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Volatile Metal and Metalloid Species (Pb, Hg, Se) in a European Urban Atmosphere (Bordeaux, France)

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Ambient air measurements of volatile metal and metalloid compounds were conducted in a European urban environment (Bordeaux, France). Air samples were collected with a cryogenic trap and analyzed by low-temperature gas chromatography with ICP/MS detection. Indoor and outdoor sites were studied. Tetraalkyllead compounds ($\text{Me}_{4-n}\text{Et}_n\text{Pb}$, $n = 0-4$) and elemental mercury were found to be the major volatile metal species. Average concentrations of 15.5 and 2.7 ng/m³ as metal have been reported respectively for total alkyllead species and elemental mercury in open area. These results illustrate the general phasing out of atmospheric lead initiated in the past decade. Accumulation of dimethyl selenide has been recorded in a building probably originating from human breath. Volatile metal species distribution in the different sites is discussed with regards to meteorological conditions and automotive traffic parameters. Occurrence of unknown volatile metal and metalloid species likely to occur in urban environment is also reported and discussed.

Introduction

Air quality in urban areas is one of fastest growing concerns with respect to environmental issues. Most of these issues are directly related with the ever increasing rise of the automotive traffic and industrial emissions. Urban air quality policies rely mostly on the determination and regulation of major gaseous pollutants such as O₃, CO, CO₂, NO₂, SO₂, and volatile organic carbons (VOC) (1). However, a clear increasing interest can be noticed for atmospheric metallic emissions from natural and anthropogenic sources due to their high potential health hazards (2–4). However, trace metal contaminant surveys are only occasionally included in urban pollution monitoring programs. When metal are included in such surveys, they are mainly evaluated via aerosols collection and analysis, regardless of the chemical species in which they occur (5). Metals and metalloids also can be found in a gaseous state under normal pressure and temperature conditions (6–11). The natural biogenic formation of volatile metal species plays a significant role in the biogeochemical

cycle of some trace metals such as selenium (11–13) or mercury (8, 14–16). The importance of the gaseous phase is specifically well illustrated in the case of mercury since volatile elemental mercury (Hg^0) represents more than 95% of the global atmospheric mercury burden (17). Biomethylation processes might also lead to volatile lead compounds emission (Me_4Pb) to the atmosphere. However, this hypothesis is currently highly controversial, though several studies tend to demonstrate natural biomethylation evidence (18). Anthropogenic activities such as the chloro-alkali industry with regards to mercury, waste treatment industry (PH_3 , AsH_3 , ...), etc. also represent a significant source of volatile metal and metalloid compounds to the atmosphere. Recently, Feldmann et al. have pointed out volatile emission of various metals and metalloids through the storage of domestic waste in dumping (19). In urban environment, attention has been paid 20 years ago to the occurrence of tetraalkyllead species which were extensively used then as antiknocking agent in gasoline (9, 20–22). The general phasing out of alkyllead in gasoline, first initiated in the U.S., has resulted in a drastic decrease in atmospheric lead content both in the U.S. and over Europe (23). Tetraalkyllead measurements have therefore gradually received less attention in the recent years. Despite of a drastic reduction of the use of leaded gasoline worldwide, a number of the EEC member states still use leaded gasoline providing thus a source of lead emission to the atmosphere. Since 1989, the French legislation stipulates that lead contents in leaded gasoline must not exceed 150 ppm. Note that the so-called unleaded gasoline naturally contains lead in concentration lower than 15 ppm. The unleaded term means here that no alkyllead compounds have been added.

In this paper, we present the distribution of different volatile metal species detected in a French urban environment (Bordeaux, France). After cryogenic sample collection, volatile metal species have been detected with the use of a multielemental low temperature/gas chromatography/ICP/MS system (LT/GC/ICP/MS). During different sampling campaigns, both outdoor and indoor locations have been considered over the total year span. The aim of this investigation was also to evaluate the role of an ICP/MS detector to identify and assess the detection of unknown volatile metal species likely to occur in urban atmosphere. On site cryofocusing and flash desorption in a low temperature/gas chromatography/ICP/MS yields excellent overall sensitivity and allows the sampling of a smaller volume of air leading to short sampling time. This results in an improved representation of the variability of air masses. Further, the use of a cryofocusing device allows an excellent stability of volatile gaseous organometallic compounds and allows then an important potential of investigation of new species.

