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Atmospheric Environment 40 (2006) 6554–6566
ATMOSPHERIC ENVIRONMENT
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Origin of atmospheric lead in Johannesburg, South Africa

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Received 28 February 2006; received in revised form 19 May 2006; accepted 25 May 2006

Abstract

The origin of lead in the atmosphere of Johannesburg, South Africa was investigated on the basis of elemental and lead isotopic analyses of coals, mine dumps, gasoline, and about 30 epiphytic lichen samples. Lead predominantly comes from automotive exhausts in urban and suburban areas, as leaded antiknock additives were still in use in South Africa at the time of the study. Although dust emissions from the numerous mine-tailing dumps were expected to contribute significantly to the heavy metal budget, the southern townships that are surrounded by the dumps (such as Soweto and other historically Black residential areas) do not appear to be more than partially influenced by them, and this influence seems to be geographically limited. Domestic coal burning, suspected to account for the total lead content in the air, is also recognised, but only acts as a minor source of lead, even in townships.

Keywords: Lichen; Lead isotope; Pollution; Mine dump; Mixing model

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1. Introduction

The city of Johannesburg was founded in 1886 after the discovery of the rich gold deposits of the Witwatersrand Basin. With 3.2 million inhabitants, it is the largest city in southern Africa and the second largest on the African continent. Most of the mining activity stopped in the immediate vicinity of the city more than a decade ago, and around 200 mine-tailing dumps, some as high as 50 m, are still exposed in the metropolis along an east–west axis (Fig. 1a). Some of the older mine dumps, however, have been reprocessed due to considerable improvements in extractive metallurgy of gold.

Although lead-free fuel was available on the market, leaded gasoline still held an 80% market share at the time of this study (leaded fuel was taken off the South African market in January 2006). Automotive exhaust gases were thus an important contributor for lead contamination in Johannesburg

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doi:10.1016/j.atmosenv.2006.05.064

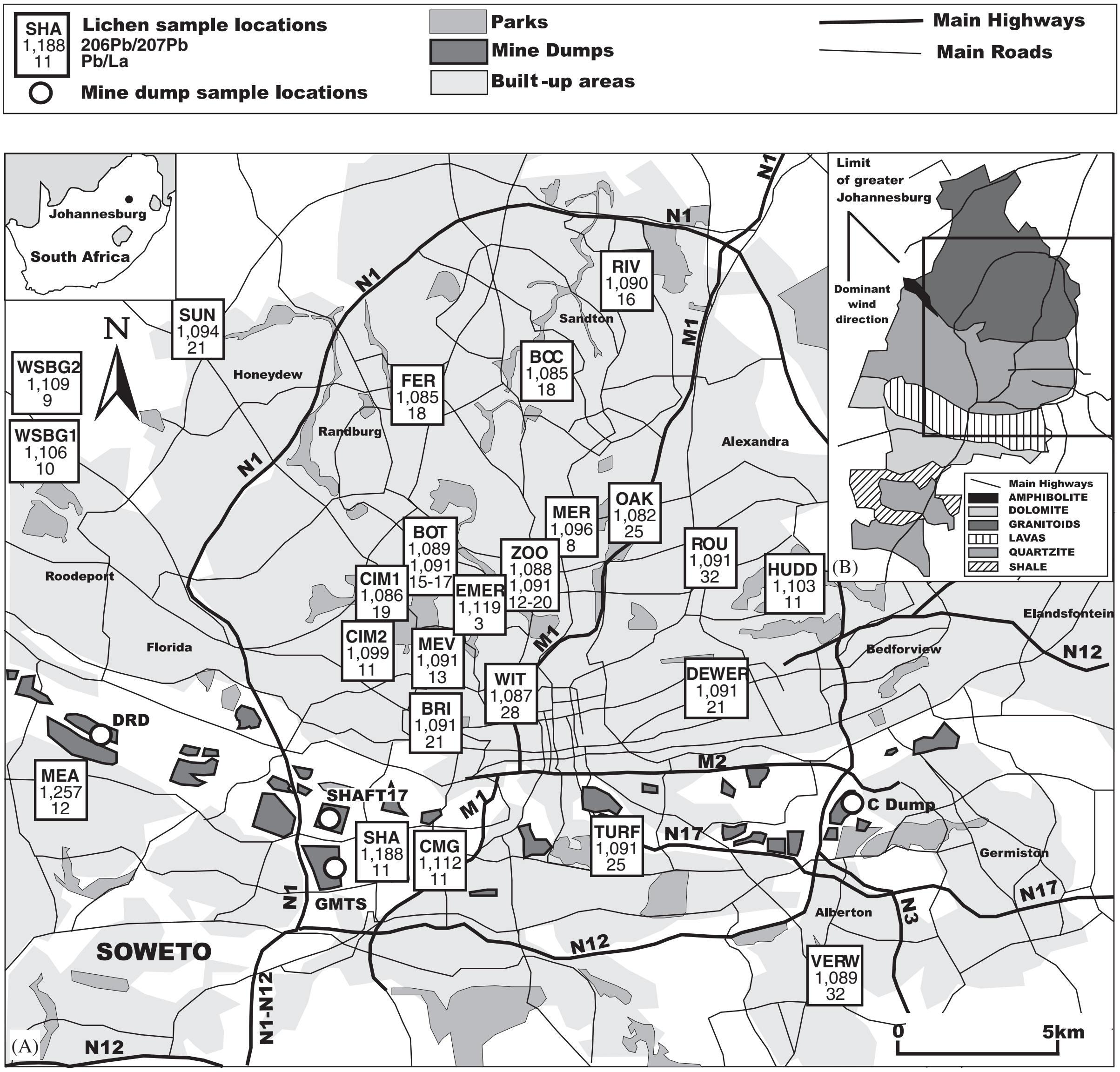


Fig. 1. (a) Map of Johannesburg and sampling sites, (b) simplified lithological map.

(Formenti et al., 1998), but many other sources may be involved, such as widespread domestic coal burning, dust from unpaved roads in poor townships, and surface mining operations. This means that in historically Black residential suburbs adjacent to mining areas, heavy metals associated with dust emissions from dumps and mining extraction are additional sources of pollution, which combine with contamination emitted by other human activities. This may enhance the breathable pollution risk level for populations living in the vicinity of mining operations. To date, exposure of historically disadvantaged communities to wind-blown mine tailings is the subject of intensive public debate.

