	-3.28	37	4185	-3.94	10.34	38

a) Parameters A and B for log (property) = A + B/T(K)

Results and Discussion

Composition of DDT Products and Their Vapors

Many countries produced technical DDT and the compositions of these mixtures are not readily available. Differing proportions are given by Spencer and Cliath (*39*): 77% *p,p'*-DDT, 22% *o,p'*-DDT and 0.1% *p,p'*-DDE, Metcalf (*40*): 48-80% *p,p'*-DDT and 11-29% *o,p'*-DDT and in compilations by Ricking and Schwarzbauer (*28*, *29*): 63-85% *p,p'*-DDT, 8-21% *o,p'*-DDT, 0.2-2% *p,p'*-DDD and 0.1-0.2% *p,p'*-DDE. The World Health Organization (*41*) gives the composition of technical DDT as 77.1% *p,p'*-DDT, 14.9% *o,p'*-DDT, 4%

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p,p′-DDE and 0.3% *p,p′*-DDD. The DDT applied at Pt. Pelee National Park (Ontario, Canada) in the 1950-60s contained 95% DDT, 5% DDE and 1% DDD (isomers not specified) (*42*). Assuming the WHO percentages and that volatilization of the compounds from the technical mixture takes place according to their P_L (eq, 1), the predicted fractions in the vapor are F_{DDTE} = 0.74, F_{DDTO} = 0.58 and F_{DDTD} = 0.99. These set upper limits to the fractions expected from evaporation of applied “fresh” technical DDT having the WHO composition.

Another potential source of DDT residues is the pesticide dicofol, which is manufactured from DDT. Dicofol in the U.S.A. has been restricted to <0.1% residual DDT since 1986 (*16*), but the dicofol made in China was contaminated with DDT residues that were especially high in *o,p′*-DDT and *o,p′*-DDE. Average concentrations of *p,p′*-DDT, *o,p′*-DDT and *o,p′*-DDE in 23 samples of dicofol obtained from 7 manufacturers in 2002 were 17±8, 114±45 and 44±25 g kg^{-1}, respectively (*16*, *17*), giving an average *p,p′*-DDT/*o,p′*-DDT ratio of 0.15 and F_{DDTO} = 0.13. Considering vapor pressure fractionation (eq 1), F_{DDTO} = 0.04 in dicofol vapor. This unique signature has been used to track “dicofol-type” DDT contamination in Chinese air (*15–18*, *27*). Some topsoils in Turkey also showed evidence of DDT contamination due to dicofol usage (*19*).

Soil-Air Exchange Experiments

The soil-air fractionation relationships (eq 1 and 2) were tested at experimental sites by collecting paired soil and overlying air samples, as described above. Ratios of DDT compounds were calculated only for events in which both species were present. Events to determine F_{DDTE} and F_{DDTO} were 22 (for each) in BC, 18 at the ON farm and 23-26 in SUSA. Fewer results were obtained for F_{DDTD} due to the lower abundance of *p,p′*-DDD in soils and air: 7 events in BC, 18 in ON and none in the SUSA.

Figure 1 shows F_{DDTE}, F_{DDTO} and F_{DDTD} in soil, measured in air over the soil, and predicted in air using either P_L or K_{OA}. The success of this approach was judged by comparing predicted/measured (P/M) compound fractions in air. F_{DDTE} in air was always lower than in soil and successfully predicted by P_L, with average P/M F_{DDTE} of 0.86-1.16 in the three locations. K_{OA} consistently overestimated F_{DDTE} in air (by underestimating the volatilization of *p,p′*-DDE), with P/M 1.9-3.4 (Figure 1a). F_{DDTO} in air was lower than F_{DDTO} in soil at the ON farm and in the SUSA, although not in BC (Figure 1b). Mean P/M for BC, ON and SUSA were 0.64, 0.89 and 1.02 using P_L, and 0.81, 1.09 and 1.19 using K_{OA}. F_{DDTD} in soil, measured in air, and predicted in air were all similar; mean P/M for BC and ON were 0.94 and 0.98 using P_L, and 0.82 and 1.12 using K_{OA} (Figure 1c). The overall comparison for all locations is summarized in Figure 1d, which shows mean P/M for F_{DDTE}, F_{DDTO} and F_{DDTD} averaging 1.00 ± 0.16, 0.86 ± 0.03 and 0.97 ± 0.04 using P_L, and 2.9 ± 3.9, 1.04 ± 0.03 and 1.04 ± 0.05 using K_{OA}.

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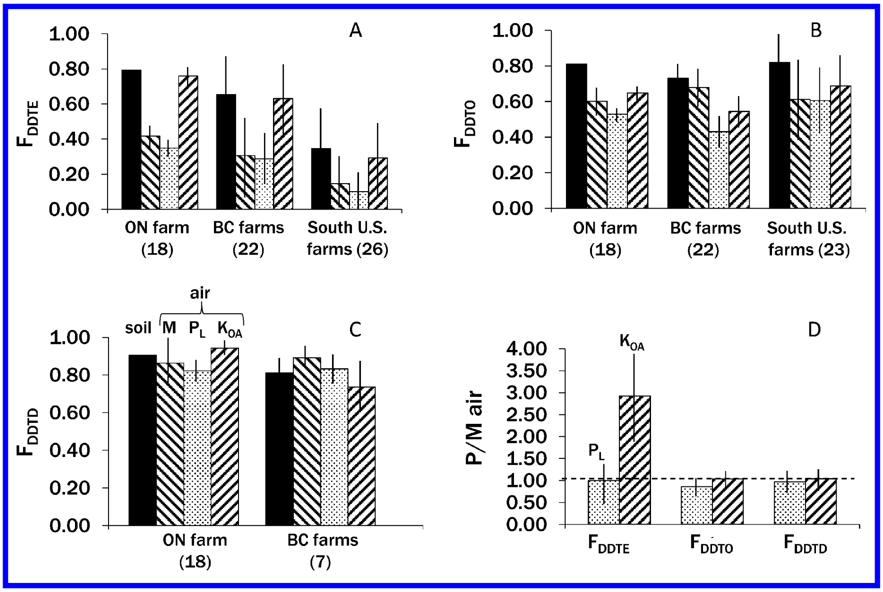

Figure 1. Panels A-C: Results of experimental studies of soil-air exchange at agricultural sites in Ontario (ON) (34, 35), British Columbia (BC) (33), and the southern United States (SUSA) (36). Shown are means and standard deviations of F_{DDTE}, F_{DDTO} and F_{DDTD} in soil and measured (M) in air at 5-40 cm above the soil, and predicted in air using the subcooled liquid-phase vapor pressure (P_L) or octanol-air partition coefficient (K_{OA}) of the DDT compounds (Table 3). Numbers of experiments are indicated in parentheses. Panel D: Summary of mean predicted/measured (P/M) compound fractions in air using either P_L or K_{OA}.

These results are reinforced by the classic experiments of Spencer and Cliath (*39*), who determined the relative volatility of DDT and its metabolites from soil by making air measurements over a farm field containing residual technical DDT. They accurately predicted ratios of *p,p'*-DDT/*p,p'*-DDE and *p,p'*-DDT/*o,p'*-DDT in air from the ratios in soil and the saturation vapor density of the compounds. Revisiting the data in Table 4 of their paper, P/M F_{DDTE} for two field trials were 1.01-1.26 using P_L and 2.56-3.21 using K_{OA}. P/M F_{DDTO} using either P_L or K_{OA} were 0.92-0.98 and 1.08-1.15. Considering that in all studies P_L and K_{OA} predicted F_{DDTO} and F_{DDTD} similarly and P_L gave better prediction of F_{DDTE} than K_{OA}, P_L was used for subsequent assessment of relative soil-air exchange.

Table 4. Estimated soil concentrations (C_S) for which soil/air fugacity ratios = 1.0, assuming air concentrations (C_A) at the Sturgeon Point IADN station[a]

			IADN C_A, ng m^{-3}				C_S, ng g^{-1}				
Months	T, °C	φ_{OM}	*p,p'*-DDT	*o,p'*-DDT	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT	*o,p'*-DDT	*p,p'*-DDE	*p,p'*-DDD	ΣDDTs
April-	15	0.05	0.0072	0.0033	0.0184	0.0010	3.1	0.61	6.5	0.74	11
September	15	0.5	0.0072	0.0033	0.0184	0.0010	31	6.1	65	7.4	110
October-	0	0.05	0.0030	0.0011	0.0051	0.0014	9.6	1.5	17	6.5	35
March	0	0.5	0.0030	0.0011	0.0051	0.0014	96	15	170	65	350

a) C_S estimated from $f_S/f_A = 1 = C_S/C_A\varphi_{OM}K_{OA}$ (see text). C_A = STP mean values, K_{OA} from Table 3.

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DDT Compounds in North American Soil and Potential for Soil Emissions

A national monitoring program for pesticides in urban and agricultural soils of the U.S.A. was conducted between 1968-1973 (*43*), and in Canada pesticide residues were surveyed in Ontario soils between 1964-1974 (*44*). Table 1 gives a more relevant summary of ΣDDT in soils of Canada, the U.S.A. and Mexico covering 1985-2009, with most measurements after 1991. Some of the highest levels occur in orchards or former orchards, (*33*, *44–49*), "muck" soils with high SOM content (*33–35*, *50*), park and recreational areas formerly sprayed with DDT (*42*, *51*, *52*), and soils in villages of Mexico where DDT was used for malaria control (*5*, *7*, *53–56*). The number of sites is given where one or more samples were collected. For example, 9 agricultural and 5 orchard sites in New Jersey were examined for DDT residues by analyzing 120 and 191 samples, respectively (*47*). Sometimes "sites" refers to an entire region due to aggregation of data; e.g. 234 measurements in the Yaqui and Mayo valleys of Mexico were reported only as "residential" and "agricultural" means for each valley (*57*).

The potential for legacy DDT residues in soils to be emitted into the atmosphere was expressed by the soil/air fugacity ratio, $f_S/f_A = C_S/(C_A\varphi_{OM}K_{OA})$, where C_S and C_A are concentrations in soil and air (mol m^{-3}) and φ_{OM} is the fraction of SOM (*58*). Conversion of soil concentrations from a mass to volume basis was done by assuming 2650 kg m^{-3} as the dry bulk density of the soil (*59*, *60*). Soil/air fugacity ratios <1, =1 and >1 imply net deposition, equilibrium and net volatilization, respectively.

An example assessment was made using mean air concentrations of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD for the six warmer months (April-September, average T = 15°C) and six colder months (October-March, average T = 0°C) at the Sturgeon Point (STP) IADN station from 2000-2005. Soil concentrations required to support these air concentrations through volatilization were calculated using the fugacity model by setting $f_S/f_A = 1$ and assuming ranges of 0-15°C and 5-50% SOM. K_{OA} values were taken from Table 3. Table 4 gives the critical soil concentrations for each compound and for ΣDDTs. Soils with ΣDDTs >11-110 ng g^{-1} are expected to be net emitters in the warm months and >35-350 ng g^{-1} in the cold months. These may be somewhat high because volatilization of *p,p'*-DDE

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appears to be underestimated using K_{OA} (see above). As can be seen from the range of ΣDDTs in Canadian and U.S. soils (Table 1), many sites exceed these criteria. A worldwide survey of 202 background soils in 2008 showed ΣDDTs ranging from 0.013-430 ng g^{-1} dry wt. and geometric mean 2.4 ng g^{-1} (*35*). Similar assessments in Mexico (*13*, *60*), Spain (*61*), across Europe (*62*) and northern China (*63*) found that the potential for emission of DDTs varied with the compounds and their concentrations, seasonal temperatures and soil properties.

F_{DDTE}, F_{DDTO} and F_{DDTD} were calculated from concentration data reported by literature sources in Table 1, using individual soil samples where possible and aggregate data (means or medians) otherwise. It was not possible to derive these fractions when "DDT, DDE and DDD" were specifically reported to be the sum of *p,p'*- and *o,p'*- isomers (*42*, *45*). In other cases reported "DDT, DDE and DDT" were assumed to be only *p,p'*-species. Descriptive statistics are given in Table 5. More data points were available from which to calculate F_{DDTE}, and frequencies of occurrence within 0.1 windows were constructed for 94 individual or aggregate measurements in the SUSA, 237 in the northern U.S.A. and Canadian provinces (NUSA-CAN), 100 in California (CA) and 47 in Mexico (MEX). These characteristic F_{DDTE} frequency profiles (Figure 2a) were similar in NUSA-Canada, CA and MEX and skewed toward lower F_{DDTE} in the SUSA. DDT metabolism in soils varies greatly due to soil management practices and microbial activity (*64*). Some soils in the southwestern U.S. were reported to have an unusually high proportion of *p,p'*-DDT which was explained by lack of microbial degradation (*65*), but this was not apparent in the SUSA soil surveys in Table 1. Compound proportions in soils from North America and other countries have also been reviewed (*28*, *29*, *35*).

There was no significant correlation between F_{DDTE} and log ΣDDT (ng g^{-1}) in the SUSA ($p = 0.59$, $n = 94$) but the trend was positive and significant in the NUSA-CAN ($r^2 = 0.037$, $p = 0.003$, $n = 237$), MEX ($r^2 = 0.29$, $p = 0.0001$, $n = 47$) and CA ($r^2 = 0.10$, $p = 0.001$, $n = 100$), meaning that soils with higher ΣDDT concentrations tend to have greater proportions of *p,p'*-DDT. Average compound fractions were also calculated by weighting for the concentration of ΣDDT in the soil using Fi = F_{DDTE}, F_{DDTO} or F_{DDTD} and ΣDDT_i of individual soil samples:

$$\text{Weighted fraction} = \Sigma(F_i{*}\Sigma DDT_i)/\Sigma(\Sigma DDT_i) \qquad (3)$$

Mean F_{DDTE} without and with concentration weighting were SUSA (0.36, 0.33), NUSA-CAN (0.59, 0.72), CA (0.49, 0.57) and MEX (0.55, 0.73). Means (unweighted or weighted) were less variable within and among regions for F_{DDTO} (0.74-0.84) and F_{DDTD} (0.75-0.94) (Table 5). The unweighted mean F_{DDTE} in 202 background soils collected globally in 1988 was 0.60 ± 0.30 (*35*).

Eq 1 was used with P_L ratios *p,p'*-DDT/*p,p'*-DDE = 0.148, *p,p'*-DDT/*o,p'*-DDE = 0.272 and *p,p'*-DDT/*p,p'*-DDD = 0.502 at 20°C (Table 3) (*37*) to estimate compound ratios and fractions in air due to emissions from soils in the four regions, and results are shown for F_{DDTE} in Figure 2b. Mean fractions in air, predicted from residues in individual soils or using concentration-weighted means, ranged from 0.07-0.28 for F_{DDTE}, 0.44-0.62 for F_{DDTO}, and 0.64-0.89 for F_{DDTD} (Table 5).

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Table 5. DDT compound fractions in soils of North America and predicted composition of the volatilized residues[a]

		SUSA	NUSA-CAN	CA	MEX
Soil					
F_{DDTE}	N	94	237	100	47
	Range	0.035-0.85	0.11-0.93	0.12-0.94	0.07-0.97
	Mean	0.36	0.59	0.49	0.55
	S.D.	0.18	0.19	0.18	0.21
	Weighted	0.33	0.72	0.57	0.73
F_{DDTO}	N	48	151	94	15
	Range	0.46-0.95	0.18-0.95	0.33-0.96	0.70-0.94
	Mean	0.84	0.81	0.81	0.79
	S.D.	0.11	0.13	0.08	0.06
	Weighted	0.74	0.82	0.82	0.82
F_{DDTD}	N	63	163	87	34
	Range	0.54-0.99	0.03-0.99	0.50-0.97	0.56-0.95
	Mean	0.88	0.75	0.86	0.83
	S.D.	0.11	0.20	0.10	0.09
	Weighted	0.94	0.90	0.90	0.84
Predicted air					
F_{DDTE}	N	94	237	100	47
	Range	0.005-0.46	0.02-0.68	0.02-0.68	0.01-0.83
	Mean	0.094	0.22	0.15	0.20
	S.D.	0.079	0.14	0.11	0.16
	Weighted	0.068	0.28	0.16	0.28
F_{DDTO}	N	48	151	94	15
	Range	0.19-0.84	0.06-0.84	0.12-0.88	0.39-0.81
	Mean	0.62	0.57	0.55	0.52
	S.D.	0.16	0.16	0.11	0.10
	Weighted	0.44	0.57	0.55	0.55
F_{DDTD}	N	63	163	87	34
	Range	0.39-0.99	0.02-0.98	0.34-0.93	0.39-0.90
	Mean	0.80	0.64	0.76	0.72
	S.D.	0.16	0.24	0.13	0.11
	Weighted	0.89	0.82	0.82	0.73

a) SUSA: Southern U.S.A.; NUSA-CAN: northern U.S.A. and southern Canada; CA: California; MEX: Mexico.

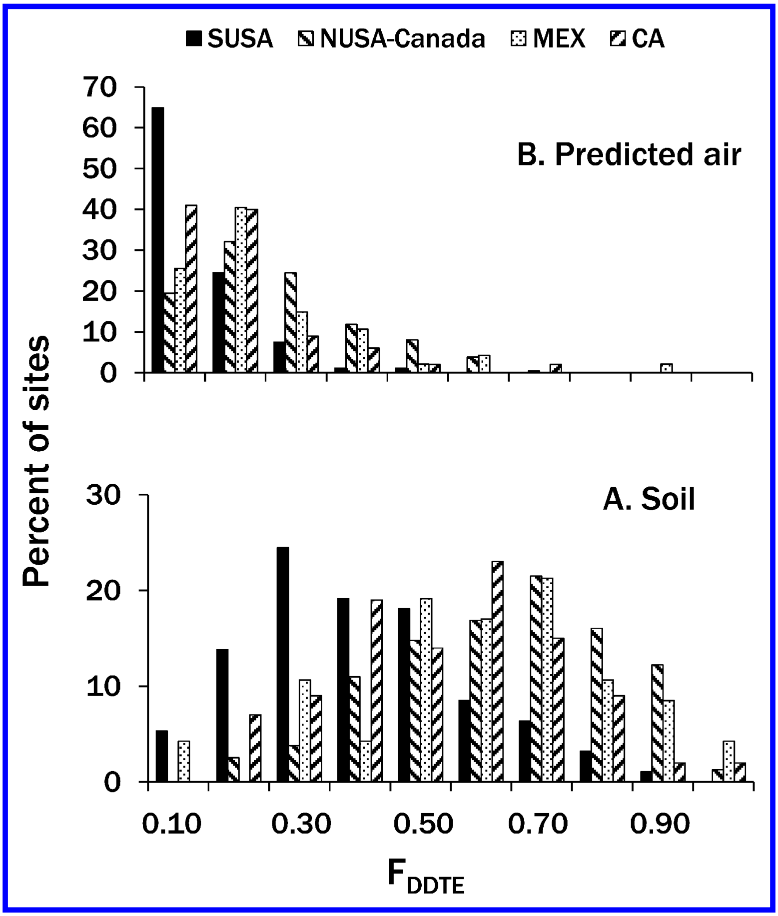

Figure 2. A: Frequency distribution of F_{DDTE} for soil residues in the southern United States (SUSA), northern U.S.A. – southern Canada (NUSA-CAN), Mexico (MEX) and California (CA). B: Predicted (using P_L) frequency distribution in air from volatilization of soil residues in the four regions.

Of the three pairs, soil-air fractionation is greatest for *p,p'*-DDT/*p,p'*-DDE. Soil having a 1:1 ratio would be expected to emit the two compounds in a ratio of 0.148 (eq 1), or $F_{DDTE} = 0.13$. and thus F_{DDTE} has the greatest forensic value in distinguishing fresh vs. and historical technical DDT sources. For this reason, most of the following discussion focuses on F_{DDTE}. Frequency distributions of predicted F_{DDTE} in air are shown in Figure 2b and compared to the soil profiles in Figure 2a. As for soil, profiles of F_{DDTE} in air are similar in NUSA-CAN, CA and MEX, and shifted toward lower F_{DDTE} in the SUSA.

DDT Compounds in the Air of North America

Long-term means of ΣDDT and compound fractions in air at IADN stations are given in Table 2. Other reports from the IADN program discuss temporal trends and relationships to environmental factors (*20–22*, *66*). Table 2 also summarizes results from shorter-term air studies in North America where the data permit calculation of compound fractions.

The ΣDDTs is elevated in some cities (Chicago, Toronto) and proximity to population centers has been identified as a significant factor in explaining variability at IADN stations (*20*, *21*). High air concentrations have also been found at sites surrounded by agricultural land; e.g. Egbert and Vineland, ON (*67*). Temperature exerts the most control over atmospheric levels of DDT compounds (*20–22*) and several studies have estimated the enthalpy of surface-air exchange from Clausius-Clapeyron plots of log partial pressure or concentration vs 1/T (K) (*23*, *46*, *68–70*).

The IADN quality assurance program and comparisons between Canadian and U.S. laboratories have been documented (*32*). Analysis of a common reference standard for DDT compounds showed only minor discrepancies ($\leq$10%) between found and accepted values. Field experiments were also done in which Canadian and U.S. groups colocated air samplers at PPT and collected ~100 sample pairs between 1998-2005. These comparisons took into account errors introduced by the sampling procedure, extraction and cleanup methods and final analytical steps. Median differences in air concentrations were not significant for *o,p'*-DDT and *p,p'*-DDD, but they were for *p,p'*-DDE ($p = 0.009$) and *p,p'*-DDT ($p < 0.001$). Resulting DDT compound fractions for the colocated experiments were Canada $F_{DDTE} = 0.14 \pm 0.05$, U.S. $F_{DDTE} = 0.35 \pm 0.22$ (n=77); Canada $F_{DDTO} = 0.39 \pm 0.09$, U.S. $F_{DDTO} = 0.74 \pm 0.13$ (n=55); Canada $F_{DDTD} = 0.82 \pm 0.13$, U.S. $F_{DDTD} = 0.80 \pm 0.20$ (n=44). Comparisons were made only for events in which both groups reported detectable concentrations of each species. The Canadian-U.S. differences make it difficult to relate compound fractions across the entire IADN network, although comparisons can be made within the groups of Canadian stations and U.S. stations. Other reports of DDTs in air and soil give quality control information in the publications, but possible interlaboratory bias in the compound fractions could not be assessed.

Mean F_{DDTE} at IADN stations (Table 2) were 0.17-0.22 at Canadian sites PPT (Lake Ontario), EGB (southern Ontario) and BNT (Lake Huron), and 0.34-0.36 at U.S. sites STP (Lake Erie) and SBD (Lake Michigan). These rural stations are close to agricultural regions and likely to be influenced by soil emissions. Recognizing a methodological offset of 0.2 between Canadian and U.S. laboratories (see above), these mean F_{DDTE} are consistent with predictions of 0.20-0.28 in air from soil emissions in NUSA-CAN or MEX, but higher than 0.07-0.09 for predicted emissions from the SUSA (Table 5). Mean F_{DDTE} were higher at the two U.S. urban stations in Chicago (IIT) and Cleveland (CLV) (0.40-0.47), and still higher at U.S. sites BRR and EGH (0.51-0.53), which are remote stations on Lake Superior.

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Long-term trends in F_{DDTE} at IADN stations are shown in plots of annual means vs. year in Figure 3. Degradation of DDTs to DDEs and DDDs has presumably increased over time (*42*), which would lower F_{DDTE} and F_{DDTD} in soils and volatilized residues. Annual means of F_{DDTE} decreased slightly, but not significantly, at PPT ($r^2 = 0.27$, $p = 0.071$, $n = 13$), BNT ($r^2 = 0.25$, $p = 0.085$, $n = 12$) and EGB ($r^2 = 0.47$, $p = 0.14$, $n = 6$), and no trend was found at STP nor IIT ($p > 0.3$). F_{DDTE} *increased* significantly at EGH ($r^2 = 0.28$, $p = 0.042$, $n = 15$) and BRR ($r^2 = 0.57$, $p = 0.050$, $n = 7$), and slightly but not significantly at SBD ($r^2 = 0.25$, $p = 0.066$, $n = 14$). Some of the F_{DDTE} values at EGH and BRR approached the $F_{DDTE} = 0.74$ for technical DDT vapor.

Further insight is provided by comparing the frequency profiles of F_{DDTE} at IADN stations with each other and with the profile predicted for soil-air exchange in NUSA-CAN (Figure 4). “Urban” profiles at IIT and CLV are symmetric and centered at 0.3-0.4. “Rural” profiles are shifted towards lower F_{DDTE} with main contributions between 0.2-0.4 at SBD and STP, and 0.1-0.3 at PPT, EGB and BNT. These are consistent with the NUSA-CAN predicted frequency distribution for soil emissions (Figure 2b), recognizing its limitations. The NUSA-CAN profile was derived from soil data collected over many years and across the continent, whereas the air profiles at a particular IADN site may be influenced by regional soils. Frequency profiles at the “remote” stations EGH and BRR are broader and have major contributions between 0.3-0.7, suggesting different sources of DDT residues to the upper and lower lakes. None of the stations exhibits a F_{DDTE} profile similar to predicted emissions from the SUSA (Figure 2b).

Mean F_{DDTE} from other atmospheric sampling studies in Canada and the U.S.A. cover a wide range from 0.08-0.88 with an overall mean of 0.37 ± 0.19 (Table 2). Four of the five highest values (0.59-0.88) were found in the Canadian Rocky Mountains on the western side of the continental divide (Revelstoke, Kananaskis, Yoho and Donald Station), suggesting the possibility of transpacific sources, while a comparative low value of 0.25 was found on the eastern side of the divide (Observation Peak) (*11*, *71*). F_{DDTE} in the air of Mexico ranged from 0.24-0.83 and was significantly higher at southerly latitudes where DDT was more recently applied (*12*).

