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The origin of particles in the atmosphere has long been subject to debate. The problem is more critical yet in urban areas, due to their negative impacts on public health. Recently, isotope tools have proved their great added value for unambiguously deciphering the origin of particles (both $PM_{2,5}$ and PM_{10}), which could help to better design management plans for reducing aerosol levels in the atmosphere. A review of several isotope systems shows that they may certainly aid in distinguishing between natural and anthropogenic, or mineral and organic origins of these particles.



Urban Aerosols



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Particulate matter (PM): source and characteristics

All urban areas have particles suspended in their atmosphere. Large cities tend to reach high levels of atmospheric pollution if the emissions-reduction measures taken are insufficient. *Figure 1* shows the relation between city size (in terms of population) and suspended particle levels: although Tokyo's population is higher, its atmosphere is less polluted than that of Beijing, Mexico or Bombay.

The sources of this particulate matter fall into three groups: (a) sea salt aerosols, (b) terrestrial aerosols (soil dust, biological emissions), (c) anthropogenic sources (industry, agriculture, burning of vegetation and fossil fuels, fertilizers). Therefore particles typically consist of a mixture of inorganic and organic chemicals, including carbon, sulfates, nitrates, metals, acids, and semi-volatile compounds.

“Anthropogenic particles typically consist of a mixture of inorganic and organic chemicals.”

Sea salt aerosols form in urban areas near the coast, notably harbour cities. Terrestrial aerosols may come from soil erosion near the collector (local source) as well as from intracontinental (external) or even intercontinental (exogenic) sources. Anthropogenic aerosols may likewise originate in the vicinity of the collector (local source) or at far greater distances (distant source). The relative abundance of particles thus depends on the scale of the production processes and the source distance. Coarser material has a shorter

The effects of atmospheric pollution on visibility in Beijing.

Les effets de la pollution atmosphérique sur la visibilité à Pékin.

© X. Liu, 2007.

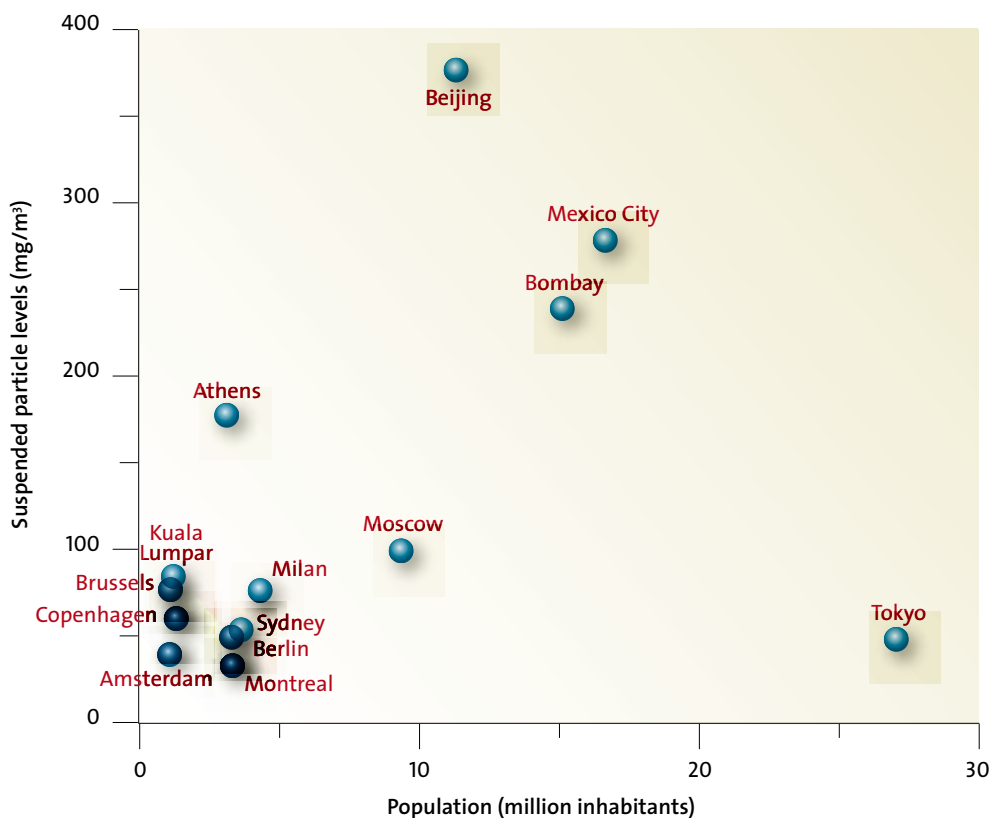


Figure 1: Relation between population size in large cities and suspended particle levels.

