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Lichens Used as Monitors of Atmospheric Pollution Around Agadir (Southwestern Morocco)—A Case Study Predating Lead-Free Gasoline

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Abstract More than 30 epiphytic lichens, collected in Agadir (Morroco) and along a 150-km transect from the Atlantic Ocean eastward, were analyzed for their metal content and lead isotopic composition. This dataset was used to evaluate atmospheric metal contamination and the impact of the city on the surrounding area. The concentrations of Cu, Pb, and Zn (average±1 SD) were 20.9±15.2 μg g^{-1}, 13.8±9.0 μg g^{-1}, and 56.6±26.6 μg g^{-1}, respectively, with the highest values observed in lichens collected within the urban area. The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in the lichens varied from 1.146 to 1.186 and from 2.423 to 2.460, respectively. Alkyllead-gasoline sold in Morocco by the major petrol companies gave isotopic ratios of $^{206}Pb/^{207}Pb=1.076–1.081$ and $^{208}Pb/^{207}Pb=2.348–2.360$. These new, homogeneous values for gasoline-derived lead improve and update the scarce isotopic database of potential lead sources in Morocco, and may be of great value to future environmental surveys on the presence of lead in natural reservoirs, where it persists over time (e.g., soils and sediments). The interest of normalizing metal concentrations in lichens to concentrations of a lithogenic element is demonstrated by the consistency of the results thus obtained

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with lead isotopic ratios. Leaded gasoline contributed less than 50% of the total amount of lead accumulated in lichens, even in areas subject to high vehicular traffic. This strongly suggests that the recent banishment of leaded gasoline in Morocco will not trigger a drastic improvement in air quality, at least in Agadir.

Keywords Atmospheric contamination · Metal · Bio-monitor · Stable lead isotopes

1 Introduction

Lichens have been widely employed as bio-monitors of metal pollution, especially because they accumulate particulate matter from the atmosphere over several years (Nimis et al. 1993; Garty et al. 1996; Bennett and Wetmore 1999; Varrica et al. 2000; Conti and Cecchetti 2001), minimizing variability in aerosol content due to sporadic events. Lichens are symbiotic, plant-like organisms composed of an association of fungi and algae. They are able to accumulate metals present in the atmosphere through wet and dry deposition, exceeding their physiological needs, by physiochemical processes or intracellular mechanisms which are not always well understood, without suffering extensive damage. Because they have no roots, the substratum on which they grow is not thought to contribute significantly to metal accumulation processes (Loppi and Pirintsos 2003). However, their elemental composition in itself does not allow for a quantitative evaluation of the mass level of metal in air, so that the extent of the exposure to pollution is often established by comparing contaminated and clean areas (e.g., Garty et al. 1997). Microclimatic conditions, individual exposure, and lichen morphology affect their trapping capacity (Conti and Cecchetti 2001; Ayrault et al. 2007). Whenever possible, studies tend to focus on a single lichen species, with individuals of the same diameter or length (i.e., supposed to be of the same age), and subjected to approximately the same exposure (Hissler et al. 2008). Another alternative is to use unpolluted individuals transplanted to contaminated areas, allowing better control of the whole experiment, and more particularly of exposure conditions (Ayrault et al. 2007). To distinguish geogenic vs. anthropogenic element sources, measured metal concentrations may be normalized by dividing them by the simultaneously measured concentration of a reference element, such as Al, Sc, or Ti, of exclusively crustal origin and not emitted in air by human activity (Carignan and Gariépy 1995; Dongarrà et al. 1995; Doucet and Carignan 2001). Calculating such ratios constitutes the first step towards the well-known computation of enrichment factors, although this procedure has been severely criticized for its intrinsic flaws, more particularly because elemental composition of uncontaminated rocks and soils cannot be considered as uniform (see Reimann and de Caritat 2000 for more details). Lead isotopes can enhance the quality of information deduced from biomonitoring. Lead isotopic abundances in geogenic materials and in anthropogenic emissions are often very different (see Komárek et al. 2008 for a complete review) allowing the sources and pathways of metal pollution to be more clearly identified (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; Farmer et al. 2010).

In the present study, we explore the metal contents (Al, Cu, Pb, Zn, Cu, Al, Ti, and Sc) and ^{208}Pb/^{207}Pb and ^{206}Pb/^{207}Pb ratios in more than 30 samples of epiphytic lichens from urban and rural Agadir (Morocco), and along a transect between the Atlantic coast of Morocco and a rural area located 150 km eastward. The field campaign took place in 2005, before lead was banned from gasoline used in Morocco (officially on January 1st 2006). The expected outcome of phasing out alkyllead gasoline is an improvement in terms of atmospheric quality, as such an improvement has been observed in countries where leaded gasoline has already been banned (e.g., Candelone et al. 1995; von Storch et al. 2003; Annibaldi et al. 2009 and references cited therein). The objectives of the present work are as follows: (1) to update the scarce environmental lead isotopic database concerning leaded gasoline sold in Morocco before its phasing out from the market, (2) to use lichen analysis to establish a reference level of atmospheric pollution at that time, which might be valuable in the near future to verify improvements resulting from environmental policies, (3) to assess the general level of urban-derived pollution along the dominant west–east wind direction, and (4) to confirm the pertinence of methodologies previously described for the study of geochemical and isotopic data obtained from lichens (Monna et al. 2006).

