

STUDY OF ATMOSPHERIC AEROSOLS IN ZAIRE BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS, ATOMIC ABSORPTION SPECTROPHOTOMETRY AND ION-EXCHANGE CHROMATOGRAPHY.

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SUMMARY

Instrumental neutron activation analysis and atomic absorption spectrophotometry were applied to the determination of trace element abundances in airborne particulate matter collected throughout Kinshasa. Elements As, Au, Ba, Br, Ce, Cd, Co, Cs, Fe, K, La, Na, Pb, Rb, Sb, Sc, Se, Sm, Th, U and Zn and gaseous pollutants under anionic forms F, Cl, NO_x, SO₄^{-x} and PO₄³⁻ were determined.

Some mathematical procedures such as frequency distribution and box-and-whiskers plots, Student's test, enrichment factors and multivariate factor analysis were applied to analytical data set in view to examine their normality, their variations among sites and to identify their sources.

Data were found to be log normally distributed for all elements, except for As. No significance differences among sites were found for Au, La and La at HO ≈ 0.05, whereas Br and Pb exhibited significance differences. Eight factors were extracted to identify pollutant sources of which the important one was earth's crust.

INTRODUCTION

Atmospheric aerosol is defined as all solid and or liquid particulate matter

suspended in air. This particulate matter can originate from natural and anthropogenic sources. Natural sources include, on a global scale, soil dust raised by winds, volcanic eruptions, natural firewood and marine spray. Anthropogenic sources comprise fuel combustion such as charcoal and oil, industrial processes, waste incineration and transport.

The strength of anthropogenic sources amounts merely to 10 - 15 % of the total particle mass production. It must be mentioned, however, that this result holds true only for global considerations. Under local urban conditions, the ambient aerosol may be totally dominated by particulate matter of human origin [1].

Although this contribution is known to be important in the northern hemisphere countries, significant variations, both, geographical and temporal, exist in the southern hemisphere countries due to the difference in anthropogenic release between urban and rural areas, to the difference in the atmospheric conditions and to the flora. Study of the aerosol chemistry in such regions also are necessary to assess by now, how the aerosol mass and chemical composition are influenced by anthropogenic sources and to establish the different types of interactions between air pollutants and natural species. Furthermore, important changes would occur in the future due to the development of industry and the explosive population growth, so that data base are to be performed now for future investigations.

In Africa, studies in aerosol chemistry in progress are up to now but limited to the northern hemisphere [2-5]. To our knowledge, the only investigations on trace elements in aerosols in the southern part of Sahara, were at a certain extent, performed in south Africa and Namibia. Less is known on the continental and tropical regions, specially concerning its regional background.

The previous reports described the plan of the work relevant to this CRP and the development of sampling and analytical methodologies to be used for environmental monitoring.

The present report deals with results on the fraction of atmospheric inorganic pollutants determined in air in Kinshasa during the period between 1985-1989.

About 204 filter samples and 146 trapping solutions of inorganic gaseous pollutants

were collected. Solid pollutants were analyzed by either instrumental neutron activation analysis or atomic absorption spectrometry whereas gaseous pollutants were analyzed by ion-exchange chromatography. Mathematical procedures were applied to describe distribution functions of data, to calculate the enrichment factors of determined air compounds and to identify their sources using multivariate factor analysis.

EXPERIMENTAL

Sites and sampling procedure

Samples herein concerned were collected during 1986-89 at 4 pilot stations installed throughout Kinshasa with the following characteristics [6-8]:

1. KCC (Kinshasa Campus Centre Nucléaire): site located on a ventilated hill, the Mont-Amba, with scattered population, low vehicle traffic and absence of industries;
2. KNR (Kinshasa Ndjili Regideso): site located beside industrial area and busy vehicle traffic road, with middle population density;
3. KNN (Kinshasa Ngiri-Ngiri): site with high population density, low vehicle traffic and absence of industries;
4. KSM (Kinshasa 20 May Stadium): populous quarter located beside an industrial area with busy vehicle traffic.

