Trace elements in total atmospheric suspended particles in a suburban area of Paris: a study carried out by INAA

Gilbert Le Petit

Jean-Paul Deschamps

Sunun Nouchpramools

Introduction

Atmospheric pollution is a major concern world-wide, in particular for the inhabitants of certain large urban areas. Its many and varied components attack the environment and health directly or indirectly. The main pollutants are sulphur dioxide, carbon monoxide, reactive hydrocarbons, nitrogen oxides, ozone, lead and particulate matter. The primary contributions to atmospheric pollution in the form of solid aerosols come from either natural sources such as redispersion of crustal material, volcanic eruptions, aerosols of marine origin and pollens or from anthropogenic sources such as combustion of fuel oil and coal, combustion of fuels related to vehicular traffic, and various emissions related to industrial and human activities. It is generally accepted that the level in the atmosphere of particulate matter of natural origin is less than 10 $\mu g.m^{-3}$. In urban areas with high population density, such as the great megalopolises in developing countries, the concentrations in the atmosphere are regularly higher than the guideline values recommended by the World Health

Organisation (WHO), which considers that the annual mean concentration should not exceed 60 μg.m^{-3}. The long-term effects on health of a high concentration of atmospheric particulates, specifically the fraction smaller than 10 μm, are serious and insidious; moreover, the quantification of metals and certain anthropogenic trace elements present in the particulate matter is necessary in order to evaluate the hazards of the atmospheric pollution in terms of long-term exposure of the population and consequently implement the means to combat them and reduce them.

The preliminary study described here focuses on neutron activation analysis (INAA) of trace elements in atmospheric particulate matter (collected using a very high flow rate (approximately 600 m^3.h^{-1}) atmospheric sampling system fitted with a large filter. Weekly samples of approximately 100,000 m^3 of filtered air, collected during 1998 close to Paris, were used to determine the amplitude of seasonal fluctuations in pollutant concentrations, evaluate the enrichment factor of specific elements in the total atmospheric suspended particles (TSP) and, if possible, identify the origin of certain pollution sources.

Situation

The Service Radioanalyse Chimie Environnement (SRCE) of the Commissariat à l'Energie Atomique (CEA) has an atmospheric sampling station located at Montlhéry (2° 14' E, 48° 37' N), 35 km south-south-west of Paris and approximately 900 metres from a main road (N 20) with high traffic levels, approximately 70,000 vehicles per day (including 15% heavy good vehicles). The sampling station has a weather station recording the following data: wind speed and direction, precipitation, temperature, humidity; the wind rose established for 1998 is predominantly south-west, north-east. The locations of the main potential sources of atmospheric pollution emissions in the outer suburbs of Paris are shown in Figure 1.

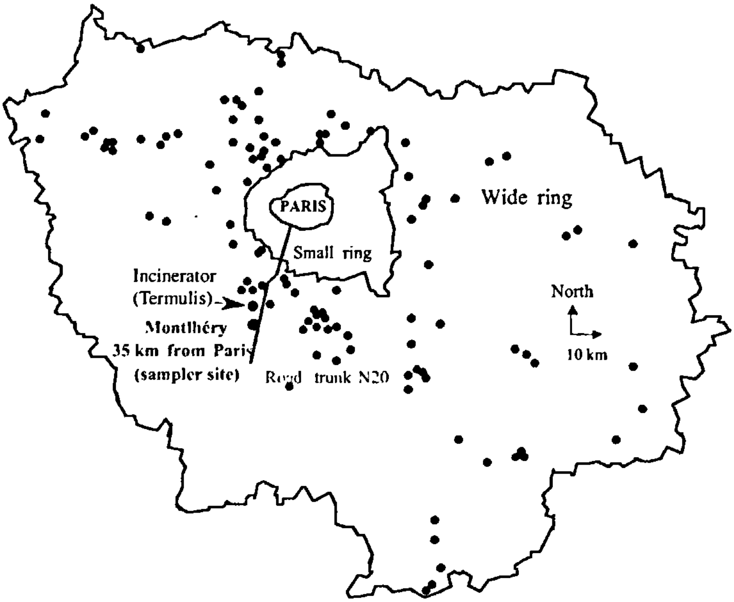


Figure 1
Air particulate sampler location and possible atmospheric emission source locations (black points).

Sampling apparatus and filter support

The atmospheric particulates sampling apparatus (Figure 2) used is the ASS500 P (Aerosols station ASS-500 Physic-Technik-Innnovation PTI & Central Laboratory for Radiological Protection CLRP (Poland), D.Fischer, Erlengen, Germany). This apparatus type equips the French Particulate Radionuclides Stations installed* as part of the world-wide network set up under the terms of the Comprehensive Test Ban Treaty (CTBT) (Schulze *et al.*, 2000) and

---

* An operational station is installed on the island of Tahiti in the South Pacific.

Figure 2 ASS500 P type sampler.

intended to monitor atmospheric radioactivity (sensitivity: 10 mBq.m^{-3} for ^{137}Cs). The high flow rate sampling apparatus can operate continuously under severe meteorological conditions. The horizontal sampling head is protected by an aluminium hood. The polypropylene filter, with a surface density of approximately 125 g.m^{-2} and effective dimensions 43x43 cm, is mounted in an air-tight manner on a calibrated grid support. The filter retention efficiency, measured experimentally, is greater than 93% for 0.15 mm particles (French standard NF X 44011). Two infrared lamps are installed above the filter to prevent icing in winter. The ASS500 P has a system giving the filtered air volume at a given time and the instantaneous flow rate. The filtered air volume is corrected for the temperature and adjusted to standard conditions (STP). For this study 54 weekly samples covering 1998 were taken; the weekly mean air flow rate, approximately 600 m^3.h^{-1}, varied significantly according to the meteorological conditions observed during sampling; at certain times of the year, when the temperature inversion layer is low, the resulting atmospheric dust level is higher, whereas at other times heavy rainfall can cause a substantial decrease in the flow rate. The weekly mean flow rates obtained during 1998 are shown in Figure 3; it can be seen that the minimum flow rate (440 $m^3.h^{-1}$) was obtained in winter.