Material and Methods

Sampling Sites. Volatile metal species were determined during three sampling campaigns throughout the year (September 1995, April 1996, and May 1996) in the vicinity of Bordeaux (700 000 inhabitants including suburbs). Thirteen sampling sites were selected. They included both indoor and outdoor locations. The sampling sites were selected to characterize industrial emissions. Sampling sites located on main streets were chosen to study the nature of automotive emission and its variation over time. Indoor and outdoor samples were collected independently. Sites characteristics and prevailing meteorological conditions are listed in Table 1.

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TABLE 1: Sites' Characteristics and Prevailing Meteorological Conditions

site	sample	date	barometric pressure (mb)	temp (°C)	wind speed (m/s)	traffic density (cars/min)	CO (ppm)
Alsace et Lorraine Street	A1	28/09/95	1017	17.5	3.3	31	3.3
	A2, A3	02/05/96	990	8.5	5.6	30	5.1
Clémenceau Street	C1, C2	02/05/96	991	13.0	10.9	35	<1
Victor Hugo Street	H1, H2	02/05/96	991	9.4	6.3	16	1.5
Intendance Street	I1	28/09/95	1018	15.3	2.9	31	2
Médoc crossroad	M1	28/05/95	1018	14.3	3.1	11	4.1
	M2–M13	05/05/96	995–999	10.8–17.2	1.9–7.4	28–45	1.4–5.7
Nancel Penard Street	P1	28/09/95	1017	15.6	4.0	13	6.7
	P2, P3	02/05/96	991	11.7	10.0	20	3.8
Vital Carles Street	V1, V2	02/05/96	991	14.0	10.9		1.4
	Park1	28/09/95					
underground car park	Park1, 2	02/05/96					
	Bat1	29/09/95	1017	16.0	1.1		
battery manufacturing plant	Ind1	29/09/95	1016	18.2	1.0		
industrial zone	Inc1a	29/09/95	1017	16.2	1.0		
incinerator	Inc2a, 2b	02/05/96	991	9.6	9.0		
day nursery	nursery1, 4	04/04/96					

Seven outdoor sites were then selected downtown in Bordeaux for their high traffic density. Sampling sites were adjusted to those of the carbon monoxide-monitoring network of the city of Bordeaux (see below). Air collection were usually performed less than 3 m from the CO sampling probes. One site (Médoc crossroad) was monitored continuously over the full day period. Air samples were collected directly in the street and 1.7 m above the ground in order to collect the fraction likely to be inhaled by pedestrians.

Three other sites were also located in the industrial zone, close to urban waste incinerators (two sites) and in the vicinity of a batteries manufacturing plant (one site). Samples collections were then performed at approximately 300 m downwind of the plant of interest. An underground car park was also sampled to characterize automotive emissions in a closed area. Finally, some air samples were also collected inside a day care center located in a quiet street but 100 m away from two main streets of Bordeaux with high traffic. This site was selected to record the ambient background of volatile metal pollutants in a building indirectly influenced by automotive emissions. Samplings were performed over a 4 h period on the first floor and in the main room.

Sample Collection and Analysis

Volatile Metal Species. Air samplings were performed with a laboratory-made portable air sampler. Air was pulled through a Teflon (PFA) sampling duct (i.d. 9 mm, 2 m of length) and placed inside a mobile laboratory unless otherwise stated. Volatile metal species were collected after online filtration of the aerosols (quartz filter 0.1 μ m, QMA Millipore) and cryogenic condensation of the vapor water in an empty U-shaped glass tube maintained at -20°C . Volatile metal species were then cryofocused at -175°C on a glass column (i.d. 5 mm, 17.5 cm of length) packed with silanized glass wool (pesticide grade). The cryofocusing temperature was regulated with an automated cryostat cooled with liquid nitrogen. The sampling air flow rate (0.8 L/min) was held constant during 18.5 min for a total volume of 15 L. In most cases two samples were collected one after the other on the same location. In the city the power to operate the air sampler was supplied by the shopkeepers, while in the industrial area an electrical unleaded gasoline generator was used. To avoid potential contamination, all samplings were performed 30 m upwind of the power generator. After collection, sample traps were sealed with Teflon caps and stored for 3 days at -196°C in a dry atmosphere cryocontainer (Voyageur 12, L'Air Liquide, Paris, France).