F_{DDTO} means at IADN stations ranged from 0.40-0.45 at Canadian sites and 0.65-0.74 at U.S. sites (Table 2). The difference reflects the offset seen in colocated sampling experiments at PPT (see above). Long-term trends in F_{DDTO} at IADN stations are shown in plots of annual means vs. year in Figure 5. F_{DDTO} were unusually low at PPT and BNT from 1997-1999, but increased again in 2000. The decrease in annual mean F_{DDTO} over time at PPT was significant whether or not the 1997-1999 “dips” were included (all years: $r^2 = 0.39$, $p = 0.022$, $n = 13$; excluding 1997-1999: $r^2 = 0.87$, $p < 0.001$, $n = 10$). The decrease at BNT was significant when the 1997-1999 data were excluded ($r^2 = 0.80$, $p = 0.0011$, $n = 9$). Data for EGB covered only 1997-2003 (with 2002 missing) and showed no significant trend in annual mean F_{DDTO}. U.S. stations did not report o,p′-DDT before 1999. Plots of annual mean F_{DDTO} vs. year show temporary increases at the U.S. stations in 2001-2003, but returned to 1999-2000 values in 2004-2005 (no data for BRR after 2002). No significant relationships were found, and a longer time series at these stations will be needed to determine temporal trends in F_{DDTO}.

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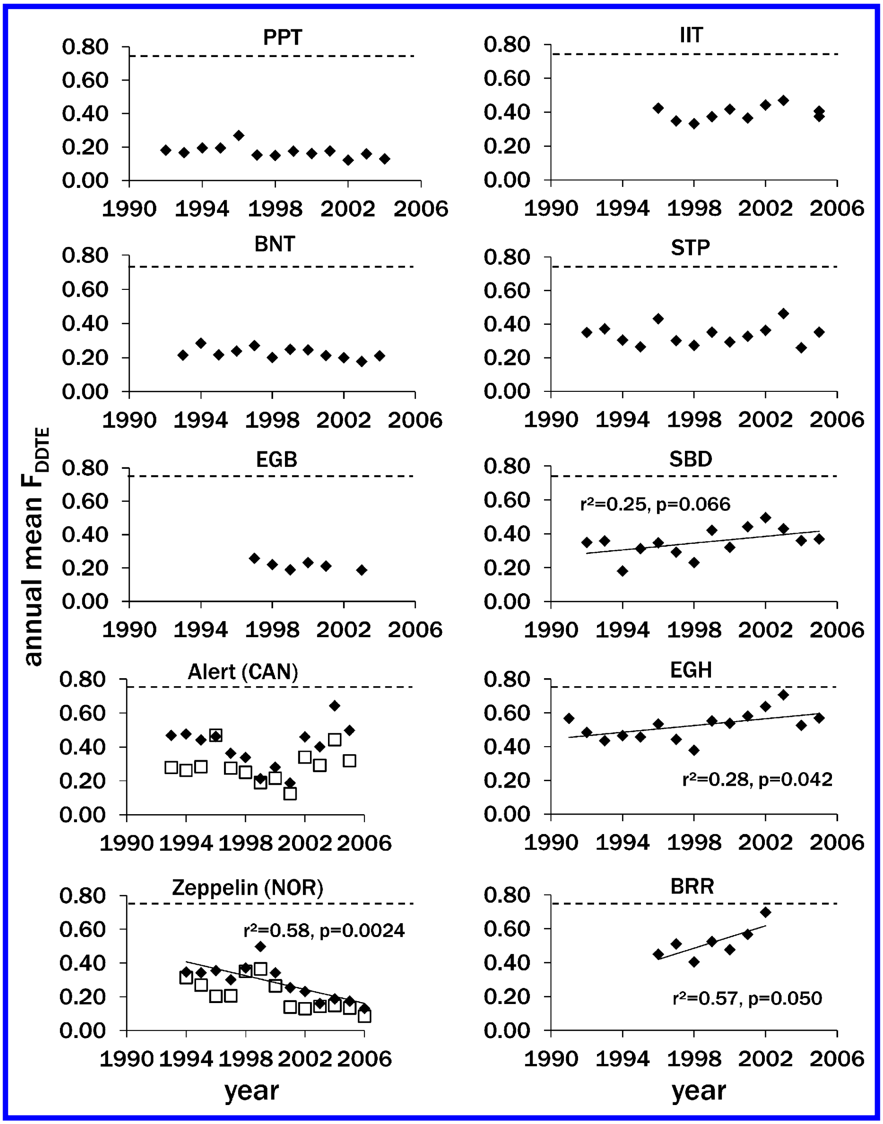

Figure 3. Temporal trends of annually averaged F_{DDTE} in air at Canadian IADN stations Point Petre (PPT), Burnt Island (BNT), Egbert (EGB), U.S. IADN stations Illinois Institute of Technology (Chicago, IIT), Sturgeon Point (STP), Sleeping Bear Dunes (SBD), Eagle Harbor (EGH) and Brule River (BRR), and arctic air monitoring stations at Alert, Canada and Zeppelin Mountain, Svalbard, Norway. Solid diamonds represent F_{DDTE} averaged from individual air samples, while open squares represent F_{DDTE} estimated from annually averaged air concentrations. The dotted line at F_{DDTE} = 0.74 indicates the predicted vapor composition of WHO technical DDT.

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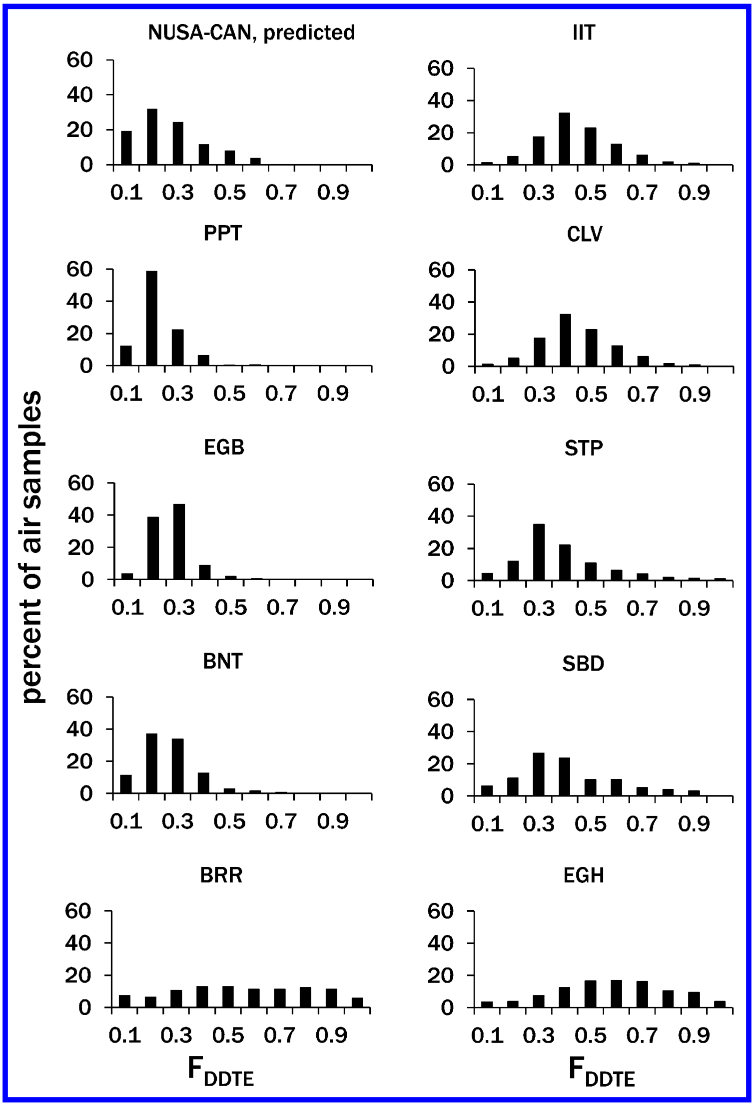

Figure 4. Frequency distribution of F_{DDTE} in air samples from IADN sites (see Figure 3 for abbreviations, CLV = Cleveland), with comparison to the frequency of F_{DDTE} predicted from emission of soil residues in the northern U.S.A. and southern Canada (NUSA-CAN).

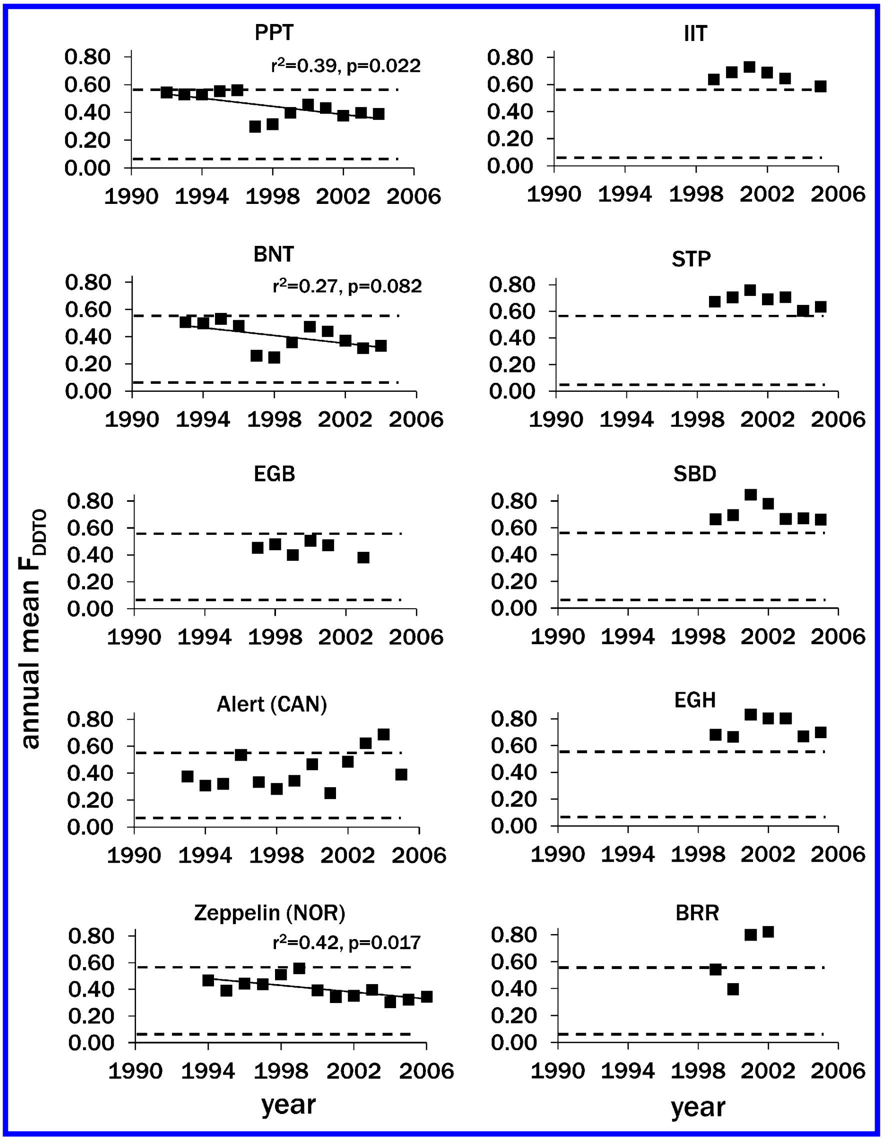

Figure 5. Temporal trends of annually averaged F_{DDTO} in air at Canadian and U.S. IADN stations, and Canadian and Norwegian arctic stations, identified in Figure 3. IADN annual means are averages for individual air samples, while those at arctic stations are estimated from annually averaged air concentrations. The dotted lines at F_{DDTO} = 0.58 and 0.04 indicate the predicted vapor compositions of WHO technical DDT and Chinese dicofol.

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Mean F_{DDTO} from other air sampling campaigns across Canada and the U.S.A. were 0.46-0.90 (overall mean 0.63 ± 0.14) and higher in Mexico (0.64-0.88, 0.76 ± 0.09) (Table 2). Predictions for soil emissions across North America were 0.44-0.62 (Table 5), which are similar to F_{DDTO} = 0.58 from evaporation of technical DDT having the WHO composition (*41*). This may imply similar rates for degradation of the two DDT isomers in soil, although there is substantial variation in the *o,p′*-DDT percentage of various technical DDT products (see above). The composition of the technical DDT manufactured in Mexico was not available for this assessment.

Mean F_{DDTD} were 0.70-0.91 at all IADN stations except BRR, where the mean was 0.46 (Table 2). Mean F_{DDTD} from other air sampling campaigns across Canada and the U.S.A. were 0.61-0.98 (overall mean 0.86 ± 0.10) and 0.80-0.98, (overall mean 0.90 ± 0.06) in Mexico (Table 2). Predictions for soil emissions were 0.71-0.89 (Table 5).

DDT Compounds in Arctic Air

Monitoring of DDT compounds and other POPs in arctic air has been conducted since the 1990s at circumpolar stations to investigate temporal trends and governing processes (*72–78*). Here we compare IADN results with temporal trends at two long-term arctic air monitoring stations, Alert (Canada, 82° 30′ N, 62° 20′ W, 1993-2005) and Zeppelin Mountain (Svalbard, Norway, 78° 54′ N, 11° 53′ E, 1994-2006).

Sources and pathways of DDTs in arctic air are complex and influenced by the compositions of technical DDT and dicofol products used in source regions, episodic transport events, different rates of rain and snow scavenging for the DDT compounds and forest fires which release DDT and other POPs from burning vegetation (*73–79*). Annual mean concentrations of ΣDDTs at Alert ranged from 0.59 pg m^{-3} in 2001 to 1.6 pg m^{-3} in 2004 (*75*). The range at Zeppelin for most years was 1.1 pg m^{-3} in 2000 to 5.4 pg m^{-3} in 1994, with an exceptionally high mean of 14.3 pg m^{-3} in 2004 (*73*). The elevated ΣDDTs at Zeppelin in 2004 were due to episodic transport of residues with high proportions of *o,p′*-DDT and *o,p′*-DDE (see below). Winter maxima and summer minima were characteristic of the DDTs and DDEs at Zeppelin in most years (*73*), but were not obvious at Alert (*78*). No significant long-term temporal trends were observed at Alert for any of the DDT compounds. At Zeppelin, times for 50% decline ranged from 4.1 y for *p,p′*-DDT to 11 y for *p,p′*-DDE using Digital Filtration Analysis (*75*), but only the decline for *p,p′*-DDT was significant using Dynamic Harmonic Regression Analysis (*73*).

F_{DDTE} at Alert and Zeppelin averaged 0.40 ± 0.13 and 0.28 ± 0.10 over 13 years of monitoring. These were calculated by converting annual averages of *p,p′*-DDT/*p,p′*-DDE ratios (*75*) to annually averaged F_{DDTE} and then taking the 13-year mean. The 13-year means were lower when F_{DDTE} was derived from annually averaged *p,p′*-DDT and *p,p′*-DDE concentrations: 0.28 ± 0.09 at Alert and 0.21 ± 0.09 at Zeppelin. The time trends of F_{DDTE} were strikingly different at the two stations (Figure 3). At Alert, F_{DDTE} decreased from 1993-2001, then increased from 2002-2005 and the overall trend from 1993-2005 was not significant. F_{DDTE} values at Zeppelin were fairly constant from 1994-2000, except for a rise in 1998-1999, and

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then dropped steadily through 2006. The decrease from 1994-2006 was significant ($r^2 = 0.58$, $p = 0.0024$, $n = 13$).

Mean F_{DDTO}, calculated from annually averaged concentration data, were 0.42 ± 0.13 and 0.40 ± 0.08 at Alert and Zeppelin, while F_{DDTD} were 0.65 ± 0.17 and 0.79 ± 0.10 at the two stations. The trend in annual mean F_{DDTO} vs year at Alert (Figure 5) was not significant from 1993-2005, but an increase was seen in recent years similar to the trend for F_{DDTE} (Figure 3). Annual mean F_{DDTO} at Zeppelin decreased steadily and significantly ($r^2 = 0.42$, $p = 0.017$, $n = 13$) from 1994-2006 (Figure 5).

Parent/metabolite ratios *p,p'*-DDT/(*p,p'*-DDE + *p,p'*-DDD) and *o,p'*-DDT/*p,p'*-DDT ratios at Zeppelin were examined in detail (*73*). The former showed dominance of *p,p'*-DDT in summer and metabolites (largely *p,p'*-DDE) in winter. Although the F_{DDTO} calculated from average annual concentrations fell within narrow limits (see above), the individual samples displayed far greater variability, with a few events of *o,p'*-DDT/*p,p'*-DDT up to 8 ($F_{DDTO} = 0.11$), which are suggestive of dicofol-type DDT sources (*73*).

Transpacific Transport

Transport of airborne dust from Asia in 1988 resulted in a “brown snow” event in the central Canadian Arctic (*80*). This snow contained levels of DDT that were 2-10 times higher than previously reported concentrations in Canadian Arctic snow. Advection of DDT in both the particle and gas phases from Asia to western Canada in 1992-1995 was documented (*81*). DDTs were measured in air on a shipboard expedition from the North Pacific to the western Arctic in 2003 (*82*). The ΣDDTs was higher in far east Asia (34-48° N, 56 ± 99 pg m^{-3}) than in the North Pacific (48-65°N, 4.2 ± 4.7 pg m^{-3}) or the Arctic (>66.7°N, 0.96 ± 1.2 pg m^{-3}). F_{DDTE} averaged 0.57 ± 0.17 in far east Asia, 0.52 ± 0.11 in North Pacific and 0.51 ± 0.17 the Arctic. Mean F_{DDTO} in these regions were 0.56 ± 0.26, 0.29 ± 0.02 and 0.42 ± 0.17, while F_{DDTD} means were 0.69 ± 0.26, 0.77 ± 0.21 and 0.63 ± 0.27. Median F_{DDTE} and F_{DDTO} at three stations in the western Arctic were higher than at three stations in the central-eastern Arctic in samples collected between 2000-2003 (*78*).

Surveys of DDTs in the air of China between 2003-2006 generally showed high F_{DDTE} (calculated either from reported compound ratios, mean or median concentrations); e.g., seasonally varying means of 0.52-0.69 in 37 cities (*27*), 0.59-0.70 in Hong Kong (*70*) and 0.46-0.71 in Guangzhou (*70*, *83*). Using eq 1, it was estimated that the air in Chinese cities contained “fresher” DDT than could be attributed to only soil emissions (*27*).

Shipboard measurements in the marginal seas of China (East, South, Yellow) found mean F_{DDTE} and F_{DDTO} = 0.43 ± 0.24 and 0.44 ± 0.26 in 2008 (*84*); 0.48 and 0.21 in 2006 (*85*); 0.49 ± 0.09 and 0.19 ± 0.10 in 2005 (*86*). A survey covering China, Japan and South Korea in 2004 found mean F_{DDTE} and F_{DDTO} = 0.46 ± 0.19 and 0.35 ± 0.14 (*87*). The proportion of technical DDT vs. dicofol-type DDT in air was estimated from product compositions and relative K_{OA} (*17*) or vapor pressures (*27*) of the compounds. According to one report, technical DDT accounted for 95% of DDT residues in the air of 37 Chinese cities, while dicofol-type DDT contributed only 5% (*27*). Another report estimated that dicofol-type DDT accounted for 72% or more of DDT residues in air of the Taihu Lake region but half or less in Hong Kong, while source media were estimated to contain 25-72% of dicofol-type DDT (*17*).

A different pattern of residues is found in India, with 2006-2007 measurements showing lower proportions of *p,p′*-DDT in cities (mean F_{DDTE} = 0.16-0.18), and higher proportions in rural and wetland areas (F_{DDTE} = 0.48-0.66) (*88*, *89*). F_{DDTO} were generally low in these studies; means ranged from 0.11-0.33. The low F_{DDTO} (high proportion of *o,p′*-DDT/*p,p′*-DDT) is surprising, because dicofol usage has not been recorded in India (*89*). A 2008 expedition to the Andaman Sea and Bay of Bengal measured DDT residues with $F_{DDTE} = 0.54 \pm 0.25$ and $F_{DDTO} = 0.50 \pm 0.17$ (*84*).

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Chiral Markers for DDT Source Identification

The two enantiomers of *o,p′*-DDT are often degraded in soil at different rates, leading to accumulation of nonracemic *o,p′*-DDT and *o,p′*-DDD (*36*, *90–94*). The enantiomer fraction, $EF = (+)/[(+) + (-)]$, is 0.5 for the racemic compound (1:1 enantiomer ratio), and <0.5 or >0.5 for preferential depletion of the (+) or (−) enantiomers. Agricultural soils in the Zhejiang Province of China showed a significant negative correlation between the *o,p′*-DDT/*p,p′*-DDT ratio and deviation of the *o,p′*-DDT EF from 0.5. Thus, enantioselective degradation was less in soils which had been more recently contaminated with dicofol-type DDT than in those historically contaminated with technical DDT (*90*).

Enantiomers have the same vapor pressures, so volatilization should transfer both to the atmosphere equally and the EF should remain the same (*92*, *93*). A problem is that *o,p′*-DDT degradation in soils is ambivalent and racemic residues or preferential degradation of either enantiomer occur with about equal frequency (*36*, *90*, *93*, *94*). Nonracemic *o,p′*-DDT has been used to trace emissions from specific fields where positive correlation was found between the EFs in soil and air (*36*). The *o,p′*-DDT in ambient air was racemic in southern Mexico, but nonracemic at sites in eastern and western Canada, and Youngstown, OH (*11*). Significant correlations were found for *o,p′*-DDT in the air of Mexico, where deviation from racemic was less for samples at more southerly latitudes ($p < 0.001$) in areas of higher DDT usage ($p = 0.03$) (*12*). Nonracemic EFs of *o,p′*-DDD in air have been reported only once, in samples from Arkansas, U.S.A. (*95*). Enantiospecific analysis has not been done for *o,p′*-DDT and *o,p′*-DDD in IADN air samples, but including this information could give additional insight to sources and age of residues.

Conclusions

Fractionation of DDTs during volatilization from soil is well described using compound ratios in soil and their P_L (eq 1), opening the possibility to estimate the contribution of soil emissions to atmospheric residues based on composition. This assessment finds that emission of legacy residues from soils in NUSA-CAN or

MEX can support mean F_{DDTE} in air of 0.20-0.28, with lower estimates for SUSA and CA (Table 5). Predictions in Figure 4 suggest that 76% of residues emitted from NUSA-CAN soils have $F_{DDTE} \leq 0.3$ and 88% ≤ 0.4, compared with $F_{DDTE} = 0.74$ from evaporation of technical DDT having the WHO composition. These results can be used as guidelines for judging whether atmospheric DDTs come from fresh sources or recycling of old residues.

Ambient air samples from IADN stations on or close to lakes Erie, Ontario, Huron and Michigan show mean F_{DDTE} (0.17-0.36) that are consistent with volatilization from NUSA-CAN soils. Mean F_{DDTE} in air at the CLV and IIT IADN urban stations were somewhat higher (0.40-0.47) and suggests less weathered DDT sources, which have not been identified, in these cities.

Interestingly, the predicted F_{DDTE} in soil emissions from the SUSA (0.07-0.09) are much lower than those found at IADN sites. This calls into question the much-discussed "southern source" of DDT to the Great Lakes, although modeling has predicted rather high loss rates from soil in this region (*96*). Air trajectories from the southern U.S. have been shown to transport elevated levels of DDTs (*23*) but these also pass over farmland in the midwestern U.S. and Ontario where they could pick up emissions from regional soils.

Still higher mean F_{DDTE} (0.51-0.53) were found at the IADN background stations EGH and BRR on Lake Superior (Table 2) where F_{DDTE} increased significantly between the early 1990s and 2005 (Figure 3). The higher means and broader frequency profiles (Figure 4) compared to those on the lower lakes suggest different DDT sources. Mean F_{DDTE} also increased at the Canadian Arctic station Alert after 2001, while a decrease occurred at the Norwegian station Zeppelin Mountain (Figure 3). Reasons for the high and increasing F_{DDTE} at the North American background air stations are not apparent. These stations have little agricultural land in their vicinities and are likely receiving DDTs from distant sources. These may be tropical countries where DDT is still applied for malaria control. Another possibility is transpacific transport, suggested by the relatively high F_{DDTE} in Chinese air. Additional possibilities are remobilization of DDTs that have been formerly deposited in cold regions that are now undergoing warming (*97*), and global "recycling" from soils and oceans (*98*, *99*).

Decreasing F_{DDTO} in air over time was statistically significant at IADN stations PPT and BNT, and at the Norwegian arctic station Zeppelin Mountain. Such decreases might be caused by increased atmospheric transport of dicofol-type DDT vs. technical DDT over time, or more rapid degradation of *p,p'*-DDT than *o,p'*-DDT in source media. If so, it is curious why increasing trends in F_{DDTO} are recently observed at Alert and why F_{DDTO} values from other air sampling campaigns in Canada, the U.S. and Mexico are generally consistent with or higher than F_{DDTO} in technical DDT or predicted from soil emissions.

This paper does not fully answer the title question, "Is there still 'new' DDT in North America?", but hopefully points the way toward improving the forensics. The estimates and conclusions depend greatly on the reliability of the soil residue data, which were gathered from many individual studies over more than two decades. Are these spatially and temporally representative of the reservoirs that supply DDT to the atmosphere today? A continent-wide soil survey for DDTs (and other POPs) would improve the ability to estimate the contributions of soil

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emissions to atmospheric levels. Better source identification could be realized by employing the chemical signatures provided by proportions of parent/metabolite compounds, isomers and enantiomers (*93*), coupled with air-surface exchange modeling (*25*, *26*, *96*). Many countries manufactured technical DDT, and varying compositions of these mixtures may be partly responsible for regional source signatures. Information on percentages of DDT compounds in the technical DDT products used in the past and today would aid speciation efforts.