Samples were collected at the 4 pilot stations using low volume samplers in such a way to collect:

1. solid suspended particles by sucking air on Whatman filter n° 41 or TFA filter n° 41;
2. inorganic pollutant gases (SO₂, NO_x, etc...) by bubbling filtered air in carbonate buffer solution as trapping solution;
3. rainwater in blackened polyethylene bottles topped with funnels.

The complete sampling procedure was described in previous papers [6-9].

ANALYTICAL TECHNIQUES

Instrumental neutron activation analysis (INAA)

Quarters of air filters were irradiated in the thermal column of the CEN - Mol BR-1 reactor at an average integrated flux of 2.9×10^{16} n·cm⁻². The counting system comprised a Ge detector with associated electronics coupled to a Canberra Series 35 PLUS analyzer. Two sets of counting conditions (600 seconds after 1-2 days decay time for short-lived radioisotopes and 6000 seconds after 10-15 days decay time for long-lived radioisotopes) were used [7,8]. Quantitation was based on a comparison with standards prepared by dropping 20 µL of solutions containing elements to be analyzed at known concentrations on Whatman 41 and irradiated along with the air filters.

Atomic absorption spectrophotometry

Quarter of air filter was dipped into 5 mL of deionized water and submitted to a 15 minute-ultrasonification shaking to extract water-soluble compounds. Atomic absorption spectrometer was applied to the solution for the determination of Cd and Pb at wave lengths 283.3 and 228.8 nm respectively using a Perkin-Elmer graphite furnace atomic absorption spectrophotometer 303. The measurement device was calibrated with Cd and Pb solutions prepared from standard solutions.

Ion - exchange chromatography

The concentrations of water-soluble airborne particulate and those of atmospheric acid gases trapped in carbonate buffer solutions were determined using a DIONEX IC 10 ion-exchange chromatography under their anionic forms. Concentrations of standards ranged in the observed sample concentrations.

Performances of analytical techniques were described in the previous reports [7,8].

RESULTS AND DISCUSSION

Analytical data were handled using STATGRAPHICS software and are reported in Tables 1-4. These results are discussed in the following sections.

1. Distribution functions and outlier rejection.

As a first step all analytical results were checked for their distribution functions graphically (plot of frequency distribution histograms, box-and-whiskers plots), and numerically (test of skewness and kurtosis). Results showed that all elements, except As, can be reasonably approximated by log-normal functions.

Box-and-whiskers plots showed outliers which were rejected prior to calculating means and variations with the individual elements.

Table 1 summarizes results of inorganic pollutants determined in air in Kinshasa. It includes the number of determinations after outlier rejection, the range of concentrations, the geometric means and the medians with their quartiles. These results show that geometric means are close to the medians for the batch of determined compounds. Relatively high atmospheric concentrations were found for: Br, Fe, K, Na, Pb, Zn. Elements Ba, F_(S1), and compounds NO₂_(S1), NO₂_(B) and P₃O₄³⁻_(B) were determined in few samples, and so, were not included in this table.

Table 2 summarizes geometric means and medians computed for all compounds determined in airborne particulate ranged by site.

2. Variations among sites.

Variations of all analyzed compounds among the 4 sampling sites were estimated using statistical t Student test for testing null hypothesis Ho at significant level = 0,05. During test, elements of sampling sites were mutually compared. Results are reported in Table 3. No significance differences among sites were found for Au, La, Rb, Cd whereas Br and Pb exhibit significance differences. For other elements, significance differences exist or not among sites.

3. Enrichment factors.

Enrichment factor (EF) is the first exploratory step in source identification. Its values close to one are indicative that the main source of the trace element is of crustal origin; whereas an EF of ten or greater is indicative that the source of the element may be anthropogenic in nature [9]. Table 4 exhibits the EF obtained for analyzed trace elements.