2 The Site

Agadir, southwestern Morocco, is located on the Atlantic coast (30°23′ N, 9°34′ W) and is the administrative capital of the Souss-Massa-Drâa region (Fig. 1). With 750,000 inhabitants, Agadir is the sixth most densely populated city in Morocco. The climate is semi-arid and tempered by winds blowing from the west all year long. Average monthly temperatures are within a narrow range: from ~14°C in January to ~22°C in July. The annual average precipitation is about 250 mm. There are no smelters or incinerators in Agadir. The economy is based on tourism, fishing, and the food-processing industry. Lead, manganese, and zinc, mined in the region, are frequently stocked on the quays, and then shipped abroad. Geologically, Agadir is located at the western edge of the Atlas Mountain fold-and-thrust belt, running from Tunisia to Agadir. The area, known as the Agadir Basin, is a part of the NW African passive margin. The geology of the study area is quite diversified, with Precambrian metamorphic rocks overlain by Palaeozoic sediments,

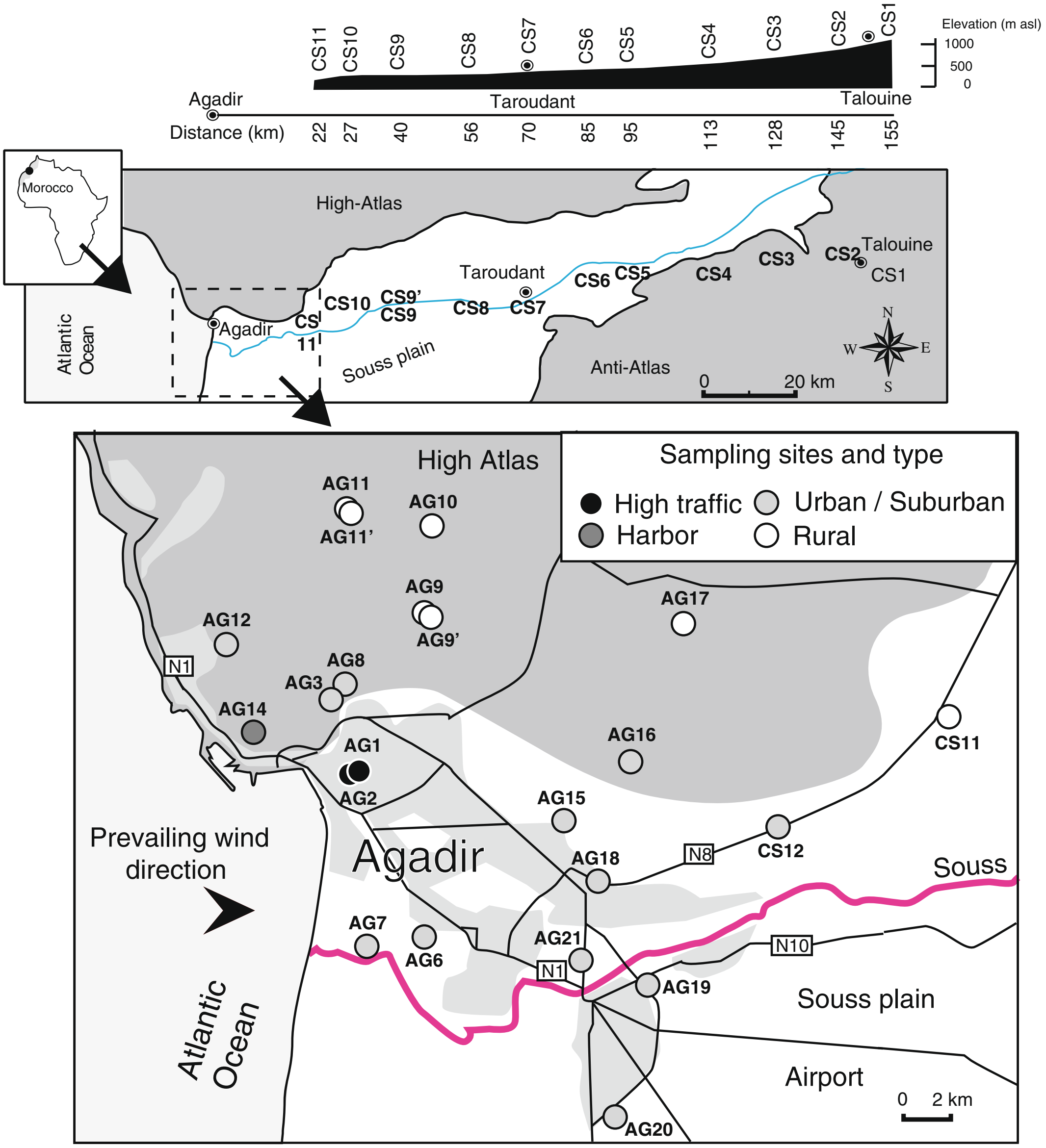


Fig. 1 Map of the Souss plain and sampling sites

intruded by granitoids, red beds, and evaporites (Trias); shallow marine carbonates of Jurassic age; Tertiary silty marls, dolomites, and phosphatic deposits; and Plio-Quaternary sediments (sands, gravels, and lacustrine limestone). Further details on the geology of the area can be found in Ambroggi (1963), Bowen and Jux (1987), and Nouidar and Chellai (2002).