Figure 1 : Rapport entre la taille des populations des mégapoles et le niveau des particules en suspension.

Source <http://www.portfolio.mvm.ed.ac.uk/studentwebs/session4/27/citydiff.htm>



lifetime while PM_{10} may remain airborne for periods ranging from a few hours to several weeks.

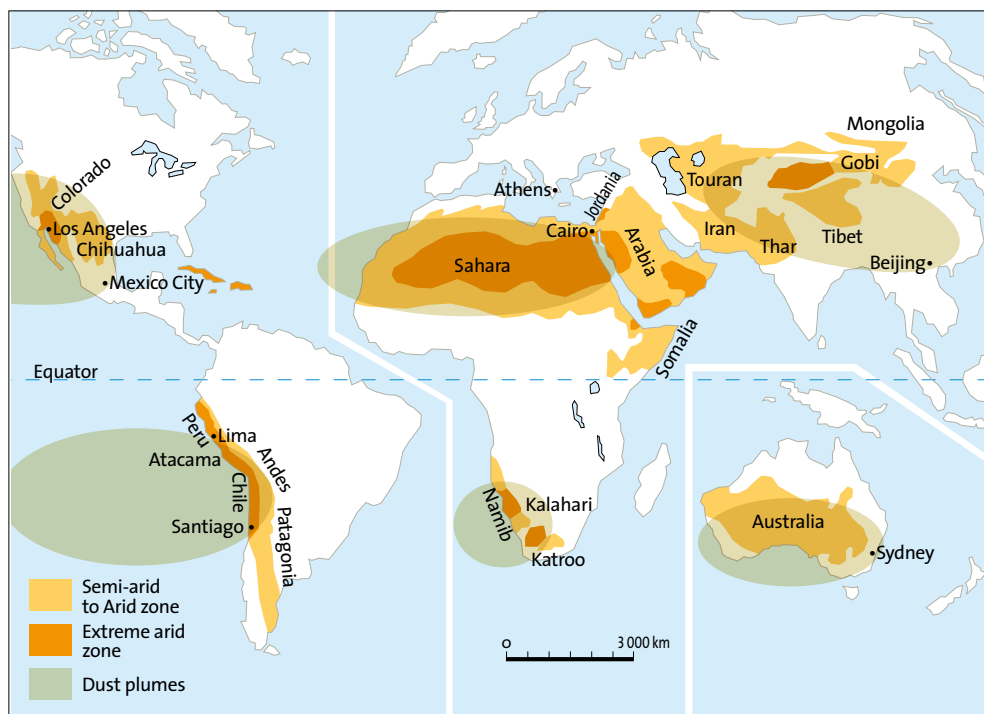
Urban particles in the context of global climate change

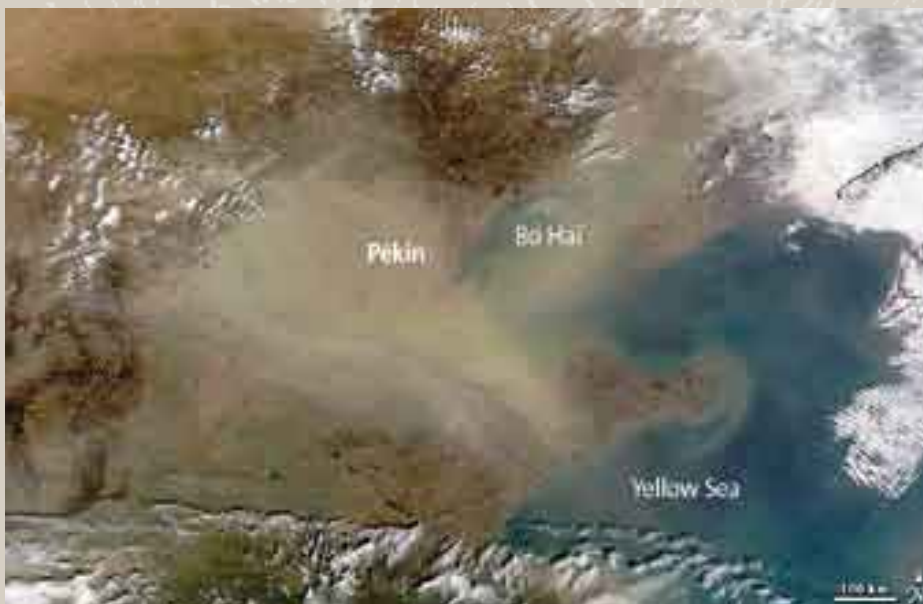
Recent information points to changes in dust events (Sahara, Australia, China) and stresses their impact on some urban areas. Climatic forcing parameters linked with global changes (draughts, deflational wind power, eolian erosion...) may be responsible for these changes, as may anthropogenic activities (figure 2). For example, dust events in 2006 generated 300 000 t of sand over Beijing, resulting directly from desertification coupled with extensive tapping of groundwater increasing soil dryness. Among the arid zones that are the main source of particles, the Sahara and Gobi deserts are the greatest contributors, although the former's impact on urban areas (in terms of number of inhabitants affected) is fairly minor (figures 3 next).

