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**Air-quality measurements in megacities: Focus on gaseous
organic and particulate pollutants and comparison
between two contrasted cities, Paris and Beijing**

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Abstract

The rapid and important development of large urban areas ('megacities'), especially in developing countries, causes and will cause serious air-quality problems. Pollutant measurements in these cities help to characterize the chemical nature and the quantity of these pollutants and to constrain air-quality models. This paper focuses on measurements of volatile organic compounds and aerosols that have an important impact on air quality. We present a brief review on existing measurements and experimental strategies in megacities and then we show results from recent measurement campaigns that took place in two contrasted megacities: Paris and Beijing. **To cite this article:** *V. Gros et al., C. R. Geoscience 339 (2007).*

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Résumé

Mesures de la qualité de l'air dans les mégapoles : zoom sur les polluants organiques gazeux et particulaires et comparaison entre deux villes contrastées, Paris et Pékin. Le développement rapide et important des grands centres urbains (« mégapoles »), tout particulièrement dans les pays émergents, cause et causera de sérieux problèmes de qualité de l'air. Les mesures des polluants gazeux et particulaires dans ces villes aident à caractériser la nature chimique et la quantité de ces polluants et à contraindre les modèles de prévision de la qualité de l'air. Dans cet article, nous nous intéresserons aux composés organiques volatils et aux aérosols qui ont un impact important sur la qualité de l'air. Nous présenterons tout d'abord une brève revue des mesures existantes et des stratégies expérimentales dans les mégapoles ; ensuite, nous montrerons des résultats obtenus lors de campagnes de mesures récentes dans deux mégapoles contrastées : Paris et Pékin. **Pour citer cet article :** *V. Gros et al., C. R. Geoscience 339 (2007).*

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1. Introduction

Studies of the anthropogenic impact on atmospheric composition have become of primary importance. Urban areas, especially megacities, are relevant to air-quality discipline, but also, and this is a new feature, to global change discipline. Models are needed to evaluate future changes of air composition and its implication on climate change (and also the climate feedback on air composition). However, before working on future scenarios, models need to be evaluated against measurements, which remain also the only means to get a ‘real’ picture of the current air pollution in megacities. In addition, observations may help to pinpoint new processes that may be specific to megacities, i.e. huge emissions of a large pool of pollutants originating from various sources (transport, industry, heating). Megacities, although generally confined on a relatively small area, are associated with such large emissions of pollutants that they can sometimes be larger than emissions from a whole country [13]. These processes can then be included, after parameterization, in the models.

The ongoing development of new megacities (eight in 1950, 41 in 2000, and 59 planned in 2015, megacities defined here as urban zones with more than 10 million inhabitants) concerns mainly developing countries where the high level of emitted pollutants constitutes a real risk for population health. In addition, most of these megacities are located in the tropical zones associated with a high level of photochemistry (which favours formation of secondary pollutant) and deep convection (which redistributes pollutants at larger scale). Therefore, organisms like the World Health Organization have initiated programs aiming at measuring (and if possible improving) air quality in these large urban centres. Pollutants that should be measured at the first place are those relevant to health issues (SO_2 , O_3 , NO_2 , CO , C_6H_6 , Pb , and aerosols). A striking point from the important data compilation produced by [3] resides also in the regional specificity of pollution, ozone, and NO_x , appearing to be the ‘common denominator’ of developed countries, whereas particulates are found at very high concentration levels in developing countries’ cities.

This paper focuses on specific gas-phase (carbon monoxide and volatile organic compounds, including benzene) and particulate-phase compounds. This choice is based on the fact that (i) these compounds cover all the important sources found in megacities (transport, industry, heating, cooking, solvent...), (ii) they have direct impact on health (CO , benzene, aerosols), and direct or indirect impact on radiative forcing (aerosols,

CO , VOCs), (iii) they are linked through the conversion from some VOCs to secondary organic aerosols, (iv) in urban centres, the photochemical regime is usually VOC-dependent (i.e. to reduce ozone levels, it is necessary to reduce VOC levels), whereas it becomes NO_x -dependent when moving to peri-urban or rural locations, and (v) monitoring of these compounds in urban centres is not yet systematic (difficulties associated with sampling and analyses of speciated VOCs, of fine particles...).

VOCs¹ include hundreds of compounds (hydrocarbons, oxygenated compounds...) and present a large variety of sources (biogenic/anthropogenic, primary/secondary) as well as a large variety of reactivity (lifetime from hours to years). The compounds of interest for megacities are the reactive anthropogenic VOCs (largely dominant in urban areas). VOCs’ main sink in the atmosphere is their reaction with the OH radical, and therefore they affect photochemical regimes, ozone formation, and organic aerosol cycle. In addition, some VOCs are toxic, as benzene, known for its carcinogenic properties. The main anthropogenic VOC sources are issued from traffic emission (fuel combustion and/or evaporation), residential emission (heating, cooking...) and industrial emissions (energy, solvent production...). Quite detailed emission databases of VOCs exist for developed countries (see for example EMEP for European countries), but are still sparse for developing countries. Most of the time, emission factors are extrapolated from those used in industrialized countries, but this extrapolation is often arbitrary (multiplication by a factor 2 for example) and not representative of the real emissions.