Annex 21

It is observed that most of elements have an EF lower than 10 and so, could originate from earth's crust. Other elements are highly enriched than 10 and so are of anthropogenic origins.

4. Factor analysis.

A second exploratory step of analytical data was the multivariate factor analysis. This mathematical procedure is among widely used methods to investigate causal factors that control the system [10]. It was applied in source identification of trace elements occurring in air in Kinshasa. The first 8 components which explained 91 % of variance were selected prior rotating by Varimax procedure to produce factor loading values. Results are reported in Table 5. Communality values over all variables exceeded 0.75 and their sum was 13,21 corresponding to the sum of the estimated variances in the system.

The factor loading values were interpreted in terms of sources occurring in air in Kinshasa.

- Factor 1: includes elements originating from dispersal crustal dust and is strongly dependant of: Fe, Sc, Th and rare earths.
- Factor 2: is alkaline elements Na and K dependant. These 2 elements could originate from fire wood or charcoal used for cooking or from crust.
- Factor 3: is associated with Zn which is known to be associated with refuse incineration.
- Factor 4: is Cd dependant which is associated with sulphide smelters.
- Factor 5: is Au dependant which could be associated with small goldsmith's works operating throughout the city.
- Factor 6: is Pb dependant; its origin is often associated with automobile exhaust.
- Factor 7: concerns Cs could originate from vegetables.

Factor 8: is Br dependant; as for Pb it is often associated with automobile exhaust. These 2 elements correlated weakly. Some raisons could be invoked: on the one hand, log normal frequency distribution histogram of Br showed 2 distinct populations of data; on the other hand, reported Pb concentrations are from only its soluble portion.

CONCLUSIONS

In spite of its ineffectiveness in the determination of interest elements Cd and Pb, it is confirmed by the present investigation that instrumental neutron activation analysis is a powerful tool for realizing the characterization airborne particulate matter where size samples do not exceed some mg.

From observations drawn out in this study, elements Ce, Fe, La, Sc, Sm and Th in air throughout Kinshasa are of crustal origin whereas other elements have doubtful or anthropogenic origins.

In order to grasp the features of airborne particulate matter in greater details in the investigated area, following steps are to be achieved:

1. instrumental neutron activation analysis of short-lived radionuclides for the determination of elements such as Al, Ti, V, Mn, Cl, Mg, Ca, S, I, Si, etc... This step has been started and is ongoing;
2. aerosol particulate fractionation for many purposes, including a better assessment of exposure to respirable toxic materials, the identification of sources of particles and quantitative apportionment of observed mass;
3. daily aerosol sampling using high volume samplers;
4. sampling of a remote area for information on the regional background;

This project being a whole Zaire concern, in a near future, a sampling programme is going to start in Shaba, to assess the contribution of mining activities to the burden of airborne particulate matter.

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Table 1: Concentrations of atmospheric inorganic pollutants in air in Kinshasa (in ng/m^3 otherwise quoted.)