All tubes and connections used in the sampler are made of Teflon (PFA, Bioblock) and were previously cleaned with

concentrated HNO_3 and thoroughly rinsed with Milli-Q water. New columns used to store the air samples were soaked in 10% HNO_3 during 2 h in an ultrasonic bath and rinsed thoroughly with Milli-Q water. The traps were then dried under laminar flow bench for 2 days at room temperature and silanized with pure hexamethyldisilazane. Columns were all blanked two times prior to use. This procedure was achieved by heating the traps for 10 min at 300°C with continuous flushing of purified He. They were then stored in double clean plastic bags until field use. Volatile metal species were analyzed in a clean room laboratory with a LT/GC/ICP/MS. The ICP/MS used here is a quadrupole MS Elan 5000 from Perkin-Elmer, Sciex. The sampling method together with the volatile metal species detection have been previously described in details elsewhere (24, 25). Samples stability during cryogenic storage was also evaluated and discussed (26).

For each sample, two isotopes of Pb ($^{206}, ^{208}\text{Pb}$), Hg ($^{200}, ^{202}\text{Hg}$), Se ($^{78}, ^{82}\text{Se}$), Sn ($^{118}, ^{120}\text{Sn}$), Cr ($^{52}, ^{53}\text{Cr}$), Ge ($^{72}, ^{74}\text{Ge}$), Cd ($^{112}, ^{114}\text{Cd}$), Ni ($^{58}, ^{60}\text{Ni}$), Te ($^{128}, ^{130}\text{Te}$), V (^{51}V), As (^{75}As), and Al (^{27}Al) were at least simultaneously recorded whenever possible. For all elements except monoisotopic elements, the isotopic abundance of at least two isotopes was systematically compared to the natural theoretical values to secure the information and correct for potential isobaric interferences. This has been carried out by comparing the measured isotopic ratio (determined after measurement of the peak area corresponding to each isotopes respectively) to the theoretical natural isotopic ratio. An agreement of 95% was considered satisfactory to assess the occurrence of an element under routine conditions. For trace level conditions, we have allowed a relative standard error less than 20%. The assignment of metal species was also achieved by comparison of the retention times with volatile metal and metalloid standards whenever they could be obtained. Quantification of the analytes was performed by injections of known amounts of volatile standards on the top of the chromatographic column via the injection port of the LT/GC/ICP/MS device. Pure organometallic standards were purchased from Strem Analytical, (Me_2Se : 99%, Me_2Se_2 : 99%, Me_4Sn : 98%, Et_4Sn : 99%, Hg^0 : 99.99%) and from Octel France (Me_4Pb : 39.4%, Et_4Pb : 99%). All concentrations are expressed with respect to the metal content.

Blanks from field columns did not contain detectable amounts of lead, tin, selenium, arsenic, and chromium species. The limit of detection based on 15 L samples is then 0.006, 0.015, and 0.3 ng/m^3 for tetraalkyllead species (Me_4Pb , Et_4Pb), alkyltin species (Me_4Sn , Et_4Sn), and alkylselenide species (Me_2Se , Me_2Se_2), respectively. After a storage time of

TABLE 2: Analysis of Air Samples (Bordeaux, France, September 1995–May 1996)^d

isotopes	R.T.	species	concn range as metal (ng/m ³)	I.R. ^a measured	I.R. ^a theoretical
208/206Pb	2.1	Me ₄ Pb	0.09–95.2	2.2–2.7	2.22
	2.3	Me ₃ EtPb	0.0–8.1	2.2–2.5	
	2.5	Me ₂ Et ₂ Pb	0.01–12.4	2.1–2.5	
	2.8	MeEt ₃ Pb	0.0–3.1	1.8–2.2	
	3.0	Et ₄ Pb	0.18–222.6	2.1–2.3	
202/200Hg	1.3	Hg ⁰	0.7–23.6	1.28–1.35	1.29
	2.5	MeHgCl ?	nq ^c	1.31–1.37	
78/82Se	1.7	Me ₂ Se	0.7–8.7	2.6–3.0	2.56
53/52Cr	2.2	ni ^b	nq ^c	0.07–0.168	

^a I.R.: isotopic ratio. ^b ni: not identified. ^c nq: not quantified. ^d mi: monoisotopic.

several days in the conditions described above, field columns blanks were found to contain less than 5 pg as Hg⁰. Under these conditions, the limit of detection based on three σ of the blank level was calculated to be less than 0.4 ng/m³ for Hg⁰.