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Chapter 9

Assessment of Persistent Organic Pollutants in the Atmosphere of Latin America

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The widespread use and distribution of pesticides, industrial and urban chemicals and their consequent release into the environment is of great worldwide relevance. Persistent Organic Pollutants (POPs) are stable organic chemicals, toxic and bioaccumulative, that undergo long-range atmospheric transport. The Latin American Atmospheric Passive Sampling Network (PROSUL-LAPAN), includes a monitoring program involving the use of pine needles and passive samplers. Passive samplers (XAD-2) are currently deployed covering 50 sites, and 30 more are expected to be installed. The network includes Antarctica and 12 countries from South America including urban, agricultural and industrial areas. Additionally, Pine needles (*Pinus sp.*) were used to evaluate latitudinal and longitudinal transport of POPs in central and Patagonian regions of Argentina and the southeast of Brazil with a 20-station network. Endosulfan was the main pesticide found, however *p,p'*-DDE, the *p,p'*-DDT metabolite, was also found in all sites independently of particular sources as a consequence

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of its intensive historical use in the region. Through the implementation of this project, new knowledge regarding the magnitude of contamination and sources of POPs in Latin America will be generated leading to more informed regulatory decisions.

Persistent Organic Pollutants (POPs): General Overview

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Persistent Organic Pollutants (POPs) constitute a group of organic chemicals that due to their physicochemical properties are toxic, bioaccumulative, persistent and semivolatile. They undergo long-range atmospheric transport (LRAT) and are detected regularly in samples from remote Polar regions (*1*). As a consequence the Stockholm Convention on Persistent Organic Pollutants was created in 2001 under the auspices of the United Nations Environmental Program (*2*). The Convention that came into effect on 17th May 2004 has today more than 152 signatories and identifies those compounds to eliminate from production and usage. Originally, there were 12 specific chemicals listed under the Stockholm Convention, called the "Dirty Dozen". Nine new chemicals were added in 2009, chlordecone, α- and β-hexachlorocyclohexane, lindane, pentachlorobenzene, hexabromobiphenyl, polybrominated diphenyl ethers (PBDEs), perfluorooctane sulfonic acids (PFOSs), tetrabromodiphenyl ether and pentabromodiphenyl ether, and endosulfan in 2011 (Table I). POPs can be produced intentionally as with organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and PBDEs or unintentionally as by-products during, for instance, chemical manufacture or incineration processes resulting in polychlorinated dibenzo[p]-dioxins and furans (PCDD/Fs).

Environmental Behavior of POPs

The distribution and fate of contaminants in environmental compartments are mainly controlled by three factors: a) physicochemical properties of the compound; b) environmental conditions (e.g., temperature, pH, solar radiation, and wind speed) and physicochemical properties of abiotic components (e.g., organic carbon content, particle size distribution of soil or sediment); and c) physiological, anatomical and behavioral characteristics of the species inhabiting exposed ecosystems. POPs are delivered into the environment during pesticide application, by leaching from dumping sites, direct discharge in effluents and

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emissions from industrial processes. Then, by volatilization, drift or attached to particulate matter, POPs may reach the atmosphere. Transport from terrestrial environments to aquatic ecosystems leads to accumulation in the biota and bottom sediments and biomagnification through trophic webs. As chemicals have been banned from further use, direct inputs to the environment are reduced; however, soil, sediments and biota are sinks of POPs and have now become secondary sources to the adjacent compartments including the atmosphere. Thus, the biogeochemical cycle of POPs depends on the amount and composition of organic matter and lipids, which are the main environmental compartments involved in adsorption/desorption processes. Many studies and worldwide programs are designed to monitor the presence of these environmental contaminants and to determine their spatial and temporal trends (*3*).

POPs may volatilize to the atmosphere from soils, plants and water bodies, and these processes play a key role in the transport and cycling of these pollutants. The long-range transport of POPs is primarily *via* the atmosphere. Some POPs, however, may also be transported through oceanic currents and eventually be transferred to air particulates via bubble bursting at the sea surface (*4*, *5*). In the atmosphere, POPs exist either in the gaseous or particle-associated form, both of which can facilitate transport over long distances. The gas/particle distribution depends on physical-chemical properties of the compounds, environmental conditions (*i.e.* temperature) and the amount and nature of the particulate matter. Therefore, their distribution will change both seasonally and spatially (*3*). Thus, POPs undergo dynamic exchange between water, soil and vegetation, and the atmosphere. These processes are important for understanding and controlling the entry of POPs into food chains, influencing their LRAT potential and, therefore, controlling their global cycling and redistribution.

The concentrations and mixtures of POPs in the atmosphere vary widely in space, time, and with compound classes. To understand the mechanisms of LRAT of POPs, it is necessary to study their partitioning between various environmental compartments. Most of the POPs contamination of remote areas is thought to be due to temperature driven atmospheric transport from warm to cold climates (*1*).

LRAT occurs along the concentration gradient through the latitudes but does not occur in one single step. The chemicals move with air masses and are deposited into other areas. Once they reach higher latitudes, such as the Arctic or Antarctic regions, their mobility is limited by the “cold trap” effect. Compounds with relatively low a vapor pressure will partition mostly to atmospheric particles and soil matrices. In the mid-latitude regions, POPs are also transferred from low to high altitudes in successive condensation-volatilization steps (“grasshopper effect”), as they are exchanged between the atmosphere and terrestrial surfaces in response to seasonal temperature variations. Thus, the occurrence of POPs in areas away from sources or pristine environments has been explained by the process of global cold-trapping (*1*). Even in very cold regions, seasonal snowmelts can facilitate revolatilization and redistribution of POPs since the equilibrium processes of these chemicals are reversible. All these processes and mechanisms lead to the “global distillation” of POPs, as evidenced by latitudinal gradients fully documented by monitoring data from sediment, soil cores, fish, water, and air samples (*1*, *6*–*9*).

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Table I. List of Persistent Organic Pollutants, Stockholm Convention on Persistent Organic Pollutants, United National Environmental Program

Compounds	*Sources - uses*
Organochlorine pesticides (OCPs) aldrin, endrin, dieldrin, heptachlor, chlordane, mirex, toxaphene, DDT, endosulfan, lindane, chlordecone, hexachlorobenzene, α− and β− hexachlorocyclohexanes, pentachlorobenzene	Agrochemicals
Hexabromobiphenyl	Industrial
Polychlorinated biphenyls (PCBs)	Use in transformers, capacitors, stable fluids, paint additives in carbonless copy paper and in plastics.
Polynuclear aromatic hydrocarbons (PAHs)	Incomplete combustion by-products, released from burning of petrol, waste, coal.
Polybrominated diphenyls ethers (PBDEs) (tetra/penta and hexa/hepta commercial mixtures)	Flame retardant chemicals in coatings and lacquers, thermoplastics, in flexible polyurethane foam for furniture and upholstery and in electronic equipment.
Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)	By-products from combustion processes and impurities in some chlorinated chemicals.
Perfluorooctane sulfonic acids, its salts, and perfluorooctyl sulfonyl fluoride (PFOSs)	Unintended degradation of related anthropogenic chemicals. Current intentional use: electric and electronic parts, fire fighting foam, photo imaging, hydraulic fluids and textiles.

For estimating the LRAT potential of substances, the atmospheric residence time can be considered as the most indicative parameter. It is defined as the time period in which the mass of the pollutant in the atmospheric boundary layer is reduced by 50%. For instance, an atmospheric residence time of 24 hours means that, at least, half of the substance is transported to a distance of 400 km or more, considering an average wind speed of 5 m s^{-1}. The atmospheric residence time is highly influenced by all removal processes from the atmospheric boundary layer, such as wet and dry deposition and photochemical degradation. This chapter focuses mainly on three points related to the study of POPs in the atmosphere: i) use of different methodologies of atmospheric POPs monitoring; ii) the current status of atmospheric POPs contamination in Latin America, based on results from natural and artificial passive samplers, and; iii) a description of ongoing research projects involving regional and international networks focused on long-term passive atmospheric monitoring of POPs.

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Measurement of POPs in the Atmosphere

Atmospheric monitoring of POPs traditionally relies on high volume air samplers. This equipment is very expensive, requiring trained operators and a electrical power. In addition, active air sampling is typically limited to short time periods of sampling. During the last years, various types of passive air samplers (PAS), including artificial, such as semi permeable membrane devices (SPMD), polyurethane foam disks (PUF) and styrene-divinylbenzene polymeric (XAD) and natural samplers, such as the use of vegetation, have been developed and used for POPs monitoring (*10*).

Artificial passive air samplers consist of an accumulating medium that has a high retention capacity for the target analytes. The sampling process is mediated by the diffusion of chemicals from a matrix where chemical's fugacity or potential is high to a matrix where its fugacity or potential is low. The sorbent is suspended directly into the sampler or housed in a stainless steel chamber, which is shaped according to the sampler type (*6*, *11*). The role of the chamber is to protect the sorbent from direct sunlight, precipitation, deposition of coarse particles and also to reduce the effect of wind speed on the uptake rate of chemicals. Quantifying the sorption of organic chemicals to the sorbent is important when determining the limits of applications of an air sampling technique, for a certain combination of polymer and target analytes. A PAS needs to operate in the linear uptake regime if time-integrated air concentrations are to be determined (*6*). Thus, depending on the characteristic of the sorbent and the chamber, PAS might be deployed over periods from weeks to years. Particularly, the XAD-resin is housed inside a cylindrical stainless steel chamber (Figure 1). The XAD-resin can be deployed for longer periods (e.g., from 3-6 months to one year or more) than the PUF-disk, which generally do not surpass three months of exposure (*6*, *12*). In both cases, most chemicals fall within the linear uptake range.

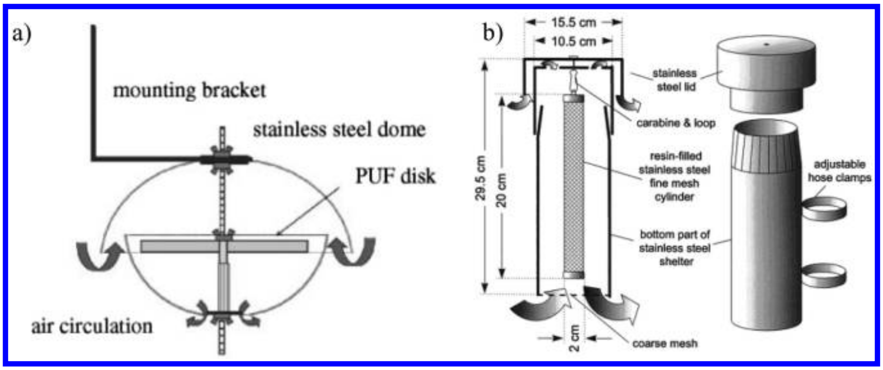

Figure 1. a) Polyurethane foam (PUF) disk passive sampler (Reproduced with permission from Moreau-Guigon et al., 2007 (13)); b) XAD-type passive sampler (Reproduced with permission from Wania et al., 2003 (6). XAD: styrene-divinylbenzene polymer.

XAD polymers are available in several formulations, differing mainly in polarity and chemical cross-linking, which allows their use for sampling a wide variety of organic chemicals from both air and water (*6*, *14*, *15*). The styrene-divinylbenzene polymers, such as XAD-2, are the most common resins used as passive samplers of organic vapors from air (*15–18*). XAD-2 is relatively non-polar, chemically inert, and has a large surface area, which allows a high sorptive capacity for organic chemicals. The resin can often be reused if properly cleaned after each sampling deployment.

Vegetation as Passive Samplers of Atmospheric Pollutants

Vegetation covers about 80% of the Earth's terrestrial surface and constitutes a key component of the land-atmosphere interface. Individual organisms, highly organized and structured, compose large areas of vegetation canopies that link the soil and air environments. Terrestrial vegetation may either take up pollutants from the air through the surfaces of above ground parts, such as leaves, stems, or bark, or directly from the soil through the roots (*19*). Particularly, the uptake of apolar airborne compounds occurs mainly *via* the leaf surface (*20*). Moreover, the epicuticular wax that covers of the outer surfaces of plants facilitates the accumulation of lipophilic compounds from the atmosphere (*21*). The extent of accumulation depends on compounds and species characteristics, in addition to environmental conditions (*22–24*). Thus, vegetation plays an important role in the deposition of hydrophobic compounds to terrestrial ecosystems. In recent years the vegetation uptake mechanisms of airborne POPs have received more attention since these processes govern the mass incorporated by vegetation and also the efficiency of vegetation as a buffer for the fractionation of POPs. However, prior to interest in their role in global fractionation, some studies used vegetation as passive sampler to identify temporal sources of POPs and for local, regional and global monitoring of contaminants (*25*, *26*).

Different species, such as evergreen tree (*Quercus ilex* and *Laurus nobilis*), epiphytes (*Thillandsia* sp.), lichens (*27*), and mosses (*28*), have been used to monitor spatial trends in air concentrations (*25*, *26*). Mosses were initially used to monitor organochlorine compounds, such as OCPs and PCBs, but lately both lichens and mosses have been used to monitor PAHs emissions from coke production, fossil fuel combustion, and aluminum and carbon electrode industries (*29*). However, conifers are among the most suitable plants, since air contaminants in the vapor phase adsorb and accumulate in the epicuticular wax of the needles (*25*). Conifers are widespread in temperate and sub-tropical areas, and due to the evergreen nature of needles it is possible to take samples of different ages from the same tree (*25*, *30*). Needles from many different pine species have been used as passive samplers of PAHs. Due to its widespread distribution throughout the Northern hemisphere, *Pinus silvestris* appears in studies from numerous European countries, such as Spain, France, Sweden, UK, and Czech Republic (*25*, *31*). Other relevant species are *Pinus strobes* in the United States (*23*) and *Pinus densiflora* and *Pinus thumbergii* in Korea (*32*).

It is known that variability of POPs concentrations in pine needles from within a single forest is low, making it possible to estimate airborne deposition of POPs

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by sampling only a few trees. So, sampling at a convenient height in the edge of the forest or in a clearing is adequate to obtain representative data (*25*).

Active and Passive Monitoring

Monitoring of atmospheric POPs using conifers can be defined as passive monitoring while other species such as lichens and epiphytes are useful tools in performing active monitoring. The Bromeliaceae family constitutes a wide group of plants with neotropic distribution including the epiphytic species from the subfamily Tillansioideae. These plants obtain nutrients and water from the atmosphere without interaction or exchange with the substrate where they live (*33*). Moreover, some of them have a high tolerance to hydric stress and are easy to re-located from their natural environments to a place of interest for active monitoring (*34*). Despite the limited number of publications about their physiological responses and accumulation potential for pollutants, epiphytes have a great potential for atmospheric pollution monitoring.

The use of epiphytes for atmospheric monitoring studies is scarce in Latin America and has been mainly focused on trace elements (heavy metals, radionucleids) (*35–37*). Most studies included species from the *Tillandsia* genus that is widely distributed in South America and were conducted by active monitoring. Argentinean and Brazilian studies have recognized the value of several species of *Tillandsia* for air quality monitoring studies. Thus, *T. capillaris* was recognized as a suitable bioindicator to assess PAHs and trace element contamination in different subtropical and tropical regions (*38*). Two other species, *T usneoides* and *T bergeri*, were defined as sensitive and low cost biomonitors for PAHs, PCDD/F, PCBs and PBDEs, since they allow distinguishing among industrial, agricultural and natural areas, as well as seasonal variability in contaminant emissions (*39–41*).

Atmospheric Pollution in Latin America

Industrial contamination is a on-going and growing problem in Latin America. However, with Latin America becoming a predominantly urban society, related contamination issues have become increasingly important on the political agenda. Air pollution is a big problem in the major urban and industrial centers of Latin America. Data on industrial contamination in the region is fragmented and lack in comparability both over time and among countries. There are indications though that levels in some Latin American cities are above the World Health Organization (WHO) (*42*) guidelines for air quality standards. Industrial and vehicular emissions constitute the main factor contributing to air contamination in urban areas.

Regarding pesticides, OCPs have been used in agriculture in Latin America over the past few decades. Although banned during the 1980's and 1990's, with endosulfan recently included in regulations, some illegal use of old stocks still occurs. Moreover, huge quantities of DDT were used for disease vector control, and currently this purpose represents the only allowed use of this insecticide

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(*43–45*). The WHO currently recommends the use of DDT for malarial outbreaks, although public health experts do not uniformly endorse its use (*46*). Particularly, an intensive DDT use was demonstrated in Mexico for growing cash crops. Historically, Mexico was the biggest consumer of DDT in Latin America followed by Brazil, but the last record of import by Brazil was in 2000 (*47*, *48*).

The Latin American and Caribbean Region (GRULAC) includes 33 countries divided in four sub-regions – Andean, Caribbean, Mesoamerica and Southern Cone. Most of GRULAC countries are parties but not all are signatories of the Stockholm Convention; only 10 out of 33 countries have completed their national implementation plans (Argentina, Barbados, Bolivia, Chile, Ecuador, Mexico, Panama, Peru, Saint Lucia, and Uruguay), including the inventories for dioxin and furan emissions, PCBs and legacy POPs . The region faces many problems related to pollution, including POPs. The United Nations Environmental Program (UNEP) issued its First Regional Monitoring Report describing the Global Monitoring Plan for Persistent Organic Pollutants under the Stockholm Convention Article 16 on effectiveness evaluation (*49*). It was launched in 2009, being the first report on POPs monitoring in core matrices, air and human milk samples, in the GRULAC region. It included the first compilation and data evaluation within the 1998-2008 period as proposed by the Stockholm Convention Secretariat (*49*). Below are summaries of recent studies of POPs in the atmosphere of some Latin American countries.

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Mexico

Measurements of organochlorine pesticides in air in Mexico were performed by Alegria et al (*50*, *51*) and Wong et al (*52*). Samples were collected with a high-volume sampler in which 500 m^3 of air was drawn through a 10-cm diameter fiber glass filter followed by a polyurethane foam (PUF) trap. Air sampling was performed in two cities in the states of Chiapas, Veracruz and Tabasco. DDT concentrations in southern Mexico reached values between 240-2400 pg/m^3 during 2002-2003 (*52*). A similar pattern to the technical DDT mixture was found in air at a farm in Chiapas, which is suggestive of fresh DDT input. A combination of ongoing regional usage and re-emission of old DDT residues from soils, based on soil analyses, was suggested as the source.

In order to determine the contamination by OCPs and PCBs in southern Mexico, another project was carried out during 2002–2004 using passive and active atmospheric samplers (*51*). Wong et al. (*52*) observed that DDT was much higher than other POPs at 239 to 2360 pg/m^3, suggesting fresh inputs in most areas. In addition, endosulfans, toxaphene and lindane were detected. Air back trajectory analysis suggests a complex pattern of regional atmospheric transport.

Chile

In an effort to characterize the spatial variability of pesticides, PCBs and PAHs in the Chilean atmosphere, a research project was performed during 12 months along three elevation gradients in Chile, including north, central and South regions using PUF disks. Transects ranged between 10 to 4400 m. The

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main pesticides found in all samples were α- and γ-HCHs, α-endosulfan and chlorotalonil, although concentrations were very low. Endosulfan increased concomitantly with altitude without marked differences among regions. In the case of chlorotalonil, the concentrations were higher in zones close to urban areas (*53*). As expected from the well-known behavior of HCBs, concentrations of this chemical in all samples were similar without any significant difference. As predicted from its physical-chemical properties, hexachlorobenzene (HCB), had largely uniform air concentrations with latitude and altitude. For this reason, HCB is usually used to derive sampler specific sampling rates for passive samplers (*53*). Other research from Chile performed by Pozo *et al.* (*54*), using PAS with PUF disks, reported the occurrence of OCPs, PCBs and PBDEs at low concentrations. Conversely, the results of Shunthirasingham *et al.* (*53*), showed a decreasing endosulfan gradient from north to south. Concentrations of PCBs and PAHs in urban particles from Santiago and Temuco were comparable to others from around the world (*55*). The occurrence of pentachlorobenzene, HCB, HCHs, PCBs and DDTs in mosses distributed over three altitude gradients of the Andean mountains in Chile showed the lowest values ever reported in remote sites, but they were slightly higher than those found in previously studied Antarctic areas (*56*).

Argentina

Argentina has a long OCPs use history due to its large fruits and row crop production. DDT was widely used in agriculture until it was officially phased out in1998 (*57*), while endosulfan use was unrestricted until 2012 (*58*). Airborne pollution assessment by pine needles (*Pinus sylvestris* L.) was performed in Mendoza, including urban and natural areas (*59*). Pine needles accumulated pesticides efficiently with mean concentrations of 25.5, 10 and 482 ng/g d.w. for *p,p′*-DDT, *p,p′*-DDE and γ−HCH, respectively. Concentrations of HCH isomers and DDTs were one or two orders of magnitude higher than concentrations from remote regions of the country. The study suggested the recent input of these compounds from local sources, possibly from insecticide spraying. In addition, among industrial POPs, PCB (congeners #28, 52, 101, 138, 153) concentrations were approximately 3 ng/g d.w., while PAH (phenantrene, anthracene, fluoranthracene) concentrations reached values of 4.6 μg/g d.w. Fifteen years later, a study performed in a nearby area (Rio Negro watershed) reported the prevalence of DDTs in pine needles collected in the Upper Valley, dedicated to fruit production during the last 50 years (*60*). In particular, concentrations of DDTs were one order of magnitude lower (2 ng/g d.w.) than those reported by Wenzel *et al.* (*59*) and in the case of the metabolite *p,p′*-DDE the concentrations ranged between 2-5 ng/g d.w. However, the current use pesticide endosulfan showed high levels in the area, with values of α-, β-isomers and endosulfan sulfate, at approximately 400 ng/g d.w. As part of the PROSUL-LAPAN project (see description below) results from the latitudinal gradient, spanning from Porto Alegre, Brazil to the southeast region of Argentina, an increase in DDT, PCBs and PBDEs (PCB 28 and BDE 47) levels were observed. Since there is no evidence of point sources for these compounds that justify the POPs pattern in the region, atmospheric transport with a possible distillation process is suggested.

Bolivia

Atmospheric concentrations of POPs were studied on the east side of the Andean mountain range in Bolivia using PUF disk samplers along an altitudinal gradient (1820-5200 masl) during 2005. The gas-phase concentration and the altitudinal and seasonal trends of OCPs and PCBs were evaluated. The main compounds detected included hexachlorocyclohexane (HCH), endosulfans, and select PCB congeners. Endosulfans and HCH concentrations increased with altitude. Air trajectory analysis indicated that the high-altitude sites were exposed to a larger air shed and hence were susceptible to LRAT from more distant regions. Endosulfans exhibited the highest air concentrations reaching ~ 1500 pg/m^3 at the two highest elevation sites. PCB air concentrations were at global background values (< 12 pg/m^3) and showed no increase with altitude (*61*).

Brazil

As a part of the Global Atmospheric Passive Sampling (GAPS) a project was performed using PUF disk samplers and including gradients in Brazilian southeastern and southern mountain regions. It was carried out from 2007 to 2008. Pesticides in air were dominated by the current use pesticides endosulfan, its metabolite endosulfan sulfate, and chlorpyrifos. Particularly endosulfans showed the highest concentration at 100-1000 pg/m^{-3}. Moreover, there was a clear seasonal variation in all sites, with pesticide concentrations one order of magnitude higher during summer as compared to winter. Along the altitudinal gradients, some pesticides had higher atmospheric concentrations at sites above 1500 m which may indicate efficient high-altitude transport from regional sources. In addition α- and γ- HCHs, dieldrin, heptachlor epoxide and *p,p′* –DDE were also detected (*62*).

Costa Rica

A study using XAD-based samplers reported average pesticide concentrations in air that were relatively low when compared to North and Central America. These results are consistent with relatively low historical domestic use and little atmospheric inflow from neighboring countries. Particularly within Central America, average air concentrations for γ-HCH were 24 pg/m^3 and appear to be very similar to concentrations of 33 and 51 pg/m^3 found using high-volume active samplers in Belize (*63*). While concentrations of DDTs in Costa Rica air were lower than those measured in Belize (*63*) and Mexico (*50*), a predominance of DDTs, dieldrin, HCHs and chlordanes in the spatial distribution of OCPs suggest regional inputs more than local sources (*64*). As a whole, measurement of POPs in the Latin America atmosphere is very limited and more studies are recommended in order to better understand POPs behavior in the south latitudes.

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Latin American Network for POPs Monitoring

As international efforts have been designed to reduce emissions of POPs into the environment, Article 16 from the Stockholm Convention on POPs indicates that "States Parties shall establish the conditions to generate comparable data for monitoring of POPs, as well as its regional and global transport and to evaluate if environmental levels are actually being reduced or eliminated" (*2*). In this context, the atmosphere is an appropriate matrix for monitoring the spatial-temporal variation of POPs, and to identify global and local sources. Thus, a passive sampler network for monitoring POPs is been established since 2010 among most of the South American countries, the so-called LAPAN – Latin American Passive Atmospheric Network. To achieve the monitoring goal, the Federal University of Rio Grande (FURG, Brazil) and the National University of Mar del Plata (UNMdP, Argentina), implemented the project PROSUL–LAPAN, "Use of passive atmospheric samplers in South America: a balance between local and global sources of Persistent Organic Pollutants". The project aims to study the sources and spatial-temporal distribution of POPs in background, urban, industrial and rural areas using PAS with the polymeric resin XAD-2 (*6*). The implementation of a network aiming for a long-term PAS monitoring allows temporal trend assessments which can be used to verify effectiveness of those measures implemented for POPs under the Stockholm Convention on POPs under the United Nations Environment Programme (UNEP), and the POPs Protocol of the Convention on Long-range Transboundary Air Pollution (CLRTAP) under the United Nations Economic Commission for Europe (UNECE) on a local and global scale. So far there are not enough networks or data sets with the spatial resolution needed to investigate the spatial and temporal global trends in POPs contamination. The Global Atmospheric Passive Sampling (GAPS) network was established beginning in December 2004 in response to this need. The PROSUL-LAPAN project will increase the number of samplers throughout South America in order to identify global and regional sources. Identifying sources related to large industrial, urban and rural areas is fundamental to identify the remaining primary and secondary sources of POPs.

The purpose of the PROSUL-LAPAN network is to conduct a permanent regional atmospheric monitoring of POPs (chlorinated pesticides, PCBs and PBDEs), through passive samplers and biomonitors (conifer needles). The network involves regions of Antarctica and 12 countries. Thus, as of 2014 up to one hundred sites will be monitored on a long-term regime using XAD-2 based PAS. Samplers will cover the main industrial, urban and rural areas of Latin America and, to comply with the UNEP Global Monitoring Plan (GMP) of the Stockholm Convention on POPs, remote areas will be also monitored. PAS are deployed to yield annually averaged concentration at each site by annual exchange of resins.