3 Material and Methods

Lichens A total of 34 samples of epiphytic lichens belonging to different species (because of sample availability): *Parmelia* sp. (21), *Ramalina* sp. (5), *Lobaria* sp. (7), and *Xanthoria* sp. (1), growing on trees, were individually sampled at 1.5–3 m above the ground. They were immediately stored in hermetically closed plastic bags. The preparation and chemical procedure mainly follows that extensively described in Monna et al. (2006). In the laboratory, lichens were air-dried, and any extraneous material was manually removed. They were then rinsed with MilliQ water in an ultrasonic bath for 1 min to eliminate dust and any remaining leaf debris (Getty et al. 1999). Tests reported in Monna et al. (2006) indicated that only ~10% of Zn, Cd, and Cu, and less than 3% of other elements were lost during the washing procedure. Lichens 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, homogeneous powder. About 50–100 mg was totally dissolved in a mixture of concentrated suprapure grade HNO_3, HF, and HCl (2 mL of each). Blanks and certified reference materials (CRMs): peach leaves NIST 1547, harbor sediment PACS-1, marine sediment BCSS-1, and basalt BCR-2, were processed with each batch of samples. Solutions, appropriately diluted with MilliQ water, were analyzed for Al, Cu, Pb, Ti, Sc, and Zn, using an ICP-AES Perkin Elmer Optima 3000 (axial view) assisted by a CETAC ultrasonic nebulization (Table 1). Concentrations in blanks were low with respect to the elemental composition of lichens, whereas values measured for CRMs did not differ from certified values by more than 10–15% for all elements considered (Table 2). Lead isotopic compositions (i.e., $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) were determined using a quadrupole-based ICP-MS Perkin Elmer Elan 6000 (University of Reading, UK) or an HR-ICP-MS Thermo Element 2 (University of Paris Diderot, France). More details about acquisition settings and mass bias corrections by bracketing a NIST SRM 981 (common lead isotopic standard) solution can be found in Monna et al. (1998, 2000). Duplicates exhibit reproducibility within the limits of instrumental error, which are typically of 2 and 6 at the third decimal place (95% confidence level) for the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios, respectively (Tables 1 and 3). Accuracy was checked by measuring the BCR-2 certified reference material, for which lead isotopic compositions are available in the literature. The results obtained: $^{206}Pb/^{207}Pb = 1.199 \pm 0.002$ and $^{208}Pb/^{207}Pb = 2.478 \pm 0.005$ (at 95% confidence level) are in good agreement with values previously measured using a more precise MC-ICP-MS instrument: $^{206}Pb/^{207}Pb = 1.2002–1.2007$ and $^{208}Pb/^{207}Pb = 2.4781–2.4796$ (Woodhead and Hergt 2000; Baker et al. 2004).

Gasoline Lead isotopic compositions in different types of gasoline (CMH, Mobil, Shell, Petrom, Afriqia, Somepi, Total, Ziz, Petromin) sold in the study area during field sampling were also measured. About 1 ml of alkylleaded gasoline was evaporated in a Savilex PTFE beaker on a hot plate. The residues were digested with 1 mL of suprapure grade HNO_3, diluted with MilliQ water, and measured for their lead isotopic compositions with an HR-ICP-MS Element 2 XR (University of Montpellier II, France). Mass bias correction was also processed by bracketing a NIST 981 solution every five samples. Accuracies of lead isotope measurements were similar for all the instruments used.

4 Results and Discussion

4.1 Data Preparation

Table 1 lists the contents of lead (Pb), copper (Cu), zinc (Zn), aluminum (Al), scandium (Sc), and titanium (Ti) measured in lichen thalli. Each element varies by approximately one order of magnitude: 5.3–54 μg g^{-1} for Pb, 17–136 μg g^{-1} for Zn, 8.4–95 μg g^{-1} for Cu, 0.24–2.4% for Al, 0.48–4.6 μg g^{-1} for Sc, and 135–1980 μg g^{-1} for Ti. The highest values for all elements were found simultaneously in the AG2 sample, a lichen of the species *Parmelia* sp.,

