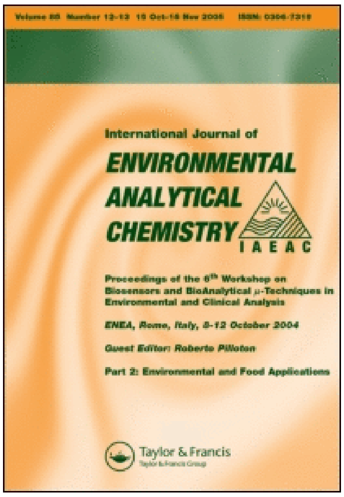

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K. C. Jones[a]; A. E. Johnston[b]; S. P. McGrath[b]
[a] Environmental Science Division, Institute of Environmental and Biological Sciences, Lancaster University, Lancaster, UK [b] Rothamsted Experimental Station, Hertfordshire, UK

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THE IMPORTANCE OF LONG- AND SHORT-TERM AIR-SOIL EXCHANGES OF ORGANIC CONTAMINANTS

K. C. JONES[1], A. E. JOHNSTON[2] and S. P. McGRATH[2]

[1]*Environmental Science Division, Institute of Environmental and Biological Sciences, LancasterUniversity, Lancaster, LA1 4YQ, UK,* [2]*Rothamsted Experimental Station, Harpenden, Hertfordshire, AL5 2JQ, UK*

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Retrospective analysis of archived soil samples collected and stored from long-term agricultural experiments in the UK has shown how soil organic chemical composition has changed over time. High molecular weight polycyclic aromatic hydrocarbons (e.g. benzo[a]pyrene) and polychlorinated dibenzo-p-dioxins and -furans have increased in concentration through this century as a result of cumulative atmospheric depositional inputs. Concentrations of polychlorinated biphenyls and low molecular weight hydrocarbons (e.g. phenanthrene) peaked in the late 1960s/early 1970s, but have declined subsequently. This reflects declining atmospheric inputs of these compounds and losses from surface soils by volatilisation back to the atmosphere and biodegradation. PCBs and low molecular weight PAHs exist predominantly in the vapour phase in air, whilst heavy PAHs and PCDD/Fs are predominantly particulate-bound. Outgassing from soils is probably the most important contemporary source of PCBs to the atmosphere in the UK. Future UK PCB air concentrations will presumably therefore be influenced (controlled) by the rate of desorption and outgassing, as soil and air concentrations move towards a condition of equilibrium partitioning. Archived soils collected and stored before the commercial manufacture of PCBs contain no PCBs indicating that there is no 'natural production' of these compounds. However, within a few hours of exposure to contemporary air these samples contain detectable quantities of PCBs. Short-term air-soil exchange, such as during soil drying in the laboratory, can lead to contamination of samples which contain low concentrations of PCBs and loss from samples which contain high concentrations.

KEY WORDS: PAHs, PCBs, PCDDs, soil samples, atmospheric deposition.

INTRODUCTION

In the 1840s in England, John Lawes and Joseph Gilbert established several unique field experiments at the Rothamsted Experimental Station, which are still being studied today by agronomists and environmental scientists. The original purpose of these experiments was to investigate the effect of various nutrients and soil amendments, added singly or in various combinations on crop yield. However, one of the most exciting unforeseen benefits of these 'Classical Experiments' has been the opportunity to study contaminant trends over time, by comparing the chemical composition of samples from the archived collection with contemporary material. In the mid-1980s we began our collaboration to look at long-term changes in soil and crop composition on the Classical Experiments, which became extended in the late-1980s to include the sewage sludge-amended plots at Woburn. Several papers have now been published on trends in metals in soils and herbage, focussing on cadmium, lead and selenium[1-8]. The various soil treatments and plots on the Classical Experiments enable inputs associated with specific sources to be identified. For example, cadmium is present as an impurity in phosphate-fertilisers, so studies comparing trends on the control (untreated) and P-treated plots have proved fruitful[9,10]. Similarly, the effects of varying organic matter content and soil pH can be studied by judious selection of the plots.

