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Identifying the origins of local atmospheric deposition in the steel industry basin of Luxembourg using the chemical and isotopic composition of the lichen *Xanthoria parietina*

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A B S T R A C T

Trace metal atmospheric contamination was assessed in one of the oldest European industrial sites of steel production situated in the southern part of the Grand-Duchy of Luxembourg. Using elemental ratios as well as Pb, Sr, and Nd isotopic compositions as tracers, we found preliminary results concerning the trace metal enrichment and the chemical/isotopic signatures of the most important emission sources using the lichen *Xanthoria parietina* sampled at 15 sites along a SW-NE transect. The concentrations of these elements decreased with increasing distance from the historical and actual steel-work areas. The combination of the different tracers (major elements, Rare Earth Element ratios, Pb, Sr and Nd isotopes) enabled us to distinguish between three principal sources: the historical steel production (old tailings corresponding to blast-furnace residues), the present steel production (industrial sites with arc electric furnace units) and the regional background (baseline) components. Other anthropogenic sources including a waste incinerator and major roads had only weak impacts on lichen chemistry and isotopic ratios. The correlation between the Sr and Nd isotope ratios indicated that the Sr–Nd isotope systems represented useful tools to trace atmospheric emissions of factories using scrap metal for steel production.

Keywords:

Air contamination

Lichen monitoring

Soils

Isotopic signatures

Lead

Strontium

Neodymium

Rare Earth Elements (REE)

Luxembourg

1. Introduction

Uncertainties in identifying the origin of atmospheric pollutants in the environment and in quantifying the impact of atmospheric contamination exist, particularly when biomonitoring

samples have been collected in strongly contaminated ecosystems. The difficulty of such estimations is based on the relative significance of both anthropogenic and natural sources of trace metals in the environment (Rasmussen, 1996; Reimann and de Caritat, 2000). The natural geochemical background is

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characterized by important variations at global, regional or local scales. Moreover, elements currently considered to be undisturbed by human activities and used as tracers of continental crust derived material (Al, Fe, REE) have become more and more involved in industrial or agricultural processes (Nriagu and Pacyna, 1988). The global production of lanthanides (REE), used in industry, medicine and agriculture, for instance, has increased exponentially from a few tons in 1950 to about 85 kt in 2000 (Haxel et al., 2002). Consequently, the presence of such anthropogenic contributions certainly interferes in the estimation of anthropogenic sources in strongly contaminated areas (e.g. using enrichment factors). On the other hand, in such areas, the concentrations of elements may be unstable during long time exposures and might have changed over time due to contamination, dilution, removal and fractionation (biological activity or other processes).

The isotope ratios do not fractionate during industrial production and only the mixing of aerosols from different sources with different isotopic characteristics can change them. In this study we observed a mixed isotope ratio, which allows, if the source characteristics were known, the quantification of the contributions of the different sources. Multi-tracer approaches combining elemental and isotope tracers may be a necessity to decrease significantly the uncertainties in identifying the origin of atmospheric pollutants in the environment. Pb isotopes have been used successfully for a long time in tracer studies and for source discrimination in environmental studies (Haack et al., 2002; and citations therein). The application of Sr and Nd isotope ratios, however, is rather new and has only very recently been successfully used for tracer studies of steel-work activities using tree bark (Lahd Geagea et al., 2007, 2008a,b).

The purpose of this preliminary study was to support this recent approach of Sr and Nd isotopes as well as REE to determine the impact of industrial atmospheric deposition in another contaminated area. In this study we applied for the first time in the Grand-Duchy of Luxembourg a multi-tracer approach combining different isotopic (Pb, Sr, Nd) and chemical tracers currently used individually in environmental studies in order to investigate the local impact of anthropogenic activity. This region suffers from substantial historical and current air contamination principally due to the presence of the steel industry, which has been active from 1875 until now. In addition to industrial or purely urban emissions, other potential sources of atmospheric emissions existing in this area are a waste incinerator and road transport. It is our hypothesis that the chemical and isotopic compositions of the lichens can be used to identify the origins of local atmospheric deposition. Epiphytic lichens were chosen because they totally derive nutrients and metals from wet precipitation, dry deposition and gaseous absorption (Rossbach et al., 1999). Therefore, they are considered to be good indicators of air quality and have been widely used to assess dispersion of trace metal contamination (Nash and Gries, 1991; Carignan and Gariépy, 1995).

2. Materials and methods

The superficial layer of soils (0–20 cm) was chosen in order to determine the local ground sources of airborne particles. We

distinguished between the four classes of lithology that cover the studied area: two calcisols developed on limestone and on the “Minette” oolitic iron sandstones in the southern Plateau region and one calcisol (marl) and one gleyic luvisol (tableland loam) that represent the valley and hills areas respectively (Fig. 1). For each soil, a composite sample was mixed from five sub-samples taken in 400 m² of a homogenous area. The samples were air dried, homogenized and sieved through a 63 µm nylon screen in order to conserve the finest particles. Complete dissolution of soil samples (100 mg) was done by acid digestion using a mixture of HF/HNO₃/HClO₄ on hot plates at atmospheric pressure.