Although it is of great importance to know the different origins of heavy metals when considering long-term strategies and environmental policies for reducing emissions, apportioning the various sources is not a trivial task. Heavy metal contents in the atmosphere are generally highly variable, depending on meteorological conditions, industrial and diurnal cycles, and density of the automotive traffic (Bergametti et al., 1989; Remoudaki et al., 1991; Monna et al., 1997; Flament et al., 2002; Chen et al., 2005). While deciphering the sources on the sole basis of heavy metal concentrations may sometimes produce ambiguous conclusions, lead isotopic abundances are particularly informative in these types of analyses as anthropogenic emissions and natural lead are usually characterised by different isotopic signatures (see the Clair C. Patterson Special Issue, Geochim. Cosmochim. Acta, 1994; Munksgaard and Parry, 1998). Furthermore, this approach often offers the opportunity to discriminate specific emissions among anthropogenic groups, e.g., alkyl lead additives, various industrial emissions, domestic wood and coal burning (i.e., Chiaradia et al., 1997; Åberg et al., 1999; Véron et al., 1999; Chiaradia and Cupelin, 2000; Kurkjian et al., 2002; Widory et al., 2004; Chen et al., 2005). Instead of collecting and measuring a large and costly set of airborne particles, some authors have chosen to apply the isotopic techniques on biological receptors such as trees, even though the meaning of the information drawn is currently subject to debate (Marcantonio et al., 1998; Tommasini et al., 2000; Bellis et al., 2002a, b; Bindler et al., 2004). Another approach consists in using moss (Kunert et al., 1999; Haack et al., 2004) and lichens (Jaakkola et al., 1983; Carignan and Gariépy, 1995; Monna et al., 1999; Getty et al., 1999; Doucet and Carignan, 2001; Carignan et al., 2002; Simonetti et al., 2003; Watmough and Hutchinson, 2004; Spiro et al., 2004; Cloquet et al., 2006), because they are supposed to represent integrated signals of atmospheric pollution. Lichens are slow-growing organisms which, over their lifespan, are expected to accumulate and retain high levels of mineral elements present in the atmosphere, but not from the host tree limb or rocks from which they are suspended (Getty et al., 1999; Loppi and Pirintsos, 2003). Their metabolism with respect to metals is not yet perfectly understood. While most of the authors state that lichens tend to average the atmospheric signal over a period of a few years (Carignan et al., 2002), some suggest quick compositional changes in relation to atmospheric pollution magnitude (Spiro et al., 2004). In any case, as their age is unknown, they cannot be used for temporal studies (Carignan and Gariépy, 1995). In the present work, we attempt to discriminate the different sources of lead in the atmosphere of Johannesburg by means of geochemical and isotopic analyses of epiphytic lichens sampled both within and around the city. To the best of our knowledge, the present set of data constitutes the first database of this type ever gathered in South Africa.

2. The site

Located at about 1700 m above sea level, the city of Johannesburg covers 1645 km^2 of mostly residential and wooded areas (Fig. 1a). The city's traffic network represents more than 9000 km of mostly (90%) tarred roads, with the M1 highway between Johannesburg and Pretoria being the busiest in the Southern hemisphere. The climate of Johannesburg is mild with north–northwest dominant winds, especially in winter. Although four seasons exist, spring and autumn are very short. Average seasonal rainfall ranges from 19 mm during the 3 months of winter to up to 563 mm during the 5 months of summer, leading to an annual precipitation of about 750 mm. Johannesburg lies on the Archaean Kaapvaal craton, which is comprised of a large variety of rocks representing different ages (3.34–2.7 billion years). To simplify a rather complex local geology, rock types of the sampling area include, from north to south, granitoids and amphibolites, quartzites, lavas and dolomite (Fig. 1b).

3. Materials and methods

3.1. Sampling and sample preparation

A total of 31 thalli of epiphytic lichens (all belonging to the Parmeliaceae family, and mostly *Parmelia sulcata*) have been collected in and around Johannesburg during two sampling campaigns undertaken in May 2001 and April 2003 (Fig. 1a). The sampling site network could not however be properly distributed because of the extreme scarcity or even absence of lichens in many areas of the city, and more particularly in Black-dominated residential suburbs. Lichens growing on trees were collected between 1 and 3 m above ground level by means of pre-cleaned plastic knives. Lichens were sometimes moistened with Milli-Q water to facilitate their removal from the trunks. They were immediately transferred into a clean plastic bag and stored in the laboratory after any remaining pieces of bark were removed from the lichens by hand. Lichens were then rinsed with Milli-Q water in an ultrasonic bath for 1 min to eliminate dust and any remaining leaf debris (Getty et al., 1999). They were then dried at 80 °C over a period of 2 days and crushed manually in a pre-cleaned agate mortar to obtain a fine and homogeneous powder.

A few millilitres of leaded-gasoline from each of the major petrol companies present in South Africa (Total, Caltex, Zenex, Engen, Shell and BP) were also collected by directly pumping the petrol into separate glass vials for each sample. In addition, several samples of sand (1 kg each) were taken from different mine-tailing dumps (DUMPC, SHAFT 17, DRD, GMTS), which lie south of the M2 motorway (Fig. 1a). Two coal samples, sold to the people of Soweto for domestic use, were also collected.