More recently, our attentions have switched to examine historical trends of trace organic contaminants and their fate and behavour in soil-plant systems. This paper will focus specifically on trace organic compounds in soils. The groups of compounds we have studied to date are the polycyclic aromatic hydrocarbons (PAHs), the polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) and the polychlorinated biphenyls (PCBs). Research interest in the environmental fate and behaviour of these compounds began in the 1960s and has been sustained to the present, because of the persistent nature of these compounds, the propensity for some of them to accumulate through the foodchain and concerns over their toxicity. All these groups of compounds are ubiquitous in the environment. Consequently one of the focusses of our work has been to investigate the nature of air-soil exchanges, by analysis of soil samples collected from the control plots, to give retrospective information about compound production and use and environmental persistence. It is important to appreciate that little reliable environmental analytical data exists for these compounds prior to the 1970s. Contemporary concentrations of these compounds in normal agricultural soils range from the pg/kg range for the PCDD/Fs, to the μg/kg range for the PAHs. It is only recently that sufficiently sensitive and reliable analytical procedures have become available to determine them. As a result, retrospective analysis of archived samples from the Classical Experiments has provided a unique and valuable insight into the influence of human activity on the inputs, environmental cycling and time trends of these contaminants.

THE COMPOUNDS OF INTERESTS

Polycyclic aromatic hydrocarbons

PAHs are primarily formed by the incomplete combustion of organic matter. Hundreds of homo – and hetero-cyclic PAHs can potentially be formed, but typically about 16 – 20 compounds are routinely analysed. These are listed by the United States Environmental Protection Agency and the European Commission as priority pollutants. Natural combustion processes (e.g. forest fires) will have released PAHs into the atmosphere since 'the advent of fire', but anthropogenic activities based around the large-scale consumption of fossil fuels have substantially increased emissions over the last century or so. In this paper we contrast the behaviour of two PAH compounds - phenanthrene and benzo(a)pyrene (see Figure 1). Phenanthrene is a 3-ringed aromatic of sufficiently low molecular weight (MW = 178) that it has a moderate aqueous solubility (1.2 mg/l), existing in the atmosphere primarily in the vapour phase. Indeed, phenanthrene dominates the total (Σ) PAH content of air[11]. Benzo(a)pyrene (B(a)P), a known carcinogen, is a 5-ringed molecule (MW = 252) of low aqueous solubility (1.6 μg/l), which binds strongly to particulate matter and rarely exists in the gaseous state under ambient conditions. Phenanthrene can be degraded by soil microflora, whilst B(a)P is very recalcitrant[12]. PAHs can be quantified by either high performance liquid