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

Sample name	Description	Genus/species	^{206}Pb/^{207}Pb	±	^{208}Pb/^{207}Pb	±	Pb (μg g^{-1})	Zn (μg g^{-1})	Cu (μg g^{-1})	Al (%)	Sc (μg g^{-1})	Ti (μg g^{-1})
Agadir and surroundings (within a 25-km radius)												
AG1	High traffic	*Parmelia* sp.	1.151	0.003	2.426	0.005	16.7	126	27.4	0.34	0.7	314
AG2	High traffic	*Parmelia* sp.	1.151	0.003	2.428	0.005	53.7	136	94.8	1.16	2.0	1,000
AG14	Ind./harbor	*Lobaria* sp.	1.156	0.002	2.432	0.004	7.4	29.7	23.8	0.24	0.5	135
AG3	Urb/suburban	*Xanthoria parietina*	1.168	0.001	2.443	0.013	18.0	81.7	39.8	1.26	2.3	978
AG6	Urb/suburban	*Parmelia* sp.	1.146	0.003	2.423	0.007	16.4	71.5	16.7	1.12	1.8	844
AG7	Urb/Suburban	*Lobaria* sp.	1.167	0.002	2.443	0.007	5.3	22.6	8.4	0.48	0.9	339
AG8	Urb/suburban	*Lobaria* sp.	1.163	0.002	2.439	0.006	16.0	38.9	18.4	0.71	1.3	593
AG12	Urb/suburban	*Ramalina* sp.	1.166	0.002	2.449	0.006	17.8	48.4	19.8	0.76	1.3	615
AG15	Urb/suburban	*Parmelia* sp.	1.169	0.001	2.450	0.002	15.8	60.0	39.1	1.08	1.7	1,050
AG16	Urb/suburban	*Parmelia* sp.	1.162	0.002	2.442	0.005	18.4	50.4	20.8	0.96	1.8	741
AG18	Urb/suburban	*Parmelia* sp.	1.161	0.003	2.444	0.005	6.7	36.8	10.1	0.46	0.8	296
AG18′	Urb/suburban	*Parmelia* sp.	1.163	0.002	2.440	0.008	17.9	81.8	23.0	1.00	1.6	827
AG19	Urb/suburban	*Parmelia* sp.	1.161	0.003	2.440	0.005	27.0	86.7	25.9	1.28	1.9	1,170
AG20	Urb/suburban	*Lobaria* sp.	1.170	0.003	2.449	0.007	5.8	26.5	9.9	0.51	1.1	373
AG21	Urb/suburban	*Parmelia* sp.	1.166	0.002	2.447	0.003	8.5	41.2	22.7	0.86	1.3	675
AG9	Rural	*Ramalina* sp.	1.170	0.005	2.445	0.005	5.7	17.3	10.6	0.51	0.8	322
AG9′	Rural	*Ramalina* sp.	1.167	0.002	2.445	0.004	10.4	32.8	14.1	0.87	1.3	524
AG10	Rural	*Ramalina* sp.	1.169	0.003	2.446	0.007	11.4	42.4	10.9	0.83	1.4	676
AG11	Rural	*Ramalina* sp.	1.165	0.002	2.442	0.005	17.9	45.8	17.0	0.79	1.5	622
AG11′	Rural	*Parmelia* sp.	1.169	0.002	2.449	0.005	25.2	83.5	29.5	2.10	3.1	1,720
AG17	Rural	*Parmelia* sp.	1.164	0.002	2.443	0.006	7.9	31.4	13.9	0.58	1.0	369
CS12	Rural	*Lobaria* sp.	1.165	0.002	2.443	0.004	15.6	55.2	24.2	0.96	1.5	741
CS11	Rural	*Lobaria* sp.	1.162	0.001	2.436	0.004	16.8	68.6	21.1	1.10	2.3	778
CS10	Rural	*Lobaria* sp.	1.167	0.002	2.447	0.007	7.4	35.8	9.0	0.55	1.1	415
Countryside												
CS9	Rural	*Parmelia* sp.	1.179	0.002	2.453	0.004	7.7	41.7	12.7	1.54	3.0	1,300
CS9′	Rural	*Parmelia* sp.	1.174	0.002	2.453	0.004	8.5	50.5	14.3	1.94	3.5	1,370
CS8	Rural	*Parmelia* sp.	1.175	0.002	2.453	0.007	5.4	39.1	9.1	0.83	1.4	709
CS7	Taroudant	*Parmelia* sp.	1.169	0.002	2.446	0.003	12.2	82.6	12.7	0.88	1.4	826
CS6	Rural	*Parmelia* sp.	1.182	0.002	2.460	0.007	11.0	49.9	19.6	1.74	3.5	1,200
CS5	Rural	*Parmelia* sp.	1.185	0.002	2.457	0.003	10.2	55.6	21.4	1.48	2.4	1,400
CS4	Rural	*Parmelia* sp.	1.186	0.002	2.455	0.004	10.4	55.0	15.0	1.15	1.9	1,310
CS3	Rural	*Parmelia* sp.	1.186	0.002	2.460	0.003	15.0	69.8	19.9	2.36	4.7	1,980
CS1	Rural	*Parmelia* sp.	1.178	0.003	2.452	0.006	13.1	63.5	19.0	1.84	3.6	1,240
CS1 bis	Rural	*Parmelia* sp.	1.181	0.002	2.458	0.006						
CS2	Rural	*Parmelia* sp.	1.182	0.003	2.457	0.007	7.5	64.2	14.6	1.36	2.2	1,030

The errors for isotopic measurements are given at a 95% confidence level; see the text for uncertainties regarding elemental concentrations

bis duplicated material

collected in the urban area of Agadir. The examination of absolute metal concentrations alone may however produce spurious interpretations in terms of anthropogenic contribution to environmental exposure. To eliminate most of the variability related to the problems mentioned above, linked to exposure, lichen

Table 2 Quality control of the analyses

	Pb	Zn	Cu	Al	Sc	Ti
LOD (ng g^{-1})	0.6	0.9	0.3	1.3	0.2	0.3
NIST 1547 (μg g^{-1})						
Measured *a*	0.58	20.8	3.8	310	nm	22
Measured *b*	0.81	18.3	3.8	256	nm	24
Certified	0.87	17.9	3.7	250	0.04[a]	–
PACS-1 (μg g^{-1})						
Measured	395	905	471	6.52[b]	14	0.38[b]
Certified	404	824	452	6.47[b]	13[c]	0.42[b]
BCSS-1 (μg g^{-1})						
Measured	25.0	106	20.3	6.62[b]	12.7	0.40[b]
Certified	22.7	119	18.5	6.26[b]	11[c]	0.44[b]

Limits of detection (LOD) are calculated on the basis of three times the standard deviation of three analytical blanks. Measured and certified/provided values of CRMs NIST 1547, PACS-1, and BCSS-1

nm not measurable, – to the best of our knowledge, no data available

[a] Provided but not certified

[b] Expressed in percents

[c] No certified values available, data compiled from Hart et al. (2005), average of 20 and 8 values for PACS-1 and BCSS-1, respectively

age, etc., it was decided to normalize metal concentrations to an element of clear crustal origin. This procedure assumes that the background elemental composition of natural mineral matter incorporated into lichens is comparable over the whole study area. In this study, Al, Sc, and Ti concentrations in lichens are highly correlated ($r>0.91$, $p<0.01$). The linear regression slopes of 0.52 (Al vs Sc), 1.4 10^{-3} (Al vs Ti), and 408 (Ti vs Sc), are of the same order of magnitude as, respectively, Al/Sc, Al/Ti, and Ti/Sc ratios in the continental crust: 0.50, 1.9 10^{-3}, and 250 (calculated from Wedepohl 1995). Furthermore, Fig. 2 shows that along the W–E transect, the Al/Ti ratio (as well as Al/Sc and Ti/Sc, not shown here) remains reasonably steady, whatever the local lithology. This suggests that Al, Ti, and Sc are similarly incorporated into all lichen species during their lifespan. Thus, the mineral components of natural origin that contribute to lichen chemistry should not drastically differ in terms of composition over the whole study area. Each of these lithophilic elements can therefore be efficiently used to normalize metal concentrations. Titanium was arbitrarily chosen as reference element.