3.2. Chemical procedure

As, Br, Cr, Fe, Sb, Sc, Th and La were measured using instrumental neutron activation analysis (INAA) by Actlabs (Ontario, Canada). Measurements of standards (WMG1 and peach leaves NIST 1547) did not differ from certified values by more than ±10% for Sc, Th and La and about ±15% for the other elements. For Pb, Zn, Cu and Cd concentration and Pb isotopic composition determinations, between 70 and 100 mg of powdered lichen were transferred to a beaker with 2 mL each of concentrated HNO_3, HF and HCl of suprapure grade (Merck, Germany). The dissolution was achieved under microwave assistance (Ethos, Milestone, 9 positions) at the F.-A. Forel Institute, University of Geneva. A blank and a peach leaves reference material (NIST 1547) were processed systematically for each of the seven-lichen batches. All the following procedures were carried out in a clean room (US class 100–1000). One-third of the solution was evaporated, retaken with concentrated HNO_3, diluted with MilliQ water, and introduced in an HP 4500 inductively coupled plasma-mass spectrometer (ICP-MS). Elemental concentrations were measured using both internal (Re, Rh) and external calibrations. Results of six NIST 1547 measurements were within ±15% of the certified values. Measurements of 19 MilliQ washing solutions of lichens indicated that approximately 10% of Zn, Cd and Cu, and less than 3% of other elements were lost during the washing procedure. Lead in the other aliquot solution was pre-concentrated using ionic resin AG1 × 4 (Biorad) and isotopic ratios were determined using the quadrupole-based HP 4500 belonging to the F.-A. Forel Institute or, for some samples, a PQ2+ ICP-MS from the University of Montpellier II, France. Mass bias was monitored and corrected by bracketing a NIST 981 isotopic lead standard every five measurements. Further details about the complete procedure and instrumental settings can be found elsewhere (Monna et al., 1998, 2000). Blank corrections were never required, as the contamination by the chemical procedure appeared negligible compared to the total amount of lead in the treated samples. Some samples were duplicated, demonstrating the reproducibility of the analytical method within errors.

Mine dump samples were treated using the same procedure as the lichens. Approximately 100 mg of powdered and ashed coal was digested in aqua regia in covered Savillex beakers for 24 h on a hot plate. One millilitre of $HClO_4$ was then added to the evaporated solution to complete the digestion (Giusti, 1988). Lead was extracted following the procedure described above and measured for its isotopes on a MAT 262 thermal ionisation-mass spectrometry (TIMS) at the Memorial University of Newfoundland, Canada following the technique described in Pillet et al. (2005). One millilitre of the six leaded petrol samples was evaporated to dryness in Savilex beakers. The residues were dissolved using 1 mL of concentrated HNO_3 overnight on a hot plate. The solutions were then diluted with MilliQ water and lead isotopic compositions were measured using the HP 4500 ICP-MS as described earlier.

4. Results

4.1. Trace element contents

Elemental concentrations and isotopic compositions of mine dumps, coals and lichens are reported in Table 1. Mine dumps and coals are characterised by rather homogeneous compositions for lithophilic elements such as Th, Sc, La or Fe and, to a lesser extent, for chalcophylic elements (Pb, Zn, Cu, etc.). There is no significant difference in isotopic signatures or elemental concentrations, using Mann–Whitney *U*-tests, between the lichens collected in 2001 and those collected in 2003 from sites with equivalent exposition to car traffic. The largest variations in lichens are observed for Pb (7–388 $\mu g\,g^{-1}$) and Sb (0.1–9.7 $\mu g\,g^{-1}$), and also for Th (0.2–6.8 $\mu g\,g^{-1}$). The other elements, and particularly La, are less variable, within approximately one order of magnitude or less. Because this study is the first of its kind in South Africa, it was necessary to characterise the isotopic compositions

Table 1
Lead isotopic compositions and trace element contents (expressed in μg g^{-1}, except iron content in percent)