Element	N	Range	Geometric mean	Median	Quartiles
As	140	0.14 - 4.29	0.92	0.93	0.59 - 1.06
Au	90	2E-3 - 1.10	0.044	0.04	0.02 - 0.10
Br	191	10.39 - 411.74	51.70	55.18	25.0 - 97.80
Cd	142	0.02 - 2.64	0.18	0.19	0.08 - 0.36
Ce	151	0.20 - 16.01	1.61	1.60	0.96 - 3.10
Co	108	0.10 - 5.79	0.68	0.70	0.40 - 1.20
Cr	163	1.30 - 38.40	6.66	6.70	4.18 - 10.29
Cs	111	0.06 - 3.09	0.42	0.41	0.22 - 0.77
Fe ($\mu\text{g}/\text{m}^3$)	192	0.42 - 9.10	1.59	1.49	0.98 - 2.47
K ($\mu\text{g}/\text{m}^3$)	184	0.15 - 5.31	1.07	1.02	0.62 - 1.20
La	169	0.13 - 7.62	1.02	1.09	0.62 - 1.79
Na ($\mu\text{g}/\text{m}^3$)	176	0.11 - 6.99	0.62	0.60	0.36 - 0.99
Pb	131	0.51 - 339.4	40.14	42.4	22.0 - 69.7
Rb	66	3.01 - 20.44	7.79	8.28	5.70 - 10.26
Sb	177	0.38 - 10.89	1.91	1.82	1.20 - 2.98
Sc	191	0.07 - 1.06	0.28	0.30	0.20 - 0.43
Sm	186	0.03 - 0.75	0.14	0.13	0.10 - 0.24
Th	170	0.08 - 2.25	0.47	0.53	0.30 - 0.78
Zn	189	11.13 - 283.88	65.93	69.8	39.30 - 105.2
F ⁻ (S)	8	0.086 - 0.71	0.28	0.33	0.165 - 0.475
Cl ⁻ (S)	138	0.45 - 9.3	1.49	1.80	0.92 - 2.38
NO ₃ ⁻ (S)	139	0.47 - 14.48	2.88	2.70	1.76 - 4.71
SO ₄ ²⁻ (S)	146	0.75 - 24.6	3.95	3.92	2.3 - 7.23
Cl ⁻ (B)	102	0.44 - 6.82	1.32	1.13	0.82 - 2.19
NO ₃ ⁻ (B)	96	0.17 - 23.0	1.44	1.17	0.53 - 3.95
SO ₄ ²⁻ (B)	105	0.22 - 21.3	1.82	1.82	1.0 - 3.45

Table 2 : Geometric means and medians at the 4 sample sites
(in nR/m³ otherwise quoted.)

Element	KCC		KNR		KSM		KNN	
	Xq	Med	Xq	Med	Xq	Med	Xq	Med
As	0.78	0.85	0.76	0.83	0.97	1.03	1.12	1.10
Au	0.04	0.045	0.04	0.04	0.05	0.04	0.05	0.04
Br	23.96	24.46	98.33	106.15	63.46	67.74	41.29	45.01
Cd	0.21	0.25	1.76	1.48	1.65	1.80	0.16	0.18
Ce	1.44	1.75	1.25	1.27	2.30	2.47	1.96	1.97
Co	0.47	0.44	0.75	0.70	0.88	1.10	0.75	0.80
Cr	5.42	4.96	6.00	5.64	7.28	8.27	8.79	9.85
Cs	0.46	0.38	0.33	0.40	0.41	0.31	0.57	0.55
Fe *	1.39	1.40	1.54	1.32	1.61	1.62	2.06	2.03
K *	0.93	0.79	1.04	0.89	1.07	1.12	1.47	1.47
La	0.90	1.01	0.90	1.04	1.16	1.26	1.26	1.30
Na *	0.46	0.49	0.67	0.53	0.60	0.54	0.92	0.89
Pb	18.94	17.30	38.27	36.85	87.17	85.40	55.41	64.40
Rb	7.28	7.54	7.69	8.19	8.40	9.10	9.06	8.97
Sb	1.23	1.10	2.07	1.95	2.32	2.23	2.23	2.38
Sc	0.24	0.27	0.23	0.22	0.34	0.32	0.35	0.40
Sm	0.12	0.12	0.13	0.12	0.18	0.20	0.16	0.16
Th	0.40	0.43	0.43	0.44	0.57	0.60	0.60	0.60
Zn	37.86	38.41	70.80	70.40	74.58	86.79	117.87	133.78
Cl ⁻ (S)	1.07	0.99	1.47	1.48	2.06	2.26	1.96	1.62
NO ₃ ⁻ (S)	2.97	2.51	2.20	1.97	3.35	3.65	3.47	3.55
SO ₄ ²⁻ (S)	3.41	2.83	4.14	4.05	4.39	4.25	3.82	3.69
F ⁻ (B)	0.95	0.92	0.67	0.76	0.81	0.89	0.66	0.65
Cl ⁻ (B)	1.42	1.25	1.18	1.11	1.17	0.98	1.96	2.16
SO ₄ ²⁻ (B)	1.06	1.30	3.39	3.41	1.45	0.98	1.46	1.21

* uG/m³

Table 3 : Variation of trace element contents among sampling sites.