Urban aerosols originate from a multitude of sources and are very diverse in chemical composition and structure. Determining their chemical composition is essential to understand their properties and reactivity, and hence their environmental effects. Fine (and coarse) particles are usually defined as particles having diameter smaller (larger) than $2.5\ \mu\text{m}$ and have shown to present contrasted chemical composition in urban atmosphere. Coarse particles in urban areas usually tend to be mechanically generated and are composed of materials such as tyre dust as well as sea salt and dust. Fine particles (accumulation and nucleation mode) tend to be produced either directly from combustion sources (black carbon and organics of primary origin), or by

¹ Although carbon monoxide is by definition not an organic compound, it is in this study implicitly involved in the generic term ‘VOCs’ (as it has similar sources and chemical behaviour as the VOCs studied here).

gas-to-particle conversion involving reaction products of sulfates, nitrates, ammonium, and organics. Urban aerosols originating from ‘megacities’ in developing countries are likely to differ in a number of ways from cities that have been studied in the USA and in Europe. Less strict regulations in these megacities will allow the production of higher levels and more complex (and possibly more toxic) aerosols. In addition, while many types of VOC and aerosol sources can be similar in megacities, many of the cities are marked by numerous and various area sources, spread across an extensive urban landscape, as opposed to traffic-related automobile emissions that characterize the emissions from large cities in industrialised countries. Finally, VOC and aerosol sources will also be changing over time as megacities develop and technology evolves.

This paper will describe briefly the existing measurements in megacities (air-quality networks and dedicated field campaigns) and will then focus on two contrasted megacities (Paris and Beijing), detailing the chemical air composition in terms of the selected species.

2. Air-quality measurements in megacities

2.1. Air-quality networks

Except the earliest urban dataset of ozone in the centre of Paris from 1877 to 1910 [30], systematic measurements of ozone and other pollutants in urban centres of developed countries are performed since some decades. These air-quality networks are managed by local authorities or independent agencies and monitor primarily regulated pollutants (see <http://ec.europa.eu/environment/air> for European norms), which include gas-phase compounds (SO₂, O₃, NO₂, CO, benzene) and aerosol compounds (PM₁₀, particulate matter –PM– for particles with aerodynamic diameter less than 10 µm). VOCs, except benzene, are rarely measured on a long-term basis, due to the large variety of compounds involved and the high costs associated with measurements of speciated VOCs.

The coordination of air-quality management issues is made by NARSTO (<http://www.narsto.org/>) for North America and by organisms such as EEA (<http://www.eea.europa.eu/>) and EMEP (<http://www.emep.int/>) for Europe. New initiatives focused on specific megacities issues are emerging (see for example <http://www.megacities.uni-koeln.de/index>). The challenge for air-quality networks already well developed is to adapt rapidly their capacity to improve existing

measurements, to measure new identified pollutants, and/or to use new measurement techniques.

For megacities located in emerging countries, air-quality measurements are more recent (Asia, South America), and sometimes still in their infancy (Africa). Current efforts should be continued to help development of air-quality measurements and subsequent improvement in these continents (see for example the initiatives from the urban program of GAW, which aims to study and improve air quality in megacities like Beijing, Moscow, or South American cities, http://www.wmo.ch/web/arep/gaw/gaw_home.html).

2.2. Brief review of existing field measurements in megacities

In the context of air-quality and health impacts, experimental strategies primarily aim to understand better the sources of ambient VOCs and aerosols at the scale of the megacity. Such studies improve and will improve the ability of regulators to enact controls that will be most effective in reducing photooxidant and aerosol pollution. Air-quality monitoring and previous campaigns in megacities from developed countries have already brought substantial information on emission inventory diagnostics, on concentrations and trends of pollutants, on the link between pollutant concentration and population exposure [2,16,18,19,23,29, and references therein]. More specifically for VOCs and aerosols that have multiple sources, exhaustive chemical characterizations are performed and serve in multivariate receptor models and/or statistic tools (such as Positive Matrix Factorization, PMF) to apportion the number of sources and their composition profiles. Many of these source-apportionment studies have been performed in megacities (see for instance [27] for Beijing, [14] for Mexico, [28] for Mumbai, [6] for São Paulo, [15] for Seoul).

In the context of climate change, intensive field campaigns that coordinate and integrate observations from ground stations, aircraft, and satellites are clearly needed here, as they will provide a rich database for improving regional and global climate models of the transport and transformations of aging urban pollutants. So far, the MILAGRO Experiment, where several ground-based stations as well as several aircrafts were deployed in March 2006 in order to characterize the air pollution of Mexico City from the local to the continental scale, represents the most accomplished large-scale experiment in one of the largest megacities in the world. Results from this campaign are currently under investigation (<http://www.eol.ucar.edu/projects/milagro/>).