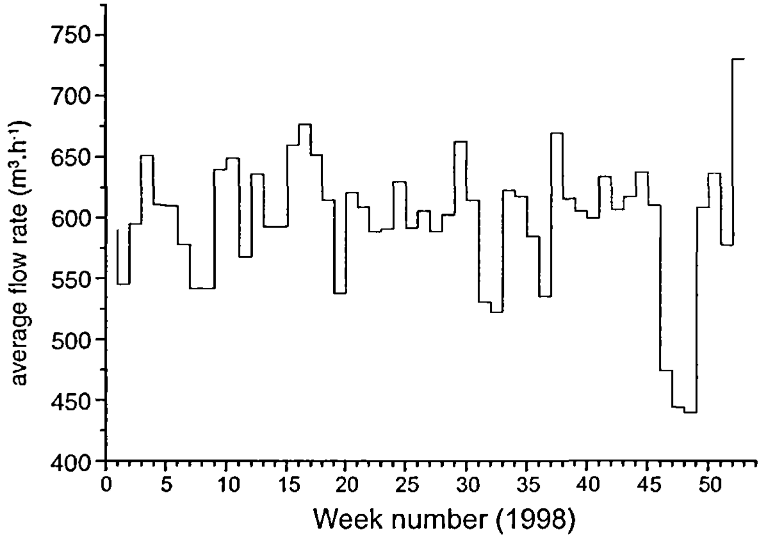


Figure 3
Average flow rate observed on the sampler during year 98.

Sample preparation protocol

The atmospheric particulate matter is sampled for one week, without particle-size cutoff. Each filter is oven-dried for 6 hours at 90° C, then weighed on a precision balance, before it is placed in the sampling apparatus. On withdrawal, the aerosol-loaded filter is dried and weighed again; the mean weight loss after drying is about 4%

of the total mass. The distribution of the aerosol masses (mg.m^{-3} filtered air) collected on each weekly filter and measured in 1998 is shown in Figure 4. It can be seen that, in winter, atmospheric dust levels in the Paris region can reach 80 mg.m^{-3} (weekly mean), a value that is slightly above the maximum annual limit adopted by the WHO (60 mg.m^{-3}).

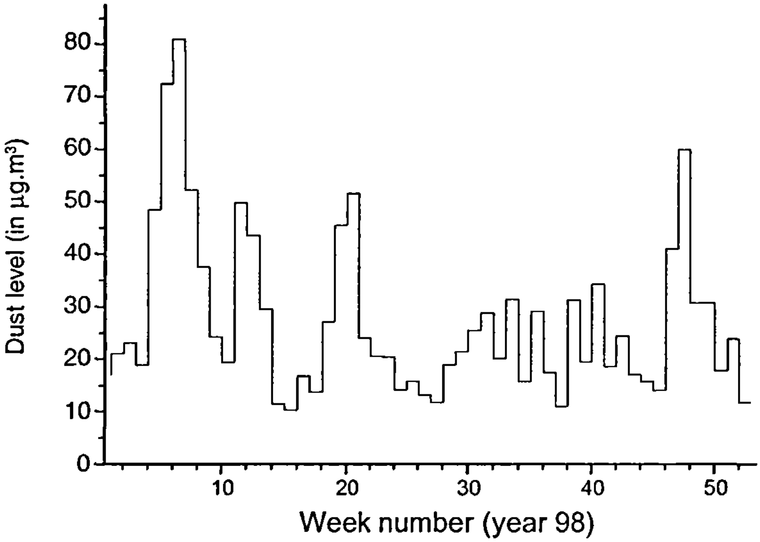


Figure 4
Dust concentration during year 98 observed at Montlhéry.

The filters are then compacted and reduced to ash in a programmable oven, using a protocol giving a slow temperature rise to 400 °C over a period of 8 hours. In parallel, blank filters loaded with stable tracers (standards), prepared under the same conditions as the samples and undergoing the same protocol, were used to determine the calcination yield after INAA analysis for each element investigated in the atmospheric aerosols (except Pb, analyzed by ICP-MS after solubilization). The reproducibility of the calcination yields obtained was verified by three independent values for each element.

After calcination, 50 mg of sample were placed in a high-purity polyethylene container and heat-sealed. A set of blank filters, prepared under identical conditions to the samples, was analyzed to identify and quantify impurities (major constituents: Al, Cl, Cu, Na, K). In addition, for the same purpose, impurity concentrations of the empty container were determined, as the gamma spectrometry measurements on the samples were made in the presence of the container (major constituents: Al, Mg). The results obtained were taken into account in the determination of the element concentrations in the atmospheric particulate matter.

Sample irradiation and induced activity measurements

Although the INAA technique cannot quantify certain elements such as Pb, Hg and S that are of particular interest as atmospheric pollutants, it is one of the most powerful non-destructive multi-element analysis techniques (Sarmani *et al.*, 1998; Djingova *et al.*, 1998), capable of determining some forty elements (lanthanides, rare earths, metals, K, Na, etc.).

The samples were irradiated using the HERMA pneumatic system installed on the periphery of the core of the OSIRIS reactor at the Centre d'Etudes Nucléaire at Saclay (CEA). This apparatus has a very fast transport system for shuttles carrying the container and the sample; the transfer time between the reactor core and the gamma spectrometry laboratory located in a peripheral gallery is about 2 to 3 seconds, which enables detection and measurement of radioelements with half-lives of a few minutes. A distributor managing eight shuttles simultaneously means that the irradiation system can sequence the irradiation cycles. The associated laboratory can perform two types of measurement: HPGe gamma spectrometry measurement and measurement of delayed neutrons by ^{3}He proportional counter for the fissile elements such as ^{235}U, ^{238}U, ^{239}Pu. The samples were irradiated in a thermal neutron flux of approximately

$1.2.10^{14}$ n.cm^{-2}.s^{-1} for 60 s. Each set of eight samples was framed by two flux guides made of ultra-pure Fe; experience has shown that, given the short duration of the irradiations, the neutron flux variation during the treatment of a set of samples can be considered negligible.

Two measurement procedures were used, depending on the elements to be analyzed. The short half-life radioelements (^{28}Al, ^{52}V, ^{66}Cu, ^{51}Ti, ^{80}Br, ^{38}Cl, ^{116m}In, ^{57}Mn, ^{56}Mn) were measured in the laboratory located close to the reactor by an HPGe detector, relative efficiency 30%, with a collimator 100 mm thick and a 10 mm aperture. The sample was positioned automatically in front of the detector by the pneumatic system. The detector was calibrated using a multigamma (^{152}Eu) solution placed and dried in a container identical to the ones used for sample irradiation; the calibration was checked using a Monte-Carlo code, taking into account the corrections due to summing effects. An initial measurement (T0) was made when the dead time of the acquisition electronics was less than 10%. Three measurements were then made at T_0+10, T_0+20 and T_0+30 min.