Earlier studies generally consider particle quantity (i.e., concentrations in g per m^3 , e.g. the review by Harrison, 2004), basic particle chemistry [Lenschow *et al.* (2001)] or both [Artiñano *et al.* (2003)]. Recent work shows that it is difficult to unravel the different atmospheric particle sources without analyzing their isotope content [Widory & Fiani (2008)].

Figure 2: Location of the world's main arid areas and the extension zones of dust plumes.

Figure 2 : Localisation des zones arides et zones d'extension des panaches de poussière.





Urban particles and health issues

Health impacts of particles in urban atmospheres have long been well documented [Pryor & Barthelmie (1996); Harrison (2004)]. Particulate matter in the air including PM_{10} (particles with an aerodynamic diameter $<10 \mu m$) directly influences mortality levels and respiratory-disease-related hospital admissions. Aerosols vary in size up to ten microns in diameter and exhibit a wide range of chemical compositions. Their origin may be either primary (direct emission into the atmosphere through processes of combustion or natural alteration) or secondary (post-emission formation in the atmosphere, e.g. nitrate in aerosols which results mainly from the degradation and conversion of gaseous nitrous oxides).

“Particulate matter in the air directly influences mortality levels and respiratory-disease-related hospital admissions.”

The air in many big cities contains high concentrations of fine particles. Concentrations of PM_{10} particles can reach $300 \mu g \cdot m^{-3}$ [Seinfeld & Pandis (1997)]. Fine atmospheric particles harmful to public health have recently raised major concern (e.g., the ERPURS project for Paris; [Dab (1998)]). Little stable-isotope work has been devoted to atmospheric particles in urban environments, and fewer studies yet have used nitrogen isotopes, despite preliminary evidence they could be a potential tracer [Widory & Fiani (2008)].

Particles $10 \mu m$ or less in size often display a bimodal distribution: fine particles (diameters $<2.5 \mu m$) and

coarse particles (diameters $2.5-10 \mu m$). The origins of these two size fractions, their chemical and physical properties, spatial distributions and deposition processes generally differ. $PM_{2.5}$ results primarily from combustion processes and gas-to-particle conversions, while particles in the coarse size fraction (PM_{10}) may be linked to mechanical processes (e.g. airborne dust).

Isotopes: applications for characterizing urban atmospheric particles

Isotopes can be used in two ways to trace the source and processes of particles in urban atmosphere. The first involves sampling, analysis and characterization of the particles in an overall context, while the second samples particles either in central or outlying areas of the city and characterizes sources (diesel, central heating, industries...). The first approach was developed in Lyon (France) using lead isotopes, while the second was applied in Paris (France) using carbon and lead isotopes and Beijing (China) using lead and strontium isotopes.

Physical characterization and lead isotopes in the Lyon atmosphere

Aerosols were collected at regular intervals in metropolitan Lyon over a 5-month interval in 1999. Their size distribution obtained by laser grain-size analysis shows that 50 % have diameters of less than $7.5 \mu m$ and at least 10 %, diameters of less than $1.5 \mu m$. These latter present the greatest threat to human health, for particle size strongly influences what happens to them. Coarser particles ($2.5 - 10 \mu m$) deposit mainly in the upper respiratory tract due to impaction, interception, gravitational sedimentation, and dispersion. Fine particles (less than $2.5 \mu m$), like those generated by combustion processes, are quite liable to penetrate the deeper areas of the respiratory tract due to their high diffusivities.