Name	Description	^{206}Pb/^{207}Pb	±	^{208}Pb/^{207}Pb	±	Pb	Cu	Zn	Cd	As	Br	Cr	Fe (%)	Sb	Sc	Th	La
Coal																	
COAL2		1.2050	0.0001	2.4691	0.0001	11	9.1	<0.2	<0.01	3.5	1.5	29	0.35	0.6	5.4	6.8	24
COAL1		1.2159	0.0002	2.4853	0.0002	17	7.8	<0.2	<0.01	1.7	1.2	28	1.2	0.6	4.9	5.0	33
Dumps																	
DRD	Mine dump	2.232	0.011	2.105	0.005	8.8	2.2	8	<0.01	7.5	<0.5	142	0.71	0.8	3.4	3.0	18
DUMPC (a)	Mine dump	2.182	0.007	1.977	0.002	21	8.7	20	<0.01	15	<0.5	144	1.5	0.9	4.1	4	20
DUMPC (b)	Mine dump	2.607	0.013	1.864	0.005	24	32	62	<0.01	77	<0.5	160	2.3	1.2	5.4	3.9	23
DUMPC (c)	Mine dump	2.735	0.016	1.817	0.005	19	33	55	<0.01	33	<0.5	139	1.6	1	4.5	3	21
GMTS1	Mine dump	2.813	0.016	1.807	0.002	14	24	33	0.05	94	0.9	185	2.9	1.7	5.3	4.4	23
GMTS2	Mine dump	2.615	0.009	1.861	0.004	8.7	14	18	0.03	62	<0.5	146	1.8	1.1	4.3	4.2	19
SHAFT17	Mine dump	2.878	0.005	1.707	0.001	23	25	64	<0.01	77	<0.5	228	2.6	1.7	6.2	4.2	31
SHAFT17bis	*Mine dump*	*2.882*	*0.006*	1.712	*0.002*	—	—	—	—	—	—	—	—	—	—	—	—
Lichens																	
BCC1	Open space urban	1.084	0.005	2.353	0.014	61	23	65	0.32	2.5	12	134	0.35	1.6	1.1	0.9	3.6
BCC2	Open space urban	1.086	0.007	2.351	0.030	63	24	53	0.55	4.6	15	91	0.27	1.5	0.8	1.3	3.4
BOT1	Open space urban	1.091	0.004	2.351	0.010	71	16	73	0.24	6.8	23	130	0.50	1.9	1.3	1.9	4.6
BOT2	Open space urban	1.089	0.003	2.344	0.008	98	32	83	0.28	5.9	15	277	0.68	2.9	2.3	2.3	6.4
BOT3	Open space urban	1.093	0.004	2.344	0.013	179	41	93	0.32	9.0	19	339	1.1	4.8	2.8	4.2	10
BRI*	Low traffic urban	1.091	0.003	2.358	0.006	186	39	227	0.25	13	46	205	1.3	5.8	3.2	3	8.9
CIM1*	Open space urban	1.086	0.003	2.351	0.005	49	16	86	0.09	3.4	17	42	0.27	1.1	0.8	0.5	2.6
CIM2*	Open space urban	1.099	0.003	2.359	0.005	90	37	121	0.29	7.7	20	175	1.2	2.2	3.9	2.3	8.5
CMG	Open space dumps	1.112	0.005	2.348	0.011	53	21	101	0.29	9.7	15	83	0.50	1.9	1.3	1.8	4.8
DEL	Open space urban	1.091	0.003	2.357	0.009	70	24	71	0.25	6.8	17	163	0.54	2.0	1.7	1.1	5.0
DEWER	Open space urban	1.091	0.006	2.365	0.013	90	21	67	0.34	6.9	21	121	0.51	2.5	1.6	1.5	4.3
EMER	Low traffic urban	1.119	0.005	2.370	0.013	41	55	70	0.14	5.3	12	90	1.6	1.6	5.6	2.8	13
FER*	Low traffic urban	1.085	0.002	2.356	0.006	217	57	162	0.25	8.2	35	482	1.3	4.7	4	4	12
HUDD	Open space suburb	1.103	0.003	2.370	0.008	47	21	82	0.23	3.8	14	147	0.54	2.2	1.7	1.1	4.2
MEA*	Open space dump	1.257	0.003	2.305	0.005	141	93	145	0.15	14	42	120	3.2	1.8	5.8	6.2	12
MER*	Low traffic urban	1.096	0.003	2.364	0.006	66	26	103	0.22	3.4	23	59	0.4	1.6	1.7	1.5	8
MEV	Low traffic urban	1.091	0.001	2.358	0.003	143	53	133	0.19	9.2	36	389	1.3	4.3	3.7	2.8	11
OAK*	Med. traffic urban	1.082	0.001	2.351	0.005	157	41	124	0.18	6.1	30	179	0.81	6.9	2.2	1.8	6.4
OAK bis	*Med. traffic urban*	*1.084*	*0.003*	2.358	*0.007*	—	—	—	—	—	—	—	—	—	—	—	—
PILA	Pilannesburg Park	1.147	0.002	2.403	0.012	6.9	15	37	0.08	2.6	5.1	256	0.38	<0.1	0.9	1.7	8.3
RIV*	High traffic urban	1.090	0.003	2.358	0.004	159	41	173	0.47	7.3	28	154	0.79	4.2	2.5	2.6	9.9
ROU*	Low traffic urban	1.091	0.003	2.364	0.006	302	81	172	0.55	10	44	158	0.93	4.6	2.4	4.7	9.4
SHA*	Open space dump	1.188	0.002	2.337	0.005	132	57	136	0.59	12	42	130	2.5	2.3	5	6.8	13
SUN*	Open space suburb	1.094	0.001	2.353	0.007	70	22	118	0.34	9.6	14	65	0.26	2.1	0.9	0.2	3.4
TURF	Open space suburb	1.091	0.007	2.360	0.013	123	27	82	0.40	6.1	15	88	0.60	1.8	1.6	0.8	4.9
VERW	Open space suburb	1.089	0.004	2.373	0.009	217	36	274	1.39	8.1	29	177	0.96	6.8	2.6	2.1	6.9
WIT*	High traffic urban	1.087	0.002	2.356	0.006	388	66	169	0.22	15	40	486	1.9	9.7	5	4.5	14
WSBG1*	Open space rural	1.106	0.001	2.358	0.003	56	34	88	0.08	5.3	18	210	0.67	1.2	2	1.6	5.7
WSBG1 bis*	*Open space rural*	*1.107*	*0.003*	2.361	*0.004*	—	—	—	—	—	—	—	—	—	—	—	—
WSBG2*	Open space rural	1.105	0.002	2.362	0.003	51	24	68	0.11	6	14	234	0.67	1	1.9	1.2	5.5
ZOO1*	Open space urban	1.088	0.003	2.356	0.007	54	15	86	0.10	2.8	16	74	0.31	1.1	1	0.7	2.7
ZOO2*	Open space urban	1.092	0.002	2.356	0.003	51	18	90	0.05	6.2	24	54	0.82	3.2	1.8	2.7	4.0
ZOO2 bis*	*Open space urban*	*1.092*	*0.001*	2.358	*0.006*	—	—	—	—	—	—	—	—	—	—	—	—
ZOO3*	Open space urban	1.094	0.003	2.364	0.006	101	45	113	0.20	9.5	17	158	0.79	2.6	2.3	3.7	7.8

The errors for isotopic measurements are given at a 95% confidence level; see the text for uncertainties regarding elemental concentrations. '*bis*' = duplicated material. *: lichen collected in May 2001; the other samples were collected in April 2003.

of the potential lead sources around Johannesburg (Tables 1 and 2). The isotopic compositions of leaded gasoline produced by Caltex, Zenex, Engen, Shell and BP are rather homogeneous with ^{206}Pb/^{207}Pb values ranging from 1.057 to 1.072, and ^{208}Pb/^{207}Pb varying from 2.330 to 2.344 (Table 2, Figs. 2a,b and 3a,b). Gasoline from Total Company is just outside this group with higher ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of 1.096 and 2.366, respectively. Raw coal samples collected in two different coal yards from the township of Soweto yield consistent $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of about 1.21 and 2.48, respectively. Since fractionation of lead isotopes is not expected during coal burning (Ault et al., 1970), the isotopic signatures of resulting fly ashes are supposed to be the same as in raw material. Samples collected from the four mine dumps are characterised by much higher $^{206}Pb/^{207}Pb$ ratios ranging from 2.182 to 2.882, due to the high uranium content of Witwatersrand goldfields (Cole, 1998; Poujol et al., 1999), and by exceptionally low $^{208}Pb/^{207}Pb$ ratios, ca. 1.707–2.105 (Table 1). A systematic analysis of the local substrate was not performed because of its complex geological diversity (Poujol and Anhaeusser, 2001). However, a few data are available in the literature (Barton et al., 1999). They concern Archaean granodiorites and tonalites constituting the Johannesburg Dome (reported as granitoids in Fig. 1b) and exhibit highly variable isotopic signatures which, in some cases, are close to those measured in mine dumps (Figs. 2a,b and 3a,b). Most of the lichens collected in or around Johannesburg display a homogeneous isotopic field slightly more radiogenic than present-day leaded gasoline (higher $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios), constrained by $^{206}Pb/^{207}Pb$ ratios within 1.082–1.103, and $^{208}Pb/^{207}Pb$ ratios within 2.344–2.373. Nonetheless, some samples (MEA, SHA, PILA, EMER and CMG, and to a lesser extent both WSBG1 and WSBG2) plot outside this group due to their higher $^{206}Pb/^{207}Pb$ ratios.