The medium and long half-life radioelements (^{46}Sc, ^{59}Fe, ^{51}Cr, ^{60}Co, ^{76}As, ^{65}Zn, ^{75}Se, ^{82}Br, ^{86}Rb, ^{99}Tc(Mo), ^{115}Cd, ^{122}Sb, ^{124}Sb, ^{131}Ba, ^{134}Cs, ^{140}La, ^{141}Ce, ^{110m}Ag, ^{152}Eu, ^{169}Y, ^{24}Na, ^{177}Lu, ^{181}Hf, ^{187}W, ^{198}Au, ^{233}Pa(Th), ^{42}K) were made in our laboratory at Bruyères le Châtel using HPGe detectors with relative efficiencies of 30 to 50%. The detector was calibrated using a multi-element gamma solution (AEA Technologie, Courtaboeuf, France) in the same geometry as the sample. All the measurements were made at a distance of 10 cm from the detector to minimize gamma summing effects. An initial measurement was made 1 day after irradiation (T_0), then further measurements at T_0+5, T_0+20 days.

The element concentrations, allowing for experimental conditions and including corrections for dead time and for decay during acquisition, are calculated (ng.m^{-3}) using the customary formula for activation analysis:

$$Conc = \frac{Ns \times A \times \lambda \times m_t \times k}{\varepsilon_{abs} \times A_b \times m_i \times I_\gamma \times N_v \times \varphi_{th} \times \sigma_{th} \times Y_c \times V_a \times (1 - e^{-\lambda \times t_i}) \times e^{-\lambda \times t_d} (1 - e^{-\lambda \times t_m})}$$

where:

k: constant
Ns: net area of the total gamma absorption peak
A: atomic number of the activated element
λ: decay constant of the activated element
ε_{abs}: absolute detection efficiency
A_b: isotopic abundance
m_i: mass of irradiated sample
m_t: total mass collected
I_λ: absolute gamma emission intensity
N_v: Avogadro's number
Y_c: calcination yield
V_a: volume of air sampled
φ_{th}: thermal flux
σ_{th}: thermal neutron absorption cross-section
t_i, t_d, t_m: irradiation, cooling and measurement times, respectively

The gamma spectrograms were processed using the GW software (Westmeir Gesellschaft für Kernspektrometrie mbH – Beratung Software). All the nuclear data (thermal neutron absorption cross-sections, gamma emission intensities) were taken from "*The K0-Consistent IRI gamma-ray Catalogue for Instrumental Neutron Analysis* (Menno Blaauw Interfacultair Reactor Instituut van de Technische Universiteit Delft, 1996) and the Neutron activation Tables (Gerhard Erdtmann, 1976). The Innovator in Elemental and Isotopic Mass Spectrometry relative. The Minimum Detectable Concentration (MDC) calculation was based on the definition of Currie (1968) and complies with the expressions defined by the international organization overseeing the CTBT (Schultze *et al.*, 2000).

$$MDC_{\left(mass/m^3\right)} = \frac{K_a \times 2.71 + 4.65\sqrt{\sum_{ROI} count_i}}{t_m \times \varepsilon_{abs} \times V_a \times K_s \times K_w \times K_c}$$

where:

ROI is defined as ± 1.25 Full Width Half Maximum on either side of the hypothetical peak K_a, K_s, K_w, K_c: respectively factors related to the conversion mass/Bq, decay corrections during activation time, between end of activation and acquisition start, during acquisition time

The overall uncertainties assigned to the results are given by the following equation, for a standard deviation:

$$\Delta Conc = Conc \times \sqrt{\frac{\Delta N_s}{N_s} + 2\frac{\Delta N_b}{N_b} + \frac{\Delta I_\gamma}{I_\gamma} + \frac{\Delta \varepsilon_{abs}}{\varepsilon_{abs}} + \frac{\Delta m_i}{m_i} + \frac{\Delta m_t}{m_t} + \frac{\Delta V_a}{N_a} + \frac{\Delta Y_c}{Y_c} + \frac{\Delta \varphi_{th}}{\varphi_{th}}}$$

where N_b: area under the gamma peak.

Validation of the experimental method

The validity and the reliability of the results obtained using our experimental method were verified by irradiating an IAEA 1632A particulate matter standard (Table 1).

Element	Certified values IAEA 1632A(ppm)	Our work (ppm)	Detection limit (ppm)
As	9.3 ± 1.0	11.1 ± 1.0	0.55
Ce	29.0 ± 2 .0	28.5 ± 1.7	1.8
Cs	2.3 ± 0.2	3.0 ± 1.8	0.7
Cr	34.3 ± 1.5	31.5 ± 1.5	4.0
Eu	0.52 ± 0.04	0.52 ± 0.06	0.1
Fe	11100 ± 200	10755 ± 220	645
Hf	1.62 ± 1.00	1.67 ± 1.00	0.3
K	4110 ± 200	4063 ± 230	1.6
La	15 +/- 2	13.5 ± 2.0	0.06
Na	828 ± 77	834 ± 69	5.2
Rb	30 +/- 2	33.7 ± 2.1	1.5
Sc	6.3 ± 0.3	6.9 ± 0.6	0.04
Th	4.5 ± 0.1	5.3 ± 1.0	0.7
Yb	1.08 ± 0.09	1.3 ± 0.4	0.6

Table 1
Comparison of measured and certified values.

Atmospheric pollution monitoring in the Paris region

AIRPARIF (1998), the entity responsible for air quality monitoring in the Paris region, has three types of station for measuring the main primary atmospheric pollutants (CO, NO, NO_2, O_3, SO_2) covering a radius of approximately 100 km around Paris:

- *urban background stations:* installed away from the direct influence of any source of industrial or vehicular pollution, for example in parks, school grounds; the AIRPARIF network includes 60 stations of this type;
- *rural background stations:* installed on the edge of the Paris conurbation, intended to measure the impact of certain pollutants generated by chemical reaction, such as O_3; the network includes 3 stations of this type;
- *proximity stations:* installed in immediate proximity to vehicular traffic; the network includes 9 stations of this type.

The concentrations of primary pollutants measured by an urban background station (located in Paris, 500 metres from the Place d'Italie), representative of climatic events observed at the scale of the Paris region, were compared with the levels in the atmosphere of the stable elements determined by this study.