Table 3 Lead isotopic compositions of leaded gasoline from the major petrol companies operating in Morocco

Company	^{206}Pb/^{207}Pb	±	^{208}Pb/^{207}Pb	±
CMH	1.080	0.001	2.357	0.006
Mobil	1.077	0.002	2.360	0.006
Mobil bis	1.076	0.001	2.357	0.002
Shell	1.079	0.003	2.353	0.004
Petrom	1.081	0.002	2.360	0.004
Afriqia	1.079	0.002	2.348	0.004
Somepi	1.080	0.003	2.355	0.005
Total	1.080	0.001	2.355	0.005
Ziz	1.081	0.002	2.357	0.004
Petromin	1.081	0.002	2.357	0.003

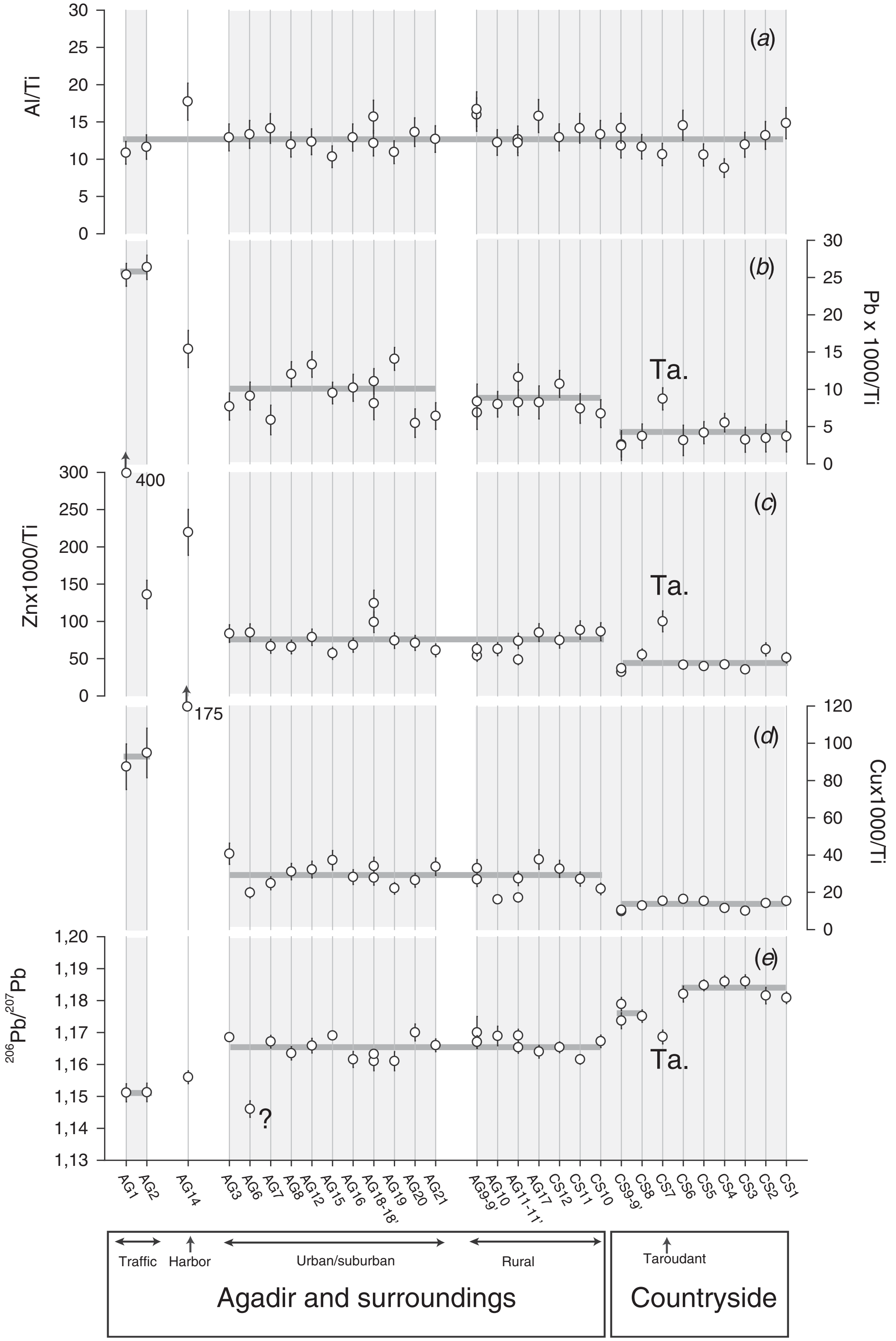
Errors are given at a 95% confidence level

bis duplicated material

4.2 Spatial Distribution of Metals Accumulated in Lichens

Figure 2 depicts variations in the Ti-normalized Pb, Zn, and Cu concentrations. Samples are ranked along a west to east axis, from the town of Agadir eastward to Talouine. The highest [metal]/[Ti] ratios are observed in lichen thalli sampled in downtown Agadir (AG1–AG2), an area exposed to high road traffic, and more generally to contaminated urban dust, and in lichen grown close to the Agadir harbor (AG14). Apart from these three samples, no significant differences were found between the values of the normalized metal ratios in both urban/suburban and rural areas situated around Agadir until sample CS10, located approximately 25 km east of Agadir (Figs. 1 and 2). From this point eastward, the Pb/Ti, Zn/Ti, and Cu/Ti ratios decrease about twofold and remain steady up to the extreme end of the transect, Talouine. Sample CS7, collected downtown in the city of Taroudant (63,000 inhabitants in 2005), is the only exception to this scenario. Its Pb/Ti and Zn/Ti ratios are higher than the average values of rural samples and are quite similar to those measured in urban/suburban samples from Agadir. It is noteworthy that while