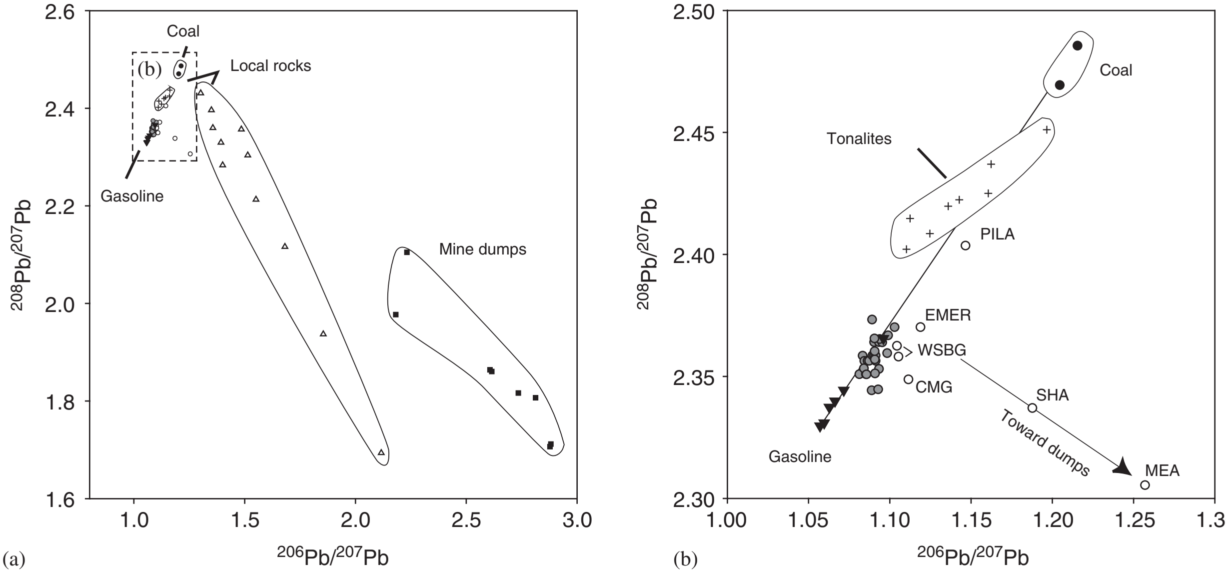
Table 2
Lead isotopic compositions of petrol from the major petrol companies

Petrol company	$^{206}Pb/^{207}Pb$	±	$^{208}Pb/^{207}Pb$	±
Total	1.096	0.004	2.366	0.006
Caltex	1.072	0.004	2.344	0.008
Zenex	1.057	0.002	2.330	0.006
Engen	1.060	0.002	2.331	0.005
Shell	1.066	0.003	2.340	0.005
BP	1.063	0.002	2.337	0.005

5. Discussion

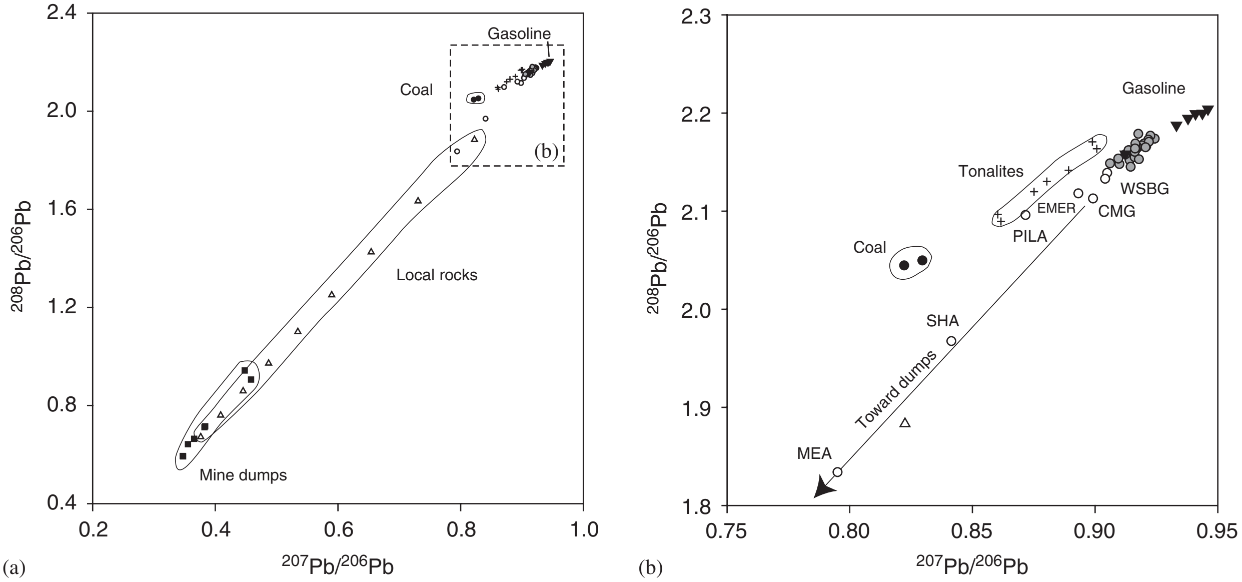
5.1. Preparation and treatment of concentration data

Elemental concentrations measured in lichens exhibit non-normal and positively skewed distributions, even after logarithmic transformation. The possible relationships between elements must therefore be examined using non-parametric statistics. In a Spearman's correlation coefficient matrix, almost all of the elements appear to be significantly correlated to one another (Table 3), with the highest



(a) (b)

Fig. 2. (a, b) $^{208}Pb/^{207}Pb$ vs. $^{206}Pb/^{207}Pb$ in leaded gasoline (▼), raw coal (●), mine dumps (■), lichens collected either in urban open space or in traffic areas (●), lichens collected close to the dumps or outside the city (○). Lead isotopic compositions of selected rocks from the Johannesburg Dome are reported for comparative purposes: granites and granodiorites (△), tonalites (+); data from Barton et al. (1999).



(a) (b)

Fig. 3. (a, b) ^{208}Pb/^{206}Pb vs. ^{207}Pb/^{206}Pb in leaded gasoline (▼), raw coal (●), mine dumps (■), lichens collected either in urban open space or in traffic areas (◍), lichens collected close to the dumps or outside the city (○). Lead isotopic compositions of selected rocks from the Johannesburg Dome are reported for comparative purposes: granites and granodiorites (△), tonalites (+); data from Barton et al., (1999).