3. Focus on two contrasted megacities: Paris and Beijing

3.1. Experimental

We have chosen to present here results obtained recently in Paris and Beijing. These two megacities represent contrasted situations in terms of development, nature of the pollutants emitting sources, meteorology, and photochemistry. Beijing, the Chinese capital, faces the challenge of improving its atmospheric environment while seeing an annual growth rate of 15% in the number of personal vehicles on the road. Note that the period of the year is slightly different for both campaigns, summer for the Beijing campaign versus spring for the Paris campaign.

A three-week experiment was performed during August 2004 in downtown Beijing. A detailed description of the sampling site is given in [10]. Briefly, the sampling site is located at 4 km west from Tiananmen Square, between the Second and the Third Ring Roads, and at the top of the Beijing Municipal Environmental Monitoring Centre (BMEMC) building, roughly about 30 m above ground level.

The LISAIR campaign took place in the centre of Paris (city hall parvis) in May 2005, a location strongly influenced by traffic of the important roads surrounding the measurement place. An instrumented truck allowed in-situ measurements, including O_3 , NO_x , CO, and NMHCs for the gas phase.

CO was monitored in situ in both campaigns, by a gas chromatograph coupled with a mercuric oxide reduction detector with an uncertainty of about 1% [8]. For determination of VOCs, two gas chromatographs equipped with flame ionization detectors (GC-FID, Chromato-Sud, France) were used in Paris, allowing measuring C_2 – C_6 and C_6 – C_{12} non-methane hydrocarbons. During the Beijing campaign, 36 flask samples were collected and were measured subsequently in laboratory by GC-FID and GC-MS [8,9] for the same non-methane hydrocarbons. The overall uncertainty of VOC measurements is estimated at better than 15%.

Aerosol samples were collected at the Paris and Beijing sites on 47-mm diameter pre-fired quartz fibre filters (QMA, Whatman) for the analysis of black carbon (BC) and organic carbon (OC) contents, and with Stacked Filter Units (SFUs) for gravimetric measurements and ion analysis. A detailed description of the methodology used for the carbon, gravimetric, and ion analyses performed on the filters can be found in [25]. The sampling time was typically of 12 h for the SFUs and quartz filters in Paris, and 6 h in Beijing. The

SFUs consist of an 8- μ m-pore-size 47-mm-diameter Nuclepore polycarbonate filter mounted in front of a 0.4- μ m-pore-size 47-mm-diameter Nuclepore filter. At our flow rate of 1 m³/h, the 50% cut-point diameter of the 8- μ m-pore-size filter was estimated to be of the order on 2- μ m aerodynamic diameter (AD). In this paper, the aerosol coarse fraction refers to the particles collected on the 8- μ m-pore-size filters and thus having a diameter larger than 2 μ m AD. PM and ion concentrations in the coarse mode were derived from the analysis of the 8- μ m-pore-size filter. Particulate organic matter (POM) and BC concentrations in the coarse mode were derived from the bulk measurements performed on the QMA filters, assuming that 75% and 90% of these species are located in the fine mode. The previous distributions between fine and coarse modes were derived from the results of low-pressure cascade impactors (13-stage Dekati Impactor) obtained during both campaigns ([10] and Favez et al., manuscript in preparation).

A chemical mass balance for fine and coarse particles was performed for Paris and Beijing aerosols, following the procedure described by [10] and [25]. Following the results reported by these authors, a calcium-to-dust conversion factor of 12 was first adopted to calculate the concentration of dust aerosols from the calcium measurements determined by ion chromatography. This value of 12 is an average of the calcium-to-dust ratios proposed by [11] for Beijing (summer 2003 and 2004) and Paris (Paris and Gonesse).

Another uncertainty arises here from filter-based measurements of semi-volatile nitrate aerosols that are likely to be affected by significant sampling artefacts, as thermodynamic equilibrium between gaseous HNO_3 and particulate NO_3^- will evolve in time with air temperature and relative humidity variations. For that reason, filter sampling duration was kept here as short as possible in order to minimize changes in gas-to-particle equilibria and subsequent sampling artefacts. Although the extent of filter sampling artefacts on nitrates was not evaluated in Paris, reliability of filter sampling nitrate measurements was assessed in Beijing by the very good agreement obtained between nitrate concentrations derived from both filter sampling and artefact-free Steam-Jet-Aerosol-Collector coupled with ion chromatography [26]. An OC-to-POM conversion factor of 1.4 was adopted here for both datasets to calculate the concentration of organic matter (in μ g/m³) from the results of OC (in μ gC/m³). This factor is commonly taken in the literature for freshly emitted carbonaceous urban aerosols. The reconstructed particulate matter (PM) – derived from the chemical analyses – is defined as the

sum of BC, POM, ammonium, sulfate, nitrate, dust, and sea-salt aerosols. This reconstructed PM was obtained for both fine and coarse modes, and it is compared in the following to the measured PM derived from the weighing of SFUs.