As part of the atmospheric regional network, PROSUL-LAPAN, a local monitoring program involving the use of pine needles is conducted. Pine needles (*Pinus sp.*) were used to evaluate latitudinal and longitudinal transport of contaminants in central and Patagonian regions of Argentina, and the southern Brazilian region, with a 20-station network.

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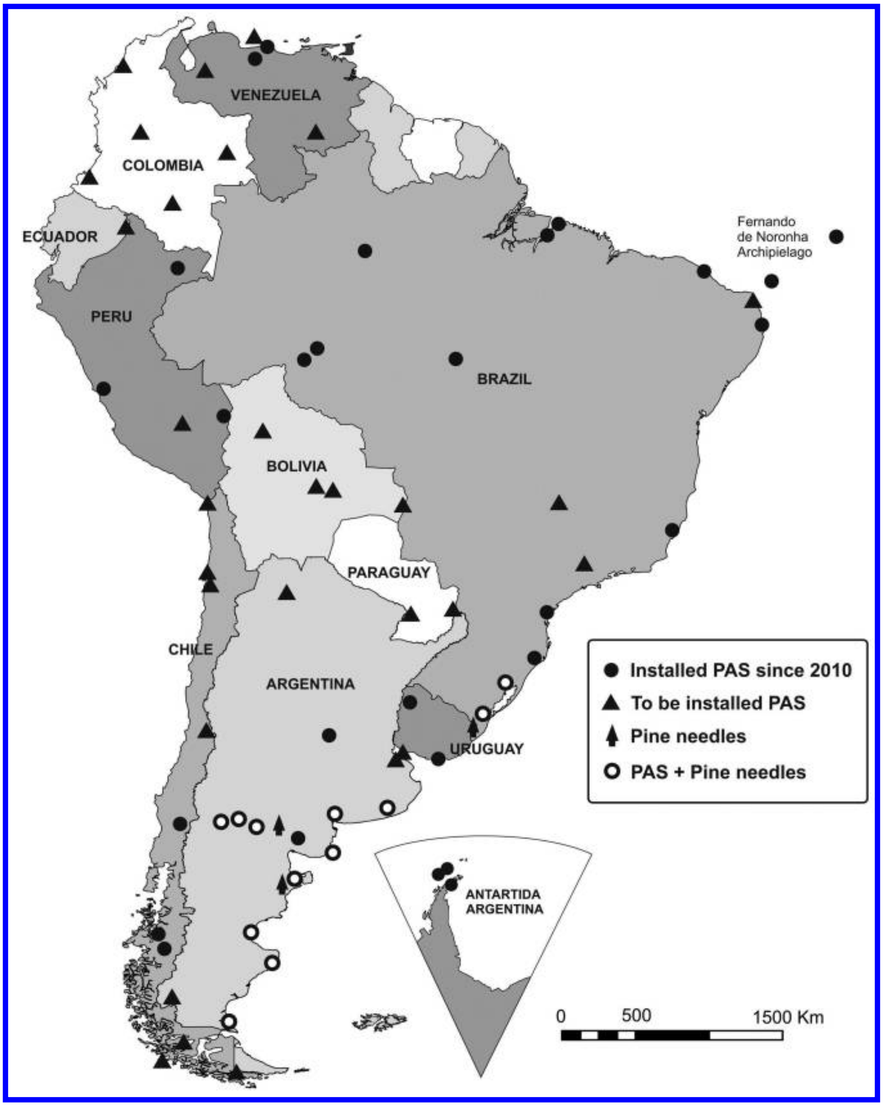

Figure 2. Sampling stations of PROSUL-LAPAN project.

Main Goals of the LAPAN-PROSUL Project

- Evaluate sources and local and temporal gradients of OCPs, PCBs and PBDEs in the Latin America region;
- Supply, in part, the needs of Latin American countries that are signatories to the Stockholm Convention on POPs implementation monitoring plan.
- Promote capacity-building for POPs among Latin American countries.

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- Consolidate the exchange of researchers between universities, promoting the implementation joint projects and the training of postgraduate students.

Monitoring Points or Stations

PAS are currently deployed at 55 stations across South America, including Argentina, Brazil, Colombia, Chile, Ecuador, Uruguay, Peru, Venezuela and Antarctica (Figure 2). Other XAD2-PAS are going to be deployed in the next few years to cover the main regions in South America to fulfill the strategy of sampling background areas, to comply with the UNEP Global Monitoring Plan, and to look for regional and local sources from urban, rural and industrial areas of South America. Pine needles sampling includes a latitudinal transect along the Rio Negro watershed, which constitutes the main basin of the Patagonian Region and a coastal longitudinal transect from São Francisco de Paula, RS, Brazil (29°27′S-50°33′W) to Rio Gallegos, Argentina (51°37′S-69°17′W).

Sampling and Chemical Analyses

Needles are collected during summer months from branches at 2.5–3 m above ground level. Pine needles are sorted into year-classes based on their position on branches and only 1 year old needles are sampled for OCPs analysis. The samples are taken, and stored in hexane-rinsed glass jars with aluminum foil-lined lids, transported to the laboratory and kept at -20°C prior to analysis. Passive samplers are deployed in specific previously chosen sites and resins are exchanged after 1 year of exposure. OCPs, PCBs and PBDEs are extracted from pine needles or XAD -2 resins following methodology described by Metcalfe and Metcalfe (*65*) with modifications from Miglioranza *et al.* (*66*). Analyses are performed by gas chromatography electron-capture detection and gas chromatography mass spectrometry (*66*, *67*). Results for pine needle samples are expressed in ng/lipid weight and for XAD-2 resins in pg/m^{-3}.

Project Outlook

Through the implementation of this project South America will meet part of the Stockholm Convention requirements for signatory countries. The Convention requires major sources and even existing POPs wastes to be identified and inventoried in order to promote actions aimed at their elimination. Data from this project should be ready to present at the Convention of the Parties to be held in 2014.

Acknowledgments

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Chapter 10

Perspective on Changes in Atmospheric Concentrations of Lindane and the Pre-Emergent Herbicides (Trifluralin, Ethalfluralin, Triallate) in the Canadian Prairies

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Air concentrations of lindane and pre-emergent herbicides were measured during 2003 and 2010 at Bratt's Lake, Saskatchewan and compared to other Canadian or worldwide sites. The removal of sales and usage of lindane in 2002 in Canada has resulted in a rapid decline in atmospheric concentrations of γ-hexachlorocyclohexane in the Canadian prairies. Pre-emergent herbicides which are used on grain and oil seed crops in the Canadian prairies show the highest atmospheric concentrations during the spring (May-June) when they are typically applied. Atmospheric concentrations of triallate are much higher than trifluralin or ethalfluralin in 2003. In 2010, there was a shift in time of the spring maximum atmospheric concentration of pre-emergent herbicides attributed to delays in seeding of wheat and canola. There was also a decline in atmospheric concentrations of triallate in 2010 as compared to 2003 which was associated with an increase in production of canola, and decline both locally and regionally in wheat production due to wet weather conditions in 2010. Ethalfluralin or triallate are potential replacement herbicides for use on canola or grain crops, and the long-range atmospheric transport of these pre-emergent herbicides should be considered together with trifluralin in future implications of potential restrictions

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developed for United Nations Economic Commission of Europe protocol on persistent organic pollutants.

Introduction

Total agriculture value in Canada has been from >$46,000,000,000 to approximately $60,000,000,000 between 2006 and 2010 (*1*). The Canadian prairie provinces of Saskatchewan, Manitoba, and Alberta account for most of the grain and oil seed production in Canada. The current study focuses around a sampling site, Bratt's Lake, located within the province of Saskatchewan which has almost half of Canada's cultivated farmland and the highest production of grain and oil seed crops. The average value of agriculture gross domestic product in Saskatchewan during 2006-2010 was $4568 Million per annum (*2*). There are 22195 farms in Saskatchewan with the average farm size of cultivated land of 1220 acres (*2*). The major crops in the prairies and Saskatchewan include spring wheat, canola, durum, barley, field peas, lentils, oats, and flaxseed. In 2003, Saskatchewan had the highest provincial usage of pesticides in Canada (*3*, *4*) and usage data was collected by soil zone. Historical atmospheric measurements of selected pesticides were also taken at other locations within Saskatchewan and Canada, and used for comparison of long-term trends in atmospheric measurements.

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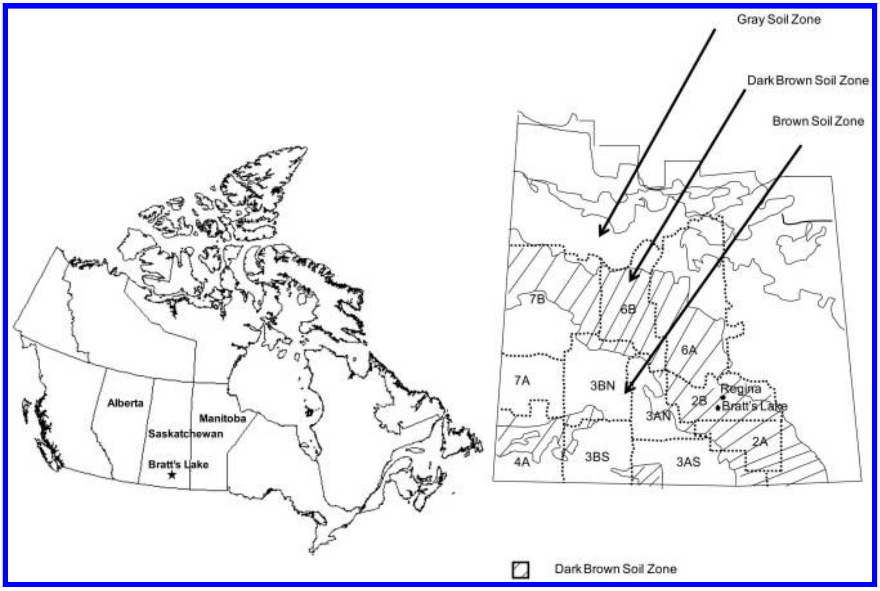

Figure 1. The prairie provinces of Canada with expanded view of location of Bratt's Lake sampling site in southern Saskatchewan. Adapted with permission from Government of Saskatchewan. Soil zone and crop district map available from (5).

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Study Site, Air Sampling and Chemical Analysis

The air sampling field site is located at Bratt's Lake, Saskatchewan (latitude 50°12′10″N, longitude 104°12′15″W) in the prairie agricultural region located within the dark brown soil zone of Saskatchewan (crop district 2 B) as shown in Figure 1 (*5*). Bratt's Lake is located 35 km southwest of Regina, Saskatchewan. The station is operated by Environment Canada where University of Regina operates two co-located PS-1 high-volume air samplers. Temperature and precipitation amounts are also available from Environment Canada for Bratt's Lake from 2003 and from Regina (International Airport) prior to 2003. Figure 2 shows the temperature variations and precipitation amounts since 2000. Precipitation amounts were lower in 2003, while 2010 observed both an increase in frequency and amounts of precipitation relative to other years. Daily maximum temperatures were slightly higher in 2003, while in 2010 temperatures were cooler along with the wet conditions during the agricultural season. Wet conditions and flooding issues were reported for prairies in 2008-2010 with a higher frequency of precipitation reported in 2010 as shown in Figure 2. Dry conditions, high atmospheric particle concentrations, and high grasshopper counts along with an increase in usage of some insecticides such as chlorpyrifos in 2003 have been associated with higher atmospheric concentrations of chlorpyrfios (*6*). In 2010 when flooding occurred on farmland, fungicides were also detected in the atmosphere for sampling with one or more days with no precipitation (*7*). Fungicides are more water soluble than the pre-emergent herbicides and can wash-out of the atmosphere during precipitation events. The agricultural season in the prairies generally is from May through to early October with the first snowfall occurring typically in late October and last snowfall commonly in April.

For the comparison discussed in this chapter, air samples were collected at Bratt's Lake between April 2, 2003 and December 19, 2003 and April 2, 2010-December 19, 2010. Two high–volume air samplers (Model PS-1, Tisch) were operated continuously at a flow rate of 225 L/min and for a sample duration of 7-days the air volume was ~2300 m^3. In 2003, air samples were collected for either 1 day, 2 days, 4 days, or 7 days with shorter time periods during the agricultural growing season (*6*), while in 2010 air samples were generally collected for 3 or 4 days during July and August, and 7 days for remainder of the sampling events (*7*). During the ~1 year period starting April, 2003, the effectiveness of the solid sorbent used for gas-phase collection of pesticides was evaluated with the two co-located PS-1 samplers, and showed all seven sorbents tested which included XAD-4 were more effective than a standard 7.6 cm polyurethane foam (PUF) (*8*). Triallate, trifluralin, ethalfluralin, and γ-hexachlorocyclohexane (γ-HCH) are predominantly in the gas phase (*9–12*), and the concentrations reported herein are gas phase concentrations obtained from a PS-1 sampler with a sampling module containing 2" PUF/ 14 g sorbent/1" PUF combination (*6*, *8*) for samples collected in 2003. The sampling module contained 2"PUF/14 g XAD-4/1"PUF combination for samples collected in 2010 (*7*). Chemical analysis is completed by gas chromatography/mass spectrometry (GC/MS) with negative chemical ionization and has been described in detail (*8*, *13*). Ions monitored for α and γ-HCH were at mass/charge of 71 and 73, and the

In Occurrence, Fate and Impact of Atmospheric Pollutants on Environmental and Human Health; McConnell, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

quantitative and confirmation ion for ethalfluralin, trifluralin, and triallate were 333/303, 335/305, and 160/161, respectively.

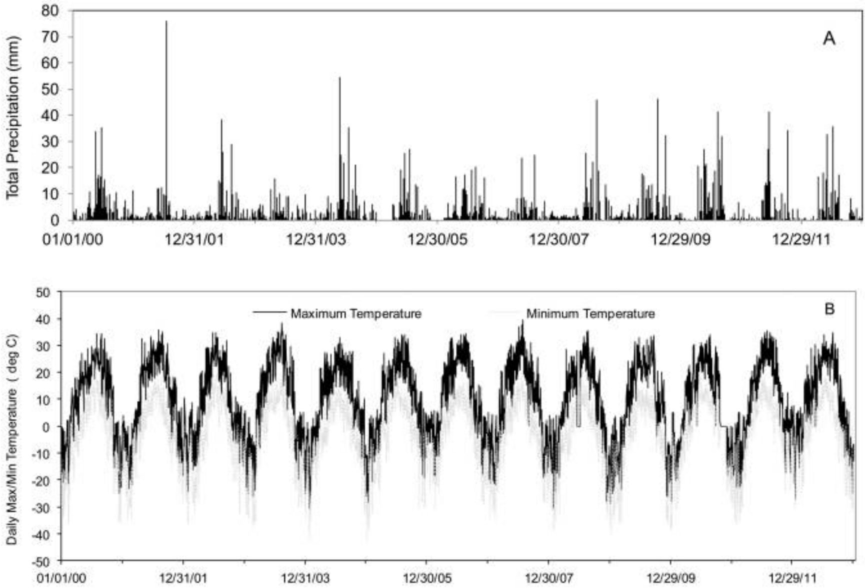

Figure 2. Total Precipitation and daily maximum and minimum temperature at Bratt's Lake, Saskatchewan. A, daily total precipitation amount, B, maximum and minimum daily temperature (2000-2002 Regina International Airport; 2003-2012 Bratt's Lake). Data source: Government of Canada, Environment Canada, Climate Services, available at http: www.climate.weatheroffice.gc.ca.

Crop Production in the Prairies

The region where cereal grain crop production dominates in North America includes the Canadian prairies (provinces of Alberta, Saskatchewan, Manitoba) as well as the north central region of the United States (Dakotas, Montana, Minnesota) (*14*). The Canadian prairie region has high production rates for wheat (spring and durum), barley, canola, mustard, flaxseed, lentils, and peas. Canola is also grown in the United States with most of its production in the late 1990s in North Dakota. The present study will focus on pesticides used for crop production on wheat and canola as well as other crops grown in the prairie agricultural region. Figure 3 show that there has been an increase in canola production in the Canadian prairies since the late 1990s with production of canola currently approaching that of wheat. In the prairie provinces there was 11.4 and 16.7 acres of canola harvested, and 23.9 and 19.3 million acres of wheat harvested in 2003 and 2010, respectively (*1*). The 10-year average (2003-2012) for wheat and canola areas harvested in the prairie provinces were 15.2 ± 3.1, and 21.8 ± 1.5 million acres harvested, respectively (*1*). Wheat production continues to be important in the Canadian prairies with Saskatchewan having the highest

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production for both canola and wheat in Canada (see Figure 3). The crop districts within Saskatchewan with the highest production of wheat, canola, barley, and oats include 2B, 6A, 6B located in the dark brown soil zone, and to a lesser extent 7A, 3BN, 3AS (see Figure 1 for location of soil zones and these crop districts). Figure 3 shows that wheat and canola production observed annual variations as influenced by pressures on farmers including climatic and economic factors, infestations, and pesticide usage for crop protection. These changes will also impact atmospheric concentrations of high usage pesticides and will be discussed in more detail with the atmospheric concentrations of pesticides.

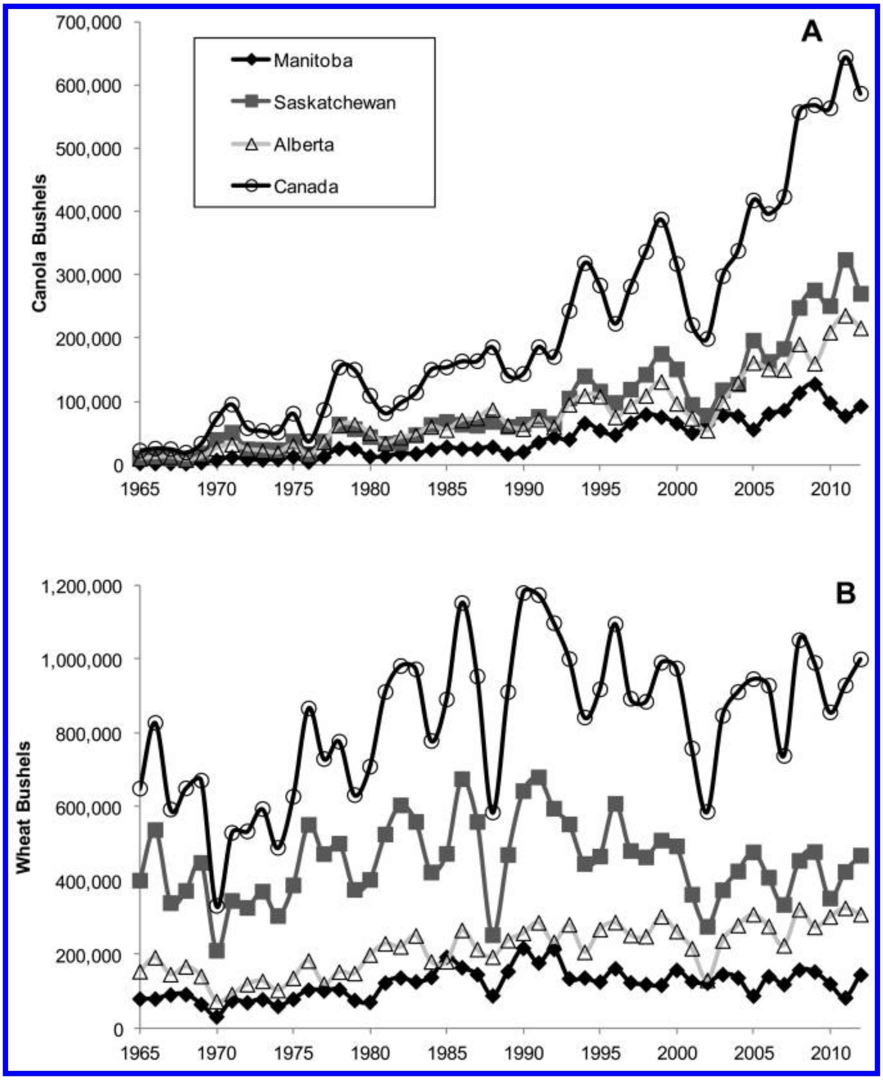

Figure 3. Production of Canola and Wheat in Canada and the Prairie Provinces. A, Canola; B, Wheat (All). Data source: Government of Canada, Statistics Canada, CANSIM tables (1).

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Pesticide Usage

A provincial based inventory for pesticide usage for the agriculture sector is available in Canada for 2003, and on a gridded basis in the United States through the Pesticide National Synthesis Project for 2002 (*3*, *4*, *14*). World and US market expenditure estimates have shown that herbicides comprise the largest fraction of pesticide usage. Total pesticide usage has increased since 2002 world-wide and in the United States primarily due to increased use of fungicides and insecticides (*15*). In United States, total herbicide usage increased in the 1990s, and since 2002 there has been a small decline (*15*). Trifluralin was ranked the 17th most commonly used conventional pesticide in the United States with its usage declining (2001, 2003, 2005, and 2007 usage range of 5.4-7.3, 3.6-4.5, 3.2-4.1, 2.3-3.2 million kg of active ingredient, respectively) (*15*). Triallate and ethalfluralin were not listed in the top 20 pesticides for the United States (*15*), and based on 2002 were ~20% of usage of trifluralin (*14*). More than 99% of triallate and ethalfluralin in Canada occurred in the Canadian prairies (*3*, *4*). Trifluralin was used on a larger variety of crops in the United States than Canada with dominate usage in Canada on grain and oil seed crops in the prairies (*3*, *4*). Canadian usage of trifluralin, ethalfluralin, and triallate in 2003 were estimated at 0.37, 0.64, and 0.75 million of kg of active ingredient, respectively (*3*, *4*). Ethalfluralin and triallate remained in the top 10 active ingredients sold in Canada in 2008 with annual usage of ethalfluralin > 0.5-1.0 million kg, and triallate and trifluralin usage was >0.1-0.5 million kg (*16*). Triallate has shown the largest reduction in usage between 2003 and 2008 particularly in the province of Alberta where annual usage declined from 0.2 to 0.1 million kg (*17*). Canadian pesticide annual usage has increased from 9.3 to 12.5 million kg from 2003 to 2008 (*16*). The prairie provinces comprise of ~60% of usage of pesticides in Canada with Saskatchewan having the highest provincial usage (*3*). Saskatchewan pesticide sales also increased from 2001 to 2003 (see Figure 4 for pre-emergent herbicides). Annual average usages between 2004-2006 in Manitoba for ethalfluralin, trifluralin, and triallate were 93100, 41700, and 7200 kg, respectively (*18*). Similar pesticide usage in 2010 and 2011 in Manitoba has been reported, although expenditures dropped due to lower cost of gylphosate in 2011 (*19*). Pesticide usage in the prairie provinces is dominated by herbicides such as glyphosate, pre-emergent herbicides (triallate, trifluralin, ethalfluralin), and acid herbicides (2,4-D, MCPA, dichlorprop,dicamba, and bromoxynil). Glyphosate has seen the largest increases in herbicide usage in the prairies provinces particularly for canola and this is expected to continue with its low cost (*16*, *18*, *19*). With the rise of herbicide resistant weeds in the prairies, the rotation of herbicides and mixed herbicide applications has become important (*20*, *21*). Historically, lindane has been widely used as an insecticide on canola and wheat crops, while chlorpyrifos is widely used for grasshopper control. Since the cancellation of lindane, usage of neonicitinoid pesticides such as clothianidin, imidacloprid, and acetamiprid have increased. The focus of this chapter will be on selected pesticides that have been used on canola and wheat as well as a variety of other crops in the prairies and include lindane and the pre-emergent herbicides (trifluralin, triallate, and ethalfluralin).

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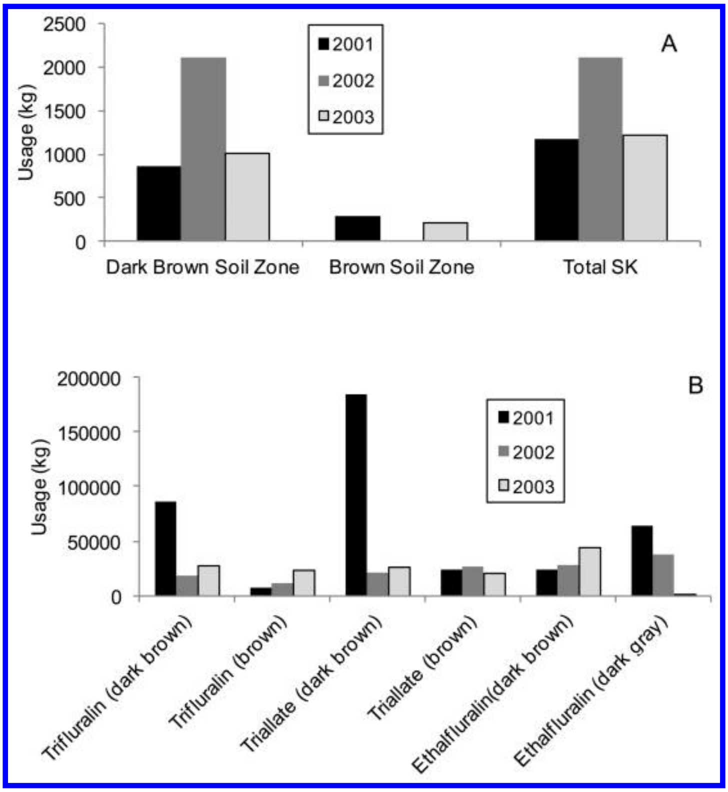

Figure 4. Usage of Selected Pesticides in Saskatchewan during 2001-2003. A, Lindane; B, Pre-Emergent Herbicides. Brackets are used to note soil zones of major pesticide usage in B. Data source: Government of Saskatchewan, Saskatchewan Agriculture and Food, unpublished data (4).