▲ **Figure 3:** (left) Influence of the Gobi desert on a dust event in China; and (right) of the Sahara over southern Europe.

Figure 3 : (gauche) Influence du désert de Gobi sur les tempêtes de poussières en Chine ; et (droite) du Sahara en Europe méridionale.

Source : NASA.



“ Following the phase-out of leaded petrol, industrial activities have now taken over as the major source of atmospheric lead. ”

The most common particle in Lyon consists of gypsum of unknown origin, with organic matter present in large quantities. Smaller particles rich in heavy metals and small minerals such as micas, feldspars and some clays make up the remainder. Lead isotopes and lead content in the aerosol samples vary little. Lead isotopes occur as three distinct end-members: natural Pb (the lead isotope signature in pre-industrial period sediments), industry (all industrial activities), and road traffic (regular and unleaded petrol are isotopically distinct, while lead concentrations in diesel emissions are below the detection limit of 1 mg L^{-1}). Simple binary calculations in 1999 found that a substantial proportion (40 to 70 %) of the lead in aerosols came from road traffic, as for other cities in France at the time. Since then, however, with the phase-out of leaded petrol, industrial sources have taken over as the main source of atmospheric lead.

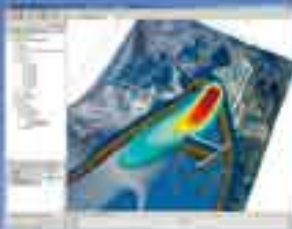
Matériels d'étude, surveillance et diagnostic pour:

Eaux souterraines et superficielles, sols, sédiments, déchets...

... Mesure - Télémessure - Acquisition et Interprétation de données



Mix/Micro/Cona/CTD-Diver



Logiciels: Visual Modflow, HydroGeo Analyst, AquiferTest Pro...



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▲
Atmospheric particles in the Paris air.
Particules atmosphériques dans le ciel de Paris.
 © PhotoAlto

Stable carbon and lead isotopes in the Paris atmosphere

The main sources of atmospheric particles in the Paris air are road traffic, heating and waste incineration. Sources were extensively sampled including motor vehicles (regular or unleaded petrol and diesel), central heating sources using all types of fuels (fuel oil and natural gas), and emissions from distinct waste incinerators. In parallel, ambient PM₁₀ particles were collected in the Paris atmosphere.

Carbon concentrations fluctuate considerably (1% to 96%, figure 4), and the corresponding δ¹³C, ranging from -22.6‰ to -38.0‰, also discriminate among the different pollution sources. Stable carbon isotopes effectively distinguish emissions from waste incineration, also discriminating diesel emissions from the rest of road traffic. While chemically similar diesel and fuel oil yield particles with comparable isotope compositions, diesel emissions contain more carbon). Waste incineration has no visible influence on particulate matter.

