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REVIEW ARTICLE

Identification of chemical tracers in the characterisation and source apportionment of inhalable inorganic airborne particles: an overview

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Abstract

The acquisition of increasingly large analytical datasets from standardized air pollution monitoring stations allows more effective characterization of the fine aerosol cocktail breathed daily by modern urban populations. It is increasingly clear from such data that there is great variability in the chemical composition of inorganic inhalable particulate matter ($PM_{10} = < 10$ µm in size) in both space and time. Such variability can be demonstrated using selected tracer elements which, combined with source apportionment techniques, allow differentiation between natural (geological) and anthropogenic sources such as traffic and various industries. These tracer elements, which are commonly toxic metals, can be shown to concentrate in the finer, more deeply inhalable PM fraction, and are thus linked to potential inflammation and oxidative stress after inhalation. Legislation concerned only with measuring physical PM mass concentrations therefore fails to address potential health effects linked to chemical variations in ambient aerosols.

Keywords: *Atmospheric PM10; inorganic chemical tracers; inhalable metal; oxidative stress*

Introduction

It is now abundantly clear that enhanced levels of airborne particulate matter small enough to be inhaled (< 10 µm: PM_{10}) significantly increase the risk of premature death: 'the inhalation of atmospheric PM reduces European human life span by 8.6 months' (WHO 2000). Exposure to atmospheric PM_{10} is associated both with acute respiratory health effects and with longer term pulmonary and cardiovascular disease and cancer (e.g. Schwatz & Meas 2000, Pope et al. 2002, 2004, Brook et al. 2002, Brunereef & Holgate 2002, Vineis & Husgafvel-Pursiainen 2005, Beelen et al. 2008). Most world cities have moved on from the dramatic acute effects of coal-related smogs such as those of London in the mid-20th century, but there is a growing concern over the chronic effects of the less visually obvious but pervasive fine aerosol cocktail breathed by modern urban populations. In its widest sense, the concentration (µg m^{-3}) of this PM mixture present in the atmosphere can be considered as a human biomarker, representing a precursor stressor linked to potential inflammation and oxidative stress after inhalation (Risom et al. 2005). However, an obvious limitation of using PM_{10} mass measurements as surrogate biomarkers derives from the fact that the particles that comprise this aerosol mixture originate from different sources, and have different sizes, shapes and chemical compositions, so that health effects are unlikely to be uniform between different samples of similar mass.

Given this potential complexity and variability of ambient PM_{10} samples, a full physicochemical characterization of such materials involving electron microscopy, X-ray diffraction and complete chemical analysis by ICPMS/AES is needed before experimental toxicological *in vitro* cell assays and *in vivo* studies are applied to determine bioreactivity. Furthermore, in order to generate a realistic idea of what people are actually breathing across our cities, and the likely epidemiological

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consequences on disease patterns, large datasets must be generated from carefully selected and standardized monitoring stations (ideally supplemented by personal exposure information e.g. Sørensen et al. 2005). For this reason, early attempts at physicochemical characterization and source apportionment of ambient atmospheric PM truly representative of the urban environment where most people live and work were limited by a lack of data. In recent years, however, the amount of air pollution information derived from monitoring sites around the world has increased enormously. Publicly available databases such as AIRBASE (http://air-climate.eionet.europa.eu/databases/airbase/index_html) provide many thousands of mass measurements of ambient PM levels, and published chemical analyses on PM samples from monitoring stations are much more abundant than even 5 years ago. The CSIC air pollution group in Barcelona, to take just one example, has produced an extensive database with thousands of ICPMS analyses of airborne PM samples since 2003, from some 40 sites across Spain. This improvement in data availability offers us far better insight into the daily reality of air pollution in the built environment, and it is becoming increasingly apparent that there is great variability in inorganic PM composition in both space and time. In this overview, examples of recent work are selected to demonstrate this chemical inhomogeneity of ambient urban atmospheric PM in modern towns and cities. Such variation is best illustrated by focusing on specific tracer elements, notably metals, that are present in atmospheric PM and that allow us both to differentiate natural from anthropogenic air pollution episodes, and identify specific types of technogenic emissions. The analytical methodology involved in obtaining these data has been published elsewhere (Querol et al. 2001, 2007, Rodriguez et al. 2002, Moreno et al. 2008a).