Lindane

Lindane is an insecticide (> 90 % γ-HCH) and was registered for pesticide use in Canada in 1951 as a seed treatment (*22*). In 1979, the first lindane product for canola was developed, which was registered for use and sold in Canada in 1980. This product also contained two fungicides (carbathiin and thiram) along with lindane. Other lindane-based products were developed for use on canola/rapeseed, and mustard seed crops to control flea beetle infestations, and on cereal crops to control wireworm. Flea beetles are a pervasive problem in Western Canada, where they are destructive to canola, rapeseed, and mustard as well as other crops grown in North America such as broccoli, brussel sprouts, cabbage, cauliflower (*23*). Other agricultural applications of lindane as an insecticide occurred in North America on wheat, barley, oats, rye, flax, corn, bean, soy bean and pea seeds for control of wireworms. Planting of lindane-treated seeds occurred primarily during April and May and manufacturing of lindane products was from November in one year to March/April in the following year with sales each crop year completed in June. The shelf-life of lindane products was two years and carry-over of use may have occurred into the following year. Lindane was also registered for use in the United States but was never registered for use on canola. In the mid-1990s canola farmers imported from Canada lindane-treated canola seeds and canola production grew in the US particularly in North Dakota, where an estimated 90% of total US production of canola occurred in the late 1990s. In 1998 US EPA confirmed its policy that lindane-treated canola seed for planting could not be imported into the US as lindane was not registered for use on canola. A conditional withdrawal agreement on lindane treated seed was also reached in Canada in late October 1999. Lindane products could be used to treat canola seed in Canada until July 1, 2001, with no stated restrictions on when treated seed could be sold or planted. In February 2002 PRMA cancelled registrations of lindane products for all of these uses. As all sales in Canada of lindane terminated by Feb 2002 it is expected that there was no subsequent new usage of lindane beyond 2003. In the United States a cancellation order for lindane took effect in October 2006 with all end uses terminated by July 2007. Figure 4 A shows usage of lindane in Saskatchewan for 2001-2003 during the time period when restrictions or cancellation occurred in Canada (*4*) with usage of lindane in 2003 similar to 2001. Usage of lindane was primarily in the dark brown soil zone in the province of Saskatchewan where crop production of canola and wheat usage would be expected to be highest in crop districts 6A, 6B, and 2B (where Bratt's Lake is located). In 1990, Canada, France, Italy, Niger, Honduras, the United States, and China were the leading lindane consuming countries with Canada's usage in 1980 and 1990 at 286 t/yr and 284.5 t/yr, respectively (*24*). Usage of lindane for canola seed treatment in the prairie region in 1997 and 1998 was estimated at 445.3 and 510.4 t/yr, respectively (*25*) showing that agricultural usage in 2001-2003 during the time of its restrictions was significantly less than prior to 2000.

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Atmospheric Concentrations of Lindane in the Canadian Prairies

The Canadian prairie provinces have been identified as a major source region for usage of lindane contributing to the loading of γ-HCH into the atmosphere prior to 2002 (*3*, *4*, *24–32*). The long-range atmospheric transport of lindane from the Canadian prairies has been identified as a possible source for the Canadian Great Lakes, Arctic, and Rocky mountains (*26*, *28*, *29*). Table I shows that the highest atmospheric concentrations of γ-HCH in the 1990s to 2001 were observed at sampling sites in Saskatchewan including Regina and Hafford with maximum γ-HCH atmospheric concentrations in excess of 2000 pg/m^3 (*33*). These sites are within a region of heavy canola cultivation. High atmospheric concentrations (>1000 pg/m^3) were also reported in Alberta (*34*). Other regions of Canada observe much lower concentrations of γ-HCH than the Canadian prairies (*35–41*). Table II, shows these atmospheric concentrations of γ-HCH in Saskatchewan are similar to other countries such as France with usage of lindane >100 t/yr during this time period (*42–44*). Passive air sampling in 2000-2001 across North America also showed that the Canadian prairies had the highest levels of γ-HCH and the lowest ratio of α/γ-HCH (ratio =0.2) (*45*). Canola production has increased since

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1980s (see Figure 3) with a decline in 2001 and 2002 relative to prior years which corresponds to the time of the start of restrictions on the use of lindane products. This region of Saskatchewan during this time period did not show any major difference in precipitation or temperature trends from the average other than one higher precipitation event in 2001 in Regina.

In 2003, the last year of reported usage of lindane in Saskatchewan, a significant reduction in atmospheric concentrations of γ-HCH at Bratt's Lake (located within 35 km of Regina where previous measurements had been taken) was observed with maximum concentrations <500 pg/m^3 and a number of sampling periods observed concentrations less than the method detection limit (MDL) of 1 pg/m^3. The detection frequency of samples collected from April 2003-December 2003 for α- and γ-HCH was 61% and 43%, respectively. Our studies which had short duration sampling also showed that α-HCH was present and could reach or exceed atmospheric concentrations observed for γ-HCH (maximum α-HCH 989 pg/m^3, γ-HCH 274 pg/m^3). During May and June, 2003 when both α- and γ- HCH were observed >MDL, the ratio of α/γ-HCH ranged from 1.1-4.4 (average 2.1) which was higher than reported from passive sampling in 2000-2001 (*45*). The high ratio of α/γ-HCH in 2003 indicates that aging of γ-HCH has occurred along with some periods of regional or local application of remaining stocks of lindane influencing atmospheric concentrations. Atmospheric concentrations of γ-HCH continued to decline in 2004 and 2005 at Bratt's Lake following the removal of lindane products from usage (see Table I). The most recent measurements during April-December 2010 show a detection frequency of α- and γ-HCH of 69% and 51%, respectively. Similar to 2003 the majority of air samples with detection of both α and γ-HCH were observed in May-June with the ratio of α/γ-HCH ranging from 0.5-1.9 (average 1.1). The concentrations of γ-HCH (<MDL-22.3 pg/m^3) in 2010 were the lowest reported on record in Saskatchewan.

As α- and γ-HCH concentrations were nearly equal in 2010, this indicates a well-aged source that is more difficult to distinguish from the global distribution of HCHs. The atmospheric concentrations of HCHs observed at Bratt's Lake, Saskatchewan in 2010 were also in a similar range to those observed in the Pacific Northwest region of North America at Mt. Bachelor Observatory, OR and sites in British Columbia in early 2000's (see Tables I and II) (*30*, *41*, *46*). Long-term trend analysis for Alert site in the Canadian Arctic also showed declining γ-HCH concentrations in the atmosphere during this time period (*47–49*).

Pre-Emergent Herbicides

The pre-emergent herbicides (triallate, trifluralin, and ethalfluralin) are among the top 10 pesticides used in the prairies in 2003. The prairie provinces accounted for ~94% of usage of trifluralin in Canada in 2003 (*3*, *4*). Trifluralin is used on a wide variety of crops in Canada with usage also in Ontario, Quebec, British Columbia, Nova Scotia, and New Brunswick (*3*). In 2003, other regions of Canada had low or no reported usage of triallate and ethalfluralin (*3*) with previous measurements in these regions generally showing atmospheric concentrations of triallate and ethalfluralin < MDL (*31*, *32*, *50*).

These pre-emergent herbicides can be applied to fields in the spring prior to crop emergence or in the fall (typically September-October prior to snowfall). They are incorporated into soils generally within 24 hours of application in the spring to prolong soil activity. They can also be applied in the fall at depth of 2 cm when soil temperature is < 4°C but before snowfall and incorporated in the spring. In 2003, Saskatchewan usage for triallate, trifluralin, and ethalfluralin were similar at 46000, 49900, and 43700 kg, respectively as shown in Figure 4B, but annual usage can vary significant as shown by higher usage of triallate and trifluralin in 2001 (*4*). A mixed formulation contains 10% triallate along with 4% trifluralin in a granular formulation and is recommended for use as pre-emergent control of wild oats, green or yellow foxtail for canola, flax, barley, and spring and durum wheat but is expected to be more heavily used on spring and durum wheat (*23*). The higher usage of triallate and trifluralin in 2001 also occurred in a year of lower production of canola in Saskatchewan (and Canada) but within the normal range of wheat production as shown in Figure 3. Figure 4 B shows that trifluralin and triallate are mainly used in the dark brown and brown soil zones where canola and wheat production are high, whereas ethalfluralin is used in the dark brown and dark gray soil zone due to its usage on a wider variety of crops. Trifluralin and ethalfluralin are more commonly used on canola in the prairies. Granular formulations can contain 5% ethalfluralin and are used for control of weeds for canola, peas (spring and fall), lentils (fall only), and dry beans (*23*). They are not recommended for use prior to seeding of wheat. There are a larger number of formulations that contain trifluralin including granulars (either 4, 5, or 10% trifluralin), an emulsified concentrate (400 g/L trifluralin), or a dry flowable (60% trifluralin) (*23*). These formulations are recommended for use on spring wheat (including durum) in Saskatchewan with application in spring prior to seeding or to summerfallow in May-July during years of a fallow-wheat rotation or in fall (September or October) (*23*). Canola, oilseed, barley or pulse crop (beans, lentils, soybean) can also be treated with trilfuralin. The pre-emergent herbicides are also relatively immobile in soil and have been detected in the upper 5 cm of soil up to 3 months or more after application (*51*, *52*). Triallate, trifluralin, and ethalfluralin have high vapour pressures and relatively low water solubilities (see Table III) such that atmospheric transport is the major transport pathway in the environment (*53*).Volatilization of trifluralin has been shown to vary with air temperature, relative humidity, and soil moisture with the major portion of these herbicides volatilized within 24 hours of application (*51*, *54*). After incorporation into soil, volatilization decreases but does not stop, leading to detection of these herbicides in the atmosphere throughout the agricultural season (*51*).

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Table I. Hexachlorocyclohexane Atmospheric Concentrations in Canada

Location	*Year*	*α-HCH (pg/m³)*	*γ-HCH (pg/m³)*	*Ref*
St. Damase, Quebec	May to Sept 2004	<MDL	<MDL-2623	(*35*)
Villeroy, Quebec Villeroy, Quebec	1992 Jan 1993-Dec 1995		1.2-367 8-269	(*36*) (*37*)
Saint Anicet, Quebec	Mar 1994-Dec 1995		5-552	(*37*)
Mingan, Quebec	June 1994-June 1995		6-119	(*37*)
Egbert, ON	July 1988-Sep 1999		4-820	(*38*)
Stony Creek, ON	Aug 1985-Mar 1989		78-490	(*10*)
Turkey Lake	Aug 1985-Mar 1989		15-190	(*10*)
Regina, SK	May-June, 1994		<13-2400	(*39*)
Regina, SK	1993 1994 2001		<MDL 1100-2800 600-940	(*33*)
Hafford-C site, SK	1998 2000		2600-7400 900-2400	(*33*)
Hafford G-site, SK	1998 2000		1000-2700 400-1000	(*33*)
Hafford, SK	May-Aug 2003		<MDL-244	(*32*)
Waskesiu, SK	1993 1994		<MDL <MDL	(*33*)
Waskesiu,SK	May-Aug 2003		<MDL-220	(*32*)
Bratt's Lake, SK	Spring-summer 2003		68.8-479 (171)	(*32*)
Bratt's Lake, SK	Apr-Dec 2003	<MDL-989	<MDL-275	This study
Bratt's Lake, SK	2004 2005	<MDL-37.6 44.4-57.6	22.6-143 58.1-120	(*40*)
Bratt's Lake, SK	Apr –Dec 2010	<MDL-38.6	<MDL-22.3	This study
Lacombe, AB	Apr-Nov 1999		<MDL-1160	(*34*)
Lethbridge, AB	Apr-Nov 1999	<MDL-20	<MDL-1150	(*34*)
Lundbreek, AB	April-Nov 1999	<MDL	<MDL-190	(*34*)
Langley, BC	Aug 2001	1.8-27.3	1.6-16.6	(*41*)
Slocan, BC	Aug 2001	10.6-24.5	3.0-13.9	(*41*)

Table II. Lindane Usage in France and Mt. Bachelor, OR

Location	*Year*	*α-HCH*	*γ-HCH (pg/m³)*	*Ref*
Mt. Bachelor Observatory, OR	Apr 2004-May 2006	2-43	<MDL-32	(*46*)
Aubure, France	April-May 1993 and June-July 1994	70-423	52-1630	(*42*)
Colmar, France		Not reported	30-3560	(*43*)
Colmar, France	April-May 1993 and June-July 1994	75-415	751-1564	(*42*)
Strasbourg, France	April-May 1993 and June-July 1994	98-481	345-3940	(*42*)
Strasbourg, France	2002 2003		29-1643 117-772	(*44*)

Based on 2002 pesticide usage maps in the United Stated, triallate was primarily used in North Dakota and Montana for weed control for wheat and barley; trifluralin was used on a wider range of crops (soybeans, cotton, alfalfa hay, and wheat) with its main usage in North Dakota, Minnesota, and Iowa; and ethalfluralin was mainly used in the Dakotas and northwest corner of Minnesota with the highest US usage on sunflower seeds, dry beans, peanuts, and soybeans (*14*).

The European Community and its Member states have also proposed trifluralin to be added to the United Nations Economic Commission for Europe protocol on persistent organic pollutants (*60*, *61*). The prairies has high usage of the pre-emergent herbicide including trifluralin. Potential restrictions on trifluralin usage in Canada are expected to lead to increases in agricultural usage of ethalfluralin and triallate in the prairies. Table III shows the physiochemical properties of the pre-emergent herbicides in comparison to HCHs which have been assessed to have a long-range transport potential (τ_R of 230 and 1100 days for α- and γ-HCH, respectively) (*62*). Potential for long-range atmospheric transport of HCHs is supported by its high volatility (4-6 mPa) and its detection in the Arctic as well as within Saskatchewan (*11*, *33*, *47*, *48*, *63–65*). Trifluralin has a half-life in the atmosphere of less than two-days, however monitoring data has supported its potential for long-range atmospheric transport (*47*, *48*, *63*, *67*). Triallate and ethalfluralin also have similar vapour pressure to trifluralin and high usage in the Canadian prairies.

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Table III. Pesticide active ingredient physicochemical properties. Data source: The Pesticide Properties Database, 2011 (*55*) unless noted.

Pesticide	*Vapour Pressure at 20-25°C (mPa)*	*Water solubility 20-25°C (mg/L)*	*Henry's law constant at 25°C (Pa m^3 mol^{-1})*	*K_{OC} (mg /g)*[b]	*Soil Dedragation DT50*[c] *(days)*	*Half-life Air (min) unless noted*[d]	*Field Half-life (days)*[e]	*% Residues remaining in soil top 10 cm*[f]
α-HCH	5.99	2.0	0.43-2.16	1888	175	2.3 d-4.4 yr		
γ-HCH	4.34	8.52	0.15	1100	121	<1 d-9.1 yr		
Trifluralin	14.7[a]	0.22	10.2	8765	181	21-193	57-126	38
Triallate	16[a]	4.1	0.89	4301	82	300	56-77	40
Ethalfluralin	11.7[a]	0.3	18.0	5356	45	120	63	24

[a] Reference (*56*). [b] K_{OC} is the soil organic carbon-water partitioning coefficient. [c] Half-life DT_{50} is a measure of the amount of time it takes for 50 percent of the parent compound to disappear from soil by transformation. [d] Reference (*57*). [e] Reference (*58*) –based on soil half-life. [f] Reference (*59*) –% residual remaining in soil (top 10 cm) 20 days after field application.

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Atmospheric Concentrations of the Pre-Emergent Herbicides

Based on 2003 usage information for Canada (*3*, *4*) >90%-100% of the usage of pre-emergent herbicides is in the prairie provinces of Canada. Table IV shows that the highest atmospheric concentrations of trifluralin in the atmosphere were observed in Saskatchewan. A maximum of 62000 pg/m^3 was reported in Melfort, Saskatchewan located in northwestern region of the province outside of the soil zones with expected highest usage of pre-emergent herbicides giving strong evidence for atmospheric transport potential (*64*). At Bratt’s Lake and study sites nearby where pre-emergent herbicides were used locally and regionally in agricultural areas, maximum atmospheric concentrations of trifluralin were generally 2000-3600 pg/m^3 for air samples collected from 1989 through 2010 (see Table IV). Bratt’s Lake and other Saskatchewan sites had the highest reported atmospheric concentrations during 1990-2010 in Canada (*12*, *40*, *50*, *65*). Passive air sampling of trifluralin at 20 sites operated under the GAPS (Global Atmospheric Passive Sampling) Network also showed the highest atmospheric concentrations of trifluralin at Bratt’s Lake (*66*). Table V shows that atmospheric concentrations > 2000 pg/m^3 have been reported in other agricultural regions outside of Canada with significant usage of trifluralin such as France and United States (Minnesota, Iowa). In Saskatchewan where measurements at Bratt’s Lake and Regina (within 35 km distance) exist for a number of years the atmospheric concentration ranges can vary on an annual basis but have remained high in 2010 (see Table IV). High concentrations of trifluralin (> 1000 pg/m^3) have also been observed in Ontario (Egbert in 1989), Quebec (St. Damase), and British Columbia (Abbotsford) where there has been reported usage of trifluralin (*3*). Atmospheric concentrations are also very dependent upon the proximity of air sampling to application region as well as application method and time of sample collection. Trifluralin has high volatility and Table IV shows much higher atmospheric concentrations at the treated field sites than those reported at Bratt’s Lake. Atmospheric concentrations of trifluralin decline with sampling height from ground. A rapid decline in atmospheric concentrations of trifluralin after incorporation of granular formulations is also observed (see Table VI) (*51*, *59*, *76*, *77*).

Table IV. Atmospheric Concentrations of Trifluralin in Canada

Location	*Year*	*Trifluralin Range (pg/m^3)*	*Ref*
St. Damase, QC	May to Sept. 2004	317-1935	(*35*)
Egbert,ON	1989	<20-3400	(*37*)
Egbert, ON	2004	<MDL-535	(*40*)
Egbert, ON	2006-2007	4.8-120.8	(*66*)
Southern Ontario Sites (Passive)	2002-2003	40-1090	(*68*)

Continued on next page.

Table IV. (Continued). Atmospheric Concentrations of Trifluralin in Canada

Location	*Year*	*Trifluralin Range (pg/m^3)*	*Ref*
Northern Ontario Lake (L375)	1990 and 1992	<1-78	(*69*)
Melfort, SK	1980-1982	<500-62000	(*64*)
Regina, SK	1980-1982	<500-2000	(*64*)
Regina, SK	1989 1990	<40-3600 <40-1990	(*70*)
Near Regina, SK farm dugout sites	May-Sept 1989 May-Sept 1990	<40-3130 <40-1400	(*12*)
Bratt's Lake, SK	May-July 2002	<MDL-570	(*65*)
Bratt's Lake, SK	Apr 2003-Feb 2004	3.2-1520	This study
Bratt's Lake, SK	2004 2005	<MDL-921 909-2570	(*40*)
Bratt's Lake, SK	May-Nov 2010	<MDL-2430	This study
Regina, SK	May-July 2002	<MDL-30	(*65*)
Hafford, SK	May-July 2002	<MDL-2730	(*65*)
Hafford, SK	May-Aug 2003	<MDL-734	(*32*)
Waskesiu, SK	May-July 2002	<MDL-210	(*65*)
Waskesiu, SK	May-Aug 2003	<MDL-24.8	(*40*)
Lacombe, AB	May-Nov 1999	<MDL-560	(*34*)
Lethbridge, AB	May-Nov 1999	10-70	(*34*)
Lundbreck, AB	May-Nov 1999	<MDL-100	(*34*)
Manitoba Zero-Tillage Research Association, MB	May-Aug, 2007	<MDL-210	(*18*)
Vineland, ON	2004	<MDL-660 40.3-2160	(*40*)
St. Ancient, QC	2004	<MDL-374 <MDL-508	(*40*)
Baie St. Francois, QC	2004 2005	60.3-481 742-2590	(*40*)
Kensington	2004 2005	<MDL-60.3 <MDL	(*40*)
Abbotsford, BC	2004 2005	<MDL-117 <MDL-2220	(*40*)

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Table V. Atmospheric Concentration of Trifluralin at Locations Outside of Canada

Location	*Year*	*Trifluralin Range (pg/m³)*	*Ref*
Jackson, MI (urban) Rolling Fork, MI (rural)	Apr-Sept 1997 Apr-Sept 1997	<MDL-760 <MDL-5500	(*71*)
Iowa City, Cedar Rapids, and Hills, IA	2000-2002	<MDL-8200	(*72*)
Kaweah Reservoir, CA	May-Sept. 1996	130-640	(*73*)
Ash Mountain, CA	May-Sept.1996	30-270	(*73*)
Lower Kawesh, CA	May-September 1996	130-280	(*73*)
Strasbourg, France	April-May 1993 and June-July 1994	743-3800	(*42*)
Strasbourg, France	2002 2003	<MDL-179 <MDL-182	(*44*)
Aubure, France	April-May 1993 and June-July 1994	400-7980	(*42*)
Colmar, France	April-May 1993 and June-July 1994	465-5640	(*42*)
Kitakyushu, Japan	July 1991 Apr 1992	<MDL 210	(*74*)

Air Sampling at Bratt's Lake during 2003 and 2010

Our studies presented herein have investigated the seasonal trend in atmospheric concentrations of pre-emergent herbicides at Bratt's Lake, Saskatchewan. The Bratt's Lake sampling location is in a region of the prairies with high atmospheric concentrations of trifluralin. Atmospheric concentrations of trifluralin at sampling sites in the other prairie provinces (Alberta and Manitoba) were lower (see Table IV). A comparison of atmospheric concentrations of trifluralin in 2003, a dry year, and 2010 a wet year with flooding issues in southern agricultural regions of Saskatchewan is shown in Figure 5. Although 2003 was a dry year in Saskatchewan with high grasshopper counts (*6*), production of crops such as wheat and canola was similar to the average production for the period 2000-2005 (see Figure 3). There was in general excellent soil moisture conditions existing in spring 2003 as a result of wet harvest weather conditions in 2002 (see Figure 2A). Figure 5 shows that atmospheric concentrations of trifluralin as well as the other pre-emergent herbicides (triallate, ethalfluralin) were highest in May and June when these herbicides are applied earlier in the crop's development to control weeds while the plant is establishing itself. Trifluralin can be used on a variety of crops including wheat, canola, barley, lentils that are grown in the vicinity of the sampling location as well as on a more regional basis in the prairies and central United States.

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Table VI. Atmospheric Concentrations of Trifluralin at Treated Field Sites

Location (crop)	*Year*	*Trifluralin Range (pg/m^3)*	*Reference*
Greenbelt Farm, Ottawa, ON (wheat)	1993		(*75*)
	day 1	409000-2520000	
	day 2	88000-513000	
Paris Basin, France (oilseed rape)	2002		(*51*)
	Before incorporation		
	0.19 m		
	0.39 m	61200000-6690000	
	0.81 m	40900000-4660000	
	1.81 m	24300000-2250000	
	Incorporation	11800000-1690000	
	0.19 m	2200-282000	
	0.39 m	2000-459000	
	0.81 m	1600-323000	
	1.81 m	1000-23000	

In 2010, a higher maximum atmospheric concentration of trifluralin was observed at Bratt's Lake than in 2003 (Table IV). Table VII shows the means were not statistically different. However, in 2010 atmospheric concentrations of trifluralin were > 1000 pg/m^3 in late May and during June, while in 2003 atmospheric concentrations of trifluralin were > 1000 pg/m^3 much earlier in May. Seeded progress was much slower in 2010 with 59% of seeding completed by May 31, 2010 as compared to 98% of seeding completed by June 8, 2003 (*78, 79*). Saturated soil conditions and continuous rain slowed seeding and farm operations in 2010. Surplus soil moisture conditions existed in a large portion of Saskatchewan including both high production crop districts 2B and 6A (*80*) with many farmers in these regions having some acres of farmland that were flooded and not suitable for planting. Some farmers were also dealing with delays due to the late harvest in 2009. Table VIII shows the production changes for the top eight crops produced in Saskatchewan for crop district 2B where Bratt's Lake is located. Production of wheat, barley, oats, durum (confidential with value not reported) and flaxseed significantly declined in 2010, while canola production saw the largest increase, and specialty crops such as lentils approximately doubled in production and acres planted. Further north in crop district 6A significant loss in production of wheat, durum, canola, oats, barley, flaxseed were reported (see Table IX) with only lentils observing a significant increase in acres harvested and production in 2010. Figure 5 shows that in 2003 high atmospheric concentrations of both triallate and trifluralin were observed early in May through to early June with atmospheric concentrations of triallate higher by a factor of 10 or more as compared to trifluralin (see Table VII). Atmospheric concentrations of triallate were lower in 2010 than in 2003 (see Table VII) suggesting a shift from preferential usage of the mixed granular formulation to formulations only containing trifluralin. The water solubility of traillate is higher than trifluralin (see Table III) and with the wet conditions experienced in 2010 this may also partially account for lower atmospheric concentrations. Triallate formulation is also generally not used widely on canola as trifluralin and ethalfluralin are most effective for weed control. The dinitroanilines (trifluralin and ethalfluralin) can also be used in a mixed application with other herbicides such as glyphosate to minimize herbicide resistant weeds (*20*, *21*). With an expected shift in granular formulations particularly for canola usage there is also a change in percentage of trifluralin in these formulations. Formulations can contain 10% trifluralin and are recommended for summerfallow use in the brown and dark brown soil zones of Saskatchewan or on canola for weed control.