The reproducibility of the whole analytical chain (i.e. from sampling to analysis) was estimated to be better than 80% after the determination of several samples collected one after the other on the same location. This procedure was used since the cryofocusing unit can only collect one sample at the same time.

Gasoline Alkyllead Content. To have a good signature of the respective distribution of alkyllead compounds in gasoline, leaded and unleaded gasoline were subsampled at two different gas stations. The pure leaded and unleaded gasoline were respectively diluted 500 and 100 times in pure methanol (Merck, spectroscopic grade). The diluted products were analyzed by direct injections (2 μ L) on the top of the chromatographic column. The five tetraalkyllead species (TAL) contained in leaded gasoline were detected in all air samples. The lead content of the gasoline were all in agreement with the French legislative limit of 150 ppm for TAL content. On all leaded gasoline samples, tetraethyllead (Et₄Pb) was found to be the major additive representing a mean proportion of 64.3% of the total TAL content. Tetramethyllead (Me₄Pb), trimethylethyllead (Me₃EtPb), dimethyldiethyllead (Me₂Et₂Pb), and triethylmethyllead (Et₃-MePb) were found to represent 11.4%, 7.7%, 11.7%, and 4.9% of the total TAL content, respectively. Unleaded gasoline samples were found to contain less than 0.25 ppm of TAL.

Carbon Monoxide and Traffic Density. Other data related to air quality were also simultaneously monitored when available. CO concentrations were provided by the CO-monitoring network of the city of Bordeaux. Twenty-four CO analyzers (AM1, Dräger) are distributed over the city and automatically record on an hourly basis the carbon monoxide concentrations. Monitoring probes are located close to the street traffic and 1.8 m above ground level. The traffic density in the vicinity of each sampling site was continuously monitored by the GERTRUDE network on a 5 min interval basis.

Results and Discussion

All samples collected during the different campaigns were analyzed using a large number of mass channels. On all samples, unidentified species to date were detected, and their occurrence will be discussed later in the text. Volatile species clearly identified by the comparison of the isotopic match and retention time from injection of standards were tetraalkyllead compounds (Me₄–_nEt_nPb, $n = 0–4$), elemental mercury (Hg⁰), and dimethylselenide (Me₂Se). Table 2 lists all the species that were considered during the three campaigns. We will discuss the results obtained with the

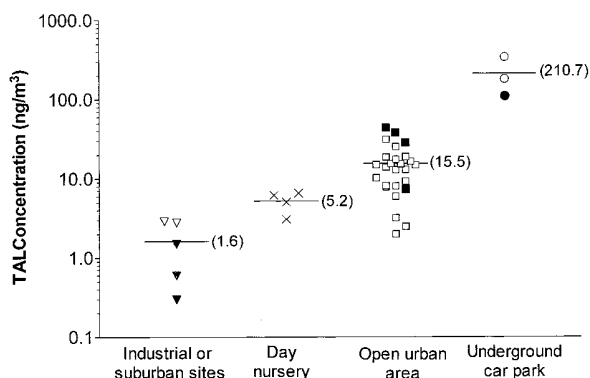


FIGURE 1. TAL concentrations measured during the three campaigns. Filled symbols represent samples collected in September 1995. (TAL mean values are indicated in brackets).

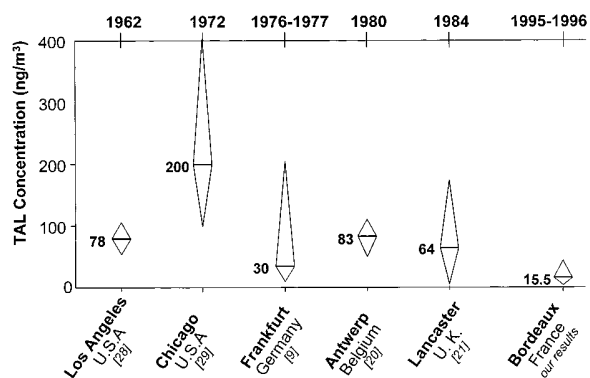


FIGURE 2. Evolution of TAL concentration in air since 1962. The mean values are indicated.

different species in the following order: alkylleads, mercury species, selenium species, and tin species and finally report on the potential occurrence of other volatile metal species.