The species *Xanthoria parietina* was sampled because of its very common presence all over the area. The samples were collected during summer 2005 along a SW–NE transect, which defines the most important regional air-mass circulation. The 15 sampling sites were chosen in order to identify the three principal sources of local atmospheric deposition as well as the local atmospheric baseline composition (Fig. 1). Some of the samples were taken as close as possible to the most important anthropogenic emission sources: a current steel-work factory (site nos. 3, 4, 5, 6, 7, 8), an old steel-work tailing area (site nos. 1, 2), and a waste incinerator (site nos. 10, 11). The other sites were chosen to characterize the local background of atmospheric deposition for each lithology that covers the investigated area. To characterize the spatial distribution of the chemical signal for a given time interval we choose in each sampling site lichens that were approximately of the same age (specimens of about 1 cm in diameter) and exhibited the same exposure characteristics to atmospheric circulation (orientation to the West and always outside forests). In order to avoid throughfall effects on the lichen chemistry, the samples were first taken from the outermost portion of tree branches of the same tree species (*Fagus sylvatica* L.). Only a few samples were collected on trunks. However, prevailing wind direction, source situation and conserving the same lichen species forced us to use different tree species from one sampling site to another in the urban environment (sites 1, 2, 4 and 5; see Table 1). Different throughfall chemistry may have influenced the lichen chemistry at these sites. For each site, a composite sample was made from different trees of the same species in order to obtain approximately 1 g dry-weight of lichen. No site replicates were collected. The samples were stored in pre-cleaned plastic flasks. The lichens were dried at 60 °C, separated from the remaining bark pieces, ground with an agate mortar and homogenized. No washing procedure of the thalli was carried out in order to avoid the leaching of soluble particles that may be adsorbed onto the thalli. The digestion was performed for at least 7 days at 105 °C using 2 ml of 40% HF and 5 ml of HNO₃ 13.5 N. Lead was separated from other elements using Bio-Rad AG1-X8 anion exchange resin and 0.6 N HBr and 6 N HCl as eluents. For Sr and Nd, Eichrom's Sr Resin in series with Eichrom's TRU Resin and Eichrom's Ln Resin were used in order to separate Sr and Nd from other elements according to Pin and Zalduegui (1996).

The precision of the analytical procedures and the variation of elemental concentrations in the composite samples were checked using triplicate mineralizations (lab splits). For each run, a blank and a reference sample (BCR-142R and