Atmospheric concentrations of triallate and trifluralin also increased during the fall of 2003 during two separate time periods (in September and late October prior to snowfall) showing the preferential use of the mixed granular formulation as compared to a 10% trifluralin (only) formulation. However, in 2010 there was no significant maximum in atmospheric concentration of trifluralin in fall, however both triallate and ethalfluralin showed increases during the fall (see Figure 5). Winter wheat was harvested earlier than other crops in 2010 (predominately in September) with harvest of canola and lentils mostly occurring in the first two weeks of October of 2010 as a result of the later seeding of these crops in spring 2010. Herbicides were expected to be applied to fields in the fall particularly for dormant fields with heavy weed infestations that were not planted with crop in 2010 due to flooding. These fall applications of herbicides can occur very late in October prior to the first snowfall which in 2010 was reported in early November. Canola and wheat can also have fall seeding and ethalfluralin can be used for canola and lentils in fall. Formulation containing triallate and/or ethalfluralin formulations for weed control on dormant fields or for its fall application for lentils or canola are potential sources of emissions. Ethalfluralin concentrations also showed high atmospheric concentrations in spring and early summer due to higher production of canola both locally (crop district 2B) and regionally (as shown for crop district 6A). Trifluralin and ethalfluralin are the most effective herbicides for weed control for canola in North America and can be used under rainfed conditions (*83*) and in combination with other herbicides. The lack of higher atmospheric concentrations of all three pre-emergent herbicides in late September for 2010 compared to 2003 (see Figure 5) is attributed to the large drop in production of grain crops such as wheat and barley both locally and regionally along with the delay in harvest. Liquid formulations of trifluralin can also be applied for post-seeding prior to crop emergence for green foxtail control in wheat and barley as well trifluralin is also recommended as a pre-plant incorporated herbicide for canola. The 10% granular formulations are recommended for summer and fall application only on canola and flax and fall applications on a variety of crops including canola and lentils (*84*). Perennial weed management with tillage and/or herbicides can be done in the fall after harvesting the crop preceding canola. Fields that are heavy infested with weeds that are not controlled by herbicides registered for use on canola are not planted with canola in the subsequent year. Crop productions in 2011 for wheat improved (see Figure 3) and may have also been influenced by weed control and seeding in fall 2010.

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Table VII. Atmospheric Concentrations of Target Pesticides at Bratt's Lake, Saskatchewan in 2003 and 2010. Time period April-December and in brackets for HCHs May-June.

	Trifluralin[a] *pg/m*^{3}		*Ethalfluralin*[a] *pg/m*^{3}		*Triallate*[a] *pg/m*^{3}		*α-HCH*[b] *pg/m*^{3}		*g-HCH*[b] *pg/m*^{3}	
Year	2003	2010	2003	2010	2003	2010	2003	2010	2003	2010
Maximum	1523	2430	1330	1860	27300	10200	989 (281)	38.6 (21.5)	275 (123)	22.3 (22.3)
Detection % (>MDL)	95	91	100	96	100	100	61 (100)	69 (100)	43 (100)	51 (100)
Median	16.9	106	19.0	80.9	525	144	48.4 (253)	8.0 (7.1)	0.5 (117)	1.6 (7.2)
25% Percentile	10.0	42.9	11.8	30.9	10.0	28.0	0.5 (173)	0.5 (6.1)	0.5 (97)	0.5 (4.7)
75% Percentile	188	255	196	208	1860	640	173 (297)	13.3 (10.1)	114 (131)	6.2 (11.0)
Standard Deviation	259	437	260	357	4050	1750	230 (164)	8.8 (5.9)	81.2 (44.0)	5.5 (7.4)
Mean	149	251	160	214	2050	770	145 (281)	9.2 (8.5)	61.3 (123)	4.3 (9.0)
p-value	0.110		0.338		0.046		0.0002		0.00001	

[a] Method Detection Limit (MDL) is 2 pg/m^3 for pre-emergent herbicides (*13*) and < MDL concentration = 0.5*MDL. [b] MDL 1 pg/m^3 for HCHs and <MDL concentration = 0.5*MDL.

Table VIII. Crop Production and Acres Harvested in 2010 for Crop District 2B (Local Crop District to Bratt's Lake, Saskatchewan). Data source: Saskatchewan Agriculture and Food, reference (*81*, *82*).

Crop	*Acres Harvested in 2003*	*Production tonnes 2003*	*Acres Harvested in 2010*	*Production tonnes 2010*
All wheat	840000	629000	479000	489000
Durum	546000	428000	confidential[a]	confidential[a]
Oats	51600	32900	12700	12200
Barley	159000	138000	88800	94800
Flaxseed	172000	70000	82700	39200
Canola	14900	56200	465000	345000
Lentils	26700	112000	414000	256100
Dry Peas (or peas)	16900	106000	117000	93600
Chick Peas	11900	4900	18500	17600

[a] Confidential not included in Saskatchewan statistics for year.

These shifts in production in various crop districts within Saskatchewan are also expected to influence the local and regional to long-range atmospheric transport contributions to atmospheric loading of pre-emergent herbicides. In 2003, local and regional contributions would be heavily influenced by both local and regional usage of the herbicides. Grain production in crop district 2B (local crop district which Bratt's Lake) declined in 2010 as compared to 2003 (see Table VII). Local usage of the pre-emergent herbicides is not available for 2010, but with decline in grain production would be expected to be lower. Further support for both local and regional contributions has been shown by measurements on a 30 m tower at Bratt's Lake where elevated levels of trifluralin and ethalfluralin were observed at 30 m compared to 1 m indicating regional atmospheric transport (*32*, *65*).

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Table IX. Crop Production and Acres Harvested in 2010 for Crop District 6A (Regional high crop production region in Saskatchewan; Watrous, Saskatchewan is located in this crop district). Data Source: Saskatchewan Agriculture and Food, reference (*81*, *82*).

Crop	*Acres Harvested in 2003*	*Production tonnes 2003*	*Acres Harvested in 2010*	*Production tonnes 2010*
All wheat	1080000	866000	521000	484000
Durum	4860000	3170000	84100	81900
Oats	1350000	995000	35200	31300
Barley	4650000	4350000	171000	157000
Flaxseed	1360000	533000	65400	29200
Canola	5650000	2680000	742000	463000
Lentils	74300	34500	240000	121000
Dry Peas (or peas)	165000	126000	181000	130000
Chick Peas	Not reported	Not reported	8810	2970

Future Considerations for the Pre-Emergent Herbicides

Fewer atmospheric studies have included or reported concentrations > MDL for triallate and ethalfluralin as compared to trifluralin. In our study at Bratt's Lake which occurred during 2003 and 2010, the highest atmospheric concentrations of triallate were reported in 2003, and were similar in magnitude to maximum atmospheric concentrations of triallate reported near Regina at farm dugout sites in prior years as shown in Table X. Maximum concentrations at these sites in Saskatchewan often ranged between 10,000 and 60,000 pg/m^3 and as noted previously are much higher than those reported for trifluralin. Maximum atmospheric concentrations of triallate were highest in the late 1990s and prior to 2004. Atmospheric concentrations of triallate in 2004 and 2010 were similar at Bratt's Lake. Alberta has reported lower atmospheric concentrations of triallate than observed in Saskatchewan, and the mixed granular formulation containing triallate and trifluralin is not recommended for use in Manitoba (*23*). Lower triallate usage has also been reported since 2003 in Canada, Alberta and Manitoba (*16–18*, *26*, *85*).

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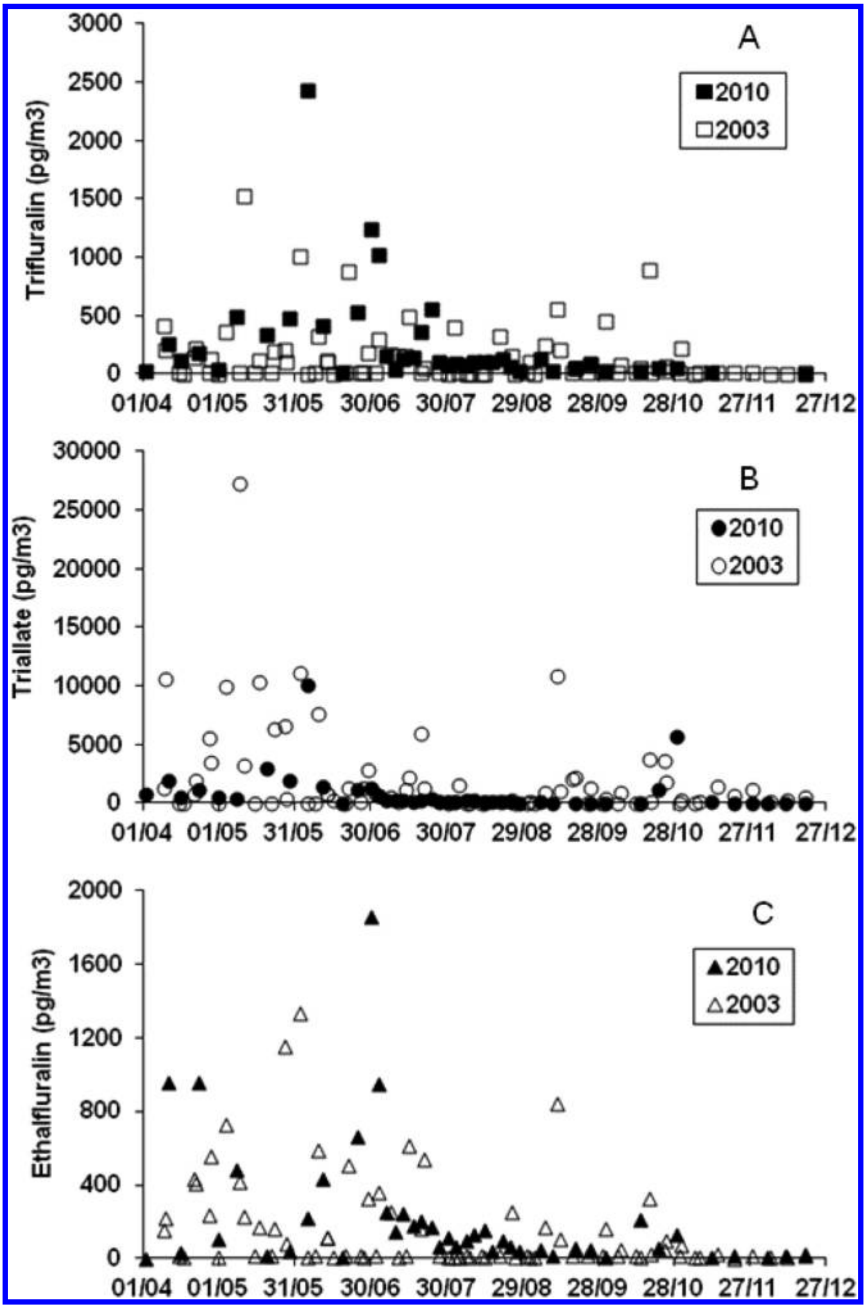

Figure 5. Atmospheric Concentrations of the Pre-Emergent Herbicides at Bratt's Lake, Saskatchewan during 2003 and 2010. A, Trifluralin; B, Triallate; C, Ethalfluralin.

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Table X. Atmospheric Concentrations of Triallate and Ethalfluralin

Location	*Year*	*Triallate Range (pg/m³)*	*Ethalfluralin (pg/m³)*	*Ref*
Northern prairie landscape		Max 25000		(*86*)
Regina and Bratt's Lake, SK	May-Sept 1989	<40-62000		(*87*)
Near Regina, SK two dugout sites, respectively	May-Aug 1989 (dugout 1 and 2) May-Sept 1990 (dugout 1)	1000[a]-60000 and <MDL-35800 1000[a]- 23700		(*11*)
Regina, SK	May-July 2002	300-5070		(*65*)
Bratt's Lake, SK	May-July 2002	120-5460		(*65*)
Bratt's Lake, SK	May-Aug 2003	402-15300	<MDL-620	(*32*)
Bratt's Lake, SK	Apr 2003-Feb 2004	<MDL-27300	<MDL-840	This study
Bratt's Lake, SK	2004 2005	<MDL-13000 963-5470	109-844 762-7570	(*40*)
Bratt's Lake, SK	2010	1.6-10140	<MDL-1856	This study
Hafford, SK	May-July 2002	Trace-200		(*65*)
Hafford, SK	May-Aug 2003	<MDL-244	<MDL-327	(*32*)
Waskesiu, SK	May-July 2002	<MDL-80		(*65*)
Waskesiu, SK	May-Aug 2003	<MDL-155	<MDL	(*32*)
Lundbreck, AB	1999	<MDL-1100	<MDL-90	(*34*)
Lacombe, AB	1999	<MDL-1070	<MDL-40	(*34*)
Lethbridge, AB	Apr-Nov 1999	<MDL-1070	<MDL-810	(*34*)

Continued on next page.

Table X. (Continued). Atmospheric Concentrations of Triallate and Ethalfluralin

Location	*Year*	*Triallate Range (pg/m^3)*	*Ethalfluralin (pg/m^3)*	*Ref*
Manitoba Zero-Tillage Research Association, MB	May-Aug, 2007	50-460	<MDL-1230	(*18*)
Iowa, USA		<MDL-800		(*72*)

[a] Minimum estimated from graphed data.

Atmospheric concentrations of ethalfluralin are only available for Bratt's Lake during 2003-2005 and 2010, with the highest concentrations in 2005 with maximum of 7570 pg/m^3 (see Table X). Atmospheric concentrations of ethalfluralin are approaching similar magnitude to that observed for trifluralin, and attributed to the rapid increase in canola production in the prairies as well as potentially increase in production of specialty crops such as lentils and decline in triallate usage. Ethalfluralin and trifluralin (as well as triallate) have similar field half-life and should be considered along with trifluralin as potential candidates for atmospheric transport and season long detection in agricultural areas of usage. With canola production continuing to rapidly increase in the prairie provinces it is expected that usage of trifluralin and ethalfluralin will remain high. Ethalfluralin usage and atmospheric concentration have been reported to exceed those of trifluralin in Manitoba in 2007 (*18*). Trifluralin is used for biennial weeds or perennial weeds by early season and is not effective for perennial weed management which can be done in the fall. Fall applications of ethalfluralin for some crops can occur from October 1 to December 31 (before snowfall). Canola production is very sensitive to certain classes of herbicides, especially certain sulfonylurea and imidazolinones such that there are a limited number of substitutes for trifluralin (or ethalfluralin) formulations. Other herbicides used for weed management canola include clopyralid, clethodim, sethoxydim,and quizalofop. Imazamox, glyphosate, and glufosinate and are approved for use on herbicide-resistant canola. With the increasing production rates for canola in the prairies preferential usage of trifluralin and ethalfluralin formulations will remain in demand as these pesticides are considered highly cost effective. In addition, with herbicide weed resistance increasing the demand for these herbicides is expected to continue due to increased practices of herbicide rotation and mixed herbicide applications (*20*, *21*). Any restrictions on trifluralin usage are likely to result in increases in usage of ethalfluralin on canola (on its own or in a mixed herbicide application). Ethalfluralin has similar properties to trifluralin (Table III) and its long-range atmospheric transport potential should also be considered. For wheat a shift to either the mixed formulation or use of triallate or ethalfluralin in a mixed herbicide application are expected to occur if restrictions on trifluralin usage occur. Triallate atmospheric concentrations still remain the highest of all pre-emergent herbicides (Table VII) although the atmospheric concentrations and usage of triallate have declined. The long-range atmospheric transport of triallate and ethalfluralin should beconsidered together with trifluralin in future implications on potential restrictions developed for United Nations Economic Commission of Europe protocol on persistent organic pollutants.

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Chapter 11

Sources, Transport and Deposition of Atmospheric Organic Pollutants in the Mediterranean Sea

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In this chapter a compilation of existing atmospheric concentration data and related deposition fluxes of organic contaminants in the Mediterranean Sea (far from the shore line) are presented. We have emphasized in compiling and discussing available data at open sea and background coastal sites which are most often scarce, but very valuable. The main objectives of this work were (a) to establish base line atmospheric concentrations of persistent organic pollutants (POPs) over the open Mediterranean Sea and to assess their spatial variability and potential sources based on existing data; (b) to estimate a total atmospheric load of POPs and related compounds at open sea based on most recent reported data. This literature review reveals that there is still a general lack of data on POPs and related contaminants in the atmosphere over the Mediterranean Sea as well as on their deposition fluxes, in particular at open sea. This data scarcity is more pronounced for organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs). This situation could have been motivated in part by the fact that existing national and international regulations and programmes dealing with marine pollution control and monitoring have relegated the atmospheric pathway to a second tier, if considered at all. The

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small amount of existing data does not allow identification of consistent trends. Atmospheric levels of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) seem to be homogeneous across the Mediterranean Sea, even comparable with those of big coastal cities, suggesting that even if there are hot spots in the Mediterranean basin the levels found at open sea are mostly driven by the atmospheric circulation patterns. Concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the atmosphere over the Mediterranean Sea seem to be within the levels first measured in the 1980s, while a general declining trend was observed for hexachlorocyclohexanes (HCHs). Available data on PBDEs suggest that background costal sites in the Eastern Mediterranean may be considered as the least polluted areas at present. Moreover, coastal sites in the Western Mediterranean may present levels comparable to those reported for some of the largest urban coastal sites in the Mediterranean Region. The total atmospheric loading of organic contaminants (PAHs + OCPs + PCBs + PBDEs + PCDD/Fs) to open Mediterranean Sea waters is estimated to vary from 2100 to 4360 tons each year. It is important to note that even if PAHs are the predominant contaminants inputted to Mediterranean waters, other highly toxic chemicals are also entering the water masses *via* the atmosphere forming a complex cocktail of contaminants. Available data show that the Mediterranean waters are not only a sink for organic contaminants but also a source, with 200-1500 tons of organic contaminants (sum of all contaminant groups) “escaping” each year to the overlying atmosphere. Interestingly, data point to volatilization of toxic contaminants from open sea waters occurring at a higher extent in the Eastern Mediterranean Basin.

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Introduction

Chemical contamination of our natural environments, due to the past and current usage of large amounts of chemicals world-wide, has become an important issue at a global scale. One of the many contaminant classes occurring at a planetary scale is semi-volatile organic chemicals, in particular persistent organic pollutants (POPs) and related compounds. These contaminants are organic chemical substances that are highly resistant to degradation processes occurring in the environment and so can persist for exceptionally long periods of time. They become widely distributed in the environment as a result of their long rage transport (LRT) potential, mainly via the atmosphere. POPs are highly bioaccumnulative, entering the food chain and are toxic to both humans and wildlife, some of them at very low doses, such as dioxins. Sources of POPs in the environment can be different depending on the contaminant class.

The fact that around 70% of the earth surface is covered by water (*1*), together with the capability of POPs to travel long distances from sources (mainly land-based), increases the potential impact of those chemicals in marine environments. The loading of POPs and related contaminants to marine environments and possible toxic effects is driven by atmospheric deposition to open waters (*2*, *3*) and riverine inputs and runoff in coastal zones (*4*, *5*). Airborne organic contaminants participate in exchange or/and deposition processes that govern their transport to the marine environment. It is therefore essential to have reliable measurements of the atmospheric levels of POPs in order to better characterize their potential inputs to the aquatic environment.

The Mediterranean Sea

This chapter focuses on the occurrence of POPs and related contaminants in the Mediterranean Sea. The Mediterranean Sea, with its ~2.5 million km^2 of surface, is a semi-enclosed marine environment, covering a small area when compared to the big oceans of the world, but with similar biogeochemistry to other oligotrophic subtropical oceans. It has an average depth of 1.5 km, a volume of 3.7 million km^3 and is around 3800km wide, from West to East. It is comprised of two main basins, the Western and the Eastern, connected by the Strait of Sicily (150km wide). The Western basin, covering an area of ~ 0.85 million km^2 and with connection to the Atlantic Ocean through the Strait of Gibraltar (15 km wide), can be subdivided in the North Western (NW) Mediterranean Sea, the South Western (SW) Mediterranean Sea, and the Tyrrhenian Sea. The Eastern Basin covers an area of some 1.65 million km^2 and has connection to the Black Sea (through the Sea of Marmara) by the Dardanelles Strait (1-7 km wide). This basin encompasses the Ionian Sea, the Central Mediterranean Sea, the Levantine Basin and the Aegean Sea (Figure 1).

The Mediterranean Sea is a unique environment with high intrinsic ecological, geographic, cultural and strategic importance. It is located in the centre of the Mediterranean Region (460 million people in 2008) (*6*), surrounded by twenty-one bordering countries representing ~46000 km of coastline including the islands (Figure 1). The Mediterranean region, in particular the coastal areas, has historically attracted millions of tourists due to its favorable climate, spectacular landscapes and sites of great historical, architectural and archaeological interest. In addition, its coastal areas have been the base for the settling and development of some of the largest cities in the region (*e.g.* Barcelona, Rome, Naples, Athens, Marseille, Alexandria, Istanbul, etc.) and many industrial facilities. It is estimated that around 30% of the 460 million inhabitants of the Mediterranean countries live in coastal areas (*6*). In addition, this stable population may be significantly increased in certain seasons of the year due to intense tourist activity, for example 275 million visitors travelled the Mediterranean region in 2008 (*6*). Moreover, more than 200 petrochemical and energy installations, chemical industries and chlorine plants are also located along the Mediterranean coast (*7*). There is no doubt that the Mediterranean Sea is under intense anthropogenic pressure (*e.g.* urbanization, industry, energy generation and consumption, transportation systems, tourism and recreation, agriculture, fisheries, forestry and mining).

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These pressures generally result in local impacts in coastal areas, although some of them may result in contaminants reaching open waters (far from the coast line) by means of a combined process implying pollutant emission - atmospheric transport - deposition. In addition, there are some specific pressures having an inherent effect at open waters, like the intense maritime traffic in the region. Among the world´s oceans, the traffic density of merchant vessels in the Mediterranean Sea is particularly important. About 30% of international sea-borne volume originates from or is directed to the 300 Mediterranean ports, or passes through the Mediterranean Sea (*8*). It has been estimated that there are around 2000 active ferry lines, 1500 cargo vessels and 2000 commercial vessels operating in the Mediterranean resulting in about 200 000 vessels crossing the Mediterranean Sea annually (*9*).

Regulatory Framework on Chemical Pollution in the Mediterranean Sea

Global, regional and national legal efforts have been undertaken in the last decades in order to reduce and control the direct and indirect inputs of organic pollutants derived from the above mentioned pressures in the Mediterranean Sea. The widest international legal framework aiming at reducing the uses of POPs and monitoring their ambient levels, not only in the Mediterranean Sea but at a global scale, is the Stockholm Convention on POPs. All Mediterranean countries have ratified this Convention (*10*). However, the program in the Mediterranean Sea, aimed at reducing, monitoring and controlling the pollution status by POPs and other contaminants is the Mediterranean Action Plan (MAP). The MAP was adopted in 1975, and one year later was completed with the adoption of the *Convention for the Protection of the Mediterranean Sea Against Pollution* also known as the Barcelona Convention. This regulation was modified some 30 years after its adoption and the amended document entered into force in 2004 with a slightly different name: *Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean*. The Barcelona Convention includes seven protocols addressing specific issues related to Mediterranean environmental conservation and pollution monitoring and control (*11*). The MED POL Programme (the marine pollution assessment and control component of MAP) is responsible for follow up work related to the implementation of those protocols. In addition, two important European regulations designed to preserve a good quality status of the Mediterranean coastal and open waters (EU Mediterranean countries, Figure 1), among other water bodies, were adopted in the last decades. First is the EU Water Framework Directive (*12*) which was adopted in 2000 to protect inland surface waters, transitional waters, coastal waters (*i.e.* surface waters at a distance ≤ 1 nautical mile, ~ 2 km, from shore line) and groundwater. Second is the EU Marine Strategy Framework Directive (*13*) which was adopted in 2008 and covers the EU marine territorial waters and coastal waters at > 1 nautical mile from the shore line. This directive requires that Member States take measures to achieve or maintain good environmental status of their water bodies by 2020. Moreover, the newly created Strategy for Water in the Mediterranean (SWM) aims at complementing and assisting the implementation of the above mentioned international and regional protocols and regulations in various key aspects including the reduction and prevention of water pollution. However, all these regulations have in common minimal attention dedicated to atmospheric sources of contaminants despite their key importance and relevancy in delivering POPs to marine waters.

First Evidence of Contaminant Atmospheric Inputs to the Mediterranean and the Current Status

The first global effort to address the main processes involved in the atmospheric transport and deposition of contaminants into the Mediterranean Sea was performed by the Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) in 1985. They reported existing data on atmospheric levels and deposition of contaminants over the Mediterranean (*14*). They authors highlighted the very limited data on organic substances and the paucity of emission data in the Mediterranean region. However, they concluded using available data that the Mediterranean basin was contaminated by atmospheric inputs. This assessment, although mainly based on inorganic contaminants, provides the first scientific evidence of the relevant role of the atmosphere in delivering contaminants to Mediterranean waters. A decade later, two mass balance studies undertaken for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the Mediterranean Sea confirmed the relevance of the atmospheric inputs of organic contaminants to Mediterranean waters (*15*, *16*). Finally in 2001 a global assessment on atmospheric inputs of POPs to the Mediterranean Sea was published (*17*). This integrative work was undertaken under the auspicious of the Mediterranean Action Plan. The reported estimations of atmospheric deposition were mainly based on modeling calculations and were only partially validated with some of the few existing experimental measurements carried out prior to the year 2000. Since then, there have been an increasing number of studies dealing with the occurrence of organic contaminants in the atmospheric compartment over the Mediterranean Sea, but the number of studies is small when compared to those focusing on other marine compartments such as, water, sediments or biota in the same region. This fact was also highlighted in a review by Albaigés (*18*) on POPs in the Mediterranean Sea published in 2005, where the author concluded that even if some progress took place during the last decade on the understanding of the occurrence of POPs in the Mediterranean basin, studies of the Mediterranean Sea atmosphere were very scarce and combined field work with modeling estimates due to the lack of experimental measurements. In addition, the poor geographical coverage, the lack of long-term monitoring and inter-calibration studies and the necessity of better and updated estimates of net fluxes of contaminants from the atmosphere and rivers to the Mediterranean Sea were also highlighted. The situation has not much changed since then. The current network of pollutant monitoring strategies and methodologies under the various regulations acting in the Mediterranean Sea require an intense harmonization of efforts. An important data gap exists on atmospheric levels of organic contaminants at open waters and background areas. These data are essential to measure temporal and spatial changes and to establish current base-line concentrations in this marine environment. In addition,

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the atmospheric pathway is still largely uncharacterized. This has resulted in a general lack of reliable and global estimates of atmospheric deposition of organic contaminants to Mediterranean waters.