Table 3
Spearman's correlation coefficient matrix between raw elemental concentrations

	Pb	Cu	Zn	Cd	As	Br	Sb	Cr	Fe	Sc	Th
Cu	0.73**										
Zn	0.77**	0.65**									
Cd	0.51**	0.24	0.25								
As	0.72**	0.63**	0.73**	0.36*							
Br	0.76**	0.61**	0.80**	0.15	0.67**						
Sb	0.81**	0.55**	0.70**	0.38*	0.65**	0.66**					
Cr	0.48**	0.45*	0.24	−0.01	0.26	0.24	0.47**				
Fe	0.60**	0.84**	0.61**	0.04	0.64**	0.65**	0.60**	0.49**			
Sc	0.60**	0.87**	0.64**	0.08	0.61**	0.60**	0.58**	0.49**	0.97**		
Th	0.62**	0.79**	0.61**	0.10	0.69**	0.69**	0.60**	0.44*	0.87**	0.84**	
La	0.57**	0.84**	0.55**	0.06	0.55**	0.54**	0.45*	0.55**	0.86**	0.88**	0.84**

**$p<0.01$; *$p<0.05$.

correlation coefficients observed between the terrigeneous elements: Fe, Sc, Th and La ($0.84<r_{\mathrm{sp}}<0.97$; $p<0.01$). A second group, comprising Pb, Zn, As, Br and Sb, is also highly inter-correlated ($0.65<r_{\mathrm{sp}}<0.81$; $p<0.01$). All of these elements present lower but significant relationships with those of the crustal group. Although Cr and Cu are correlated to most of the other elements, they tend to be more closely correlated to those belonging to the terrigeneous group. Finally Cd does not show a clear relationship with the other elements, except with Pb ($r_{\mathrm{sp}} = 0.51$; $p<0.01$) and, in a lesser extent, with Sb and As.

Such correlations are common and are generally induced by factors that are not directly linked to the local atmospheric depositional fluxes but rather to accumulation efficiency and the life span of lichens. Indeed, as the sampled lichens are not necessarily of the same age, the older may have accumulated more trace elements than the younger ones. Lichens might have also been exposed to varying amounts of particle fall-out and their specific morphologies may have affected their trapping capacities (Carignan et al., 2002). Variable combinations of these factors can lead to large differences in chemical compositions inducing correlations between all elements.

A common geochemical approach may consist in normalising elemental concentrations to those of an element that has no anthropogenic origin such as Sc, Ti, Al or La (Dongarrà et al., 1995; Carignan and Gariépy, 1995; Doucet and Carignan, 2001). If we consider that all the elements are continuously and similarly accumulated in lichens during their lifetime, the resulting ratio should be proportional to the enrichment with respect to the crust-derived contribution. Hence, a new matrix of Spearman's correlation coefficients was computed after normalising elemental concentrations to La contents (Table 4). It must, however, be kept in mind that parametric correlations of ratios formed of pairs which have parts in common are often spurious because induced high correlations are expected, more particularly when the coefficient of variation of the common denominator is greater than those of the variables used at the numerator places (Rollinson, 1993). In our case, the coefficient of variations of Pb, Cd, Zn, Sb, As and Br are higher than that of La. Moreover, non-parametric Spearman's correlation coefficients should be less affected by the above-mentioned problems than Pearson's correlation coefficients when outlier samples are present. In Table 4, all ratios including potentially anthropogenic elements (Pb/La, Zn/La, Cd/La, Sb/La, As/La and Br/La) still appear to be significantly intercorrelated, but they are no longer correlated with those calculated from elements belonging to the terrigenous group (Th/La, Fe/La and Sc/La), which pleads in favour of the statistical relevance of the normalisation procedure. The differences observed between the two matrices (Tables 3 and 4) tend therefore to prove that most of the variations related to the age, growing rate, exposition and morphology of the lichens have been efficiently removed using the La normalisation. These correlations do not necessarily mean that Pb, Zn, Cd, Sb, As and Br come from a common anthropogenic source, but simply that anthropogenic activities have introduced these elements into the atmosphere in larger magnitude than natural emissions. It is worth noticing that normalisation produces almost normal new distributions. A principal component analysis (PCA) computed on the standardized new set of variables is reported in Fig. 4, which depicts the projection of samples on the factor-plane F2 vs. F1 with both axes representing more than 60% of the total variance. There is no clear pattern, except that samples MEA and SHA, collected near the mine dumps, plot in the upper part of the diagram, while the PILA sample, collected in the Pilanesberg National Park some 250 km to the west of the city plots in the opposite direction. The other samples do not define any clear clusters, which might indicate a pollution gradient within the city or possibly a particular pollution point source.

5.2. Mixing model on the basis of lead isotopes

Lead isotopic compositions reflect the relative contributions and isotopic signatures of the different sources involved, so that the isotopic approach is generally more robust in identifying the origin of lead than models built from bulk concentrations alone. There is no urban incinerator, smelter, lead ore exploitation, or heavy industry using lead around Johannesburg. The clustering of most of the lichens observed in Figs. 2 and 3, and more particularly those collected either in urban open spaces or in traffic areas, therefore indicates that leaded gasoline is an important lead contributor. Similar isotopic compositions have already been measured in airborne particulate matter sampled during the late 90s in Cape Town and Pretoria

Table 4
Spearman's correlation coefficient matrix between elemental concentrations normalised to lanthanum contents

	Pb/La	Zn/La	Cu/La	Cd/La	Sb/La	As/La	Br/La	Th/La	Sc/La
Zn/La	0.54**								
Cu/La	0.50**	0.42*							
Cd/La	0.50**	0.54**	0.33						
Sb/La	0.74**	0.61**	0.30	0.42*					
As/La	0.39*	0.53**	0.28	0.40*	0.37*				
Br/La	0.49**	0.69**	0.44*	0.34	0.51**	0.62**			
Th/La	0.10	−0.07	0.10	−0.02	0.22	0.28	0.19		
Sc/La	−0.09	−0.03	0.09	−0.24	0.06	0.04	0.16	0.21	
Fe/La	0.04	−0.04	0.03	−0.27	0.12	0.13	0.22	0.30	0.89**