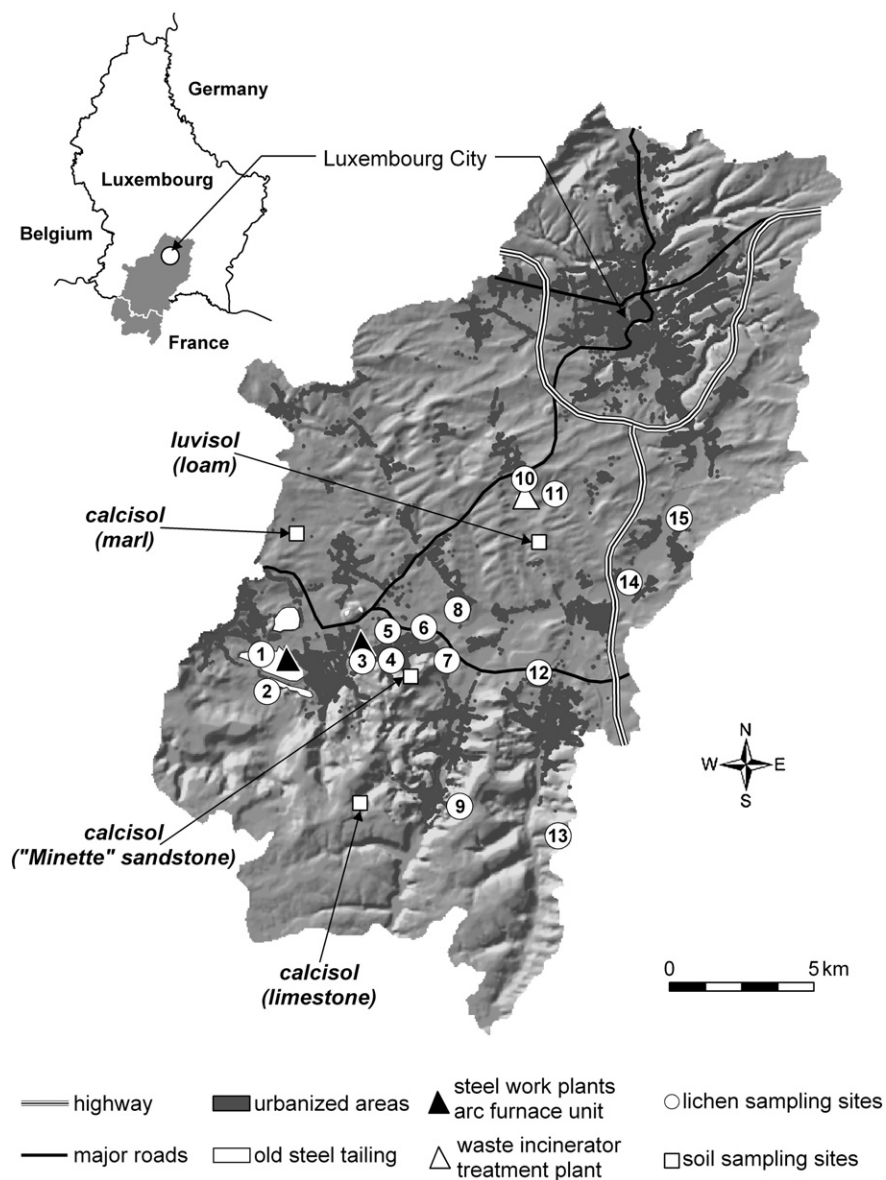


Fig. 1 – Lichen sampling sites in the upper Alzette River basin, located in the south-western part of the Grand-Duchy of Luxembourg.

NCSZC73001 for soils and IAEA-386 for lichens) were analysed using the same procedure to control for any possible contamination and the accuracy of the analytical methods. Blanks were always measured below the detection limit. For all the elements analyzed, our results were in good agreement with those of the certified reference materials and were within acceptable levels of uncertainty. The variation in elemental concentrations, tested on three replicates of lichen and soil samples, was less than 5% for all elements listed in Table 1, which tabulates the means. The variation of elemental concentrations in the samples was negligible in comparison to the variation we observed among the different samples.

The major and trace element concentrations in soil samples were determined by Inductively Coupled Plasma Optical Emission Spectrometry (Al, Mn, Fe) and Inductively Coupled Plasma Mass Spectrometry (Nd, Sm and Pb) at the Ecole Normale Supérieure Agronomique (INP Toulouse, France) and

the Laboratoire des Mécanismes et Transfert en Géologie (Toulouse, France), respectively. The major and trace element concentrations in lichen samples were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (Al, Mn, Fe) and Inductively Coupled Plasma Mass Spectrometry (Nd, Sm and Pb) at the Centre de Géochimie de la Surface (CGS; Université Louis Pasteur, Strasbourg). The errors of measurement were <5%. The detection limits for each element were determined by 10 replicate analyses of a known standard, whose standard deviation was then multiplied by three. All measurements were above the detection limits.

The Sr and Pb isotopic compositions were determined at the CGS using a fully automatic VG Sector thermal ionization mass spectrometer with a 5-cup multicollector after enrichment and separation from the bulk sample (Lahd Geagea et al., 2008a). During the measurement period, the NBS 987 Sr standard yielded $^{87}\text{Sr}/^{86}\text{Sr}=0.710271$ (± 7 stdev, $n=9$). The

Table 1 – Average concentrations of major and trace elements and isotopic ratios of Pb, Sr and Nd of three lab split samples of *Xanthoria parietina*