Fig. 2 Evolution of the Al/Ti, (Pb/Ti) ×1,000, (Zn/Ti) ×1,000, (Cu/Ti) ×1,000, and ^{206}Pb/^{207}Pb ratios. Ta for Taroudant. *Agadir and surroundings* corresponds to lichens collected within a 25-km radius circle centered on Agadir; *Countryside* is for the remaining samples ▶


(a)
Al/Ti
0
5
10
15
20
25
30
(b)
Pb x 1000/Ti
0
5
10
15
20
25
30
Ta.
(c)
Znx1000/Ti
0
50
100
150
200
250
300
400
Ta.
175
(d)
Cux1000/Ti
0
20
40
60
80
100
120
(e)
$^{206}Pb/^{207}Pb$
1,13
1,14
1,15
1,16
1,17
1,18
1,19
1,20
?
Ta.
AG1
AG2
AG14
AG3
AG6
AG7
AG8
AG12
AG15
AG16
AG18-18'
AG19
AG20
AG21
AG9-9'
AG10
AG11-11'
AG17
CS12
CS11
CS10
CS9-9'
CS8
CS7
CS6
CS5
CS4
CS3
CS2
CS1
Traffic
Harbor
Urban/suburban
Rural
Taroudant
Agadir and surroundings
Countryside

the elemental concentrations of pairs of lichens collected at the same sampling site may differ by a factor of 3 (see AG9–AG9′, AG11–AG11′, AG18–AG18′, CS9–CS9′), the proposed normalization to titanium provides consistent values (Fig. 2b to d). Given the coherence of results along the transect, these findings suggest that titanium normalization makes element compositions comparable, even when the lichens belong to different species. The polluting influence of Agadir (~25 km) is five times that observed around Metz (~5 km), a French city of comparable size (Cloquet et al. 2006). One possible reason for this discrepancy could be the persistence and the strength of prevailing winds from the west in Agadir.

4.3 Origin of Lead Accumulated in Lichens

The ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios in the lichens analyzed vary from 1.146 to 1.186 and from 2.423 to 2.460, respectively (Table 1, Fig. 3). The ^{206}Pb/^{207}Pb ratios mirror well the evolution observed for Pb/Ti ratios (Fig. 2). Moreover, all pairs of lichens collected at the same site (i.e., AG9–AG9′, AG11–AG11′, AG18–AG18′, CS9–CS9′) yield comparable lead isotopic compositions. With the exception of sample AG6, the least radiogenic values are found in lichens from the harbor and from downtown Agadir, an area exposed to high traffic. The more radiogenic ratios are measured in lichens growing at the eastern end of the sampling transect (Fig. 2).

Lead isotopic compositions could show to some extent the contamination sources of lead found in these samples. The first step is to identify potential sources and to constrain them as much as possible by their isotopic signatures. Leaded gasoline sold by the nine major petrol companies during the sampling campaign (i.e., 2005) exhibits a homogeneous isotope signature with ^{206}Pb/^{207}Pb ratios of 1.076–1.081 and ^{208}Pb/^{207}Pb ratios of 2.348–2.360, respectively (Table 3, Fig. 3). These match the ratios observed in alkyllead gasoline used in South Africa (Monna et