**$p<0.01$; *$p<0.05$.

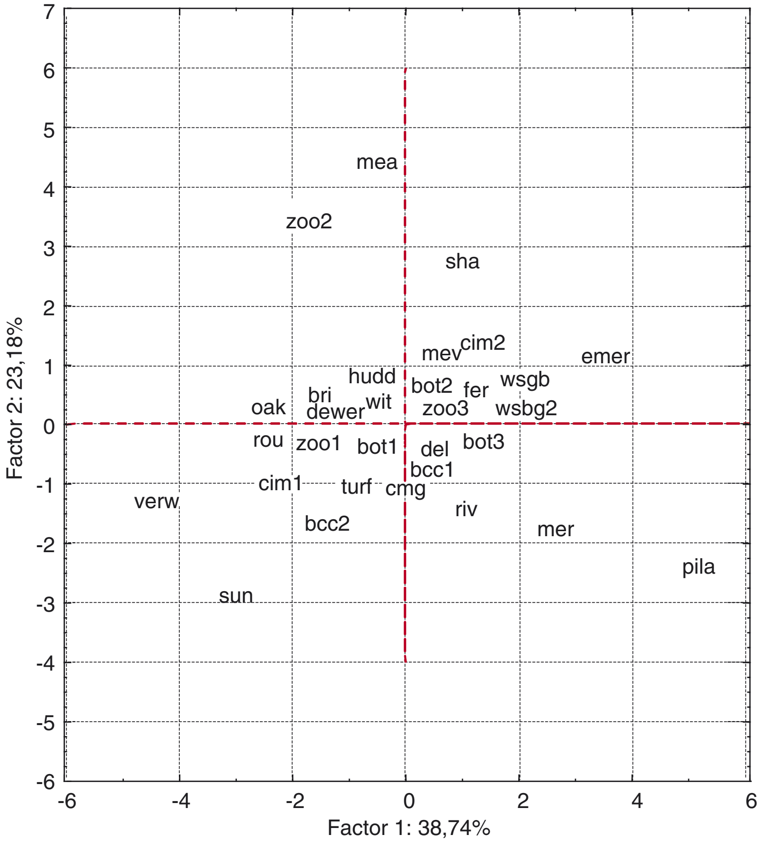


Fig. 4. Principal component analysis, projection of the lichens (see Table 1 for lichen abbreviations) on the factor plane.

($^{206}Pb/^{207}Pb$~1.067–1.090), and were also interpreted as the result of a dominant contribution of alkyl lead from gasoline (Bollhöfer and Rosman, 2000). In Johannesburg, however, none of the lichens exactly matches the average isotopic composition of gasoline. This implies that minor inputs from another source (or from several other sources) are involved. In both Figs. 2 and 3, most of the lichens collected either in urban open spaces or in traffic areas fall close to a straight line limited by the gasoline field and by the coal end-members. Similar results are reported by Coetzee et al. (2004) for lead isotope ratios determined on blood samples from children living in Johannesburg. However, tonalites reported by Barton et al. (1999) also appear in colinear position between gasoline and coals, but they cannot represent alone the average geological background contribution. Because of its homogeneous isotopic composition, lead emitted by domestic coal burning is therefore a better candidate, as a small but significant participant in the total lead budget of lichens. Isotope ratios then suggest that, in samples collected either in urban open spaces or in traffic areas, between 80% and 90% of the lead comes from automotive traffic, the remainder coming probably from coal burning. Among the other samples (open circles in Figs. 2 and 3), both WSBG1 and WSBG2 lichens developed in the Walter Sisulu National Botanical Garden, about 20 km outside the city. Their isotopic compositions do not match those of the lichens collected inside the city, suggesting a slightly lower contribution from gasoline. Further away from the gasoline field in Figs. 2 and 3 is the PILA sample collected in the Pilanesberg National Park, about 250 km away from the city. A gradient of lead pollution linked to automotive traffic is therefore observed from inside to outside the city.

Lichens sampled near Johannesburg's townships in the immediate vicinity of dumps (MEA, SHA and CMG) do not fit this overall scenario. Unlike the other lichens, they all plot, as shown in Figs. 2 and 3, in the direction of mine dumps. Particles from the tailing dumps are likely to be resuspended by winds and incorporated in the lichens growing nearby but, due to their low lead content they do not contribute more than 15% of the total lead (calculated upon the basis of isotopic mixings), with the remaining lead content being mainly related to automotive traffic (cf. Figs. 2 and 3). It is interesting to note that the lichens sampled just at few kilometres away from the goldfields, even in open spaces or low traffic areas, do not show any impact from mine dumps (i.e., see DEWER, CIM1 and CIM2 in Fig. 1). Long-distance transport of any significance is doubtful because of the large size of particles from dumps, so that this source is progressively and rapidly obliterated by diffuse lead emissions from cars.

5.3. Combining lead isotope and La/Pb ratios

In a classic mixing model combining concentrations and isotopic compositions, the 1/Pb ratio