3.2. Chemical air composition

3.2.1. Chemical air composition for selected VOCs

Fig. 1 represents the chemical air composition in $\mu\text{g}/\text{m}^3$ for selected VOCs measured in both megacities. Note that the lifetime of selected compounds ranges from a few hours (xylenes) to a few weeks (ethane). Keeping in mind that these measurements were performed at different times and with different measurement methods, this comparison gives some information on pollutant levels and on the polluting source influences. At first, we note that the overall concentration (for the measured VOCs) is half in Paris ($47 \mu\text{g}/\text{m}^3$) than in Beijing ($97 \mu\text{g}/\text{m}^3$). Then the study of individual species contribution shows significant differences, with for example a higher (lower) contribution of toluene and isopentane (benzene) in Paris than in Beijing. Therefore, the ratio benzene/toluene (ppb/ppb), often used in the literature as a photochemical air marker, differs significantly in both cities (0.98 ± 0.23 for Beijing, 0.15 ± 0.11 for Paris). Benzene and toluene have been shown to be emitted by automobiles in a ratio of approximately 0.50 ± 0.05 ([5,24] and references therein) depending on the motor type and the technology applied. The lower ratio observed in Paris is mainly due to the decrease of the benzene level (decrease of 85% between 1994 and 2006,

[1]), due to the reduction of the benzene content of fuels (European Directive No. 98/70/Ec, 1998). The relatively high benzene/toluene ratio measured in Beijing reflects the importance of other polluting sources, like charcoal combustions used for cooking, as suggested by the relatively high abundance of acetylene and other compounds emitted by combustion (CO, black carbon).

A first attempt to perform source apportionment on the Paris dataset [20] has suggested one dominant source for the heavier hydrocarbons (C6–C12), probably emission due to traffic (which would explain 79% of the observed variability). For the light hydrocarbons, the first three principal components are needed to explain 76% of the total variability (46%, 19%, and 11%, respectively). In addition to traffic, lighter compounds (C2–C5) were influenced by two additional sources. One source is probably due to fuel evaporation, as suggested by the high level of isopentane (typical tracer of the evaporation source) and its covariation with temperature. Indeed, the campaign was characterized by two different temperature regimes: from 18 to 23 May, the temperature range was $10\text{--}20^\circ\text{C}$, whereas from 24 until 26 May, it was $15\text{--}30^\circ\text{C}$. Contrary to acetylene, which shows no significant difference between both periods with similar baseline levels, isopentane shows an enhanced baseline level during the second period. This can be illustrated by comparing values recorded during the night, when traffic emissions were not yet active. For example, during the night of the 23 May (26 May), at 3.00 a.m., values of acetylene, isopentane, and temperature were $275 \mu\text{g}/\text{m}^3$ ($228 \mu\text{g}/\text{m}^3$), $897 \mu\text{g}/\text{m}^3$ ($3480 \mu\text{g}/\text{m}^3$), and 11.4°C (17.5°C), respectively. The second additional

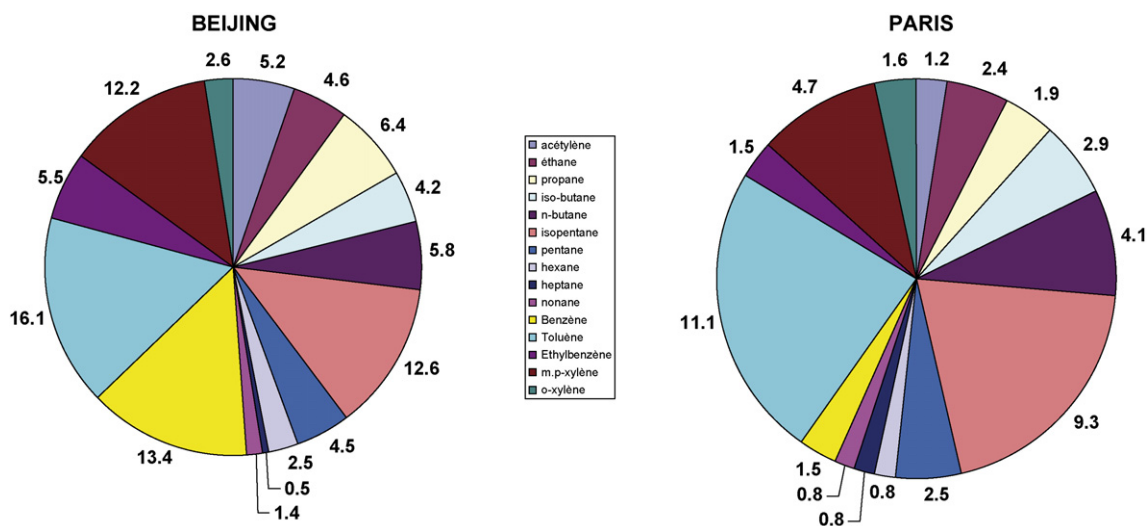


Fig. 1. Chemical air composition in $\mu\text{g}/\text{m}^3$ for selected VOCs in Beijing (a) and Paris (b).

Fig. 1. Composition chimique de l'air en $\mu\text{g}/\text{m}^3$ pour des COV sélectionnés à Pékin (a) et à Paris (b).

source contributing to the light compounds has not been identified, but these could come from long-range transport, as the lighter hydrocarbons have a relatively long lifetime.