Lead Compounds. Relative Distribution. The TAL concentrations recorded range by increasing order of concentration respectively between 0.3 and 2.9 ng/m³ in industrial or suburban areas, 2.0 and 43.8 ng/m³ in the urban samples, and 110.4 to 341.3 ng/m³ in the underground car park (Figure 1).

The relative distribution of the different TAL in air samples is slightly different from those recorded in the gasoline samples. Average calculation on all samples obtained gave the following distribution: 31% for Me₄Pb, 3% for Me₃EtPb, 6% for Me₂Et₂Pb, 1.5% MeEt₃Pb, and 58% for Et₄Pb. Except for Me₄Pb, the relative proportion of the different TAL presents a slight decrease in relative concentrations when compared with the leaded gasoline data. On the contrary, the Me₄Pb percentage rises from 11 to 31%. This relative enrichment has already been previously observed in the 1980s and was attributed to the higher volatility, thermal, and photochemical stability of Me₄Pb compared to the other compounds (9, 20, 27).

Open Urban Sites TAL Concentrations. Outdoors total TAL concentrations recorded in this study were always lower than those previously reported by several authors in urban environments (Figure 2). Nielsen et al. reported total TAL concentrations ranging between 11 and 77 ng/m³ in Stockholm in 1979 (22). De Jonghe et al. found similar levels (83 \pm 19 ng/m³) in Antwerp in 1980 (20). Hewitt et al. reported daily mean concentrations ranging from 50 to 90 ng/m³ with peaks up to 150 ng/m³ in March 1984 in Lancaster (21). Our results represent, to our knowledge, a new set of data collected after the general phasing out of the use of lead in gasoline in European countries. They are also the first ones reported

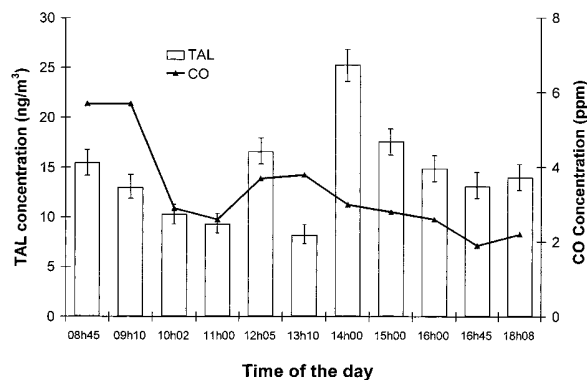


FIGURE 3. TAL and CO concentrations recorded on the same site during 1 day (May 1996).

in a French city. Despite the difficulty of direct comparison of the data with respect to similar collection protocols and nature of the sampling sites, we can confirm the general evidence of decreasing concentrations of TAL in air.

The TAL concentrations are highly variable from site to site. This high variability can certainly be related to the local topography, the traffic density, and atmospheric turbulence during the sampling period. Though most samples collected one after the other on the same location displayed TAL concentration changes less than 20%, two exceptional cases were observed with variations of 88% and 100% between two repeated sample collections. These large differences may originate from the high variability of parameters such as traffic density, quality of the cars using different gasoline, and the micrometeorological conditions during the short time of sampling (18.5 min). In both cases, the total number of cars driving past the monitoring point is quite similar from one sample to one another which rules out the impact of the traffic density factor. The decomposition of alkylleads in the atmosphere under our working conditions (lifetime ~ 10 h for Me_4Pb and ~ 2 for Et_4Pb) cannot explain these discrepancies, but a minor contribution should not be excluded. The average TAL values measured during September 1995 were found to yield higher TAL concentrations compared to those recorded in May 1996 with similar traffic density conditions. The September 1995 campaign meteorological status was characterized by anticyclonic conditions which are likely to enhance the accumulation of gaseous pollutants over the city (wind speed ranging from 1 up to 4 m/s). On the contrary, the prevailing meteorological conditions occurring in May 1996 favored the pollutants dispersion (wind speed ranging from 1.9 up to 10.9 m/s). The differences obtained between the two sets of TAL concentrations may then directly be related to the general ventilation of the atmosphere. This hypothesis is corroborated by the principal components analysis data treatment and will be discussed later in the text.