Improving air quality in Beijing: the added value of isotopes

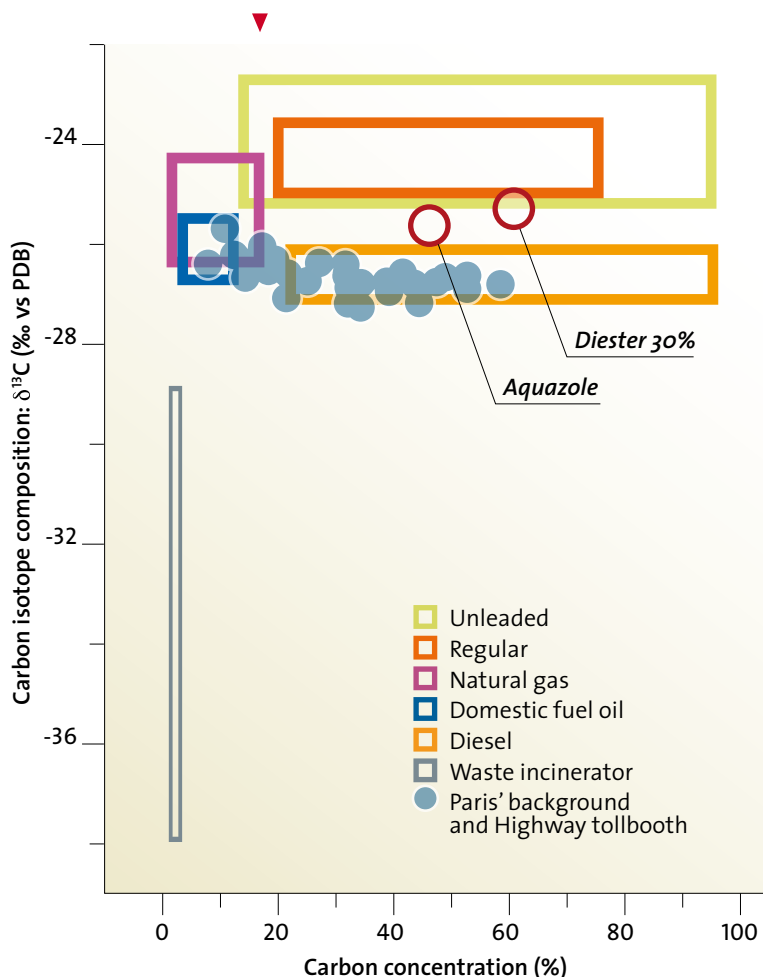
Traffic is progressively being eliminated as one of the main vectors of lead air pollution due to the prevalence of unleaded gas. The shift in the aerosol signature in the Paris atmosphere towards the industrial one (cf. boxed text) suggests that it is a reliable tracking tool for aerosol sources.

Figure 4: Tracking the origin of particles in the atmosphere of Paris and its vicinity via a coupled approach between carbon concentrations and isotope compositions (δ¹³C).

From Widory and Fiani, 2008.

Figure 4 : Traçage de l'origine des particules dans l'atmosphère de la région parisienne par une approche couplée entre les teneurs en carbone et les isotopes (δ¹³C).

D'après Widory et Fiani, 2008.



With the 2008 Olympics on the horizon, Beijing awoke to the need to improve its air quality. Lead gas was phased out in 1997. However, while its atmospheric concentrations have decreased slightly, levels can still reach $0.3 - 0.4 \mu\text{g}\cdot\text{m}^{-3}$. Industrial emissions such as non-ferrous metal or coal-combustion industries are typical suspects, but so far classical chemical methods have been unsuccessful in determining respective source contributions.

To this end, we adopted a two-step methodology to test lead and strontium isotope systematics: 1) characterization of all potential pollution sources, i.e. typical Chinese soils, coal combustion fly ash, cement factories, smelters and lead refining plants and 2) dual-isotope characterization of ambient air samples (total suspended particles and fine fractions) to identify their main source and determine respective contributions.

► ISOTOPES: A METHOD TO CHARACTERIZE AND MONITOR PARTICLES IN URBAN ATMOSPHERES

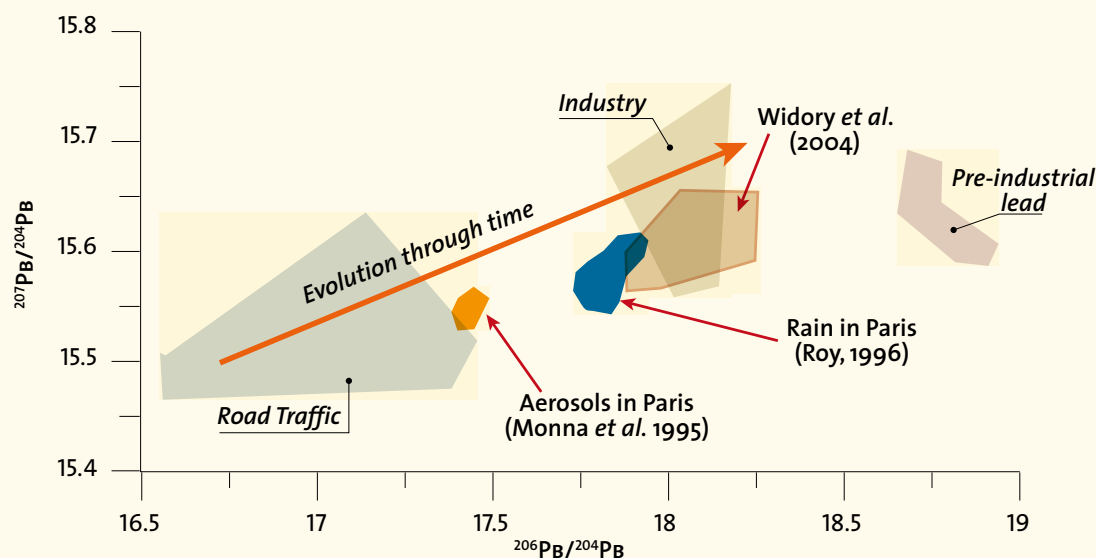
Atoms consist of a nucleus surrounded by electrons that are negatively charged; the nucleus is composed of neutrons with no electric charge and positively charged protons. The number of protons is equal to the number of electrons, so the atom as a whole is electrically neutral. The sum of protons and neutrons is the nuclear mass number. In the most abundant nuclides of the light elements, the numbers of protons and neutrons are equal, while for the heavy elements the number of neutrons far exceeds the number of protons. Thus, instabilities are caused by an excess of protons or neutrons: for instance ^3H or ^{14}C are unstable (or radioactive).