The VOC levels measured in Beijing and Paris are compared with measurements performed in other megacities of developing countries in Table 1. This comparison is done for the C₆–C₁₂ hydrocarbons, as the lighter ones were not measured in the experiments referenced here. The main findings of this comparison are (i) the large range of variability observed for VOC levels in these megacities (a factor 10 between toluene level at Karachi and at Cairo), (ii) the significant difference between levels observed in Paris and in megacities of developing countries (this will be further commented in section III), (iii) the VOC main source in most of these megacities, identified as emissions from vehicle exhaust (one exception is the megacity of Mumbai, dominated by evaporative emission), and (iv) the need to perform more systematic measurements. Although these preliminary studies bring first information on the level and variability of VOCs in megacities, these results must be taken with caution for the following reasons. At first, most of these measurements rely on samples analysed later on in the laboratory and not on in-situ measurements. It is known that storage in such supports (canister, tubes filled with adsorbents) may induce measurement artefacts [21]. In addition, use of different calibration scales for VOC calibration is an important issue and makes difficult any comparison between absolute levels measured by different laboratories. Rappengluck et al. [22] have recently pointed out this issue in an international exercise

of VOC measurement intercomparison. Finally, and as pointed by the authors of these studies, the measurements reported here are representative of a given moment and therefore do not reflect the variability of the main processes controlling VOC levels and variations (emission, dynamics, and photochemistry).

3.2.2. Aerosol chemical mass balance

3.2.2.1. Beijing. The reconstructed versus measured PM for the 56 fine aerosol data points has shown a slope close to one (0.96) and good correlation coefficients ($r^2 = 0.94$), demonstrating the consistencies of our previous hypotheses. Using the methodology reported by [11,12] – which is based on the best fit between gravimetric and chemically derived aerosol mass –, a calcium-to-dust conversion factor of 0.09 (instead of 0.12) was taken here for the coarse mode. Sulfate and nitrate are almost fully neutralized by ammonium in the fine mode ($[\text{NH}_4^+](\text{nequiv}/\text{m}^3) = 0.90 ([\text{SO}_4^{2-}](\text{nequiv}/\text{m}^3) + [\text{NO}_3^-](\text{nequiv}/\text{m}^3)) - 0.02$; $r^2 = 0.98$; $N = 52$). Associated here with ammonium, nitrate exhibits a semi-volatile pattern that has shown to be mainly controlled by the physical state (dry/wet) of aerosols, leading to a complete volatilization for relative humidity rates below 60% [26]. The relatively high BC/OC ratios (0.55 ± 0.30 on average) in the fine mode suggest an important contribution of organic aerosols of primary origin. On the other hand, the poor correlation between BC and OC ($r^2 = 0.62$) suggests that these two components do not have a single origin (such as traffic), but most probably result from the mixing of multi-combustion sources, which is in line with the previous findings on VOC.

Table 1
Ambient concentrations of VOCs ($\mu\text{g}/\text{m}^3$) from studies referenced in § 3.2.1

Tableau 1
Concentrations ambiantes de COV ($\mu\text{g}/\text{m}^3$) d'après les études référencées au § 3.2.1

	Beijing	Cairo	Karachi	Manilla	Paris	São Paulo
Reference	This work	K2007	B2002	G1998	This work	G1998
Period	Summer 2004	Summer 2004	Winter 98	1995	Summer 2005	1995
Sampling	C	T	C	T	Online	T
Measurement	FID + MS	GC–FID	FID + MS	GC–FID	GC–FID	GC–FID
Sample number	36	12	78	?	—	?
Hexane	2.5	123.5	26.9	9.5	0.8	
Heptane	0.5	70.6	16.3	8.4	0.8	11.1
Benzene	13.4	87.2	16.9	12.6	1.45	16.7
Toluene	16.1	213.8	27.2	168	11.1	28.1
Ethylbenzene	5.4	43.3		21.9	1.5	6
<i>m,p</i> -Xylene	12.2	140.8	13.7	55.8	4.7	18.5
<i>o</i> -Xylene	2.6	73.8	4.9	16.8	1.6	6.2

G1998: Gee and Sollars [7], B2002: Barletta et al. [4], K2007: Khoder [17].

T: sampling on a tube filled with adsorbents, C: sampling in a stainless steel canister previously evacuated, GC–FID: gas chromatograph coupled with a ion-flame detector, GC–MS: gas chromatograph coupled with a mass spectrometer.