Diurnal Variability. The TAL concentrations were monitored over time at a heavy traffic crossroad. Results are presented in Figure 3 and presented a high variability over time as expected. Highest TAL concentrations were observed at 8h45, 12h00, 14h00, and 18h00 which correspond to typical rush hours with heaviest traffic density. No direct correlation could however be observed in detail between the TAL concentrations, traffic density expressed as the number of cars, and the CO levels. General trends between these different factors however agreed.

Underground Car Park. The TAL concentrations determined in the underground car park differ significantly from those detected in open area. The average concentration of TAL was 210 ng/m^3 and differs by more than 1 order of magnitude over concentrations recorded in the open areas.

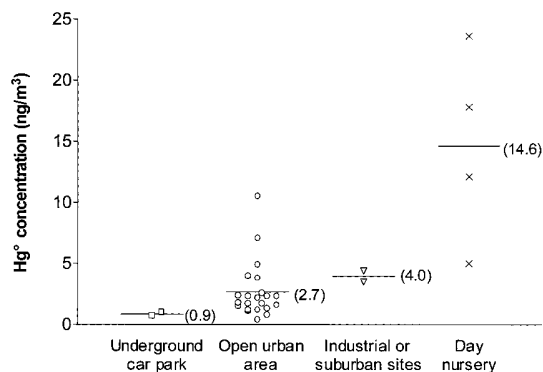


FIGURE 4. Hg^0 concentrations measured during the in April and May 1996. (Mean values are indicated in brackets.)

Important variations have here also been observed with respect to time of sampling and traffic density. In this case, the contribution of the meteorological conditions was considered to be negligible. The high levels recorded (up to 340 ng/m^3) underline the accumulation of pollutants despite the ventilation installations.

Indoors Location, Day Care Center. Samples collected in the nursery displayed TAL levels in the same range of those detected in the surrounding main streets during the following May 1996 campaign. The traffic density close to the nursery was not recorded, but the traffic was much lower than in the two main streets surrounding the sampling location. The tetraalkyllead levels determined inside of the day care can be thought to reflect the passive automotive traffic and could be considered as urban background levels. These results suggest that short-range atmospheric transport can lead to accumulation of TAL levels in buildings and result in similar concentrations to those occurring in busy traffic streets.

Suburban and Industrial Locations. Low TAL concentrations were detected in suburban and industrial areas. This area presented good air masses mixing conditions and low traffic density. Samples collected downwind from the incinerator sites displayed levels of TAL only slightly lower (3 ng/m^3) than those observed in urban sampling sites. These results may have been affected by the contribution of a nearby highway.

Mercury Compounds. Hg^0 was the only mercury species clearly identified in all samples. Trace amounts of methylmercury chloride were suspected to occur in some samples similar to the work reported by previous authors (30, 31). However, the chromatographic resolution was not sufficient to secure the assignment and the quantification of this species at such low levels.

The atmospheric mercury concentrations are displayed in Figure 4. Average concentration of Hg^0 determined in the different types of sampling sites ranged from 0.9 ng/m^3 in the underground car park to 14.6 ng/m^3 in the day care center. The open urban area value was 2.7 ng/m^3 . The September 1995 campaign values were discarded due to high Hg^0 blanks.

Open Urban Sites and Underground Car Park. The mercury concentrations were found to be spread between 0.4 and 10.5 ng/m^3 . Similarly to what has been observed with the TAL species, the samples collected one after the other at the same location showed generally mercury levels variation less than 30%.