All the isotopes of a chemical element have the same atomic number (same number of protons), the same name and are located at the same place in the periodic table of the elements: only their atomic mass ($p+n$) differs.

In the case of radioactive isotopes, isotopic proportions change over time, whereas with stable isotopes, proportions remain constant unless modified by isotope fractionation related to physical/chemical/biological processes. Such modifications can be detected by isotopic ratio measurements, thus highlighting specific processes, which then helps reconstruct the element's "story". Radiogenic isotopes of heavy elements, on the other hand, are not fractionated by these processes. For such isotopic tools, there is therefore a direct link between the source and the receptor (Sr for $^{87}\text{Sr}/^{86}\text{Sr}$, Pb for $^{206}\text{Pb}/^{204}\text{Pb}$).

An illustration can be drawn from the use of lead isotopes in the Paris atmosphere. Since the mid 90's, emissions from many atmospheric-Pb sources in France have been isotopically characterized. Results distinguish three end-members,

corresponding to 1) road traffic, 2) industry, and 3) pre-industrial sediments. Lead in aerosols in Paris (*see figure*) is mainly industrial in origin, although specific samples may reflect a natural input. Lead-isotope ratios can also be used to monitor the evolution of atmospheric-Pb origin over approximately the past decade in Paris. Aerosols collected in 1995 unquestionably designate road traffic as the main pollution source, while data after 1996 suggest that samples are moving from petrol towards the industry end-member. This trend is confirmed by recent results [Widory *et al.* (2004)], the contribution of road traffic being proven to be minor. In nearly ten years' time, the main source of atmospheric lead in Paris shifted from road traffic to industry, clearly due to the phasing out of tetraethyl lead from gasoline. ■



► Discriminating lead sources in the Paris atmosphere based on isotope ratios. Evolution of the impact of Pb sources in the atmosphere over time.

In Widory *et al.*, 2004.

Utilisation des isotopes du plomb pour discriminer les sources de plomb dans l'atmosphère de Paris. Evolution de l'impact des sources de Pb dans l'atmosphère au cours du temps.

D'après Widory *et al.*, 2004.