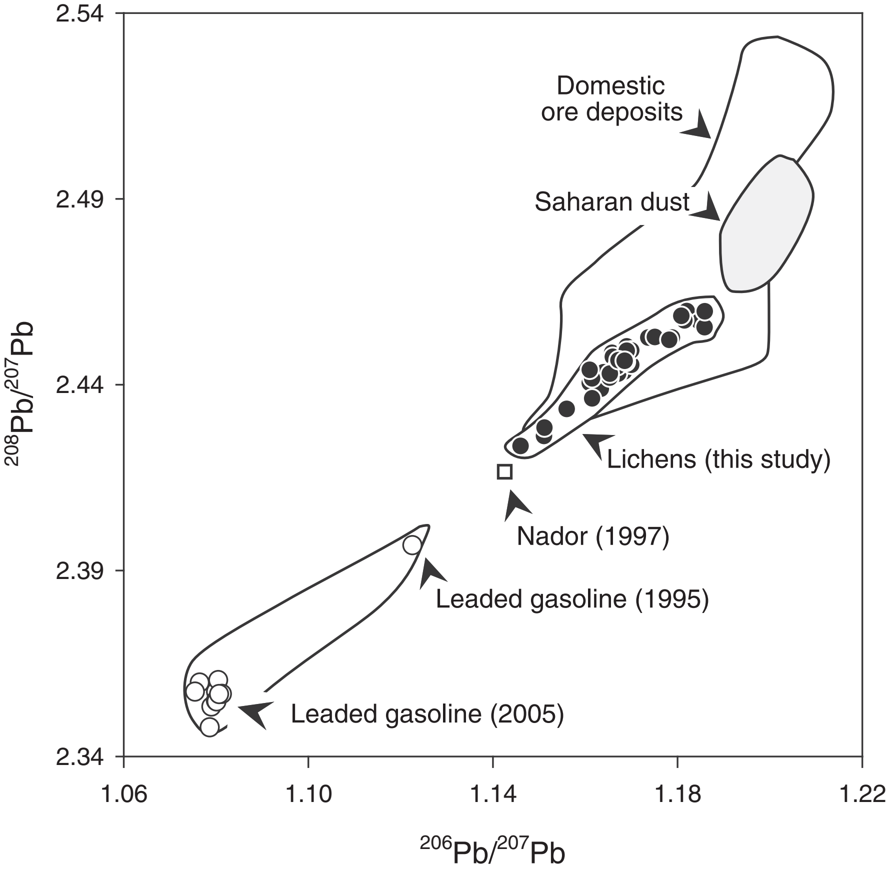


Fig. 3 ^{208}Pb/^{207}Pb vs ^{206}Pb/^{207}Pb in leaded gasoline (*open circles*), and in lichens (*closed circles*). For comparative purposes, leaded gasoline sampled in 1995 (Alleman 1997) and airborne particulate matter sampled in 1997 in Nador (Bollhöfer and Rosman 2000) have also been reported as well as the isotopic compositions of domestic ore deposits (Jébrak et al. 1998; Marcoux and Wadjinny 2005; Marcoux et al. 2008) and Saharan dust (Grousset et al. 1995; Bollhöfer and Rosman 2001; Abouchami and Zabel 2003)

al. 2006), pointing to lead derived from Precambrian ore deposits. Alleman (1997) reported a more radiogenic ^{206}Pb/^{207}Pb ratio of ~1.12 for leaded gasoline sold in Morocco in 1995 (Fig. 3). It seems, therefore, that significant changes in the natural forms of lead added to gasoline occurred during the 10 years preceding our sampling. Although the geology of the study area is quite varied, Saharan dust could provide some insight into the average isotopic signature of lead from natural mineral matter. The values reported in the literature (Grousset et al. 1995; Bollhöfer and Rosman 2000; Abouchami and Zabel 2003) are around 1.19–1.20 and 2.45–2.50 for ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb, respectively. Furthermore, lead exploited in Morocco may also contaminate the lower atmosphere of the study area. First, because ores from several mines located in High-Atlas and Anti-Atlas are stocked in the open air on the quays of Agadir harbor, and because indigenous lead is commonly used by local industries and craftsmen. Unfortunately, it is rather difficult to constrain this source from an isotopic point of view, due to the diversity of metallogenic events that led to the formation of massive polymetallic sulfides exploited in Morocco. As a consequence, only a broad domain can be defined by compiling several studies undertaken for metallogenic purposes (Jébrak et al. 1998; Marcoux and Wadjinny 2005; Marcoux et al. 2008, Fig. 3).

It is evident from Fig. 3 that none of the collected lichens isotopically matches modern leaded gasoline or the gasoline sold 10 years before our sampling. Their position on the plot is rather the result of a complex mixture of several components, including anthropogenic and natural sources. Our inventory is not exhaustive (the isotopic signatures of manmade sources may have changed over time). A major problem with such a plot is that the end-members appear in collinear positions, so that mixing involving more than two sources cannot be mathematically resolved. In other words, it is not possible to calculate precisely the fraction of gasoline-derived lead pollution.

Although deciphering all terms of the mixture may not be possible, the average lead isotopic composition of the anthropogenic component alone can be roughly assessed using a ^{206}Pb/^{207}Pb vs Ti/Pb diagram (Fig. 4). In this plot, data on lichen samples collected far from Agadir lie in the upper part of the diagram, while the most polluted lichens plot in the left part. The rectangle in the upper right-hand corner of the diagram indicates the area of the Ti/(Pbx1000) ratio of the upper continental crust (Wedepohl 1995), and the Pb isotopic compositions of Saharan dusts (Grousset et al. 1995; Bollhöfer and Rosman 2001; Abouchami and Zabel 2003). This domain represents a supposed background end-member, which is well aligned with both rural and urban lichens. The *X*-axis of Fig. 4 may also be regarded as the percentage of the anthropogenic contribution to the total lead content of individuals: ~100% when the Ti/(Pbx1000) ratio is close to 0, and ~0% when the same ratio is ~0.19. In such a representation, the desired information (i.e., the average Pb isotopic composition of the anthropogenic component alone) corresponds to the *Y*-axis intercept of the straight lines linking background to contaminated samples (see Monna et al. 2006 for a specific use with lichens). Thus, lichens collected in and around the town of Agadir present a ^{206}Pb/^{207}Pb signature of the anthropogenic component ranging from 1.145 to 1.160. There is only between 10% and 50% of anthropogenic lead in lichens sampled in rural areas. This percentage increases for lichens collected in Taroudant and within a 25-km radius around Agadir (ca. 60–80%) and may reach 90% in high traffic areas. Taking into account lead from gasoline (assumed to be characterized by a mean ^{206}Pb/^{207}Pb ratio of ~1.09 over the last 10 years), and two industrial components each situated at the extreme end of the ^{206}Pb/^{207}Pb ratio range (i.e., at 1.15 and 1.20), it can be calculated that lead deriving from automotive exhausts does not contribute more than 50% to the total anthropogenic lead content of lichens sampled in the high traffic areas of Agadir, and obviously contributes much less when considering the total lead content (including natural contribution), especially for lichens sampled far from Agadir.

Literature is particularly scanty for lead isotope analyses of Moroccan environmental samples. Bollhöfer and Rosman (2001) report ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of 1.141 and 2.418, respectively, for airborne particulate matter collected in 1997 at Nador, on the Mediterranean coast of Morocco, which did not match the gasoline sold at that time (^{206}Pb/^{207}Pb ~1.12, Alleman 1997). These authors proposed that either Saharan dust or industrial lead was responsible for the relatively high radiogenic value.