Large variations in the Hg^0 level were observed from site to site and also over time at the same location (site M) during the continuous day sampling program. The mean concentration of Hg^0 recorded in the urban areas was calculated after the campaign of May 1996 and gave an average value of 2.7 ng/m^3 . These levels can be compared and are in the

TABLE 3: Correlation Matrix (Base 19) of the Parameters Used for the Principal Components Analysis

	temp	barometric pressure	wind speed	CO	traffic density	TAL	Hg ⁰
temp	1	0.8021	0.2125	-0.3734	0.5718	0.0420	-0.4583
pressure	0.8021	1	-0.3521	0.0682	0.6537	0.1468	-0.5925
wind speed	0.2125	-0.3521	1	-0.6112	-0.2788	-0.0722	0.1846
CO	-0.3734	0.0682	-0.6112	1	0.1179	0.5741	-0.4892
traffic density	0.5718	0.6537	-0.2788	0.1179	1	0.0740	-0.6284
TAL	0.0420	0.1468	-0.0722	0.5741	0.0740	1	-0.5239
Hg	-0.4583	-0.5925	0.1846	-0.4892	-0.6284	-0.5239	1

same range than those previously reported in unpolluted areas of western Europe (17, 32). The highest mercury concentrations were recorded on site H (10.5 and 7.1 ng/m³ respectively). It is worthwhile noticing that this sampling site was located close to two dentists' offices. Dentist activities are known to contribute significantly to Hg⁰ emissions via dental amalgam uses (33).

Samples collected inside the underground car park displayed very low mercury levels (0.7 and 1.0 ng/m³, respectively). These results suggest that automotive activity does not contribute to Hg contamination and that Hg⁰ concentrations could be assigned to the outdoor air masses.

Incinerator. Samples collected downwind of the incinerator sampling point presented average concentrations slightly higher (4.0 ng/m³) than those recorded in the urban areas (2.7 ng/m³). The number of samples collected on this site is however limited to significantly identifying the possible contribution of this plant.

Day Nursery. Four air samples (15 L, 18.5 min) were successively collected every 45 min, over a 3 h period. The mercury concentrations levels recorded in the day care center were found to be significantly higher than in the outdoors locations. Concentrations ranged from 5.0 up to 23.6 ng/m³. The origin of mercury inside the nursery was not identified. These values are however lower than the guideline value of the World Health Organization (1000 ng/m³).

Selenium. Samples collected in open areas did not reveal the occurrence of any volatile selenium species except for the industrial zone in an area located over a brook where levels reached 0.7 ng/m³ of Se. Previous studies performed in rural environment have also pointed out the occurrence of such species in similar concentration ranges (0.4–0.9 ng/m³) (7, 24, 34). Dimethylselenide can indeed be formed in the environment via biomethylation processes from bacteria (35), plants (36), soil (37), and water (13). Very few authors have detected this compound in open atmosphere. The occurrence of dimethylselenide in this sample is then highly suspected to originate from the brook or surrounding vegetation.

Dimethylselenide was also systematically detected in the nursery with concentrations ranging from 0.8 up to 8.7 ng/m³. Concentrations were found to increase linearly ($r^2 = 0.9989$) with time with an accumulation rate of 3.2 ng m⁻³ h⁻¹. This accumulation of Se species is suspected to originate from human biological activity through perspiration or breathing. Feldmann et al. have recently identified this selenium species in human breath with levels ranging between 0.08 and 0.98 µg/m³ (38). They estimated that 11% up to 23% of the daily selenium intake of noncontaminated persons could be excreted through this biological activity.

Unidentified Species. During sample detection, many mass channels were monitored simultaneously in order to investigate the possible occurrence of new species. Many unidentified signatures have been recorded on mass channels of Cr, Ni, Te, V, Al, As, Cd, and Ge in almost all samples. Low signals were recorded on the ^{60/58}Ni, ^{130/128}Te, ^{114/112}Cd, and ^{74/72}Ge mass channels, but spectroscopic interferences are

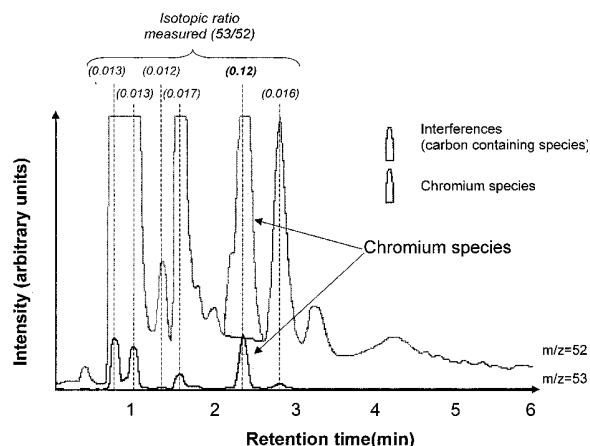


FIGURE 5. Typical chromatogram recorded on chromium channels (masses 52 and 53). Isotopic ratio measured (⁵³Cr/⁵²Cr) for each species is indicated in brackets.