Table 2

Concentration and associated standard deviations of the main chemical species of fine and coarse aerosols (in $\mu\text{g}/\text{m}^3$) in Paris and Beijing

Tableau 2

Concentration et déviations standard associées des principales espèces chimiques d'aérosols fins et grossiers (en $\mu\text{g}/\text{m}^3$) à Paris et à Pékin

Chemical species	Paris Fine mode (A.D. < 2.0 μm)	Paris Coarse mode (A.D. > 2.0 μm)	Beijing Fine mode (A.D. < 2.0 μm)	Beijing Coarse mode (A.D. > 2.0 μm)
PM	18.4 ± 7.3	19.2 ± 9.7	56.7 ± 42.8	72.2 ± 48.6
Sulfate	2.3 ± 1.1	0.7 ± 0.4	13.5 ± 14.7	5.5 ± 7.5
Nitrate	1.5 ± 1.7	1.4 ± 0.6	6.7 ± 7.9	4.9 ± 4.0
Ammonium	1.3 ± 1.0	0.1 ± 0.1	10.0 ± 18.0	1.0 ± 1.8
POM ^a	10.2 ± 6.2	3.4 ± 2.1	15.1 ± 6.4	5.0 ± 2.2
BC	1.8 ± 1.2	0.2 ± 0.1	6.1 ± 3.8	0.8 ± 1.0
dust ^b	0.4 ± 0.4	12.0 ± 8.3	5.8 ± 4.5	44.9 ± 30.2

Chemical composition of fine/coarse aerosols (in $\mu\text{g}/\text{m}^3$) in Paris and Beijing.^a [POM] = 1.4 [OC].^b [dust] = [Ca²⁺]/0.12.

3.2.2.2. *Paris.* The reconstructed versus measured PM for fine and coarse aerosols have shown slopes close to 1 (0.98 and 0.97, respectively), but contrasted correlation coefficients ($r^2 = 0.67$ and 0.94, respectively). The poor agreement found here in the fine mode is not fully understood yet, but it could possibly originate from quartz-filter sampling artefacts inherent to the determination of semi-volatile organic species that have been shown recently to contribute significantly to the levels of POM in Paris during summertime (Favez et al., Atmos. Environ., submitted). As shown in Table 2, PM is equally distributed in the fine and coarse modes (18.4 and $19.2 \mu\text{g}/\text{m}^3$, respectively), although the distribution of the main chemical components shows a much larger discrepancy (Fig. 2). Inorganic salts and carbonaceous aerosols are the main chemical components of fine aerosols (more than 90% of the PM in the fine mode). Their contribution in the coarse mode is much weaker (roughly 30% of the PM) compared to dust particles, which totalize almost 65% of the PM in this coarse aerosol fraction. The BC/OC ratio averages 0.25 ± 0.06

for the duration campaign, a factor of 2 lower than that recorded in Beijing and in the lower range of ratios commonly reported in urban areas. The good correlation between BC and OC ($r^2 = 0.83$) strongly suggests a unique and similar source (traffic).

3.3. A comparative study of compounds level and variability in Beijing and in Paris

3.3.1. Carbon monoxide and benzene level and variability

Fig. 3(a and b) shows the carbon monoxide and benzene variations over one week for both campaigns. The difference in absolute levels of compounds is noteworthy, with a mean of $1703 \pm 1038 \mu\text{g}/\text{m}^3$ (1460 ± 890 ppb) CO and $13.4 \pm 7.2 \mu\text{g}/\text{m}^3$ (4134 ± 2200 ppt) benzene in Beijing, and $399 \pm 221 \mu\text{g}/\text{m}^3$ (342 ± 190 ppb) CO and $1.0 \pm 0.9 \mu\text{g}/\text{m}^3$ (319 ± 279 ppt) benzene in Paris. The values measured in Paris are in good agreement with the monthly means of CO ($357 \pm 92 \mu\text{g}/\text{m}^3$) and benzene ($0.9 \pm 0.4 \mu\text{g}/\text{m}^3$)

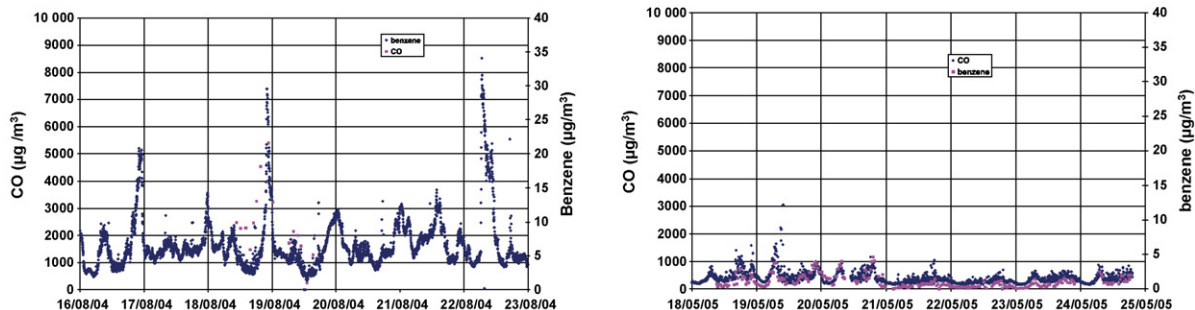


Fig. 2. One-week CO and benzene dataset in Beijing (a) and in Paris (b).

Fig. 2. Ensemble de données sur le monoxyde de carbone et le benzène, recueillies sur une durée d'une semaine à Pékin (a) et à Paris (b).