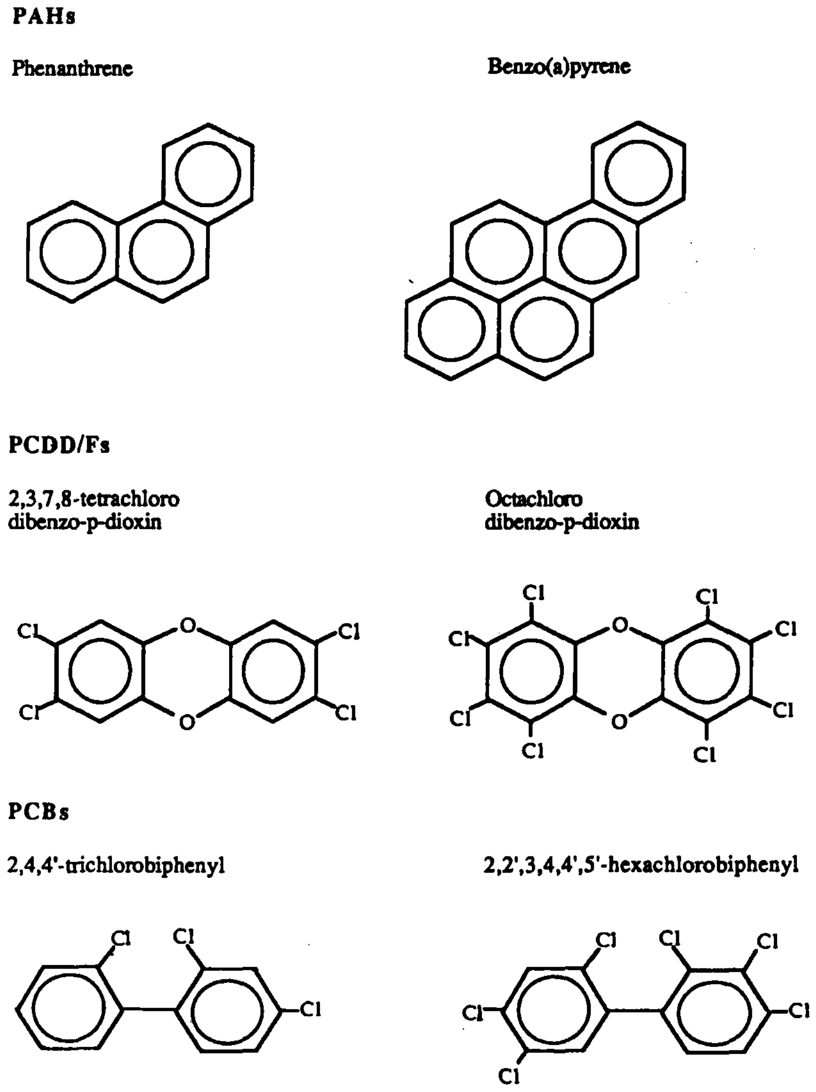

Figure 1 Compounds compared in this paper.

chromatography with fluorescence or diode array detection, or capillary gas chromatography with flame ionisation or mass selective detection.

Polychlorinated dibenzo-p-dioxins and -furans

PCDD/Fs are formed via two major routes; by combustion and 'accidentally' during the production of organochlorine chemicals, such as chlorophenols and phenoxyacetic acid herbicides[13]. Over two hundred different PCDD/F compounds can exist, with as few as one and as many as eight chlorine atoms. One particular PCDD, 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD) has been called 'the most toxic chemical known to man', but it's concentrations in environmental samples are usually miniscule. The PCDD/Fs have the propensity to become substantially accumulated through foodchains (particularly in aquatic environments), so toxic effects have been reported in freshwater and marine top predators[14]. Two PCDD/Fs will be compared here; 2,3,7,8-TCDD and the octachlorinated dioxin (OCDD). PCDD/Fs are determined in soils by high resolution gas chromatography – mass spectrometry after extensive liquid chromatography column clean-up of solvent extracts.

Polychlorinated biphenyls

PCBs were first synthesized in 1929. About 2 x 10^9 kg of PCBs have been manufactured worldwide, primarily for use as electrical insulating fluids in transformers and capacitors. They are very persistent compounds, which are mobile through the environment because of their ability to volatilise and exist in the vapour phase in air. They are lipophilic (accumulate in fat) and concerns over high concentrations in top predators in the late-1960s lead to restrictions and ultimately bans on their use in the UK and elsewhere in the mid-/late-1970s. Nonetheless, they are still being linked to subtle ecotoxicological effects on reproductive potential and the immune system in marine mammals[15]. Two PCB congeners are considered here: the low molecular weight 2,4,4'-triCB (IUPAC number 28) and the 2,2',3,4,4',5'-hexaCB (IUPAC number 138). Both are amongst the most abundant congeners in environmental samples[16]. Following Soxhlet extraction and sample clean-up, PCBs are quantified by capillary gas chromatography with electron capture and/or mass selective detection.

RESULTS AND DISCUSSION

Net changes in soil composition due to air-soil interactions

In soils organic chemicals are subject to: a) sorption to the soil – either reversibly or irreversibly; b) removal from the plough layer to the sub-surface zone or following crops uptake at harvest; c) biotic or abiotic degradation; d) volatilisation. Hence, analysis of the archived samples yields information about net changes in the extractable soil composition after these various processes have occurred. Soils generally have a capacity to store contaminants by sorption. Hence, the soil can become a significant long-term sink for contaminants which come into contact with it[17]. Indeed, budget calculations show that surface soils represent the most substantial 'reservoir' of PAHs, PCDD/Fs and PCBs in the UK environment[13,18,19], so that large-scale net changes in soil composition can have a profound effect on the total amount of these chemicals in the environment as a whole. As mentioned earlier, studies on PAHs, PCDD/F and PCB trends in the long-term experiments have focussed on the control plots where changes in plough layer (0 – 23 cm) depth soil and vegetation will be influenced by air-soil exchanges[12, 20–24]. Table 1 presents information on the six selected compounds in the control soils from the Broadbalk winter wheat experiment and an experiment started at Woburn in 1942. The latter is included because samples have been taken more frequently from this site, giving better temporal resolution of trends in more recent decades. The Table highlights the contrasting behaviour of the compounds, both within

Table 1 Summary properties of the 6 selected compounds.