Geological tracers

Atmospheric aerosols derived from the physical and chemical weathering of continental rocks and soils are commonly referred to as ‘crustal’ or ‘geological’ PM and the chemical composition of most of them ultimately reflects that of parent rock forming minerals. Given the dominance of felsic silicates in the upper continental lithosphere this means those elements associated with feldspars, quartz, micas and their weathering products (mostly clay minerals), i.e. Si, Al, K, Na, Ca and associated trace elements such as Ba, Sr, Rb, and Li. In addition there will be accessory silicates (notably zircon, titanite and epidote), and representatives from the minority non-silicate mineral groups, namely carbonates, sulphates, oxides, hydroxides and phosphates. A small number of these minerals are of particular interest because they host a disproportionately high amount of chemically incompatible trace elements and have a high resistance to physical and chemical attack during weathering and transport. Thus Zr and Hf are hosted by zircon, Ti, Nb and Ta by rutile, and La and Ce by monazite. With increasing weathering and transport, high field strength elements (HFSE) such as Zr, Hf, Nb and Ta, will tend to become concentrated in resistant detrital PM relative to the large ion lithophile elements (LILE) Rb, Sr, Cs, and Ba which are more susceptible to weathering and loss in solution (Figure 1A). Thus, in desert dust for example, although clay adsorption will also play a role, HFSE are mostly contained within tiny, durable nuggets of phosphates and Ti-oxides (e.g. Poitrasson et al. 2002).

Given the distinctive chemistry of geological dust, application of receptor modelling techniques (e.g. principal component analysis) readily identifies the ‘crustal’ component of a PM sample, on the basis of grouping typical tracer elements such as Ce, Rb, Sr, K, Ti, Al and Si. A much greater problem exists in trying to separate different types of crustal PM sources, because these materials commonly have a long history of transport, mixing and resuspension. In southern Europe, for example, the massive amounts of crustal PM regularly introduced by dust intrusions from North Africa mingle with European soil dusts released by agricultural work, and both are repeatedly resuspended by wind and anthropogenic processes such as traffic movement. Within the urban environment in particular both traffic resuspension and release of crustal aerosols from construction and demolition work add greatly to the ambient PM loading. Although none of this extensive mixing and recycling is likely to have a dramatic effect on the geochemistry of these silicate-rich dusts, a long history of transport will favour contamination of the crustal PM by anthropogenic emissions. The adsorption of fine metal aerosols on to the surface of quartz and clay mineral particles, for example, will potentially alter the toxicological impact of these mostly coarse ($>2.5\,\mu m$) materials which at legal concentrations ($<50\ \mu g\,m^{-3}$) are otherwise normally held to be of relatively low health concern.

Technogenic tracers

With respect to the links between inorganic atmospheric PM and human disease it is the trace metals associated with anthropogenic pollution emissions which are of greatest interest in terms of potential candidate biomarkers (e.g. Adamson et al. 2000, Schaumann et al. 2004, Nawrot et al. 2006). The primary sources of metalliferous aerosols are from industrial point sources and traffic emissions, although there are other, commonly overlooked, pollution events (such as firework combustion) that expose populations to high metal PM