For this purpose the daily measurements made by AIRPARIF in 1998 have been matched to the corresponding weeks of ASS500 P atmospheric sampling.

Results and discussion

A certain number of elements present in the aerosols are used as markers of certain sources of atmospheric pollution, of anthropogenic or natural origin. The various sources of urban pollution (main elements As, Se, Zn, Sb) and the natural sources, derived essentially from crustal material and the ocean, (main elements Al, Cl, Fe, La, Mn, Na, Ce, Sm) are listed in Table 2.

Sources	Markers
Crustal material	Al, Mn, Fe, Sc, Rare Earth Elements
Marine aerosols	Na, Cl
Coal combustion	As, Se, Hg
Oil combustion	V, La, Sm
Refineries	La, Sm
Motor vehicles	Br, Zn, Sb, Pb, Cu (La, Ce, Al, Fe)*
Wood burning	K
Incinerators	Na, K, Cl, In, Hg
Industrial urban areas	V, Zn, Se, Mo, Sb
Iron/steel works	Fe, Zn, Se, Mo, Sb,
Ni, Cu extraction	Hg, As, Se
Zn, Cd, Pb smelting extraction	In, As, Se, Co, Cd, Cr
Aluminium plants	Al, Mg, Hg
Paint	Ba, Ti
Precious metal	Au, Cr, Mo
	* *Catalytic converter*

I Table 2
Sources of atmospheric particulates and their elemental markers (from reference [18]).

An effective approach for revealing any atmospheric pollution of anthropogenic origin consists in calculating an enrichment factor (EF) for each element, defined as the ratio of the element of interest in the sample to a reference element in the sample $(Xi/Ci)_{SAMPLE}$ divided by the same ratio in a reference material $(Xi/Ci)_{REF}$. In this work the table of crustal abundance given by Taylor (1972) was used, with respect to Sc as the reference element because of its low volatility and lack of anthropogenic sources. The mean enrichment

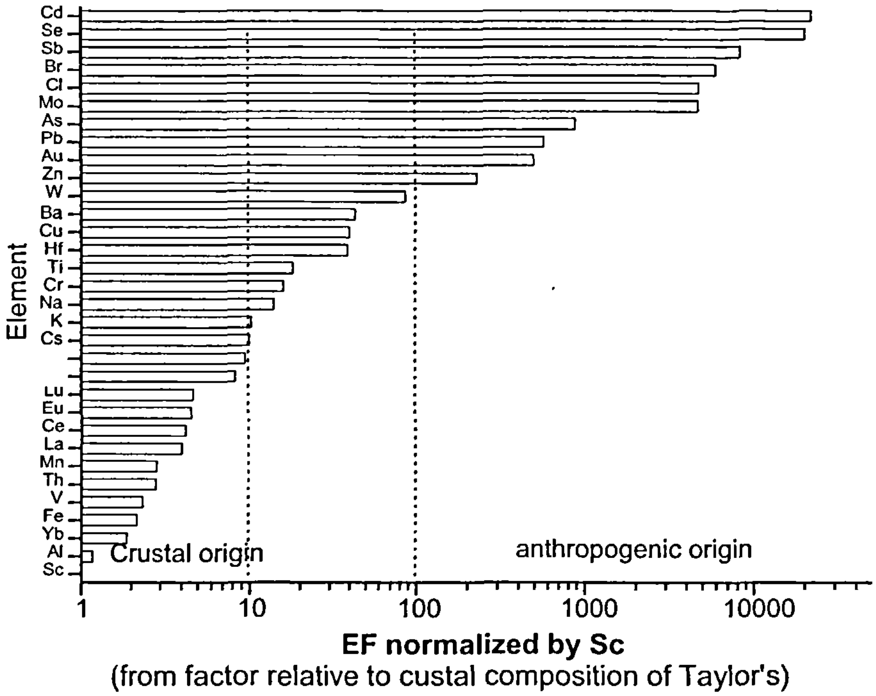


Figure 5
Enrichment factors related to TSP.

factor for each stable element, calculated from the 54 weekly atmospheric samples taken in 1998, is shown in Figure 5. The mean enrichment factors show a very wide range of variation (10^0 to 10^4). The hypothesis of emission sources of anthropogenic origin is highly probable for certain elements showing an EF greater than 10^2 (Cd, Se, Sb, Br, Cl, As, Pb, Mo, Au, Zn). Low enrichment factors, below 10, were observed for certain elements such as Al, Co, Cs, Hf, K, Mg, Mn, Th and the rare earths; it can be assumed that these elements correspond to the redispersion of materials from superficial layers of the ground in the investigated area. A few elements have moderate enrichment (Cr, V, Ti, Ba, Cu, W). Samples taken from the ground surface in the immediate vicinity of the sampling apparatus were sampled and analyzed by neutron activation. The EF values calculated as described above are given in Figure 6; it can be seen

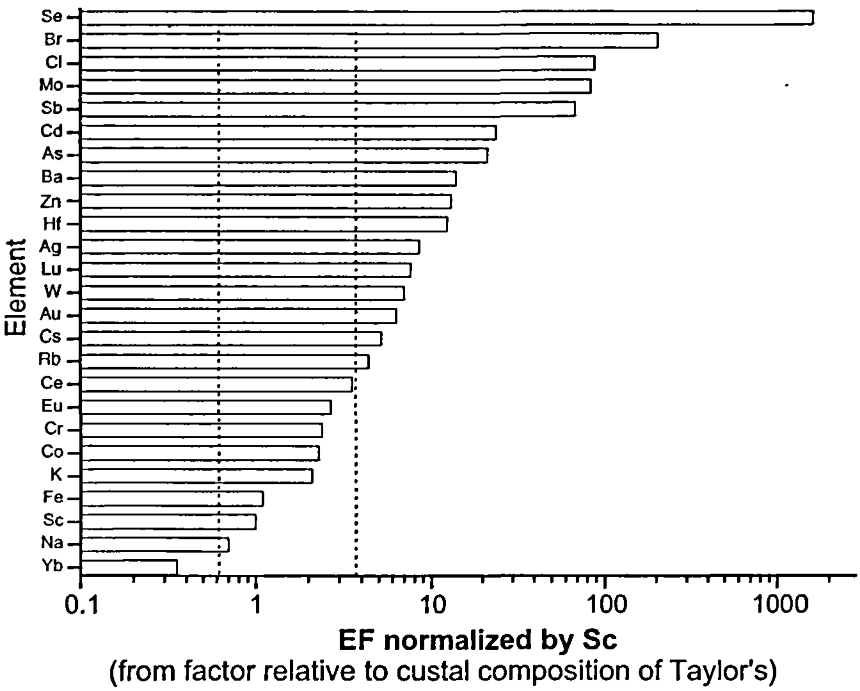


Figure 6
Enrichment factors in soils close to the sampler.