Compound	*Volatilisation potential*[a]	*Log octanol: water partition coefficient*[b]	*Susceptibility to biodegradation*[c]
Phenanthrene	High	5.6	Yes
Benzo(a)pyrene	None	6.3	No
2,3,7,8-TCDD	Low	6.8	Very slow
OCDD	None	8.2	Very slow
PCB-28	High	5.6	Yes, but slow
PCB-138	Medium	6.7	Slow

[a] Criteria applied as defined in Wild and Jones[25].

[b] Generally the higher the log Kow, the greater the strength of compound binding to soil. Data obtained from refs 28 and 29

[c] Data summarised from refs 28 and 29.

and between homologue groups. Four of the chemicals were detectable in the earliest samples (phenanthrene; B(a)P; 2,3,7,8-TCDD and OCDD) – indicating that 'natural' levels of these compounds occur. This observation is consistent with combustion as a source to the environment. All four compounds also increase in concentration through the time series – again supporting the assertion that anthropogenic activities have increased their atmospheric burden (and hence deposition) during this century. However, phenanthrene concentrations clearly peaked in the 1960s and have declined subsequently, whilst B(a)P, 2,3,7,8-TCDD and OCDD concentrations have either continued to increase up to the present or have stabilized. This observation can be explained from our knowledge of the potential volatility of phenenthrene[25] and/or its

Table 2 Concentrations of the 6 selected compounds in soils from the control plots at Broadbalk and Woburn (0 – 23 cm depth).

Broadbalk					*Year*					
	1846	*1856*	*1881*	*1893*	*1914*	*1944*	*1956*	*1966*	*1980*	*1986*
Phenanthrene[a]	46		68	45	89	110	120	160	140	48
Benzo(a)pyrene[a]	18		6.7		12	23	73	28	120	72
2,3,7,8-TCDD[b]		33		29	40	40	49	60	79	110
OCDD[c]		7.6		11	11	10	13	32	20	25
PCB-28[a]	–	–	–	–	–	1.7	3.4	106	1.9	
PCB-138[a]	–	–	–	–	–	0.26	<0.15	3.4	0.21	

Woburn					*Year*			
	1942	*1951*	*1960*	*1966/67*	*1972*	*1980*	*1984*	*1992*
Phenanthrene[a]	17	110	340	250	130	160	150	
Benzo(a)pyrene[a]	17	18	30	38	45	39	35	
PCB-28[a]	9.7	50	154	146	183	110	4.1	0.38
PCB-138[a]	0.6	<1.2	4.5	3.9	5.5	2.7	2.3	1.0

[a]µg/kg
[b]pg/kg
[c]ng/kg

– indicates not detected.
space indicates not analysed

susceptibility to biological degradation[26] (see Table 2), but it implies that the input function of PAHs has declined in recent years. Various lines of evidence indicate that this is the case. Archived vegetation samples analysed for PAHs, for example, show a decline in ΣPAH concentrations since the 1960s[21,22], while data from dated lake sediment cores indicates maximum ΣPAH deposition fluxes in the 1950s[27]. Coal consumption is thought to be the largest contemporary source of PAHs to the UK environment[19,20], and total UK consumption peaked in the 1950s. In addition, there has been a shift in coal usage away from the relatively inefficient domestic combustion of coal at lower temperatures to high temperature combustion in very large quantities at power stations[20]. It is therefore interesting to note that despite the reductions in input the concentrations of B(a)P have not declined in the soils at Broadbalk and Wobum (Table 1). As Table 2 suggests, however, once in the soil the potential loss pathways for B(a)P are very limited. In other words B(a)P has a long residence time in soils[12]. The continued increase in concentrations of 2,3,7,8-TCDD and OCDD through the twentieth century again appear consistent with our knowledge of the likely input function[22] and their physicochemical properties (Table 2). PCDD/Fs can be formed and released from a variety of sources[13] and it seems likely that contemporary inputs have remained high, notably from municipal waste incineration and combustion. The temporal trends of the PCBs in the two experiments most closely resemble phenanthrene (see Table 1). There is a clear peak in concentrations of both PCB-28 and PCB-138 in the 1960/70s, although this is most marked for PCB-28. Contemporary concentrations are much lower (Table 2). These trends are consistent with our knowledge of the production and use history of these compounds in the UK[24]; the peak in usage worldwide was the late 1960s[18].