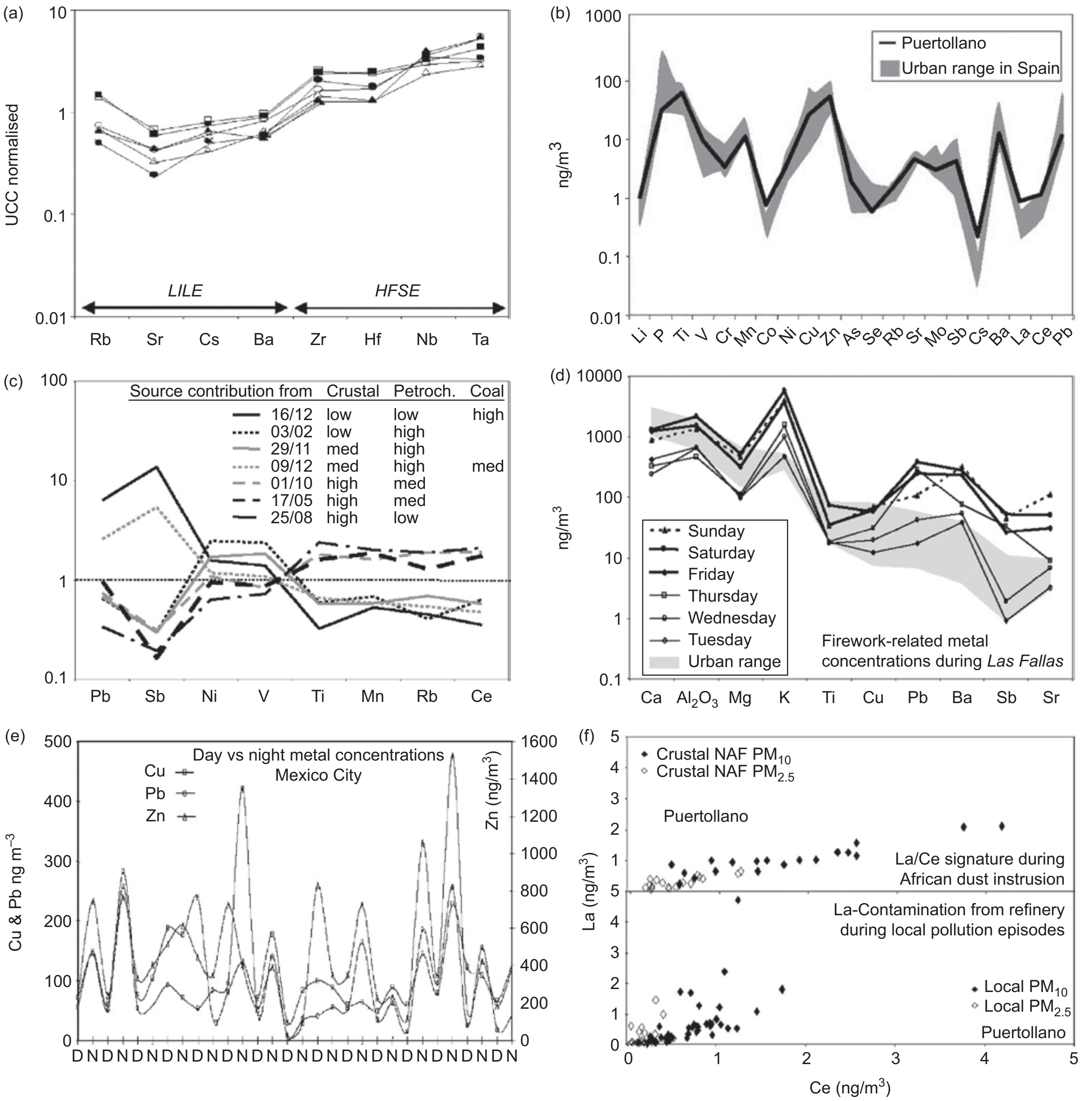


Figure 1. Graphical demonstrations of the chemical variability of inhalable particulate matter (PM). (A) Preferential loss of large ion lithophile elements (LILE) compared with high field strength elements (HSFE) in Saharan desert dusts (adapted from Moreno et al. 2006a); (B) comparison of annual average chemistry of a selected site (Puertollano) with average urban backgrounds (see text for details, adapted from Moreno et al. 2007a); (C) contrasting chemical signatures of PM collected under different types of pollution episodes, daily levels for each element divided by its annual mean concentration (see text for details, adapted from Moreno et al. 2006b); (D) progressively increasing loading of atmospheric metalliferous aerosols during 6-day fiesta (Las Fallas, adapted from Moreno et al. 2007b); (E) prominent nocturnal spikes in metalliferous aerosol concentrations in Mexico City (Moreno et al. 2008b); (F) contrasting La/Ce signatures of aerosols contaminated with crustal dusts transported from North Africa (NAF) with locally-derived La-contaminated PM sourced from a nearby refinery (Moreno et al. 2008c).

concentrations. Smokestack emissions from industrial processes form visually obvious anthropogenic contributions to atmospheric pollution, and the chemical signature of emissions from specific industries can usually be unequivocally demonstrated relatively easily. Thus for example the steel industry creates abnormally elevated atmospheric concentrations of Cr, Ni and Mo, copper metallurgy produces abundant Cu and As aerosols, and ceramic industries raise ambient levels of Ce, Zr, and Pb (Querol et al. 2007). Monitoring campaigns need to be carefully targeted at individual plumes, especially when there is a large number of potential sources: in the Mexico

City Metropolitan Area for example it has been estimated that there are around 30 000 industries, many of which involve using metallurgical processes (Baez et al. 2007).