Objectives and Data Research Strategy

The main objectives of this work were (a) to establish base line atmospheric concentrations of POPs over the open Mediterranean Sea and to assess their spatial variability and potential sources based on existing data; (b) to estimate a total atmospheric load of POPs and related compounds at open sea based on the most recently reported data.

Our strategy was to search for available data (last 30 years) mostly in the peer-review literature by using Scopus (http://www.scopus.com/) and different keyword combinations. Most relevant scientific reports/book chapters on organic contaminants in the Mediterranean Sea reporting on the atmospheric compartment have also been considered. Data on atmospheric levels of POPs and related compounds (gas and particulate phases), atmospheric deposition fluxes (derived from atmospheric concentrations or directly measured by using deposition samplers) were considered. Although the focus was on data at open sea (far from the coast), due to scarcity of data, background and non-to-moderated impacted coastal sites were also considered. In addition, and for comparative purposes only, data reported for a number of large Mediterranean coastal cities was included when available. However, it was out of the aim of this work to compile data on atmospheric levels and deposition of pollutants in urban sites. Data on contaminants reported for the Mediterranean Sea in other matrixes, such as water, sediments and biota, etc. have not been considered in this literature survey. The data quality control was performed by a rigorous analysis of the experimental methodologies and assumption adopted by the authors. In addition, studies based on only one sample were considered only as reference values, but not for estimating the atmospheric inputs.

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Organic Contaminants Included

Atmospheric concentrations and deposition data in the Mediterranean open Sea, background and non to moderate-impacted coastal sites were gathered on highly toxic organic contaminants as reported in the peer-reviewed literature. Data availability of POPs is for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), PCBs, some organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs). Figure 2 shows some of the organic contaminants reported in the atmosphere over the Mediterranean Sea belonging to the above mentioned groups. These contaminant families have been reported to exhibit a wide range of adverse effect in biota and humans, including carcinogenicity, reproductive and developmental toxicity, disruption of the endocrine system, induction of enzymes, and anti-estrogenic effects among others (*19–24*). The closely related PAHs have also proven high toxicity in the environment (*25*).

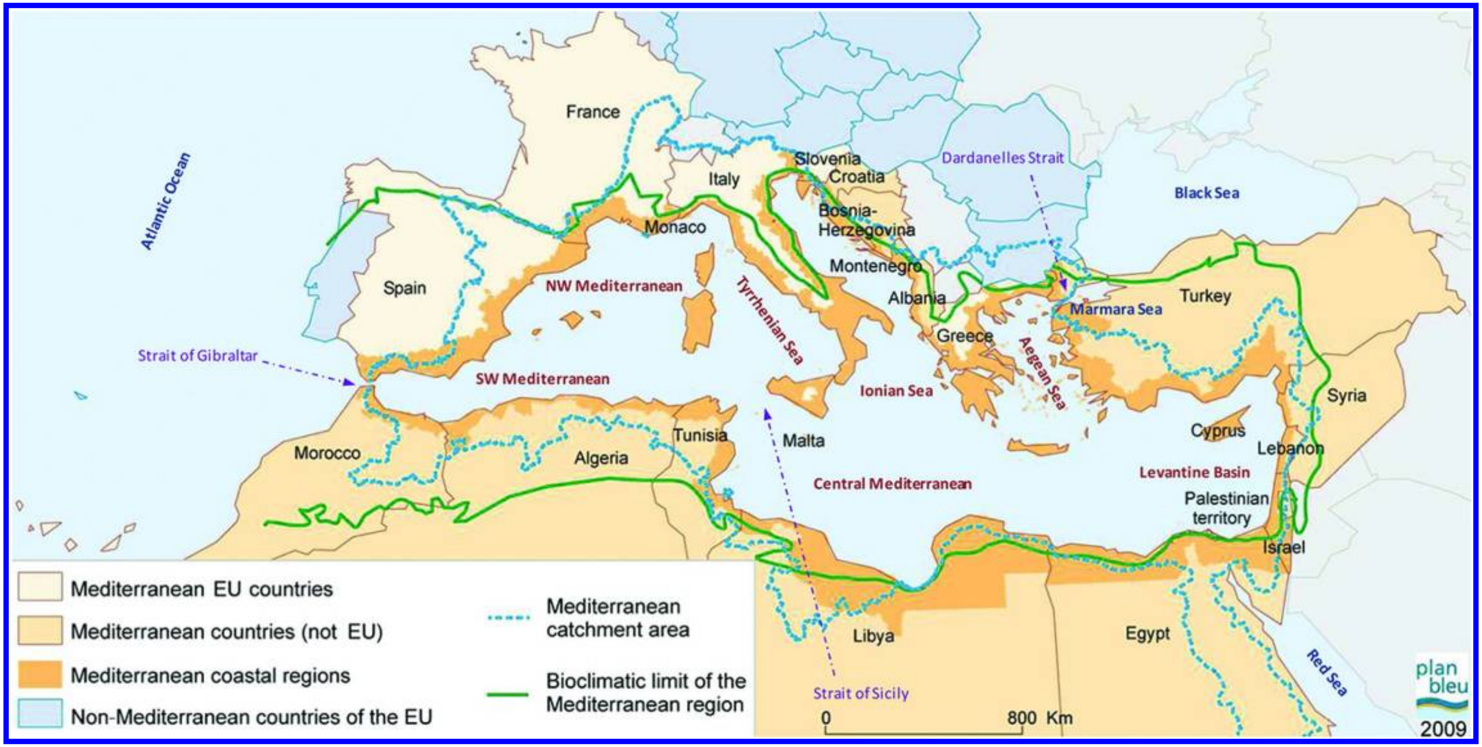

Figure 1. The Mediterranean Region and location of the main Mediterranean sea sub-basins. (adapted with permission from: Plan Bleu, 2009; ref (6)) (see color insert)

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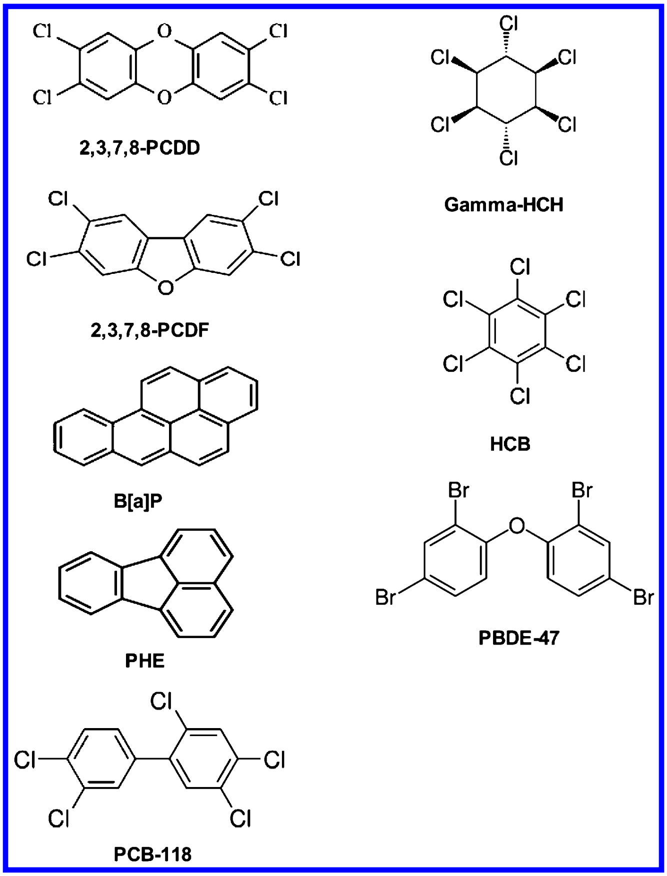

Figure 2. Molecular structures of selected organic contaminants reported in the atmosphere over the Mediterranean Sea.

Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

PCDD/Fs occur as unintentional byproducts of chemical manufacturing and incineration processes (*26*, *27*). Emissions from waste incineration and industrial processes such as metal reclamation and domestic heating (especially in central Europe) are considered as current sources of PCDD/Fs to the environment (*28–31*). Among the 210 different PCDD/Fs congeners, the isomers presenting chlorine in the 2,3,7,8 positions have been reported as the most toxic ones to exposed organisms. Since these congeners occur in complex mixtures in the environment, with the aim of facilitate their risk assessment and regulatory control of exposure, Toxicity Equivalency Factors (TEF) relative to the 2,3,7,8-TCDD (the most toxic one) have been assigned for the seventeen 2,3,7,8-PCDD/Fs (*21*, *32*). It is common in the literature to find atmospheric levels of dioxins and furans reported both as absolute concentrations (*e.g.* fg m^{-3}) or as toxic equivalent (TEQ) concentrations (*e.g.* TEQ pg m^{-3}), the later being helpful for regulatory and comparative purposes. However, in spite of its utility to check compliance with legal thresholds or to compare different studies, it has been recommended to restrict the use of TEQ to biotic matrixes, where TEQs provide in addition relevant toxicological information and can be used for human risk assessment (*32*). In this chapter we will use both ways of expressing concentrations in order to facilitate data comparability.

Polycyclic Aromatic Hydrocarbons

PAHs are semi-volatile organic contaminants which are ubiquitous in the environment. Even if these chemicals have sometimes been regarded as POPs, and have been even included as target pollutants in the Protocol on POPs from the UNECE-CLRTAP, they are generally not as persistent in the environment as other POPs. Some of the sources are similar to PCDD/Fs (*e.g.* combustion sources). PAHs are thought to be formed and released to the atmosphere due to the incomplete combustion of coal, oil, petrol and wood (*33*), even though natural sources (*e.g.* forest fires, volcano eruptions, biogenic formation) may also have a significant regional influence on the PAH occurrence (*34*, *35*).

Polychlorinated Biphenyls

PCBs were used in industry for decades before evidence of accumulation in nature and perhaps problems for human health and the environment were observed (*36*). PCBs were mainly used by the power industry in electrical transformers, capacitors, hydraulic equipment, and as lubricants. These compounds were also added to many products used directly by the public like adhesives, waxes and inks. Since the mid-1970s PCBs have been removed from active use in most countries. However, PCBs can be detected in almost all environmental compartments. Current emissions to the environment are urban/industrial centers, landfills, open burning of products containing PCBs, waste incinerations and accidental fires (*37*). Re-volatilization of PCBs from other environmental reservoirs, such as formerly exposed soils has also been reported as source (*38*). Similarly to PCDD/Fs, there are 209 possible PCB congeners and mostly all of them have been detected in the environment during the last decades (first, as complex mixtures, such as Arochlors and then employing congener-specific analyses). However, even though data exist for many of those hundreds of congeners, two main groups have been traditionally studied. On the one hand, twelve (CB-81, 77, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189) out of the 209 existing PCB congeners have been identified as dioxin- like PCBs (DL-PCBs) and TEFs have also been assigned to them (*21*, *32*). Due to certain molecular characteristics, which make them similar to the 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), such as the fact that they can adopt a co-planar configuration, they exhibit a very similar toxicity mechanism to dioxins (*39*). However, their much lower ambient concentrations compared to other PCB congeners make their analysis complex and expensive resulting in a limited data availability. On other hand, a considerable higher amount of data exists for the 'indicator' PCBs (CB-28, 52, 101, 138, 153 and 180, sometimes CB-118). These congeners are ubiquitous in all environmental compartments and occur at higher concentrations allowing an

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easier and less expensive analysis. In this chapter we have compiled existing information on DL-PCBs and indicator PCBs. In addition, other congeners have been included depending on data availability.

Organochlorine Pesticides

OCPs are a group of pesticides including many types of compounds. These chemicals are often targeted together with PCBs. OCPs can be considered as legacy POPs and most of the modern studies world-wide focus in the pesticides included in the first list of the Stockholm Convention of POPs (*i.e.* aldrin, chlordane, DDTs, dieldrin, eldrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene) and to a lesser extent on the new pesticides recently added to the Convention as new POPs (*i.e.* alpha and beta hexachlorocyclohexanes, cholordecone, lindane, pentachlorobencene, and endosulfans). Since pesticides are applied to soils and crops, major sources to the atmosphere come from the volatilization during application processes and re-volatilization from soils under favorable environmental conditions. However, the differences in their physical-chemical properties influence their environmental behavior. Background information regarding production, application and current sources can be found in the web site from the Stockholm Convention (*40*). Limited data have been found for the atmosphere over the Mediterranean Sea, mainly restricted to HCHs, DDTs and HCB.

Polybrominated Diphenyl Ethers

PBDEs constitute an important group of brominated flame retardants (*41*) and have been used in different kinds of resins, polymers, textiles and in circuit boards, electrical components, panels, coatings, etc. (*42*). Three major PBDE commercial mixtures are commonly used: Deca-BDE, Octa-BDE and Penta-BDE, accounting for 7600, 610 and 150 tons used in Europe in 2001, respectively (*43*). Environmental studies conducted primarily in Europe, Japan and North America indicate that PBDEs are ubiquitous in the atmosphere, sediment and biota (*24*). Very limited data exist for PBDEs in the atmosphere over the Mediterranean Sea. Indeed, only two studies were found.

Results and Discussion

Ambient Levels

Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

PCDD/F atmospheric levels over the Mediterranean open Sea were reported in 2010 based on a unique set of air samples collected during two West-East surveys performed in 2006 and 2007 in the Mediterranean (*44*). ∑2,3,7,8-PCDD/Fs atmospheric levels (gas+particle phase) over the Mediterranean Sea varied from 60 to 1040 fg m^{-3} (3 – 27 WHO$_{98}$-TEQ fg m^{-3}). Slightly higher values were

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measured in 2007-2008 (67 – 1700 fg m^{-3}) in a Mediterranean coastal site in France (*45*). The higher concentrations corresponded to the winter months. Interestingly, open sea and costal atmospheric levels were comparable to those measured in two of the largest Mediterranean coastal cities, Athens (Greece) and Barcelona (Spain) where ∑2,3,7,8-PCDD/Fs concentrations of 702 and 572 – 1162 fg m^{-3} were reported, respectively (Table I) (*46*, *47*). This observation together with the lack of significant differences in the atmospheric levels between the Western and the Eastern Mediterranean basins (*44*) suggest a homogeneous distribution of atmospheric PCDD/Fs over the Mediterranean Sea. These results indicate that even if there are hot spots in the Mediterranean basin, the levels found in open sea are mostly driven by the atmospheric circulation patterns. In-depth analysis of the PCDD/F congener patterns and air mass back trajectories of samples collected in open waters revealed that PCDD/Fs were transported to the open sea waters from continental areas and across the Atlantic and that emissions from ships may be significant sources to the open Mediterranean (*44*). However, no information on emissions of PCDD/Fs from ships has been reported for the Mediterranean Sea.

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Polycyclic Aromatic Hydrocarbons

The first measurements of PAHs in the atmospheric gas and particle phases over the Mediterranean Sea date back to the mid 80s (*48*). $\sum_{19}$PAH concentrations from samples taken in a costal background site in the Western Mediterranean (Corsica, France) varied from 24 to 76 and from 0.3 to 4.6 ng m^{-3} in the gas and the particle phase, respectively. Since then, other studies have been undertaken both in the Western and Eastern Mediterranean basins ((*46*, *49–56*), Table II). The first cruise measurements of PAH atmospheric concentrations in the Eastern Mediterranean were undertaken in summer 2000 and 2001. $\sum_{18-24}$PAH concentrations varied from 20 and 76 ng m^{-3} in the gas phase and from 0.2 to 7 ng m^{-3} in the particle phase (*46*, *49*). However, the first comprehensive assessment of gas and particle phase PAH concentrations from across the Mediterranean Sea comes from the above mentioned surveys performed in 2006 and 2007 (*50*). PAH atmospheric concentrations were dominated by gas phase levels due to the high contribution of phenanthrene, dibenzothiophene and their alkylated derivates. $\sum_{30}$ PAH gas phase concentrations over the Mediterranean Sea ranged from 13 to 86 ng m^{-3}. The highest $\sum_{30}$PAH concentration was measured in the Western Mediterranean (26 - 86 ng m^{-3}), whereas the lowest levels were measured in the SE Mediterranean (13 - 28 ng m^{-3}). $\sum_{30}$PAH concentrations in the atmospheric particle phase over the Mediterranean Sea varied from 0.5 to 3 ng m^{-3}. Contrary to gas phase levels, a similar range of $\sum_{30}$PAH particle concentrations were measured in all the Mediterranean sub-basins but showing a high within-basin variability. It is interesting to note that in SE Mediterranean the highest particle phase levels were measured in the proximity of the Nile Delta and Alexandria (Egypt) urban area (*50*) suggesting particle phase sources are important in this specific zone within the basin.

Table I. PCDD/Fs (gas + particle phase) ambient air concentrations (fg m^{-3}) in the open Mediterranean Sea, coastal sites and selected large coastal cities in the area

Location	Sampling site	Site description	Sampling date	∑2,3,7,8-PCDDs	∑2,3,7,8-PCDFs	∑2,3,7,8-PCDD/Fs	WHO-TEQ$_{98}$^{a}	WHO-TEQ$_{05}$^{a}	Reference
Whole Mediterranean Sea	All basins	Cruise sampling	June 2006, Jun/July	21 - 973	26 - 404	60 - 1040	3 - 27	2 - 24	(44)
Western Mediterranean Sea / FR	Thau Lagoon	Coastal site	Feb 2007-2008	39 - 1210	18 - 775	67 - 1700	2 - 135	2 - 103	(45)
Athens / GR	Thisio, Ymittos	Urban	July 2000	305	397	702	73	62	(46)
Barcelona / SP	Sant Adriá del Besós	Urban/Industrial	March-April 2005	355 - 885	217 - 276	572 - 1162	22 - 26	19 - 22	(47)

[a] TEQ values are upper bound concentrations; FR = France, GR= Greece, SP= Spain

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Table II. PAH ambient air concentrations in the open Mediterranean Sea, coastal sites and selected large coastal cities in the area

Location	Sampling site	Site description	Sampling date	Compounds (conc., ng m^{-3}) GAS	PARTICLE	Reference
Whole Mediterranean Sea	All basins	Cruise sampling	June 2006, Jun/July 2007	Σ_{30}PAHs (13 - 86)	Σ_{30}PAHs (0.5 - 3)	(50)
Eastern Mediterranean Sea	Aegean Sea	Cruise sampling	July 2001	$\Sigma_{18\text{-}24}$PAH (20- 76)	$\Sigma_{18\text{-}24}$PAH (0.2 -7)	(49)
Eastern Mediterranean Sea / GR	Saronikos Gulf (Aegean Sea)	Cruise sampling	July 2000	Σ_{20}PAH (22)	Σ_{20}PAH (1)	(46)
Western Mediterranean Sea / FR	Banyuls-sur-Mer	Coastal site	March, July 2002	Σ_{15}PAH (11 - 19)	Σ_{15}PAH (0.6 -2)	(51)
Eastern Mediterranean Sea / GR	Finokalia (Crete)	Background Coastal site	Nov 2000-July 2002	Σ_{10}PAH (4 - 15)	n.r	(52)
Eastern Mediterranean Sea/ GR	Finokalia (Crete)	Background Coastal site	Feb 2000-2002	Σ_{37}PAH (4 - 56)	Σ_{37}PAH (0.3 - 2)	(53)
Western Mediterranean Sea /SP	Mallorca	Coastal site	Oct-Nov 1990	n.r	Σ_{16}PAH (0.2 - 1)	(54)
Western Mediterranean Sea / FR	Cap Ferrat	Coastal site	April-May 1990	n.r	Σ_{10}PAH (1 - 1.4)	(55)
Western Mediterranean Sea/ FR	Corsica	Background Coastal site	March-April 1986	Σ_{19}PAH (24 - 76)	Σ_{19}PAH (0.3 - 4.6)	(48)
Eastern Mediterranean Sea /IT	Venice Lagoon	Coastal site	March 2002-July 2003	Σ_{15}PAH (0.5 - 11)	n.r	(56)
Athens / GR	Athens city	Urban/Industrial	June, Nov-Dec 2003	Σ_{14}PAH (7 - 124)	Σ_{14}PAH (0.4 - 13)	(59)
Barcelona /SP	Barcelona coast	Urban/Industrial	March, July 2002	Σ_{15}PAH (43 - 46)	Σ_{15}PAH (4 -7)	(51)
Alexandria / EG	Alexandria coast	Urban/Industrial	July 2010, Jan 2011	Σ_{42}PAH (240 - 1100)	n.r	(60)
Rome / IT	Not specified	Urban	Feb 2000 - Jan 2001	n.r	Σ_{10}PAH (2 - 44)	(61)

n.r = not reported; FR = France, GR = Greece, SP = Spain, IT = Italy, EG = Egypt

In spite of variability in the historical data due to different sampling and analytical approaches, PAHs levels reported for the mid 80s and at the present time are very similar. Atmospheric half-lives of PAHs have been reported to range from few hours to few days (*57*, *58*) resulting in a constant depletion of PAHs in the atmosphere. However, the present situation points to continuous emissions of PAHs to the atmosphere, maintaining relatively stable airborne PAH levels over the atmosphere of the open Mediterranean Sea and over coastal sites during the last decades. The other interesting observation is that current ∑PAH gas and particle phase atmospheric levels at open sea fall generally within the range of those of some of the largest Mediterranean coastal cities such as Barcelona or Athens ((*51*, *59*), Table II), but are generally lower than values reported for Alexandria (up to 1100 ng m^{-3} in the gas phase) or Rome (up to 44 ng m^{-3} in the particle phase) ((*60*, *61*), Table II). So, it is difficult to derive clear conclusions from the available data.

Polychlorinated Biphenyls

Existing data on atmospheric levels of PCBs are scarce in the Mediterranean Sea, where current significant geographical data gaps exist and the available records come mainly from local studies. First reported PCB concentrations in the coastal and open sea atmosphere over the Mediterranean Sea date back to punctual measurements undertaken between 1975 and 1977. PCB concentrations ranging from 160 to 340 pg m^{-3} were reported. However, it is unclear which atmospheric phases were sampled as well as the number of PCB congeners analyzed (*62*, *63*). First cruise measurements in the Mediterranean Sea were performed in June/July 1989 and atmospheric gas phase concentrations of $\sum_{40}$PCBs derived from only 2 samples (transects) gathered at open sea ranged from 170 to 490 pg m^{-3} (*64*). Results from the West-East cruises undertaken in 2006 and 2007 provide again the most comprehensive assessment of PCB atmospheric levels in Mediterranean Sea open waters. $\sum_{41}$PCB gas phase concentrations across the Mediterranean Sea ranged from 82 to 930 pg m^{-3}, whereas particle phase levels varied from ~1 to 36 pg m^{-3} (*65*). Higher PCB concentrations were generally measured in the Western Mediterranean.

These levels are generally within the range of the first reported measurements and of levels measured in other coastal sites in the Eastern and Western Mediterranean ((*66–68*), Table III). However, PCB data comparability may be tricky since different sampling and analytical methods were employed and different number and type of PCBs may be included in the sums reported. A more meaningful data comparison would be congener-specific, but this is out of the scope of this work. Reported PCB atmospheric concentrations over some of the largest Mediterranean coastal cities (Barcelona, Rome and Izmir) are generally higher than levels at open sea ((*61*, *67*, *69*), Table III), except for the case of Athens (*46*). There results indicate the importance of the current PCB urban/industrial sources in the region. In addition, existing data suggest

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a limited decline in PCB atmospheric concentrations in the last decade for the Mediterranean region. It is also worth noting that very limited data exist on the most toxic PCBs, DL-PCBs, in the atmosphere of the Mediterranean Sea. Only two studies reported concentrations of more than 3 DL-PCB congeners. One reported the whole set of DL-PCB in a coastal site in the Western Mediterranean, with DL-PCB concentrations raging from 1 to 7 pg m^{-3} and 0.1 to 0.7 pg m^{-3} in the gas and the particle phases, respectively (*45*). The only study measuring DL-PCB concentrations in the Mediterranean atmosphere at open sea reported mono-ortho PCB ($\sum_8$DL-PCBs) levels of 0.03-1.5 and 0.001-0.2 pg m^{-3} for the gas and particle phases (*65*).

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Organochlorine Pesticides

Only two studies reported atmospheric levels of OCPs over the open Mediterranean Sea. As for PCBs, the first cruise measurements in the Mediterranean were performed in June/July 1989 by Iwata and co-workers (*64*) for a limited number of OCPs (Table IV). Mean atmospheric gas phase concentrations were of 150, 75 and 18 pg m^{-3} for α-HCH, γ-HCH and, $\sum_3$DDTs, respectively (*64*). Data comparability is not easy due to the general lack of data on atmospheric levels of OCPs over Mediterranean waters. In addition, the degree of uncertainty in the comparisons is high due to the different sampling and analytical methods used as previously mentioned. Cruise measurements undertaken almost two decades later across the Mediterranean revealed slightly lower mean levels of α-HCH (23 pg m^{-3}) and γ-HCH (44 pg m^{-3}) in the atmospheric gas phase (*65*). Unlike for α-HCH (higher gas phase values measured in the samples taken in the Eastern Mediterranean basin), γ-HCH, δ-HCH and HCB exhibited peak values in the Western Mediterranean Sea. Thus, the highest values for γ-HCH and δ-HCH were measured in samples taken between Barcelona and Mallorca while HCB peak values were detected in a sample collected between Mallorca and Sardinia. This fact highlights the differential environmental behavior and potential sources of OCPs.

Interestingly, the reported mean concentrations of α-HCH and γ-HCH in the late 80s in the atmosphere over the open Mediterranean Sea (*64*) are within the same range of those reported for residential areas in Turkish coastal Mediterranean city of Izmir (the only large Mediterranean coastal city for which data on atmospheric OCP are reported), where mean values measured in 2003 (gas+particle phases) were of 110 and 117 pg m^{-3} for α-HCH and γ-HCH, respectively (*70*). However, the comparison of the most recent measurements (*65*) with the same urban values as well as the first measurement at open sea suggest a general declining of HCH atmospheric concentrations over the Mediterranean, in particular for α-HCH, and a clearer differentiation between source areas and open sea. Other OCPs such as *trans*- and *cis*-chlordanes and *trans*-nonachlor seem to have followed a different evolution and levels at open sea are much lower than those in urban regions (*70*).