One interesting aspect of the PCB time trend data is the rapid loss of these congeners from the soil through the 1970s and subsequently. Table 2 indicates that the likely predominant loss pathway for these compounds from soil is volatilisation. In other words, transfer back to the atmosphere from where they came. In fact, air-soil exchange can be regarded as a process of equilibrium partitioning[30]. PCBs are very 'dynamic' in the environment and may continue to re-cycle between air and soil (as well as water and air) over long periods of time[31] as they move towards their equilbrium partitioning between different environmental compartments[30]. However, the kinetics of these exchange processes will presumably differ between congeners. PCB-138 is bound more firmly to soil organic matter than PCB-28 and will volatilise less readily because of it's lower vapour pressure[28].

In summary, the high moleculer weight PAHs and PCDD/Fs can be expected to reside in soils over many years/decades, firmly sorbed to soil constituents. In contrast, UK soils – such as those at Rothamsted – now appear to be acting as a source of PCBs and low molecular weight PAHs back to the atmosphere. This is of significance for the global cycling of these compounds.

Implications of the Rothamsted soil trends for the global cycling of PCBs

One fascinating feature of the time trend data is that ΣPCB concentrations (defined as the sum of several individual congeners measured by Alcock *et al.*,[24]) at Broadbalk have now apparently reverted to levels close to those in the mid-1940s, albeit with a somewhat different congener composition, with the heavier homologues constituting a greater proportion of the ΣPCB content. Clearly, manufactured Aroclor (commercially synthesized mixtures of PCBs) inputs now exert far less influence on ΣPCB levels at these sites than during the years of peak use. As an illustration of the scale of the reduction in levels of PCBs, if it is assumed that concentrations at Broadbalk, Woburn (and other sites studied by Alcock *et al.*,[24]) were/are representative of those in the UK generally (total surface area is 2.475×10^{11} m^2), that soil density averages 1300 kg/m^3, and that the soils were sampled to plough layer depth (23 cm), the ΣPCB burden of UK soils has declined from ca: 26,600 t to ca. 1,500 t in the last two decades.

It is interesting to speculate on the ultimate fate of the PCBs lost from these soils. As already stated, the most likely loss process is volatilization. Biodegradation is likely to be minor, since it has already been established that aerobic degradation is slow, especially for the more recalcitrant congeners[32]. Moza *et al.*,[33] showed that volatilisation losses of ^{14}C-labelled tri, tetra-, and pentachlorinated PCBs from soils was substantial and accounted for the majority of the compound lost. Volatilisation fluxes are temperature - dependent[34] and may result in PCBs from temperate latitudes, such as the UK, migrating by 'cold condensation' processes to the sub-Artctic and Arctic regions[35], where high concentrations have been observed far from local sources[36].

If it is assumed that volatilisation has been the only loss mechanism over the last 20 years, the above estimates of 26,600 t in UK soils in 1970 reducing to a burden of 1,500 t in 1990 imply that the net annually averaged volatilisation flux over this 20 year period has been ~ 5 mg m^{-2} $year^{-1}$ or ~ 14 μg m^{-2} day^{-1}. To put this in context, Achman *et al.*[31] reported volatilisation rates to the air above the highly contaminated Green Bay, Lake Michigan sediment water system of 0.013 - 1.3 μg m^{-2} day^{-1} in the height of summer. This is relevant, because it has been argued that the Great Lakes are a significant source of PCBs to the overlying air and hence to the Canadian Arctic[37]. Clearly this implies that soil outgassing is potentially a major contributor to the atmospheric burden of PCBs, which may account for the majority of PCBs entering UK air at the present time[18]. Presumably this, in turn, will be subject to long range atmospheric transport. It is therefore of considerable interest to establish the equilibrium partitioning between the soil and that in the overlying atmosphere. This will enable predictions of future trends to be made.

The possible natural production of PCBs

In recent years there has been some debate about whether PCBs existed in the environment prior to 1929 (i.e. prior to their industrial synthesis), perhaps produced by combustion processes in trace amounts, in the same manner as PCDD/Fs[18]. The archived soil collection has provided an opportunity to investigate this issue.