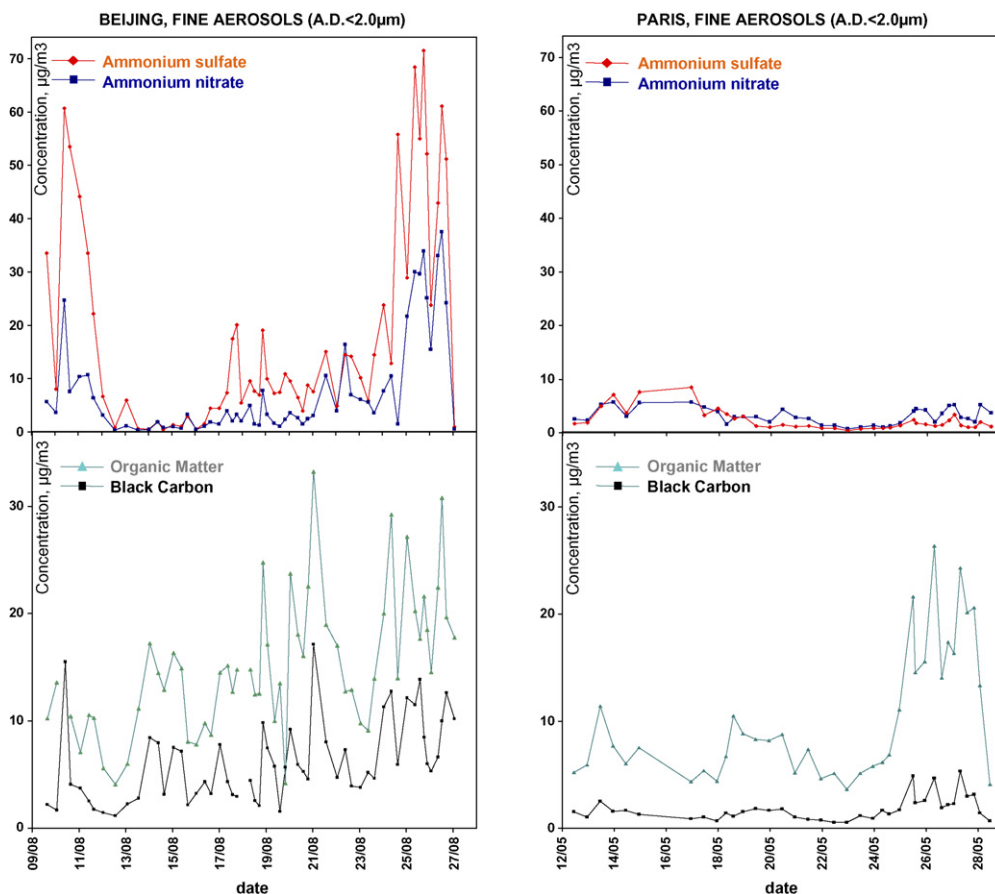


Fig. 3. Percentage mass contribution of the main chemical components of fine aerosols in Beijing and Paris.

Fig. 3. Pourcentage de la contribution en masse des aérosols fins à Pékin et à Paris (mai 2005).

measured at a close monitoring station (Châtelet) in May 2005 by the air-quality network Airparif (<http://www.airparif.asso.fr/>). As the values measured by Airparif in August 2004 ($312 \pm 74 \mu\text{g}/\text{m}^3$ CO, $0.7 \pm 0.5 \mu\text{g}/\text{m}^3$ benzene) are slightly lower than in May 2005, this means that the difference between the absolute values measured in Beijing and in Paris would be even greater if the measurements were made at the same time. Note that the difference observed between August 2004 and May 2005 is rather due to the seasonal variation than to the interannual variation. Therefore, the differences in absolute levels of pollutants between Paris and Beijing are real and reflect the very high rate of development of the megacity of Beijing in the course of these last years versus the already developed city of Paris. Note that the EU limit values (Directive 2000/59/EC) are $1000 \mu\text{g}/\text{m}^3$ (862 ppb) for CO (since 2005), whereas for benzene the limit applied in 2010 will be $5 \mu\text{g}/\text{m}^3$ (~ 1.5 ppb). The ratio benzene/CO (ppt/ppb) differs also significantly (0.9 in Paris, 2.8 in Beijing), in

agreement with the previous suggestion of a more complex mixture of polluting sources in Beijing.

A reproducible diurnal cycle of benzene and CO is observed in Paris, with values decreasing during the night and peaking in the early morning and in the late afternoon. This diurnal cycle is typical for cities influenced mainly by vehicular emissions. Note that on the weekend (21–22 May), there is only one broad peak during the day and the overall amplitude is lower, reflecting the lowering of the source related to traffic emissions during the weekend. As CO and benzene have quite a long lifetime (a couple of days for benzene, about 2 months for CO), photochemistry does not play a significant role in their diurnal variation. The main processes driving their diurnal cycle are rather the timing of the emissions and the boundary layer's height evolution, which varies from about 0.4 km during the night to 2 km during the day [20].