Element	KCC/KNR	KCC/KSM	KCC/KNN	KNR/KSM	KNR/KNN	KSM/KNN
Au	No	No	No	No	No	No
Br	Yes	Yes	Yes	Yes	Yes	Yes
Ce	No	Yes	No	Yes	Yes	No
Cr	No	Yes	Yes	No	Yes	No
Co	Yes	Yes	Yes	No	No	No
Cs	No	No	No	No	Yes	No
Fe	No	No	Yes	No	No	No
La	No	No	No	No	No	No
K	No	No	Yes	No	Yes	No
Na	Yes	No	Yes	No	No	Yes
Rb	No	No	No	No	No	No
Sb	Yes	Yes	Yes	No	No	No
Sc	No	Yes	Yes	Yes	Yes	No
Th	No	Yes	No	No	No	No
Zn	Yes	Yes	Yes	No	Yes	Yes
Cd	No	No	No	No	No	No
Pb	Yes	Yes	Yes	Yes	Yes	Yes

Table 4: Enrichment factors of atmospheric trace elements in Kinshasa

EF range	Elements
0.4 - 1.0	Sc, Sm, Co
1.0 - 5.0	Ce, La, Cr, K, Na, Th, Rb
5.0 - 10.0	Cs
10.0 - 40.0	As, Cd
40.0 - 100.0	Zn
> 100.0	Pb, Sb, Br, Au

Table 5 : Varimax rotated factor matrix of atmospheric trace elements
in Kinshasa.

Variable/Factor	1	2	3	4	5	6	7	8
As	0.63034	0.32419	0.41153	0.32275	0.27039	0.10215	-0.17492	-0.09280
Au	0.18819	0.01186	0.03363	0.10719	0.99115	0.11058	0.04164	0.05746
Bp	0.49879	0.15132	0.06899	0.10657	0.07445	0.01524	-0.04574	0.84008
Co	0.89289	0.09501	0.24022	0.09664	-0.17683	-0.03826	0.15900	0.25120
Co	0.40667	0.43746	0.45748	0.30871	-0.35586	0.29104	0.33593	0.11450
Cr	0.51916	0.33455	0.06888	0.16211	0.25346	0.35984	0.12973	0.11992
Cs	0.02099	0.03915	-0.00288	0.00438	0.03886	-0.00212	0.99288	-0.03150
Fr	0.76404	0.09862	0.42420	0.03918	0.18039	0.03195	-0.01394	0.29843
K	0.36136	0.77446	0.13042	0.38932	0.05635	0.05774	0.08965	0.07836
La	0.89832	0.33095	0.13186	0.04135	0.05545	0.12775	0.01617	0.08194
Na	0.16704	0.53037	0.04643	-0.14902	-0.03689	-0.10651	-0.02300	0.07255
Pb	0.63071	0.19713	0.33656	0.33300	0.40690	0.02006	0.02750	0.29394
Sb	0.68432	0.21956	-0.03763	0.41742	-0.14389	0.19090	0.06552	0.10490
So	0.83833	0.27162	0.04114	0.12894	0.24764	0.12777	0.02029	0.12137
Sm	0.92930	0.02356	0.05633	0.15165	0.08253	-0.01978	-0.03627	0.13075
Th	0.82483	0.29928	0.23170	0.09079	0.28934	0.20457	0.01671	0.08332
Zn	0.23390	0.07917	0.97747	0.11548	0.03494	0.06989	-0.00261	0.04856
Cd	0.16213	0.00616	0.11316	0.91885	0.09435	-0.00212	0.00106	0.05018
Pb	0.11795	-0.02741	0.07708	0.00353	0.09009	0.96231	-0.00764	0.00163