Sub-samples had been taken from the collection and transferred to Lancaster where they were milled for heavy metals analysis in 1985[1]. In the early 1990s, these sub-samples were used for PCB analysis. Clearly detectable levels of PCBs were present in the pre-1929 soils. Given the potential significance of these results, further studies were undertaken. In late 1991/early 1992 further samples were collected from the archive. On this occasion three wax-sealed, previously unopened bottles containing pre-1929 soil were removed and brought to Lancaster. The outside of the jars were meticulously cleaned, to remove all trace of dust. The jars were opened and ca. 100g of soil removed from the middle of the jar, below the surface of the stored soil. This was immediately transferred to the Soxhlet apparatus and extracted and analysed as described above, together with the appropriate blanks. Replicate 20g samples were extracted. On this occasion, no PCBs were detected in the soils. Figure 2a shows a GC-ECD chromatogram of a previously unopened 1914 soil from Broadbalk. These results suggested that the first pre-1929 sub-samples had become contaminated since collection from the field. This hypothesis was tested, as follows.

Replicate 10 g sub-samples of the previously unopened bottle containing the 1914 Broadbalk soil were placed into hexane-rinsed aluminium foil trays and placed in a laboratory for different periods of time. At various intervals the soils were covered to prevent further contact with the atmosphere and then analysed as described above. The ΣPCB results from this experiment are presented in Figure 3. Within a few hours, detectable concentrations of several congeners were present in the soils. Exposure to laboratory air for several days gave ΣPCBs concentrations of several μg/kg (see Figure 3), similar to those in contemporary UK field soils[24]. Figure 2b shows the chromatogram of a soil left in contact with laboratory air for 40 days. The chromatogram illustrates the predominance of lighter PCB congeners. During the experiment, a sample of the laboratory air (~ 100 m^3) was obtained using a High Volume air sampler, purchased from General Metals Works Inc., USA. These samplers trap the particulate-bound PCBs on a Whatman GFA filter, whilst vapour phase PCBs are retained on carefully pre-extracted polyurethane foam plugs. They are being deployed to monitor ambient levels of toxic organics at several sites in the UK[11]. Typically, over 85% of the PCBs burden of air is present in the vapour phase[23], which is dominated by the lighter congeners, such as 28, 52, 44, 61 and 66[11]. Urban air from Manchester city centre averaged ~ 1 ng ΣPCB/m^3 throughout 1991/92[11] and never exceeded 2.5 ng/m^3. Concentrations at a rural site ca. 1 km from Lancaster University are typically 0.3 – 0.6 ng/m^3. The sample of laboratoly air contained 3.8 ng ΣPCB/m^3. The chromatogram of this sample of indoor air is shown in Figure 2c. Clearly the soil sample (Figure 2b) strongly reflects the congener composition of the air (Figure 2c). Other workers have reported previously that concentrations of PCBs and other organochlorines can be elevated in indoor air[38,39]. Replicate soil trays were exposed for the same length of time in different rooms and buildings, to see whether the laboratory contained unusually high concentrations of PCBs for indoor air. No significant differences were noted.

Preliminary experiments on air-soil equilibrium partitioning of PCBs

By extending the experiment described in the previous section, it is possible to gain an understanding of the dynamics and mechanisms of air-soil exchange identified earlier as a controlling factor on the global cycling of PCBs. Equilibrium partitioning will vary between soils of different properties. In addition, desorption may be kinetically limited such that the characteristic biphasic nature of desorption may result in the PCB concentration of a soil with a previous history of exposure approaching a different 'equilibrium concentration' than a previously uncontaminated soil, when exposed simultaneously to the same air concentration. In other words, a proportion of the PCBs bound in soils may take a very long time to be desorbed. Again, the archived soil collection provides a unique opportunity to investigate such proeesses and to move towards a predictive model of future air-soil concentrations. For example, a sample of Broadbalk 1966 soil containing ~ 500 μg ΣPCB/kg has been exposed to laboratory air at the same time as the 1914 soil. After 60 days, the ΣPCB content of this sample declined to ~ 220 μg/kg, presumably due to volatilisation losses[24], whilst the 1914 sample has increased from non-detectable concentrations to ~ 42 μg/kg over the same period (see Figure 3). This implies that both soils are moving towards equilibrium air : soil partitioning conditions with respect to their PCB content.