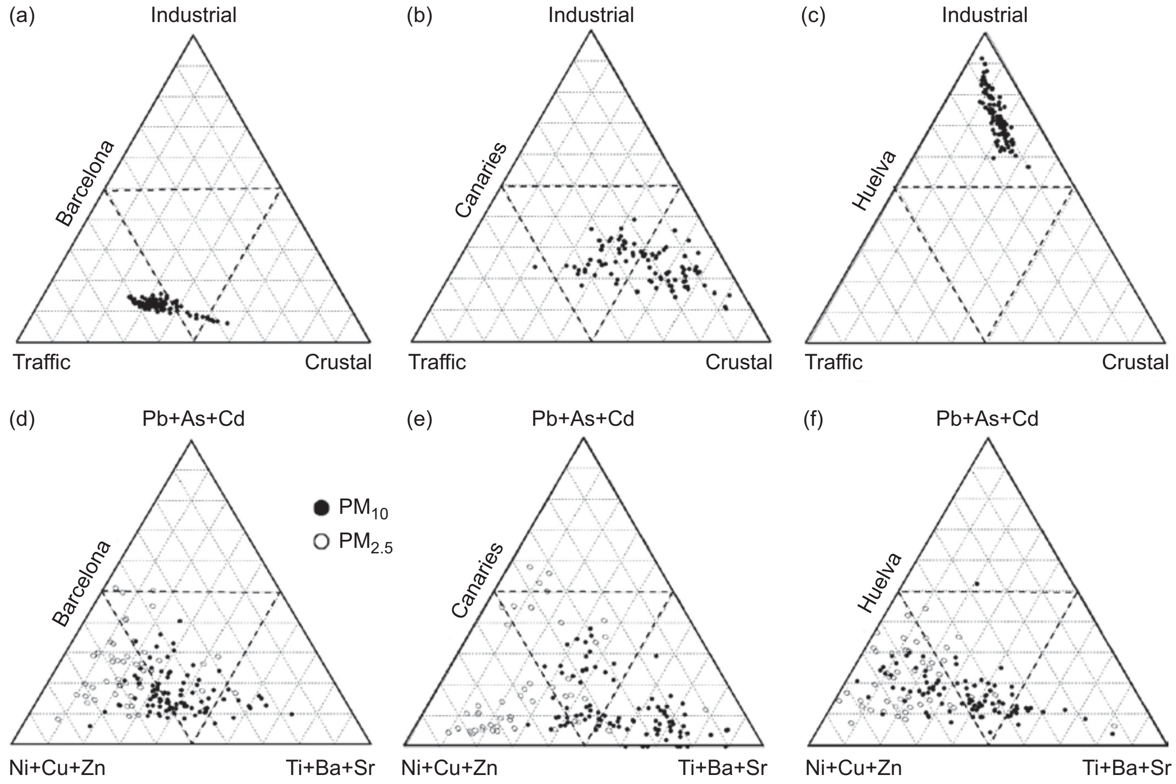
In addition to targeting specific emission sites, the monitoring of daily PM chemistry over timescales of months and years allows comparison of anthropogenic air pollution hotspots with regional and urban background levels, and thus the scale of the problem to be better appreciated. This approach is illustrated on Figure 1B which compares the average atmospheric concentrations of trace elements in Spanish cities with those in Puertollano, Central Spain (population 50 000). The presence of heavy industry (refinery, coal mine, power stations) just south of Puertollano raises average atmospheric concentrations of metal aerosols (e.g. Ti, V, Cr, Co, Ni, Zn, As and Sb) to levels much higher than would be predicted from such a small town. Chemical data such as those shown on Figure 1B are based on 24-h sampling intervals and can be integrated with meteorological data and source apportionment analysis to identify specific pathfinder elements for different types of pollution episodes which occur during the year. Figure 1C again uses a study in Puertollano to contrast different types of daily pollution episodes (when PM_{10} mass exceeded 50 µm m^{-3}) when aerosols were dominated by either petrochemical emissions (high in Ni and V), coal burning (high in Pb and Sb) or crustal particles (high in Ti, Mn, Rb, Ce). Another approach is to use intensive sampling and analysis campaigns targeted at specific pollution events, a good example being provided by our recent study in Valencia of Lãs Fallas, one of the most popular (and polluting) firework and bonfire festivals in Spain. Monitoring of 24-h PM chemistry in the city centre during the 6-day fiesta records a progressive increase in background fine metalliferous aerosols, with concentration spikes in metals especially characteristic of firework combustion (namely K, Pb, Ba, Sb and Sr) (Figure 1D).

Further refinement of time series studies can be made if chemical sampling campaigns can be achieved at 12-h rather than daily intervals, thus providing the opportunity to compare diurnal and nocturnal concentrations of tracer elements. Figure 1E provides a recent illustration of the value of such an approach, revealing striking increases in concentrations of Cu, Zn and Pb in the nightly atmosphere of Mexico City. Such increases in the metalliferous content of nocturnal atmospheres will occur wherever industrial pollutants become trapped in a cold layer of air prior to the vertical growth, mixing and dispersal of the pollution cloud during the day, a meteorological scenario unfortunately common in many world cities. Urban PM data can demonstrate that such pollution is not homogeneously distributed. In the case of the recent Mexico City study, transient concentration spikes in different metals were recorded on the same night in different places: e.g. a 'copper event' of Cu PM_{10} 281 ng m^{-3} in the centre, and a 'zinc event' of Zn PM_{10} 1481 ng m^{-3} on the NE edge of the city (Moreno et al. 2008b).