In Beijing, one observed also a large range of variability during the day, but the diurnal cycles are

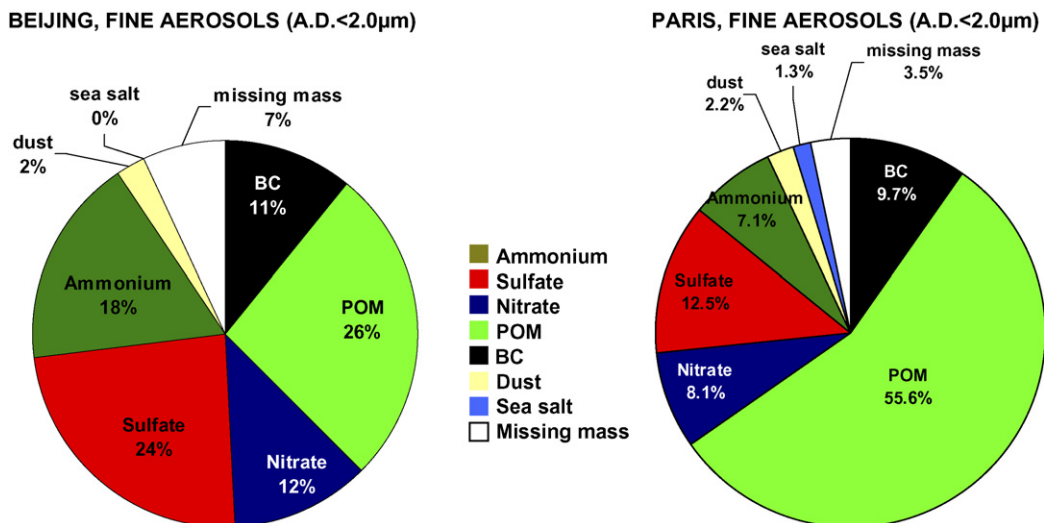


Fig. 4. Temporal variations of the main chemical components of fine aerosols in Beijing (August 2004) and Paris (May 2005).

Fig. 4. Variations au cours du temps des principaux constituants des aérosols fins à Pékin (août 2004) et à Paris (mai 2005).

different from one day to the other. This confirms that there is a much more complex mixture of sources in Beijing than in Paris. The peaks regularly observed during the night are noteworthy. Correlations with other tracers (black carbon for combustion, trichloroethene for industry) suggest that both diesel emissions from trucks (allowed to circulate only during the night) and from industries (some of them are allowed to work only during the night) could be at the origin of this nighttime peak. We note also that the diurnal variation of CO observed during the weekend (21–22 August) is as high as during the weekdays, which is also a difference with the feature observed in Paris.

3.3.2. Aerosol levels and temporal variability

The temporal variations of the main chemical components of fine aerosols are reported in Fig. 4 for the Beijing and Paris sites. Similar scales have been adopted for inorganic salts (ammonium nitrate, ammonium sulfate) and correspond to the double of the scales adopted for carbonaceous aerosols (BC, POM). As evidenced in this figure, the levels of inorganic salts in Beijing are highly variable (ranging from 0.4 to 71.5 $\mu\text{g}/\text{m}^3$) and have been shown to be governed primarily by air masses origin and ventilation [26,31], southern weak winds from the highly populated Hebei province and observed at the beginning and at the end of the campaign (9–11 and 23–27 August) bringing the highest levels of sulfate and nitrate aerosols. During these periods, inorganic salts contribute to more than 70% of the PM in the fine mode and – associated with

elevated humidity – are responsible for drastic reduction of visibility (from 10–20 km to 1 km). As pointed out by Guinot [10], this feature denotes the major influence of the elevated regional background levels of sulfate and nitrate aerosols in controlling the air-quality standards in the Beijing city. Interestingly, this pattern is not reproduced by carbonaceous aerosols, which show a much lesser variability and appear to be poorly affected by air-mass origin. A local (more than a regional) origin for C aerosols would explain such a feature, which is supported by the high BC/OC ratio reported previously.

By comparison with Beijing, the levels of inorganic salts in Paris are lower by almost one order of magnitude and do not present any particular variability. More interesting is the level of POM, which is almost comparable (33% lower) to POM concentrations in Beijing. This small discrepancy (relatively to BC, which exhibits more than a factor of 3 difference) is not clearly understood yet and could originate from many factors, such as combustion sources in Beijing, producing relatively small amounts of organics (relatively to BC).

4. Conclusion

Preliminary results on the chemical composition of VOCs and aerosols in Paris and Beijing have revealed a complex and multi-combustion source in Beijing, contrasting with a single traffic pollution source in Paris. Regional inputs of inorganic salts (sulfate and nitrate aerosols) have been shown to play a key role in the Beijing air-pollution levels, whereas carbonaceous

aerosols were more likely originating from the city itself. This preliminary study comparing contrasted megacities shows the importance of further investigating air quality in megacities. This will involve studies on emissions and processes as well as modelling exercises in order to be able to evaluate the impact of the expected large increase of pollutant emissions in the next decades.

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