that the values obtained are, in general, an order of magnitude lower than those of the atmospheric aerosols; substantial marking of the ground samples for certain elements (Se, Br, Cd, Mo, Sb) is clearly apparent, corresponding with the highest EF values recorded for the aerosol samples. These results can be interpreted by considering a process of deposition of atmospheric aerosols enriched with stable elements under the effect of favourable climatic conditions. It should be noted that the concentration of the element Sc (10 ppm), used as reference for the enrichment factor calculations, is compatible with the value given by Taylor (20 ppm) (Taylor, 1972).

The trace element concentrations determined in TSP and presented in this work are in all cases equivalent to the levels found in industrialized suburban areas of the major European cities. The mean concentrations (1998) of stable elements measured in the Paris suburbs, expressed in ng.m^{-3}, the values published by several authors (Chung *et al.*, 1997; Gallorini *et al.*, 1998; Querol *et al.*, 1997; Krivan & Egger, 1986) for different cities in Europe and in Asia, and the minima and maxima for the USA are given in Table 3. The mean concentrations measured near Paris are characteristic of the major industrial cities and give an idea, despite the wide seasonal variation, of the total quantities of trace elements present in atmospheric aerosols in urban areas and of the nature of the main pollutants; these data, coupled with other parameters such as meteorological data, are essential clues for identifying the emission sources.

The mean Br/Na ratio calculated for 1998 (0.045) is an order of magnitude greater than the oceanic ratio (0.0062) (Nouchpramool *et al.*, 1998); this result indicates a local emission source for the element Na; the probable origin is an incinerator located 10 km from the sampling point (Figure 1), Na and Cl being characteristic markers of this type of pollution (Gone *et al.*, 2000).

The Cl/Pb ratio is an indication of fresh particles emitted in the exhaust by engines burning petrol; this ratio is about 0.14 (Ozben *et al.*, 1998). However, it should be noted that this ratio can be significantly different in France depending on the type of fuel produced. In this work the Cl/Br ratio was found to be 91, a very high value, which supports the hypothesis of the incinerator as potential emission source.

The Br/Pb ratio, a characteristic of fuel quality, can vary from 0.28 to 0.47 (Ozben *et al.*, 1998). The mean annual Br/Pb ratio found in this work is close to 2; this result, much higher than the expected value considering the sampling apparatus is located 800 metres from a main road with heavy traffic, may indicate the involvement of a substantial emission source for Br, independent of the one related to road traffic.

In contrast the high enrichment factors for elements Cd, Pb and Sb can be assumed to indicate pollution for which the main emission source is road traffic; other elements (Cu, Ce, La, etc.) could have the same origin, as suggested by Huang *et al.* (1994).

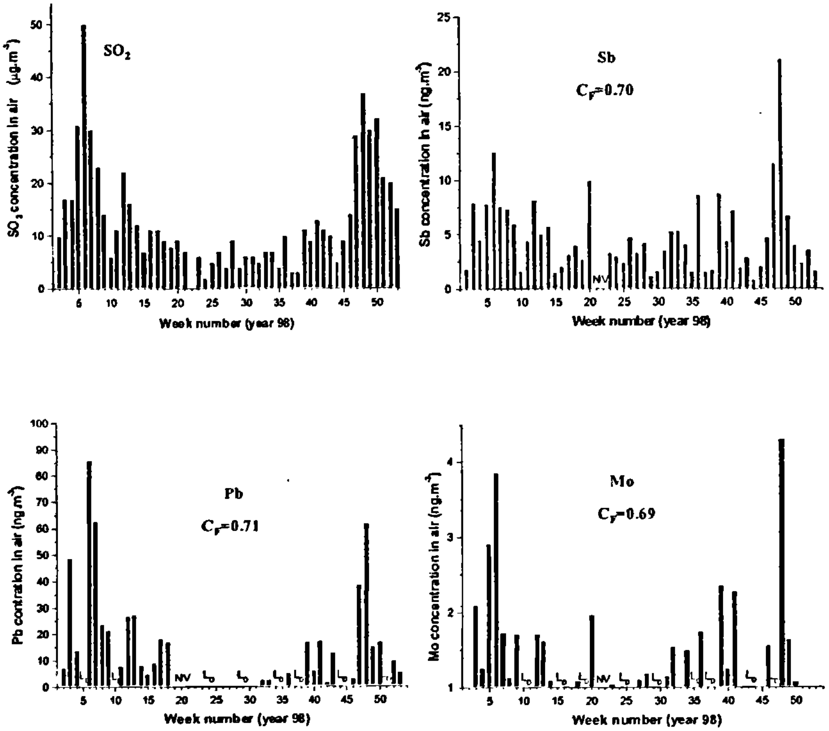
The elements As and Se, in trace amounts in the atmospheric aerosols but showing high EF values, could originate in the use of fossil fuels (district heating, etc.).