strongly suspected due to the lack of fitting between the theoretical and measured isotopic ratios. These comments do not rule out the possible occurrence of these species. The importance of an isotopic match for species identification is specifically well illustrated in the case of chromium detection in air. The mass channels 52 and 53 recorded numerous peaks, but only one species with a retention time of 2.2 min had a proper isotopic ratio between isotopes 52 and 53 (Figure 5). For this species, the measured isotopic ratio (⁵³Cr/⁵²Cr) is 0.12 and is very similar to the theoretical isotopic ratio (0.11). This result certainly suggests the occurrence of volatile chromium species in urban areas. Recent work of Feldmann et al. has suggested the occurrence of volatile species of W and Mo (39). These species were identified as carbonyl forms after applying similar procedures as described in this paper. We would therefore suggest that Cr carbonyls could occur in urban areas. The other Cr peaks recorded in Figure 5 can be attributed to carbon mass spectroscopic interferences with different combinations such as ⁴⁰Ar¹²C⁺ on ⁵²Cr⁺ and ⁴⁰Ar¹³C⁺ on ⁵³Cr⁺. These suggestions are made since the isotopic ratio recorded are similar to the ¹³C/¹²C isotopic ratio ($I.R._{theoretical} = 0.011$). Finally, for monoisotopic elements such as ⁵¹V, ²⁷Al, and ⁷⁵As, the signals obtained could not be validated by lack of isotopic comparison. However, these light elements are very much likely to be affected by polyatomic interferences such as ¹⁶O³⁵Cl⁺ on ⁵¹V⁺, ¹⁴N¹³C⁺ on ²⁷Al⁺, and ³⁵Cl⁴⁰Ar⁺ on ⁷⁵As⁺. Nonetheless, further information should be gained on these species. Many of the uncertainty occurring at the present time should be raised by the use of optical detector such as ICP/AES or with a high-resolution ICP/MS instrument.

Multivariate Approach. A principal components analysis was performed on all sampling campaigns (outdoors sites) including the different parameters such as TAL, Hg⁰, CO, traffic density, and meteorological data. This approach was made to evidence the main trends associated with the distribution of the TAL and Hg⁰ concentrations. Table 3 and

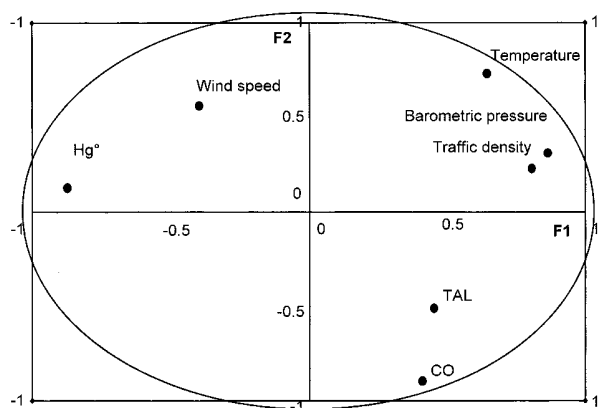


FIGURE 6. Principal components analysis representation of TAL, Hg^0 , CO concentrations, traffic density, and meteorological parameters recorded in September 1995 and May 1996.

Figure 6 describe the results of the calculations. The correlation coefficients obtained in the correlation matrix are around 0.6 for the best set of parameters. These correlation factors illustrate the complexity of the system studied. Figure 6 plots the two-dimensional representation of the system according to the first two main axes, which represent 74% of the information. These results clearly indicate that the TAL and CO parameters present similar planar projection suggesting possible covariance. This trend had been previously mentioned during the diurnal study. Both sets of parameters appear to be anticorrelated to the wind speed and the Hg^0 values. The anticorrelation between TAL and wind speed is logic since the wind speed will dilute the analytes. The TAL and Hg^0 anticorrelation underline the fact that distinct sources may occur. The Hg^0 values are certainly not associated with the car traffic. The large difference observed between the low indoor values from the car park and the surrounding outdoor levels suggests that they have a distinct origin that still needs to be identified for Hg.

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