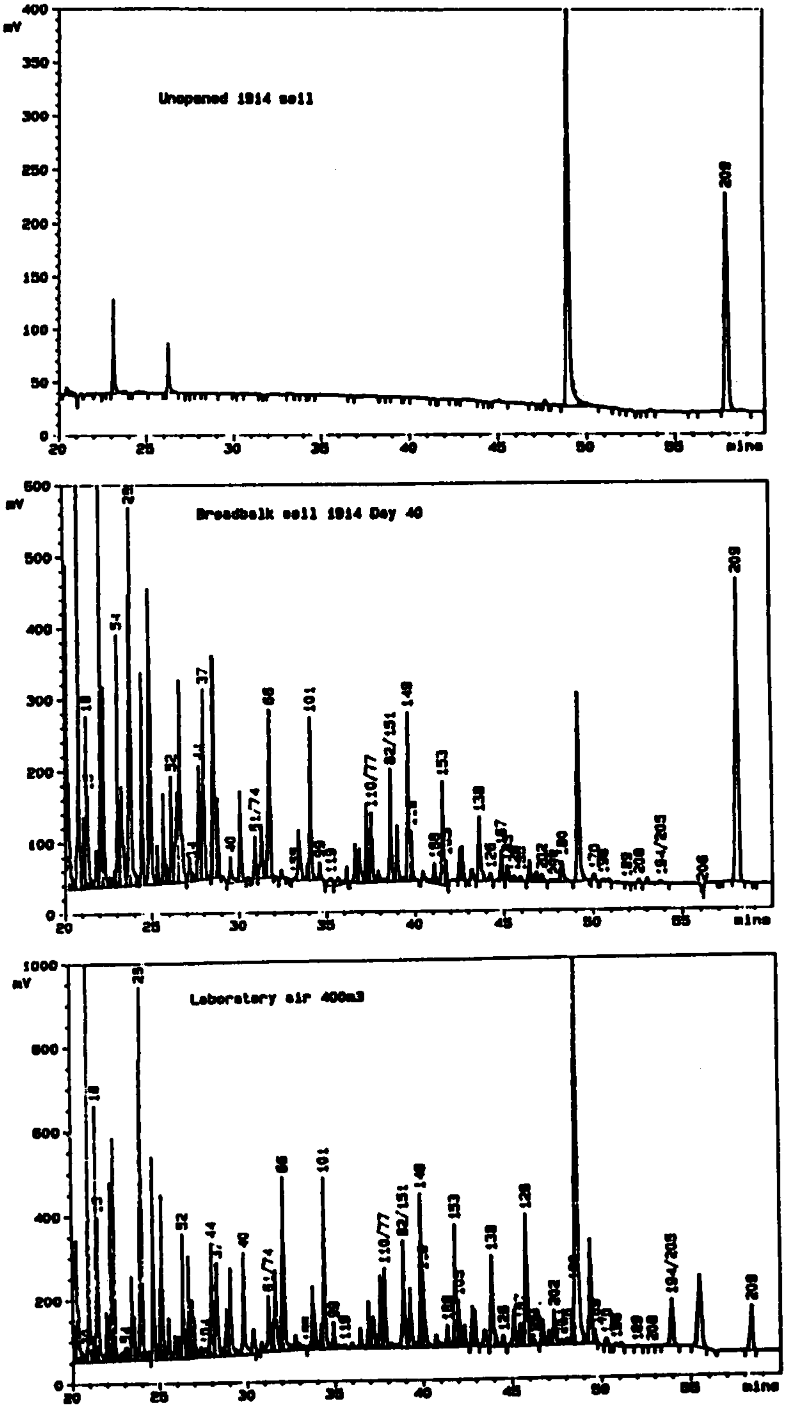

Figure 2 GE-ECD chromatograms of : a).1914 sealed soil sample from apreviously unopened bottle; b). 1914 soil sample exposed to modern air for 40 days; c). Indoor air.