Element	Paris (our work)					Milan			Ulm	Castellon	Europe		Bangkok	Seoul	Mexico	USA	
	Median		Min	Max	MDC	Median	Min	Max	Median	Median	Min	max	Median	Median	higher values	Min	Max
			ng m^{-3}				ng.m^{-3}		ng.m^{-3}	ng.m^{-3}	ng.m^{-3}		ng.m^{-3}	ng m^{-3}	ng.m^{-3}	ng.m^{-3}	
Al	286	*(18%)*	*61*	*597*	*7.8*								3950	2407			
As	4.1	*(18%)*	*1.1*	*13*	*0.24*	4.9	*0.5*	*12*	0.99	33	1	700	174.4	6.85		2	2320
Au	0.0035	*(20%)*	*0.0010*	*0.0040*	*0.00060*	0.12	*0.005*	*0.6*	0.017					0.007	3120		
Ba	55	*(18%)*	*9.1*	*149*	*6.3*				25	111							
Br	46	*(19%)*	*6.3*	*136*	*0.11*	387	*43*	*872*	71	72	24	433	23.79	12.1		32	1720
Cd	13	*(19%)*	*1.2*	*33*	*1.5*	8	*3.3*	*45*	1.33	1.8	1.3	27		6.96	270	0.2	7000
Ce	0.78	*(18%)*	*0.15*	*2.3*	*0.11*	1.8	*0.3*	*2.8*	0.62		0.4	14	3.26	0.44		0.8	13
Cl	1935	*(20%)*	*30*	*5740*	*8.5*	1350	*150*	*3692*			153	2500	995	639	3620	366	1500
Co	0.74	*(22%)*	*0.14*	*2.0*	*0.05*	4.3	*0.8*	*16*	0.32	4.2	0.25	18.3		0.81	60830	0.14	83
Cr	5	*(21%)*	*0.90*	*12*	*0.19*	70	*2*	*264*	16	34	3.7	6.7	3.01	1.86	15750	0.029	2.1
Cs	0.089	*(23%)*	*0.020*	*0.22*	*0.030*	0.14.	*0.1*	*3.7*	0.28		0.2	0.6	2.26	0.44			
Cu	15	*(67%)*	*4.4*	*51*	*7.1*	43	*6*	*130*	64	1.4	17	64			52	3	5140
Eu	0.029	*(69%)*	*0.010*	*0.083*	*0.017*	0.05	*0.02*	*0.08*	0.024		0.014	0.1				0.03	0.09
Fe	377	*(21%)*	*385*	*931*	*12*	2170	*300*	*3600*	930	1800	520	3500	2040	160		130	13800
Hf	0.093	*(23%)*	*0.030*	*0.70*	*0.015*	0.1	*0.05*	*0.45*	0.056	175	0.02	0.06		0.19			
K	675	*(21%)*	*223*	*2460*	*25.5*					5000				383	740		
La	0.37	*(20%)*	*0.075*	*1.1*	*0.025*	1.5	*0.4*	*1.8*	0.48		0.2	3.4	1.68	0.14		0.5	9.1
Lu	0.0070	*(72%)*	*0.0030*	*0.016*	*0.006*									0.11			
Mg	185	*(19%)*	*87*	*272*	*42*								212		320		
Mn	8.1	*(18%)*	*2.1*	*17*	*0.089*	40	*16*	*282*	20		13	390	58.74	13.7	190	23	850
Mo	1.5	*(27%)*	*0.37*	*4.3*	*0.57*				2.8	8.9							
Na	1020	*(18%)*	*276*	*3500*	*50*				370	5300			977.5	168	7880		
Pb	21	*(15%)*	*1.6*	*86*	*3.2*	775	*75*	*4000*	365		235	365				30	96270
Sb	5.0	*(18%)*	*0.80*	*21*	*0.015*	29	*14*	*124*	9.1	4.3	0.5	51	4.05	8.52		0.5	171
Sc	0.066	*(20%)*	*0.026*	*0.11*	*0.0015*	1.6	*0.5*	*3.7*	0.046	1.7	0.04	0.8	466	0.03		0.1	3.1
Se	3.0	*(18%)*	*0.11*	*7.0*		0.6	*0.3*	*1.6*	1	8.1			550.8	4.53			
Th	0.081	*(30%)*	*0.017*	*0.21*	*0.03*	0.03	*0.01*	*0.08*	0.095	4.9	0.05	0.1		0.2		0.02	0.42
Ti	307	*(19%)*	*92*	*427*	*23*	60	*40*	*85*					177.9			36	180
V	6.7	*(19%)*	*2.2*	*8.2*	*0.21*	31	*9.1*	*61*					19.65	14.5	7116	0.40	760
W	0.43	*(28%)*	*0.036*	*1.8*	*0.08*	1	*0.08*	*3.5*	<0.4		11	73					
Yb	0.017	*(32%)*	*0.0030*	*0.065*	*0.005*				0.022					0.12			
Zn	51	*(20%)*	*2.1*	*156*	*0.75*	85	*31*	*270*	170	256	80	200	282	0.0148		58	741

Table 3

Analytical results of Total Suspended Particles in suburban area of Paris and comparison with other studies.

Figure 7 shows the distribution of the concentrations of three heavy elements (Mo, Sb and Pb), characterized by high potential toxicity, in the 54 weekly atmospheric samples collected in 1998. As a comparison, the variation in a primary pollutant (SO_2) measured by AIRPARIF over the same period is shown. There is high seasonal variability; the maximum concentrations are observed in winter periods that favour temperature inversions and climatic episodes



$$r=\frac{\frac{1}{n}\Sigma(x_i-\mu_x)(y_i-\mu_y)}{\sqrt{\frac{1}{n}\Sigma(x_i-\mu_x)^2}\times\sqrt{\frac{1}{n}\Sigma(y_i-\mu_y)^2}}$$

Correlation factor (C_r)

LD : Detection Limit
NV : None Value

with x_i, y_i observed data (SO_2 and stable element concentration)
μ_x, μ_y : means of populations x_i and y_i

I Figure 7
Comparison between the variation of concentration of some trace heavy elements inTSP observed at Monthlery during year 98 and the variation of SO_2 measured by AIRPARIF at Paris arear.

involving anticyclonic stability and lack of wind. Moreover, there is considerable similarity between the annual variation of primary pollutants (SO_2, NO, etc.) and that of trace elements in the atmospheric particulates; as an example, analysis of the covariance of the data for SO_2 and for the metallic elements gives a correlation coefficient (r) close to 0.7. This can be explained by the fact that the stable particulate pollutants and the chemical pollutants come from emission sources that are very probably of different origins, but are produced in a diffuse manner, thus obeying the same dispersion rules dependent on the same climatic conditions. This hypothesis is plausible, since no correlation is observed between variation in Pb and Sb concentrations and variation in road traffic (Figure 8) in the immediate vicinity of the sampling apparatus.