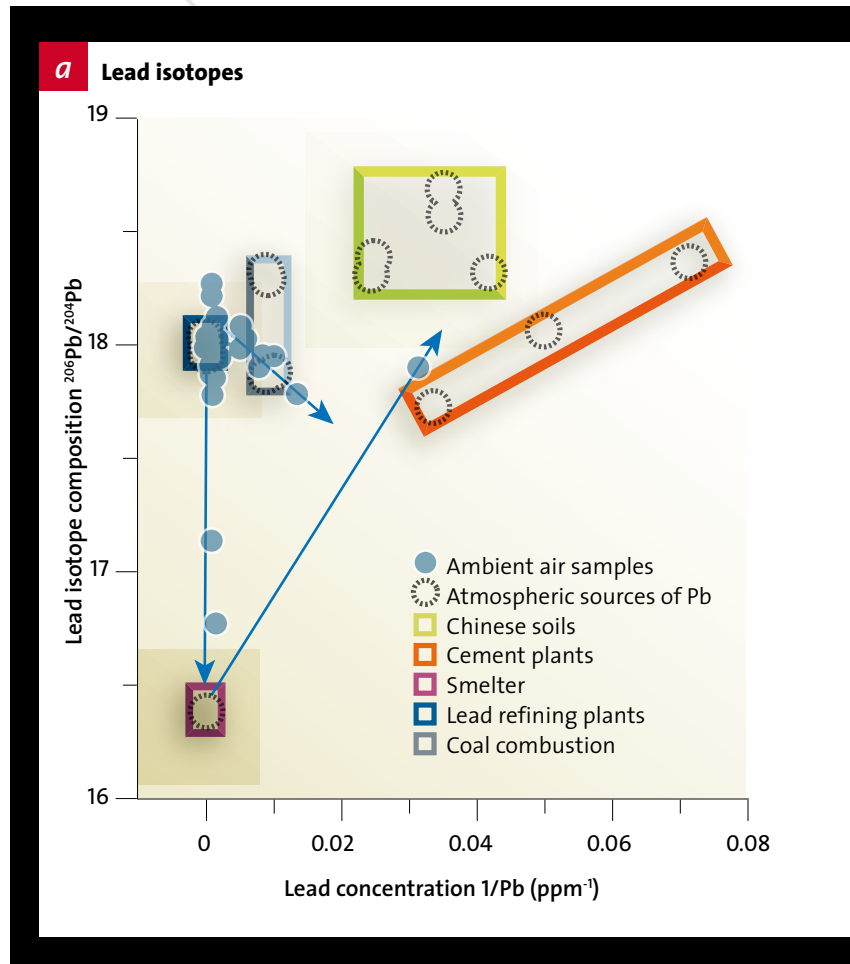
Pollution sources are significantly discriminated by lead and strontium isotope ratios (figures 5a and 5b), confirming that these are reliable tools usable as direct tracers of pollution vectors. Ambient air samples from three different locations in and around the capital city (Chegongzhuang, Liangxiang and Changping) show that the atmospheric lead budget is mainly controlled by a ternary mixing relationship, indicating that:

– Emissions from lead refineries are the main vector of lead in the air (total suspended particles or fine fraction), followed by coal combustion in the total suspended particle fraction. Emissions from smelters are isotopically detectable under specific weather conditions in both total suspended particles and fine fractions.

– The strontium isotope systematic confirms the implication of the studied sources in the overall aerosol budget. Coal combustion and emissions from cement plants are major contributors to Sr levels in the city’s atmosphere, but emissions from both smelters (fine fraction) and “Chinese soils” (total suspended particles fraction) are isotopically detectable.

This confirms that aerosols must be seen as a potential integrator of emissions from distinct origins depending on the studied isotope systematics. These results should help local authorities define an improved air-quality management plan to lower aerosol lead levels.

“Aerosols must be considered as a potential integrator of emissions from several distinct origins.”



“Classical” carbon and lead isotopes emerge as useful tools both for discriminating sources of aerosols in the urban atmosphere and the semi-quantification of their respective contributions at any given time and location:

– Carbon isotope ratios relate directly to pollution sources. While emissions from diesel traffic are still subject to debate, carbon isotopes emerge as a major vector of pollution in the PM₁₀ fraction, and the only one in PM_{2.5}, whatever the sampling environment (background or influenced by road traffic).

– Before its phase-out in 2000, lead isotopes were able to discriminate road traffic from industrial sources and “terrigenous” lead (in sediments), but discrimination between these pollution sources is now no longer possible. In some cases like China, however, their use is still valuable, especially in identifying the environmental impact of industrial emissions.

– The heterogeneity of pollution origins evidenced by different isotope systematics (for identical samples)