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Table III. PCB ambient air concentrations in the open Mediterranean Sea, coastal sites and selected large coastal cities in the area

Location	Sampling site	Site description	Sampling date	Compounds (conc., pg m^{-3}) GAS	PARTICLE	Reference
Whole Mediterranean Sea	All basins	Cruise sampling	June 2006, Jun/July 2007	$\sum_{41}$PCBs (82 - 932)	$\sum_{41}$PCBs (0.8 - 36)	(65)
Eastern Mediterranean Sea / GR	Saronikos Gulf (Aegean Sea)	Cruise sampling	July 2000	$\sum_{38}$PCBs (180)	$\sum_{38}$PCBs (3)	(46)
Eastern Mediterranean Sea / GR	Finokalia (Crete)	Background Coastal site	July-august 2006	$\sum_{39}$PCBs (33 - 128)	$\sum_{39}$PCBs (nd - 15)	(68)
Eastern Mediterranean Sea / GR	Finokalia (Crete)	Background Coastal site	April 1999-March 2001	$\sum_{54}$PCBs (35 - 137)	$\sum_{54}$PCBs (0.7 - 9.4)	(66)
Western Mediterranean Sea / FR	Thau Lagoon	Coastal site	Feb 2007-2008	$\sum_{18}$PCBs (12 - 91)	$\sum_{18}$PCBs (0.6 - 8)	(45)
Western/Eastern Mediterranean Sea	Two basins	Cruise sampling	Jun-July 1989	$\sum_{40}$PCBs (170 - 490)	n.r	(64)
Western Mediterranean Sea / FR	Banyuls-sur-Mer	Coastal site	Sept 2001, July 2002	$\sum_{41}$PCBs (30 - 860)	$\sum_{41}$PCBs (10 - 40)	(67)
Athens / GR	Thisio, Ymittos	Urban	July 2000	$\sum_{38}$PCBs (345)[a]	$\sum_{38}$PCBs (3.7)[a]	(46)
Barcelona / SP	Barcelona coast	Urban	Sept 2001, June 2002	$\sum_{41}$PCBs (390 - 1400)	$\sum_{41}$PCBs (28 - 78)	(67)
Rome / IT	Not specified	Urban	Feb 2000 - Jan 2001	$\sum_{64}$PCBs (310 - 1200)	n.r	(61)
Izmir / TR	Aliaga county	Urban/Industrial	March-April 2005	$\sum_{36}$PCBs (314 - 3140)[b]		(69)

[a] mean value (n=4); [b] mean value (n=6-7) concentrations are gas+particle phase; n.r = not reported

FR = France, GR = Greece, SP = Spain, IT = Italy, TR = Turkey

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Table IV. OCP ambient air concentrations in the open Mediterranean Sea, coastal sites and selected large coastal cities in the area

Location	Sampling site/description	Sampling date	*a*-HCH		*γ*-HCH		*δ*-HCH		HCB		∑DDTs		*t*- chlor[b]		*c*- chlor[c]		*t*- nona[d]		Reference
			GAS	PART	GAS	PART	GAS	PART	GAS	PART	GAS	PART	GAS	PART	GAS	PART	GAS	PART	
Whole Med. Sea	All basins (cruise)	June 2006, Jun/July 2007	n.d - 87	n.r	n.d - 296	n.r	n.d - 376	n.r	n.d - 420	n.d - 7	n.a	n.a	n.r	n.r	n.r	n.r	n.r	n.r	(65)
Western/Eastern Med. Sea	Two basins (cruise)	Jun-July 1989	100 - 200	n.r	42 - 110	n.r	n.r	n.r	n.r	n.r	14 - 22[a]	n.r	<0.5 -18	n.r	<0.3 - 11	n.r	<0.2 - 5	n.r	(64)
Izmir / TR	Kaynaklar (residential)	May 2003[e]	4 - 460		1 - 670		24 - 50		n.r		13 - 120[f]		13 - 895		n.r		2 - 390		(70)

Compounds (conc., pg m^{-3})

n.d = not detected; n.r= not reported; n.a=not analyzed; [a]∑DDTs=p-p´-DDE+o,p´-DDT+ p,p´-DDT; [b]trans-chlordane, [c]cis-chlordane, [d]trans-nonachlor

[e] reported concentrations are the sum of gas+aerosol phases; [f] ∑DDTs=p-p´-DDE+p-p´-DDD + p,p´-DDT

TR = Turkey

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Polybrominated Diphenyl Ethers

There is no availability of cruise measurement of PBDEs in the atmosphere over the open Mediterranean Sea. Data are very limited, and restricted to coastal areas. Only two studies were found, one in the Eastern Mediterranean and the other one in the Western basin (Table V). The former reported $\sum_{15}$PBDEs mean atmospheric levels in a background coastal site of ~4 and ~1 pg m^{-3} in the gas and particle phase, respectively (*68*). The latter revealed higher atmospheric levels for a coastal Mediterranean Lagoon located in France. $\sum_8$PBDE atmospheric levels ranged from 155 to 230 and from 1 to 18 pg m^{-3} in the gas and particle phase, respectively (*45*). These studies have in common the predominant contribution of the gas phase PBDEs to the total atmospheric concentration. Data were found for two large Mediterranean coastal cities for comparison, Athens (*71*) and Izmir (*72*) (Table V). In contrast to coastal sites, the contribution of the particle phase to the total atmospheric levels predominated. This may be the result of a higher particulate concentrations in the urban atmosphere and the sampling season (winter for urban sites) and summer (for coastal areas). PBDEs 47 and 99 were reported as predominant in all the studies except for the one in Izmir where PBDE-209 was the predominant congener, followed by PBDE-47 and 99. More data are needed for a precise evaluation. However, available data suggest that background costal sites in the Eastern Mediterranean exhibited the lowest levels of PBDEs relative to other areas. Moreover, levels over coastal sites in Western Mediterranean appear to be similar to those reported for some of the largest urban coastal cities in the Mediterranean region.

Atmospheric Deposition

When enough data are available, atmospheric deposition can be characterized by estimating the dry, wet and diffusive fluxes (air-water exchange in the case of aquatic ecosystems). The relative importance of one process over the other will depend on the physico-chemical properties of the pollutant targeted and the environmental conditions (*e.g.* temperature, wind speed, precipitation rates, etc.). For instance, dry deposition may drive the atmospheric loading for those contaminants highly associated to the atmospheric particle phase (*e.g.* higher molecular weight PCDD/Fs and PAHs), while diffusive fluxes will dominate for those contaminants with larger fractions present in the atmospheric gas phase such as PCBs, especially low molecular weight congeners and low molecular weight PAHs (*e.g.* phenanthrene).

In this section a compilation of reported atmospheric deposition fluxes for the main organic pollutants measured in the atmosphere over the open Mediterranean Sea, non-impacted coastal sites and Mediterranean background sites is presented and discussed. The literature review shows that the existing data are limited, in particular at open sea (Table VI), although some improvement on the spatial coverage since last reports (*17*, *18*) has been produced. All the relevant studies found reported dry deposition fluxes, but only a few of them wet and diffusive fluxes. There was only one investigation carried out in a background site in the

Eastern Mediterranean reporting the three above mentioned fluxes (*73*). Although the first estimations of the atmospheric deposition to Mediterranean Sea waters were made in the mid 80s based on just one 12-day integrated sample collected in a coastal site in the Western Mediterranean (*74*), the rest of the studies have been performed in the last two decades ((*44*, *45*, *50*, *51*, *54*, *65*, *73*, *75–77*), Table VI). With the aim of providing the most up-to-date and rigorously reviewed compilation of reported fluxes, we have only considered studies where more than one sample were taken, and in particular those performed at open sea or background sites (Table VI).

Estimation of Total Atmospheric Loading

As explained above, the total atmospheric loading of contaminants into Mediterranean waters depends on the magnitude of three deposition processes which result in dry, wet and diffusive fluxes of contaminants. However, as most of the existing investigations do not report these three processes for the same study; therefore, data from more than one study have been combined in order to provide with an estimate of the atmospheric loading of contaminants including the three above mentioned components. In some cases data on only single process were available, like in the case of PBDEs (wet deposition flux), so the estimations were performed with available information. We are aware of the limitations of these estimations due to data scarcity. Table VII presents an estimation of the total atmospheric loading of toxic chemicals to Mediterranean waters as well as the dry, wet and net diffusive deposition fluxes considered for this calculation. In order to estimate the total atmospheric loading for the Mediterranean Sea (ton yr^{-1}) a surface of 2.5 x 10^{12} m^2 was used. The year of the measurement, locations and the study reference are also indicated in order to better follow the discussion. An estimation of the lower (MIN) and upper (MAX) bounds of deposition rates was performed using data from those selected studies (*44*, *45*, *50*, *65*, *73*, *75*, *76*). The lower bound estimations were calculated by just using the lower reported fluxes; whereas the highest deposition fluxes reported were considered for the upper bound estimations. Note that for some cases the estimated minimum and maximum values are the same simply due to the fact that only an average flux was reported in the study.

From the available data it is clear that the dominant organic compounds deposited to the Mediterranean waters *via* the atmosphere are PAHs. The total atmospheric input of organic contaminants to open Mediterranean sea waters is estimated to varied from 2100 to 4360 ton yr^{-1}. It is important to note that even if PAHs are the predominant contaminants inputted to Mediterranean waters, other highly toxic chemicals are also entering the water masses *via* the atmosphere contributing to a complex cocktail of contaminants. Thus, in addition to the 2000-4100 tons of PAHs, from 3 to 230 tons of OCPs, from ~3 to 20 tons of PCBs, ~1 ton of PBDEs and from 60 to 260 kg of 2,3,7,8-PCDD/Fs are expected to be deposited every year in Mediterranean open waters from the atmosphere. Since deposition fluxes were mostly for open waters and background sites, the

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calculated loading could be considered as the "base line" atmospheric input to the Mediterranean Sea waters. Deposition fluxes are expected to increase in the proximity of the coast in particular for those areas close to medium and large coastal Mediterranean cities or in the proximity of coastal industrial facilities. Figure 3 shows the relative importance of each atmospheric deposition process for each contaminant class considering the highest deposition fluxes reported (upper bound fluxes, Table VII). Diffusive fluxes clearly dominate for PAHs and HCB and represent also an important part of the atmospheric loading of PCBs. However, dry deposition dominates the atmospheric loading of PCDD/Fs to Mediterranean waters and has some relevance for PCBs as well (high molecular weight congeners). In the case of PAHs, the net diffusive fluxes were dominated by the low molecular weight compounds as indicated above.

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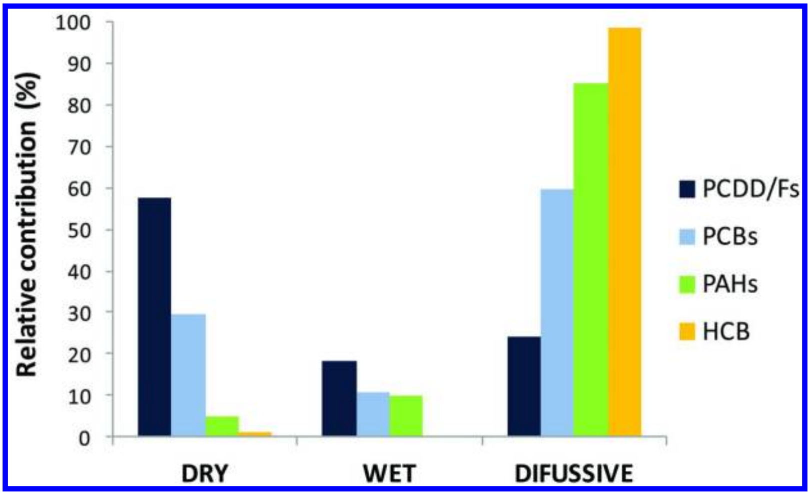

Figure 3. Relative contribution of each atmospheric deposition process to the total input (only upper bound fluxes considered) (see color insert)

This comparison provides only a rough picture of the relative contribution of depositional process by contaminant groups. In the reported summed concentrations/fluxes various congeners/compounds with a wide arrange of physico-chemical properties were considered in each family, masking the relative importance of each process for single contaminants. However, the scope of this section was not to discuss on the differential behavior of single contaminants within families, but offering an overview on the total loading of contaminants to Mediterranean Sea waters and most relevant processes.

Table V. PBDE ambient air concentrations in coastal sites and selected large coastal cities in the area

Location	Sampling site	Site description	Sampling date	Compounds (conc., pg m^{-3})		Reference
				GAS	PARTICLE	
Eastern Mediterranean Sea / GR	Finokalia (Crete)	Background Coastal site	July-august 2006	$\sum_{15}$PBDEs (2 - 11)	$\sum_{15}$PBDEs (0.5 - 2)	(68)
Western Mediterranean Sea / FR	Thau Lagoon	Coastal site	May-August 2007	$\sum_{8}$PBDEs (155 -230)	$\sum_{8}$PBDEs (1 - 18)	(45)
Athens / GR	Athens city center, Heraklion	Urban	December 2006	$\sum_{12}$PBDEs (6 -7)	$\sum_{12}$PBDEs (15 -23)	(71)
Izmir / TR	Yesildere, Horozgedigi village	Urban/Industrial[a]	Sept 2004, Feb-March 2005	$\sum_{7}$PBDEs (9 -30)	$\sum_{7}$PBDEs (27 -62)	(72)

[a] concentrations are mean values and represent the range or urban and Industrial sites

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Table VI. Compilation of reported atmospheric deposition fluxes in the last two decades for the open Mediterranean Sea and Mediterranean background and coastal sites

Compounds	**Atmospheric Deposition Flux**			**Year**	**Location**	**Reference**
	DRY	*WET*	*DIFFUSIVE*			
PCDD/Fs	[ng m^{-2} yr^{-1}]	[ng m^{-2} yr^{-1}]	[ng m^{-2} yr^{-1}]			
∑2,3,7,8-PCDD/Fs [a]	2 - 60	n.r	3 - 25	2006, 2007	All basins (open MED)	(44)
∑2,3,7,8-PCDD/Fs [a], [c]	23	19	n.r	2007-2008	Western MED (coastal)	(45)
PCBs	[ng m^{-2} yr^{-1}]	[ng m^{-2} yr^{-1}]	[ng m^{-2} yr^{-1}]			
$\sum_{18}$PCBs [a]	136	125	n.r	2007-2008	Western MED (coastal)	(45)
$\sum_{54}$PCBs [b]	36 - 400	820 [c]	n.r	2001	Eastern MED (Background)	(75,76)
$\sum_{41}$PCBs [a]	50 - 2250	n.r	187 - 4585	2006, 2007	All basins (open MED)	(65)
PAHs	[**ug** m^{-2} yr^{-1}]	[**ug** m^{-2} yr^{-1}]	[**ug** m^{-2} yr^{-1}]			
$\sum_{30}$PAHs [c]	70 - 80	n.r	600 -1400	2006, 2007	All basins (open MED)	(50)
$\sum_{35}$PAHs [b], [c]	60	165	700	2001, 2002	Eastern MED (Background)	(73)
$\sum_{15}$PAHs	n.r	n.r	335 - 510	2002	Western MED (coastal)	(51)
$\sum_{11}$PAHs [a]	15 - 35	10 -40	n.r	1990	Western MED (coastal)	(54)
OCPs	[ng m^{-2} yr^{-1}]		[**ug** m^{-2} yr^{-1}]			
HCB [a]	4 - 18	n.r	0.03 - 1.4	2006, 2007	All basins (open MED)	(65)
HCHs [a]	n.r	n.r	1 - 90	2006, 2007	All basins (open MED)	(65)
PBDEs	[ng m^{-2} yr^{-1}]					
$\sum_{8}$PBDEs [a]	230	n.r	n.r	2007-2008	Western MED (coastal)	Est. from data in (45)
$\sum_{5}$PBDEs [b]	4 - 90	n.r	n.r	2001-2003	Western MED (coastal)	(77)

[a] Samples collected using high volume samplers (gas and aerosol phases); [b] Samples collected using deposition samplers; [c] Mean values; n.r = not reported

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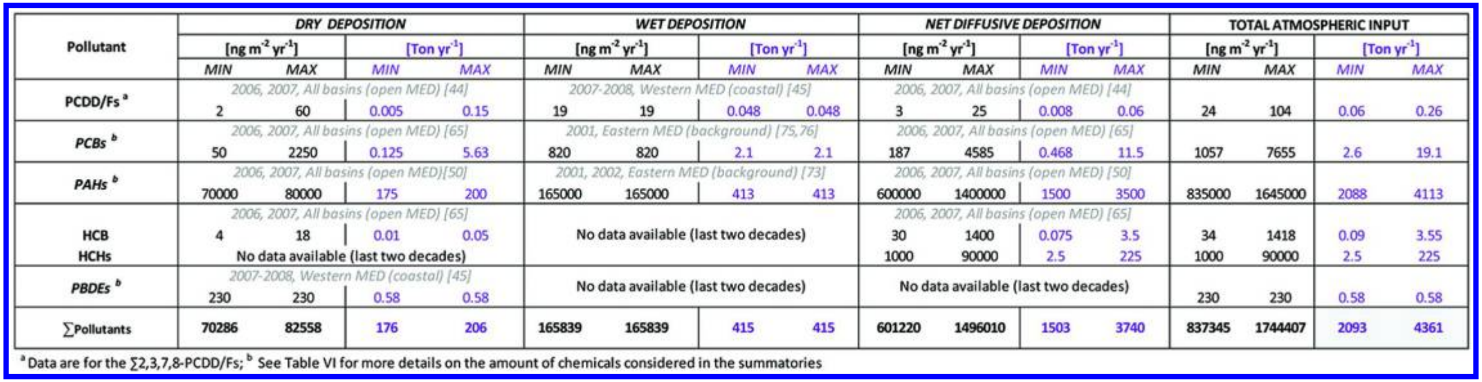
Table VII. Estimation of the dry, wet, net diffusive deposition fluxes and of the total atmospheric loading of toxic chemicals to the Mediterranean Sea



Pollutant	DRY DEPOSITION				WET DEPOSITION				NET DIFFUSIVE DEPOSITION				TOTAL ATMOSPHERIC INPUT			
	[ng m^{-2} yr^{-1}]		[Ton yr^{-1}]		[ng m^{-2} yr^{-1}]		[Ton yr^{-1}]		[ng m^{-2} yr^{-1}]		[Ton yr^{-1}]		[ng m^{-2} yr^{-1}]		[Ton yr^{-1}]	
	MIN	*MAX*	*MIN*	*MAX*	*MIN*	*MAX*	*MIN*	*MAX*	*MIN*	*MAX*	*MIN*	*MAX*	*MIN*	*MAX*	*MIN*	*MAX*
PCDD/Fs[a]	*2006, 2007, All basins (open MED) [44]*				*2007-2008, Western MED (coastal) [45]*				*2006, 2007, All basins (open MED) [44]*							
	2	60	0.005	0.15	19	19	0.048	0.048	3	25	0.008	0.06	24	104	0.06	0.26
PCBs[b]	*2006, 2007, All basins (open MED) [65]*				*2001, Eastern MED (background) [75,76]*				*2006, 2007, All basins (open MED) [65]*							
	50	2250	0.125	5.63	820	820	2.1	2.1	187	4585	0.468	11.5	1057	7655	2.6	19.1
PAHs[b]	*2006, 2007, All basins (open MED)[50]*				*2001, 2002, Eastern MED (background) [73]*				*2006, 2007, All basins (open MED) [50]*							
	70000	80000	175	200	165000	165000	413	413	600000	1400000	1500	3500	835000	1645000	2088	4113
	2006, 2007, All basins (open MED) [65]								*2006, 2007, All basins (open MED) [65]*							
HCB	4	18	0.01	0.05	No data available (last two decades)				30	1400	0.075	3.5	34	1418	0.09	3.55
HCHs	No data available (last two decades)								1000	90000	2.5	225	1000	90000	2.5	225
PBDEs[b]	*2007-2008, Western MED (coastal) [45]*				No data available (last two decades)				No data available (last two decades)							
	230	230	0.58	0.58									230	230	0.58	0.58
∑Pollutants	**70286**	**82558**	**176**	**206**	**165839**	**165839**	**415**	**415**	**601220**	**1496010**	**1503**	**3740**	**837345**	**1744407**	**2093**	**4361**

[a] Data are for the ∑2,3,7,8-PCDD/Fs; [b] See Table VI for more details on the amount of chemicals considered in the summatories

Table VIII. Compilation of reported net diffusive volatilization fluxes from Mediterranean Sea waters

Compounds	*Diffusive voltilization flux*	Year	Location	Reference
PCDD/Fs	[ng m^{-2} yr^{-1}]			
$\sum$2,3,7,8-PCDD/Fs [a]	0.7 -1.3 (Hx-, Oct- PCDDs)	2006, 2007	All basins (open MED)	(44)
PCBs	[ng m^{-2} yr^{-1}]			
$\sum_{54}$PCBs [b]	1600 ($\sum_{54}$PCBs)	2001	Eastern MED (Background)	(75,76)
$\sum_{41}$PCBs [a]	73 - 13500 ($\sum_{2-13}$PCBs)	2006, 2007	All basins (open MED)	(65)
PAHs	[**ug** m^{-2} yr^{-1}]			
$\sum_{30}$PAHs [c]	3 - 315 ($\sum_{2-5}$PAHs)	2006, 2007	All basins (open MED)	(50)
$\sum_{15}$PAHs	275 - 3130 ($\sum_{2-3}$PAHs)	2002	Western MED (coastal)	(51)
OCPs	[ng m^{-2} yr^{-1}]			
HCB [a]	75 - 280	2006, 2007	All basins (open MED)	(65)

[a] Samples collected using high volume samplers (gas and aerosol phases)

[b] Samples collected using deposition samplers

[c] Mean values

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Sink or Source Character of the Mediterranean Sea

One of the main scientific open questions at present is whether the Mediterranean open sea waters behave as a sink (*i.e.* absorbing contaminants) or source (*i.e.* emitting contaminants). From the presented figures, one could arrive at the conclusion of the Mediterranean Sea being a net sink of pollutants. However, the situation is more complicated. Net volatilization fluxes for high chlorinated PCDDs, certain PCB congeners, and HCBs have been reported too in the same selected studies. For the purpose of this discussion it was decided to treat separately the net absorption data from the net volatilization data. However, it is important to note that the absorption of an specific contaminant and its volatilization from surface waters take place simultaneously, and the predominance of one process over the other determines the net contaminant diffusive flux through the air-water interphase. Table VIII summarizes the volatilization fluxes estimated in the selected studies. The estimation (as performed by the deposition fluxes) of the total mass of contaminants volatilized from Mediterranean waters indicates that from 8 to 790 tons of PAHs (sum 30 PAHs), 190 to700 tons of HCB, 0.2 to 34 tons of PCBs (sum of 2-13 PCBs), and from 2 to 3 kg of hexa- and octa-PCDDs “escape” from Mediterranean waters into the overlaying atmospheric boundary layer per year. These figures result in a total volatilization flux of organic contaminants (sum of all contaminant groups) ranging from 200 to 1500 tons a year. Interestingly data point out to a volatilization of toxic contaminants from open sea water occurring at a higher extent in the Eastern Mediterranean Basin. Most probably the higher average temperatures compared to the Western basin may play a role in combination with the more pronounced oligotrophic character of the Eastern Mediterranean that may imply lower removal fluxes. The removal fluxes are mainly degradation (*78*, *79*) and the biological pump. If pollutants are not removed efficiently from the surface waters, they will accumulate in the water column, and eventually, when temperature rises and during periods of high wind speed, they will volatilize.

Conclusions

This work reveals that there is still a general lack of data on POPs and related contaminants in the atmosphere over the Mediterranean Sea as well as on their deposition fluxes, in particular at open sea (far from the shore line). This data scarcity is more pronounced for OCPs and PBDEs. Existing national and international regulations and programmes dealing with marine pollution control have relegated the atmospheric pathway to a low priority, if considered at all. There is therefore a necessity to raise awareness regarding the importance of this compartment in existing regulatory programs. In addition, in the case of the Mediterranean Sea, highly impacted by an intense marine traffic, more information is needed on POP emission from ships. This information is especially relevant for some of the most toxic organic contaminants such as PCDD/Fs and PAHs due to the nature of their sources (mainly combustion sources). Thus, an emissions inventory of maritime industry sources, in particular ships, for POPs in the Mediterranean Sea should be created. Moreover, there are no data on transects from coast to open sea. This kind of data will provide valuable information on short-range contaminant transport within specific Mediterranean areas.

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Atmospheric deposition fluxes, dominated by diffusive exchange for most compounds, also depend on the levels of organic pollutants in surface waters. In coastal waters net volatilization is generally observed due to high levels in surface waters from continental inputs. However, at open sea, the dissolved phase concentrations are controlled by biogeochemical processes, such as the trophic status, as has been described for OCP, PCBs and PAHs (*78*, *79*). Future research, should also address the coupling between water column biogeochemistry and atmospheric deposition.

There is no information on emerging pollutants with known atmospheric contributions such as organophosphorus flame retardants, which are gaining increasing attention in recent years as substitutes of the PBDEs. These compounds have already been found in the atmosphere of other marine environment such us the North Sea (*80*) and the Pacific, Indian, Arctic and Southern Oceans (*81*). An updated mass balance considering main inputs-output pathways including atmosphere for the presented contaminants is necessary to fully understand the fate of these compounds in the various basins of the Mediterranean Sea. In addition, specific strategies at Mediterranean scale should be adopted to tackle "new" potential contaminants. For example, a pioneering study in the Mediterranean Sea revealed that atmospheric concentration of fullerenes C_{60} and C_{70} at open sea are in the range of those found for PAHs (*82*). These carbon nanoparticles used in numerous industrial and research applications may represent a health risk (*83*, *84*) and should be included in future monitoring programs.

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