The variation during the year of the concentrations of certain elements of non-anthropogenic origin is shown in Figure 9. No correlation with the variation of primary pollutants is observed; this is a

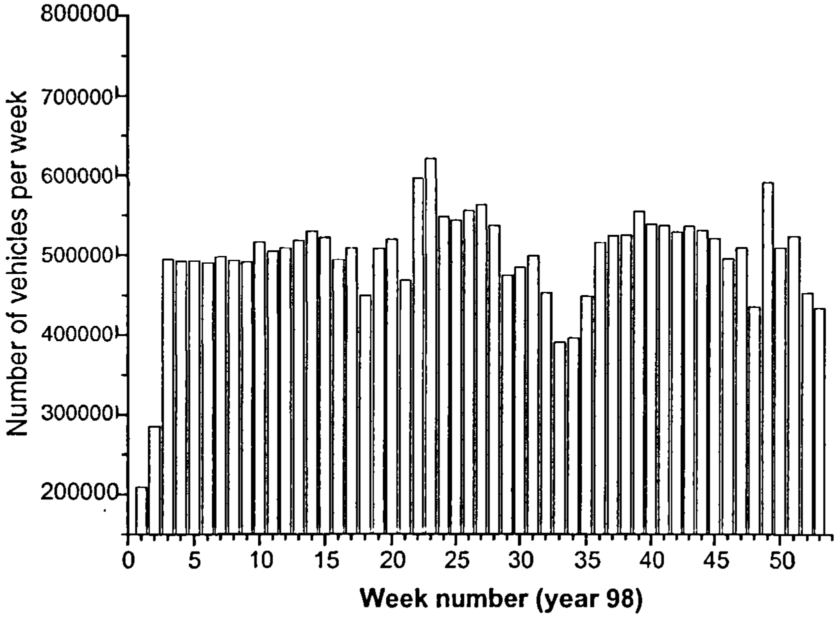


Figure 8
Trafic density related to the road trunk N20 located at 800 m of the sampler.

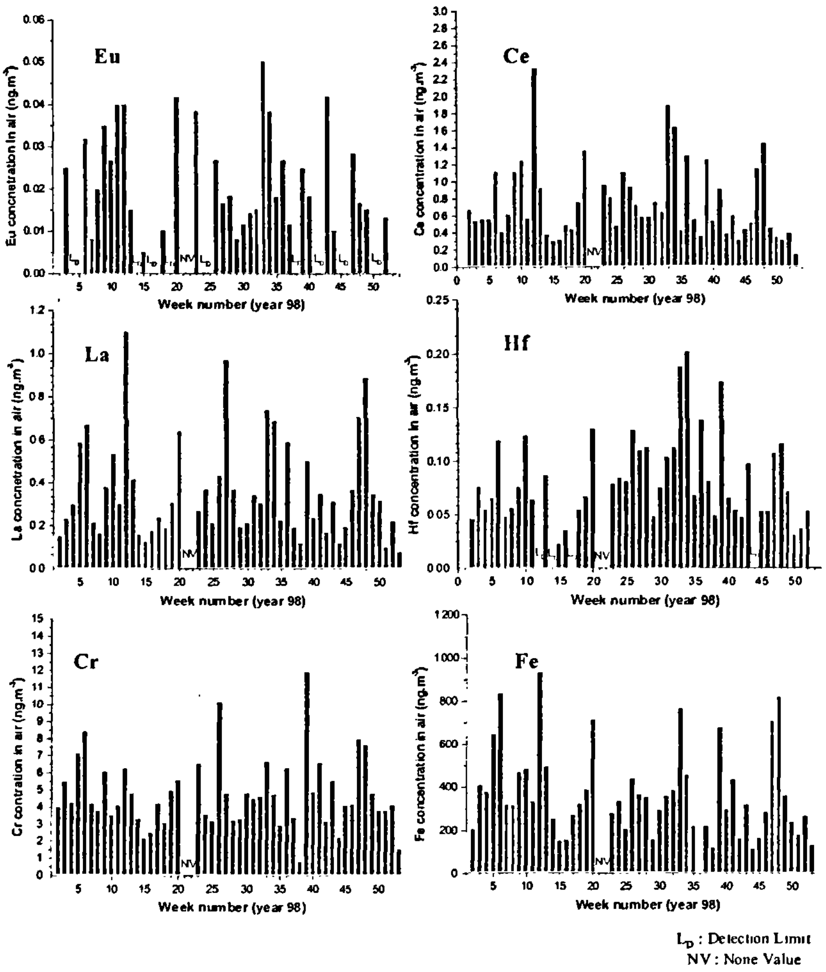


Figure 9
Variation of some trace element concentrations inTSP at Montlhery related to weak EF elements during year 98.

general trend for all the elements quantified in the atmospheric aerosols showing a low EF value and mainly of crustal origin. The low measured concentrations of these elements and the fact that the sampling apparatus is installed in a semi-urban area suggests a nearby origin, related to natural redispersion phenomena.

The annual variation of certain elements with high EF values is shown in Figure 10. Poor correlation of these elements with the variation of primary pollutants is observed, which might indicate the presence of a point source close to the sampling area.