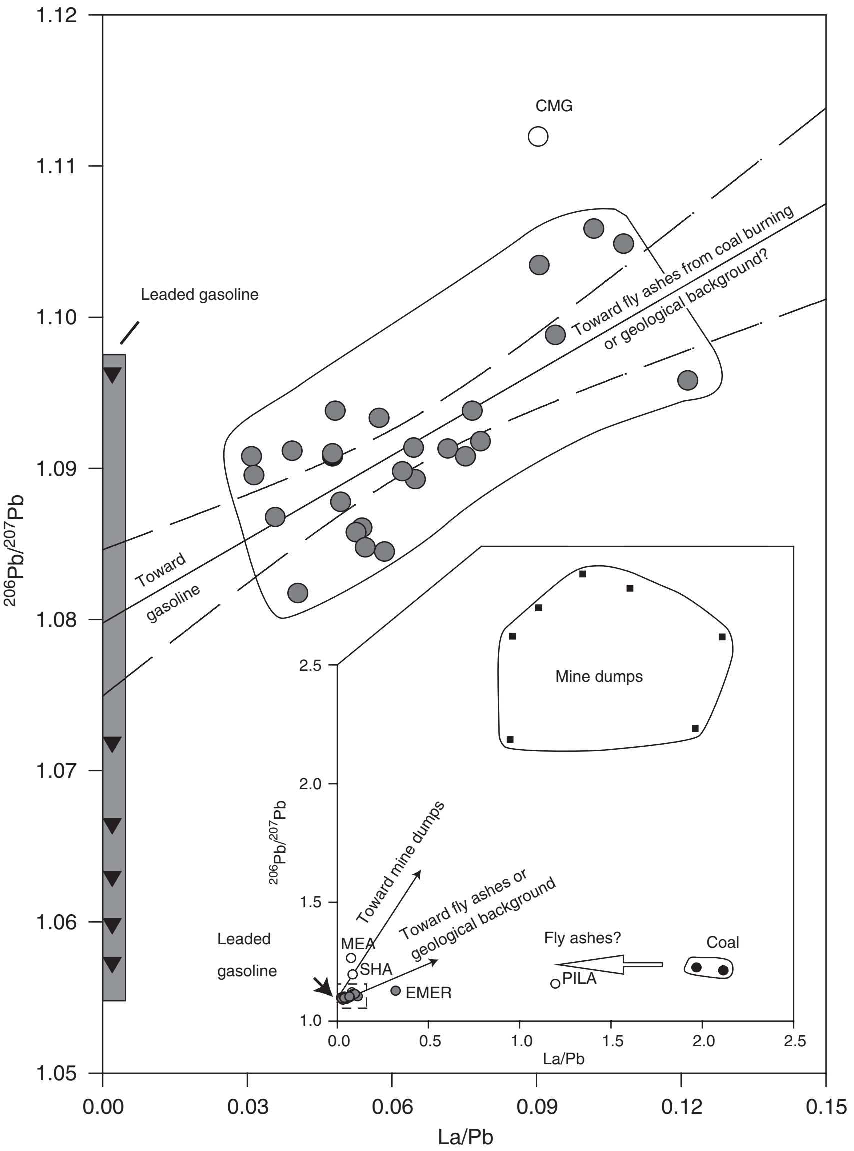


Fig. 5. $^{206}Pb/^{207}Pb$ vs. La/Pb in leaded gasoline (▼), raw coal (●), mine dumps (■), lichens collected either in urban open space or in traffic areas (●), and those collected close to the dumps or outside the city (○). The possible fly ash position from coal burning is given by an arrow, see text for details. The linear regression is calculated only from lichens collected either in urban open spaces or in traffic areas, $r = 0.73$, $p < 0.01$, and the long dash curves correspond to the 95% confidence intervals of the linear regression.

represents the *X*-axis and one of the Pb/Pb ratios the *Y*-axis: see e.g. Faure (1986) for fundamentals and Cloquet et al. (2006) for specific use in lichens. However, this procedure may not be the most advisable solution here because lead content in lichens is expected to vary, not only as a function of atmospheric pollution magnitude, but also because of the age, growing rate, exposition, morphologies or trapping capacities of the different lichens. Consequently, the La/Pb ratio was preferred to the 1/Pb ratio (Fig. 5) as was recently the case with Sc/Pb for the study of a long-term pollution record in a peat bog (Monna et al., 2004), and with Al/Pb for the identification of the impact of a Cu smelter in Russia using lichen transplants (Spiro et al., 2004). As a matter of fact, the La/Pb ratio somehow reflects the way in which anthropogenic lead exceeds the natural contribution, independently from the above-mentioned factors that are expected to influence Pb concentrations. Although La/Pb ratios of raw coal materials are fairly homogeneous between 0.3 and 0.5, lithophilic elements are known to be far less volatile than chalcophylic metals (Tolvanen, 2004), so that fly ashes are likely to present lower La/Pb ratios than original coal materials (shown in Fig. 5 by an arrow). The present-day leaded gasoline field is plotted directly on the *Y*-axis because of the negligible amounts of La compared to Pb in automotive exhaust emissions, while the mine dumps have La/Pb ratios between 1 and 2. Lichens collected either in urban open spaces or in traffic areas present very low La/Pb ratios which undoubtedly indicate high anthropogenic lead contamination. They also plot close to the gasoline field, confirming again the preponderance of lead from automotive exhausts in the Johannesburg's atmosphere. These same samples define a significant linear pattern ($r = 0.73$, $p < 0.01$, see Fig. 5) interpreted as the result of a binary mixing between gasoline and one other minor source that likely results from coal burning. Again, samples collected close to mine dumps, CMG, SHA and MEA, are found outside the group formed by the other lichens, and plot in the direction of mine dumps. The $^{206}Pb/^{207}Pb$ vs. La/Pb graphical representation produces a coherent picture of the complex multi-component mixings observed in the Johannesburg's atmosphere, suggesting that the fractionation between lanthanum and lead during their absorption and retention in the lichens is not significant. In this type of study where lichens are used as bioaccumulators, La normalisation is therefore particularly efficient and complementary to the examination of lead isotope ratios to apportion the different sources involved.

6. Conclusion

Isotopic compositions of potential pollution sources in Johannesburg are extremely contrasted with $^{206}Pb/^{207}Pb$ ratios from 1.06 to about 2.9, and $^{208}Pb/^{206}Pb$ between 0.6 and 2.20. Such a wide range is very rarely encountered because uranium-rich sources like mine dumps are infrequently involved in the surface cycle of lead. This specificity considerably extends the discrimination power of the isotopic method, especially when isotopic information is combined with elemental concentrations expressed as La/Pb ratios. The La normalisation is necessary because absolute concentrations are perturbed by other factors than atmospheric pollution. Lead associated with dust transported by winds from the numerous mine dumps is recorded in small amounts within the immediate vicinity of the dumps, but quickly becomes insignificant just a few kilometres away. Lead emitted by domestic coal burning in historically Black residential areas never contributes more than 20% of the total lead budget. Everywhere in the city, all of these sources are obliterated by leaded antiknock compounds added to the gasoline, which constituted the major lead emitter for the Johannesburg's atmosphere at the time of the study. Consequently, the promotion of unleaded petrol in South Africa will drastically decrease lead concentrations in the atmosphere.

Acknowledgements

This work has been funded in part by a CNRS/NRF agreement (13281 CNRS/NRF 2002). We greatly thank Olivier Bruguier and Pierre Yves Favargé for their technical assistance in measuring lichens, Sylvain Salavy for his help during sampling, Jean Carignan and Carmela Chateau for their precious experience and discussions. We also wish to express special thanks to two anonymous reviewers who greatly improved the manuscript by their thoughtful comments.

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