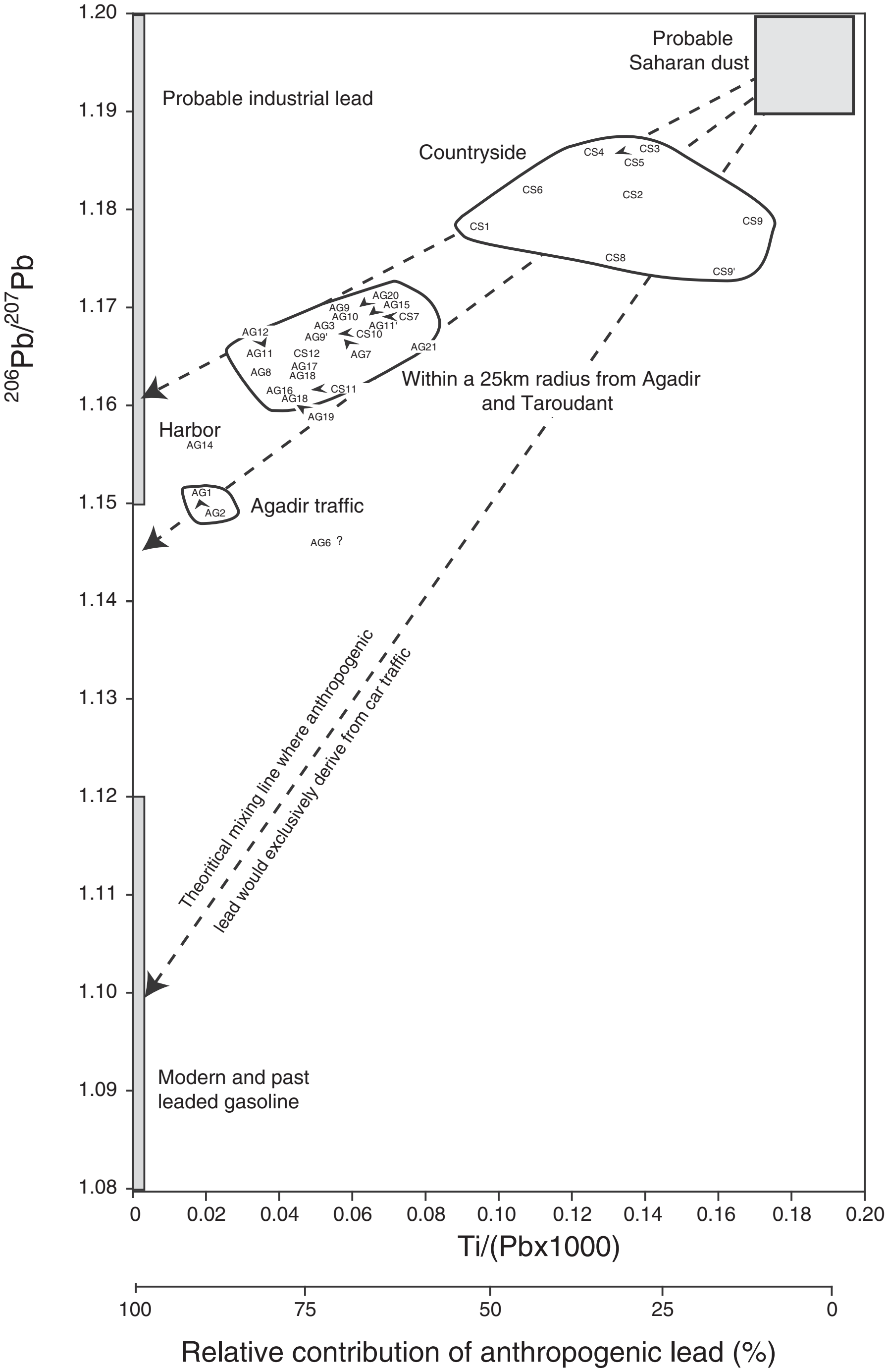


Fig. 4 $^{206}Pb/^{207}Pb$ vs Ti/Pb in lichens collected in Agadir and along a west–east transect up to Taroudant. The positions of Saharan dust, constructed using data from (Wedepohl 1995; Grousset et al. 1995; Bollhöfer and Rosman 2001; Abouchami and Zabel 2003), and gasoline-derived lead (Alleman 1997 and this study) are presented for comparison

In addition to providing new data about lead isotopes in Morocco, these results are important because they show that, within the limits imposed by data uncertainties, the response in terms of air quality to the recent banishment of lead from gasoline could be far less spectacular than expected, especially in urban areas.

5 Conclusions

This study demonstrates that normalization to a crustal element of chemical data from lichens may be necessary to increase the possibility of correct interpretations, making elemental compositions of different samples comparable, especially when the collected thalli belong to different species. This simple procedure appears to be efficient in eliminating most of the variability related to lichen exposure, morphology, age, and even species, a result strongly supported by lead isotope abundances. In addition, the lead isotope ratios point to several components responsible for the atmospheric presence of Pb, and therefore probably of Cu and Zn. It has been estimated that the gasoline contribution to total lead in lichens did not exceed 50%, even in high traffic areas. This point may be important for evaluating the improvements ensuing from environmental policies, and to assess the effectiveness of actions reducing the release of lead into the environment. The present study provides reference levels of local air pollution just before lead was finally phased out from gasoline. Lead isotopic composition measurements of leaded petrol collected before it became unavailable in Morocco improve the scarce database regarding potential lead sources in Northern Africa. This new dataset should be of great value for future studies involving environmental reservoirs where lead has a long residence time, such as soils and sediments.

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