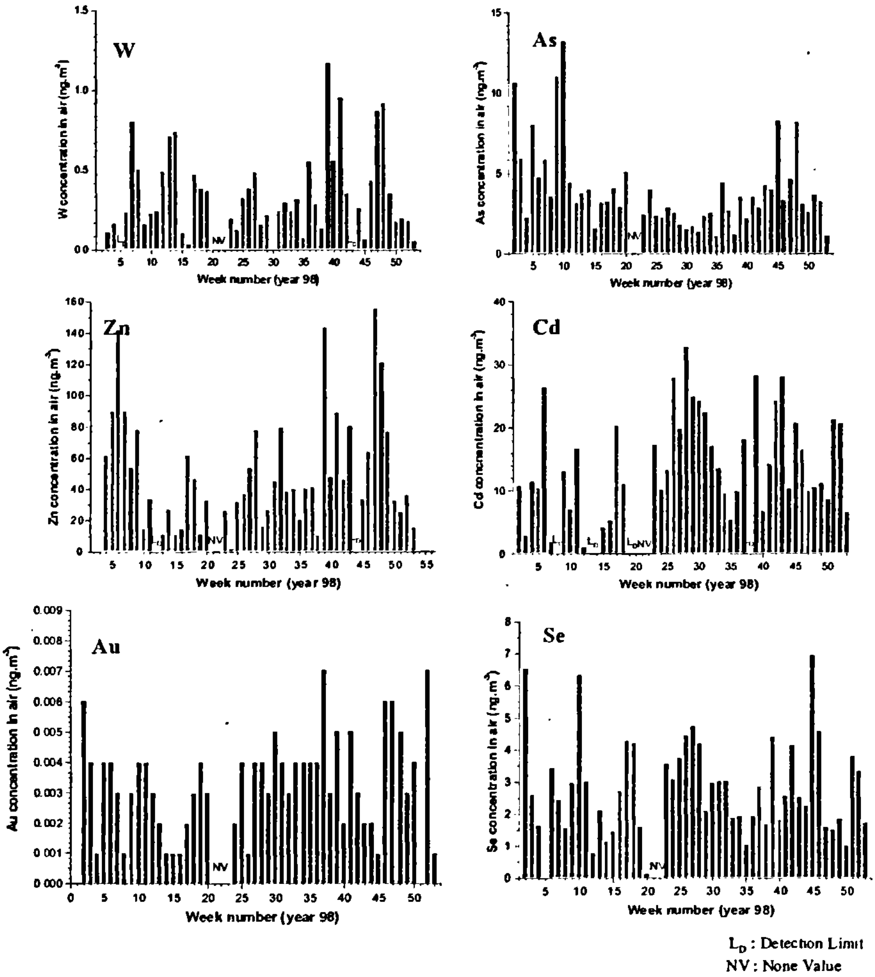


Figure 10
Variation of some trace element concentrations inTSP at Montlhery during year 98 related to high EF elements.

Conclusion

The characterization of trace elements in suspended particulate matter in major industrial cities has recently become a subject of research, since the public authorities became aware of the absence or deficit of data on possible toxicological and physiological impacts of certain elements on health. Furthermore, standards for maximum permitted concentrations in the atmosphere, including for the aerosol fraction smaller than 2.5 mm, the most harmful to the human respiratory system, are now being introduced. Although the data provided by this study concern only the total atmospheric suspended particulates (TSP), the entire particle-size range was included, as the efficiency of the filter medium remains high down to submicron particle sizes. However, the relationship between the analysis and the particle size class was not studied. The nature of the elements and the concentrations detected in the atmosphere during 1998 identify the major anthropogenic pollutants and show their seasonal variations. These data provide a guide for further investigation of the impact on man. This study is the first of its type carried out in France; the results obtained could be used as reference indicators for evaluating the long-term overall variation of atmospheric pollution in the Paris region, particularly the heavy metal levels.

Furthermore, in addition to the measurements provided by the type of study described here, it is necessary to set up collaborations with the various protagonists concerned to a greater or lesser extent by urban pollution in order to obtain the most complete possible synthesis of the available data, in particular those relating to the emissions of the various industrial activities, which are rarely published. Knowledge of these data, coupled with atmospheric modelling taking into account local weather, should enable more precise determination of the origin of emission sources for the major pollutants.

This study has also shown that neutron activation analysis remains a powerful, non-destructive, multi-element analysis method, with a measurement sensitivity that remains acceptable for this type of study. Nevertheless, although more than 30 elements were measured by this technique, knowledge of the atmospheric concentrations of certain elements (Pb, Hg, S) that are of particular interest in terms of their impact on man necessitate the use of other techniques in addition to neutron activation (ICP-AE, ICP-MS, ED-XRF, AAS, etc.).

Acknowledgements

The authors wish greatly to thanks J. C. Carbonnelle, J. Moro, F. Raynaud and F. Mietlicki (AIRPARIF) for their participation in this work.

Bibliography

AIRPARIF, 1998 —
Surveillance de la qualité de l'air en Ile-de-France. Rapport d'activité, 108 p.

CHUNG Y. S., CHUNG Y. J., JEONG E. S., CHO S. Y., 1998 —
Study on air pollution monitoring in Korea using instrumental neutron activation analysis. *Journal of Rdioanalytical Nuclear Chemistry,* 217 (1): 83-89.

CURRIE L. A., 1968 —
Abundances,of Naturally Occuring Isotopes. *Anal. Chem.,* 40: 586-593.

DE BIEVRE P., BRANES I. L., 1992 –
Handbook of Chemistry and Physics 73rd Edition. CRC Press: 11,28 – 11,132.

DJINGOVA R., IVANOVA J. U., KULEFF I., 1998 —
Comparative evaluation of the possibilities of INAA, ED-XRF, ICP-AES and AAS in the analysis of plants. *Journal of Rdioanalytical Chemistry,* 237 (1-2): 25-34.

GALLORINI M., BORRINI P. A., BONARDI M., ROLLA A., 1998 —
Trace elements in the atmospheric particulate of Milan and suburban areas: a study carried out by INAA. *Journal of Radioanalytical and Nuclear Chemistry,* 235 (1-2): 241-247.

ERDTMANN G., 1976 —
"Neutron activation Tables ". *In: Kernchemie in Einzeldarstellangen.* New York, Verlagchemie, t.VI.

QUEROL X., ALASTUEY A., LOPEZ-SOLER A., 1997 —
Trace element contents in atmospheric suspended particules: Interferences from instrumental neutron activation analysis Fresenius. *J. Anal. Chem.,* 357: 934-940.

SARMANI S., ABUGASSA I., HAMZAH A., 1998 —
Instrument neutron activation analysis of environmental samples using the K_0-standardization method. *Journal of Radioanalytical Chemistry,* 234 (1-2): 17-20.

SCHULZE J., AUER M., RWERZI R., 2000 —
Low level radioactivity measurement in support of the CTBTO. *Applied Radiation and Isotopes,* 52: 23-30.

TAYLOR S. R., 1972 —
Abundance of chemical elements in

the continental crust : a new table. *Geochim. and Cosmochim. Acta,* 28: 1973-1985.

KRIVAN V., EGGER K. P., 1986 — Multielementanalyse von Schwebstäuben der Stadt Ulm und Vergleich der Lufbelastung mit anderen Regionen Frezenus Z. *Analytical Chemistry,* 325: 41-49.

NOUCHPRAMOOL N., SUMITRA T., LEENANUPHUNT V., 1998 — "Characterization of fine airbone particulates in Bangkok urban area by neutron activation analysis". *In: Nuclear Analytical Methods in the Life Sciences (NAMLS),* Beijing, China, October 26-30, 5p.

GONE J. K., OLMEZ I., AMES M. R., 2000 — Size distribution and probable sources of trace elements in submicron atmospheric particulate material. *Journal of Radioanalytical and Nuclear Chemistry,* 244 (1): 133-139.

OZBEN C., BELIN B., GÜVEN H., 1998 — Analysis of aerosols at the Bosphorus bridge of Istanbul. *Journal of Radioanalytical and Nuclear Chemistry,* 238 (1-2): 101-104.

HUANG X., OLMEZ L., ARAS N. K., 1994 — *Journal of Atmospheric Environment,* 28: 1385-1990.