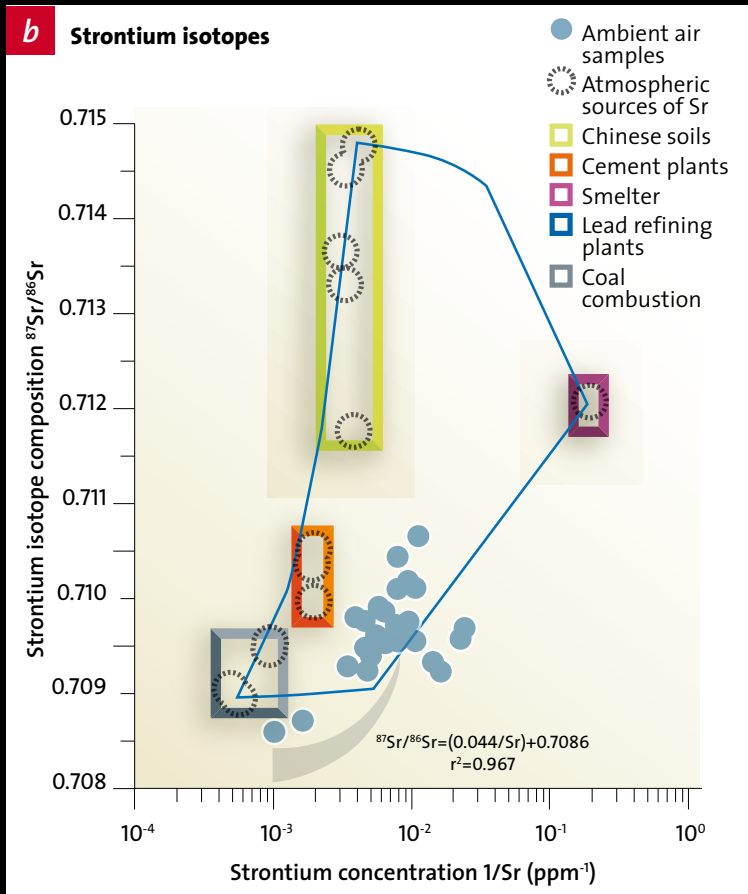


Figure 5a and 5b:
Improving knowledge
of air quality in Beijing
in view of the '08 Olympics
using the dual-isotope
approach (lead & strontium).

From Widory and Fiani, 2008.

Figure 5a-5b :
Améliorer la connaissance
de la qualité de l'air à Pékin
dans le cadre des Jeux
Olympiques de 2008 par une
approche isotopique couplée
(plomb et strontium).

D'après Widory et Fiani, 2008.

confirms the idea that aerosols are atmospheric integrators of various scenarios. For example, in the same PM_{10} sample, $\delta^{13}\text{C}$ may identify diesel as the main source of carbon, while another systematic, such as $^{87}\text{Sr}/^{86}\text{Sr}$, may show that strontium is from waste incineration. Different size fractions from distinct origins can coagulate, post-emission, within a single final particle size. Furthermore, conclusions about differences between carbon- and lead-isotopes (e.g. Paris) underline differing behaviours of organic and inorganic phases in aerosols. These may have various origins and their own specific isotope compositions. Post-emission processes in the atmosphere then form particles with distinct isotope signatures. The isotope combination initially believed to be a unique tracer of atmospheric particle sources actually turns out to be a combination of two distinct tracers, each procuring a better definition of the origin of both organic and inorganic phases in the aerosols.

This probably paves the way for a wider field of investigation based on the study of other isotope systematics. Recent developments, particularly in the field of MC-ICP-MS analyses, now allow precise isotope analyses (with an analytical precision of a few nanograms, compatible with levels observed in ambient air) of elements such as Cr, Hg, Zn or Cd (species recognized as deleterious to public health). First results show that Cd and Zn isotope systematics (and their coupling [Widory and Fiani (2008)]) are excellent discrimination tools to track the origin of these metals in the atmosphere. ■



Particules atmosphériques urbaines

L'origine des particules dans l'atmosphère urbaine ainsi que les impacts des multiples sources potentielles prêtent toujours à débat, de nos jours, dans la communauté scientifique. L'approche chimique « classique » (généralement utilisée dans cette problématique) ne peut permettre de lever sans ambiguïté l'incertitude sur l'origine des particules, mettant ainsi en exergue le besoin pour de nouveaux paramètres et outils. Cet article balaie l'ensemble des méthodes isotopiques récemment employées et d'intérêt fort dans la problématique du traçage des sources de particules dans l'atmosphère des villes. Leur application dans des villes d'importance comme Paris, Lyon et Pékin est présentée, et les outils mis en œuvre dans ces études discutés en termes de potentiel et de limites. Ces nouveaux outils permettent de tracer les sources majeures de particules impliquées dans la pollution des zones urbaines (origine naturelle, industrielle, liée aux véhicules, au chauffage collectif...), mais également de mieux caractériser et quantifier les processus secondaires pouvant affecter le budget des particules atmosphériques. Les systématiques isotopiques discutées sont celles du carbone (^{12}C & ^{13}C), de l'azote (^{14}N & ^{15}N), du plomb (^{204}Pb , ^{206}Pb , ^{207}Pb & ^{208}Pb) et du strontium (^{87}Sr & ^{86}Sr).