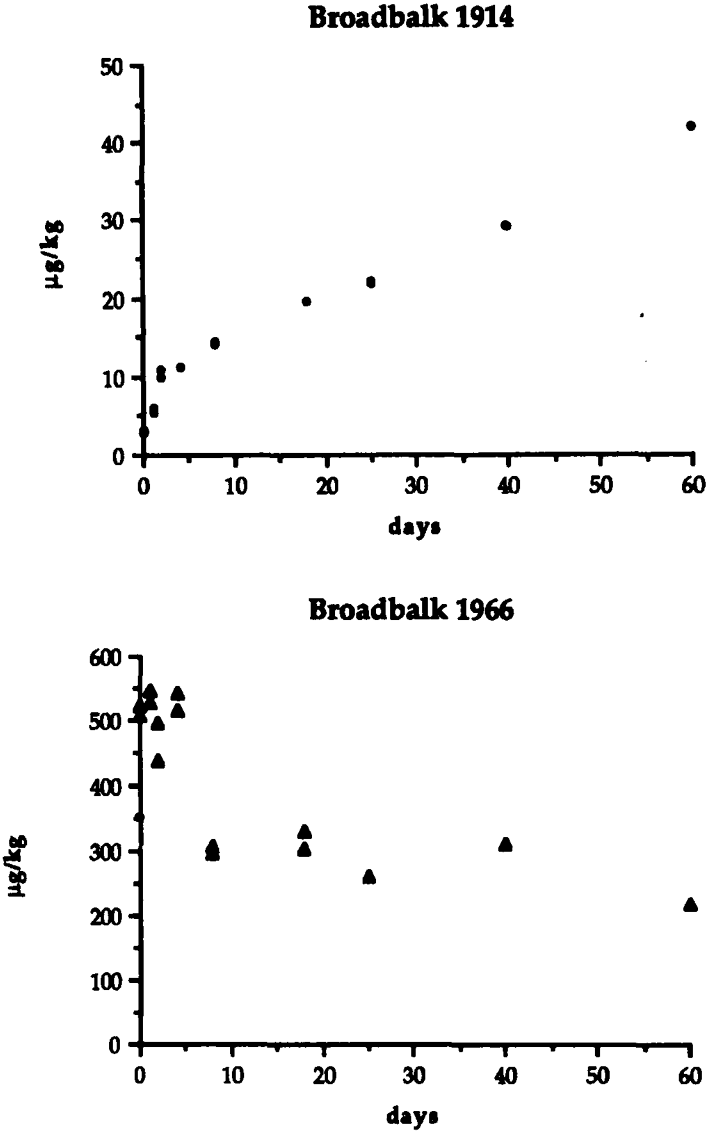

Figure 3 ΣPCB concentrations in samples of stored soils collected in 1914 and 1966 and exposed to laboratory air for different periods of time.

CONCLUDING REMARKS

Long-term air-soil exchange

In this paper we have shown how archived samples from the Rothamsted Classical Experiments have helped us look back in time to gain information about chemicals/substances which could not be analysed until recently (indeed were unheard of a few decades ago), but which have nevertheless been present in the environment. We contend that the net effects of the processes of atmospheric deposition and volatilisation influence the trace organic content of soils at a regional scale (not just at Rothamsted), such that the soil can be a key long-term sink (and source) of contaminants cycling through the environment. In addition, we have shown how the Rothamsted Classical Experiments can help us look forward, to move towards making reliable predictions about the behaviour of chemicals on a regional scale in the future. In the process, we have demonstrated that the Rothamsted archive may contain samples which are unique in another respect. The old unopened bottles, unexposed to modern air, are uncontaminated with respect to chemicals which are ubiquitous in the contemporary environment.

Short-term air-soil exchange

It is clearly very easy to contaminate environmental samples which contain low levels of PCBs, just by contact with ambient air. Indoor air often contains higher concentrations of PCBs than outdoor air (presumably from various past indoor uses of these compounds), which exacerbates the problems. Equally, relatively contaminated samples may loose PCBs to the atmosphere, if there is an imbalance thermodynamically between the PCB content of the sample and the air. Air-drying should therefore be avoided, except perhaps in a desiccator. Whenever possible, samples should be extracted immediately they are brought into the laboratory. If the moisture content is high, anhydrous sodium sulphate can be added.

The issue of 'natural production' of PCBs (and other organohalogens) remains unresolved, but these data and those presented in Alcock *et al.*,[24] clearly show that: a) anthropogenic production of PCBs greatly exceeds any natural production of these compounds, if this does indeed occur; and b) given the great ease with which samples can beeome contaminated (and the high sensitivity of current ECD and MSD techniques), *extreme* caution needs to be exercised when interpreting data purporting to show the 'natural production' of these compounds.

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