Cu, Zn and Pb concentrations in atmospheric PM, as utilized in the Mexico City study mentioned above, are especially useful pollution markers as these are the commonest trace transition metals that are primarily of anthropogenic origin. These metals are not only produced by industrial smokestacks, but are also a readily identifiable component of traffic emissions, and therefore spread pervasively throughout the built environment. Notable sources of traffic metal PM emissions include not only those from the vehicle tailpipe (PGE, Ce, Mo, Zn) but also from the mechanical abrasion of tyres (Zn) and brakes (Ba, Cu, Sb) (Sternbeck et al. 2002, Harrison et al. 2003, Maricq 2007). In cases where trace metals are released by more than one technogenic process, it can be useful to use element ratios: e.g. Cu/Sb values in PM released from traffic brake wear are significantly higher than those of waste incineration fly-ash samples (Weckwerth 2001, Sternbeck et al. 2002). Similarly, certain industrial processes, and the use of catalytic converters in road traffic, result in atmospheric fractionation of lanthanoid elements (La to Lu), creating distinctive anthropogenic geochemical anomalies, because these elements are rarely fractionated by natural geological processes. Thus PM emitted from oil refineries using La-rich zeolitic fluid catalytic converters (FCC), or from power stations burning oils previously contaminated by FCC, will show La/Ce values markedly higher than the 0.5 typical of most crustal materials (Olmez & Gordon 1985, Kulkarni 2006). In contrast, anomalously low La/Ce values are characteristic of ceramic works using Ce as a pigment (Querol et al. 2007), and vehicle tailpipe particles derived from the thermal and mechanical wear of catalytic converters typically similarly exhibit extremely low La/Ce values which can differ from crustal ratios by over x200 (Angelone et al. 2007). Figure 1F demonstrates this use of comparisons between concentrations of La and Ce, again using Puertollano data which reveals La-enrichment of local, FCC refinery-derived PM compared with crustal PM derived from the intrusion of African dust.

Conclusions

The acquisition and interrogation of large databases on atmospheric PM chemistry is making it increasingly clear that there are large differences in the chemistry of inhaled aerosols between and within cities and towns. Legislation based only on the physical mass of inhaled material fails to address the different potential health effects of, for example, breathing air laden with coarse African desert dust or air contaminated with a fine cocktail of metals from traffic or local industry. This point



Average		Barcelona	Canaries	Huelva
PM_{10}	µg/m^3	**41.0**	**37.3**	**37.5**
Pb-As-Cd	ng/m^3	59	16	43
Ni-Cu-Zn		153	41	124
Ti-Ba-Sr		130	77	80
$PM_{2.5}$	µg/m^3	**27.7**	**18.6**	**19.3**
Pb-As-Cd	ng/m^3	42	13	32
Ni-Cu-Zn		92	35	79
Ti-Ba-Sr		37	20	26

Figure 2. Three-component triangular diagrams illustrating variations in sources. (A–C) and metal aerosol content (D–F) of PM samples collected from three contrasting settings in Spain (adapted from Moreno et al. 2006c).

can be graphically made using 3-component diagrams such as those depicted on Figure 2. Figure 2A–C plots source apportionment data and demonstrates the relative importance of PM derived from traffic, industry and natural crustal material from three contrasting settings in Spain: Barcelona city, the Canary Islands and the industrial town of Huelva, all of which have similar average annual PM concentrations of between 37 and 41 µg m^{-3}. Ambient PM_{10} in Barcelona is clearly sourced mainly from traffic, accompanied by a considerable amount of repeatedly resuspended crustal mineral material (Figure 2A). Such crustal material is much more important in the Canaries (Figure 2B), due to regular dust intrusions from the Saharan-Sahel dust corridor to the east, whereas Huelva PM mostly originates from local industry (Figure 2C). Figure 2D–F shows metal aerosol concentration data in both PM_{10} and $PM_{2.5}$ for the same sites, comparing three metal groups on the basis of their relative toxicity (High = Pb, As, Cd; Medium = Ni, Cu, Zn; Low = Ti, Ba, Sr). Once again the crustal nature of Canaries PM is apparent, especially within the coarser component (PM_{10}). Also obvious is the tendency for the more toxic metals to reside within the finer particles, namely those more deeply inhalable and thus more likely to be linked to potential inflammation and oxidative stress within the human body.

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