Site	Tree species	Distance to steel activity	$\mu\text{g g}^{-1}$													$^{143}\text{Nd}/^{144}\text{Nd}$
			Al	Fe	Mn	Nd	Sm	Pb	Fe/Al	Mn/Al	Sm/Nd	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{87}\text{Sr}/^{86}\text{Sr}$	
1	<i>Betula pendula</i> Roth	350	3258	17102	338	0.38	0.07	107	5.2	0.10	0.196	18.55	15.67	38.75	0.7109	0.51186
2	<i>Betula pendula</i> Roth	789	4521	27816	494	0.44	0.09	50	6.2	0.11	0.206	18.09	15.54	37.86		
3	<i>Fagus sylvatica</i> L.	303	4379	16540	1613	0.49	0.09	99	3.8	0.37	0.174	18.00	15.61	37.91	0.7113	0.51193
4	<i>Betula pendula</i> Roth	671	2374	9409	601	0.20	0.04	82	4.0	0.25	0.199	18.04	15.61	37.95		
5	<i>Populus</i> L.	1174	1398	6550	461	0.10	0.02	59	4.7	0.33	0.206	17.98	15.56	37.77		
6	<i>Fagus sylvatica</i> L.	2265	1095	4256	284	0.08	0.02	26	3.9	0.26	0.209	18.03	15.60	37.91		
7	<i>Fagus sylvatica</i> L.	1517	1462	5001	215	0.10	0.02	32	3.4	0.15	0.214	18.05	15.60	37.94		
8	<i>Fagus sylvatica</i> L.	3546	1472	3874	138	0.11	0.02	34	2.6	0.09	0.191	18.08	15.61	38.02		
9	<i>Fagus sylvatica</i> L.	6212	769	1239	31	0.06	0.01	4	1.6	0.04	0.197	18.08	15.56	37.80		
10	<i>Fagus sylvatica</i> L.	8447	2826	2704	128	0.17	0.03	16	1.0	0.05	0.188	18.07	15.55	37.77	0.7152	0.51205
11	<i>Fagus sylvatica</i> L.	8512	1556	2025	83	0.08	0.01	10	1.3	0.05	0.184	18.03	15.54	37.73		
12	<i>Fagus sylvatica</i> L.	5799	1286	2408	81	0.08	0.02	12	1.9	0.06	0.189	18.04	15.54	37.75		
13	<i>Fagus sylvatica</i> L.	9380	1358	2423	87	0.13	0.03	12	1.8	0.06	0.206	18.10	15.57	37.86		
14	<i>Fagus sylvatica</i> L.	9300	2020	3383	118	0.13	0.03	18	1.7	0.06	0.197	18.08	15.55	37.78		
15	<i>Fagus sylvatica</i> L.	12022	782	1355	67	0.04	0.01	7	1.7	0.09	0.189	18.11	15.59	37.88		

The variation of elemental concentrations in the samples was negligible in comparison to the variation we observed between the different samples. The species of host tree and the distance from the sampling sites to the steel plants (based on ARCGIS® calculation at ± 1.0 m) are also tabulated.

isotopic Pb data presented here were adjusted for mass fractionation by repeated analyses ($n=27$) of the NBS 981 standard. The 2σ -errors of the reported isotopic ratios are for $(^{206}\text{Pb}/^{204}\text{Pb}) < \pm 0.022$, $(^{207}\text{Pb}/^{204}\text{Pb}) < \pm 0.025$ and for $(^{208}\text{Pb}/^{204}\text{Pb}) < \pm 0.079$. Nd isotopic compositions were determined using a Nu instrument high precision Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the branch of Isotope Geology at the University of Bern. The in-house standard yielded $^{143}\text{Nd}/^{144}\text{Nd} = 0.511061$ (± 3 stdev, $n=23$), corresponding to a La Jolla standard value of 0.511843.

3. Results and discussion

3.1. Elemental concentrations in lichens

The elemental concentrations found in our lichens were comparable with other *X. parietina* samples (Scerbo et al., 2002; Di Lella et al., 2004; Brunialti and Frati, 2007). The variability of elemental concentrations found in lichen may be related to species differences in age and size, or to microclimatic differences. However, the variation of the concentrations we observed for the same lichen species of similar age from the Luxembourg basin can be explained by different atmospheric dust concentrations. The lichens collected near the steel-work areas exhibited the highest concentrations. The high levels of concentrations found there rapidly decreased with increasing distance for all elements (Table 1). As already observed in other contaminated sites (Sensen and Richardson, 2002), the trace element concentration-distance relationship revealed that the most important part of local atmospheric fallout from the industrial activity did not occur beyond a distance of 5 km. Further away, element concentrations reached the local geochemical background, which was estimated with the lichens collected in remote areas (Sites 9, 12, 13, 14, 15). Closer to the emission sources, the different chemical elements, including elements generally considered as conservative and non-disturbed by human activities (Al, REE) have higher concentrations than the local background level. Anthropogenic activities generate more atmospheric dust and cause more important dust deposition close to a polluting source than at more remote sampling sites. Moreover, the anthropogenic sources cause fractionation between Nd and Sm in comparison to remote sampling sites (see Sm/Nd ratios in Table 1).

3.2. Tracers of atmospheric deposition in lichens

Using Fe/Al and Mn/Al ratios we distinguished the chemical signatures of the two steel production areas (actual metallurgical sites (P) and historical steel-works tailings (T)) and a regional background signature measured in the lichens of the remote areas (R). Lichens at the latter sites showed Fe/Al (1.0 to 1.9) and Mn/Al (0.04 to 0.09) ratios close to values found in the luvisol and calcisols (marl and limestone) of the basin. Strong iron enrichment (Fe/Al ratios > 5) characterized the lichens collected close to the old steel tailing area T (Sites 1 and 2—black plots in Fig. 2a). This enrichment may be due to the rich “Minette” iron ore used in the blast-furnace of steel-works during the last century. The sites located near the present steel-work activity (Sites 3 to 8—grey plots in Fig. 3a) were

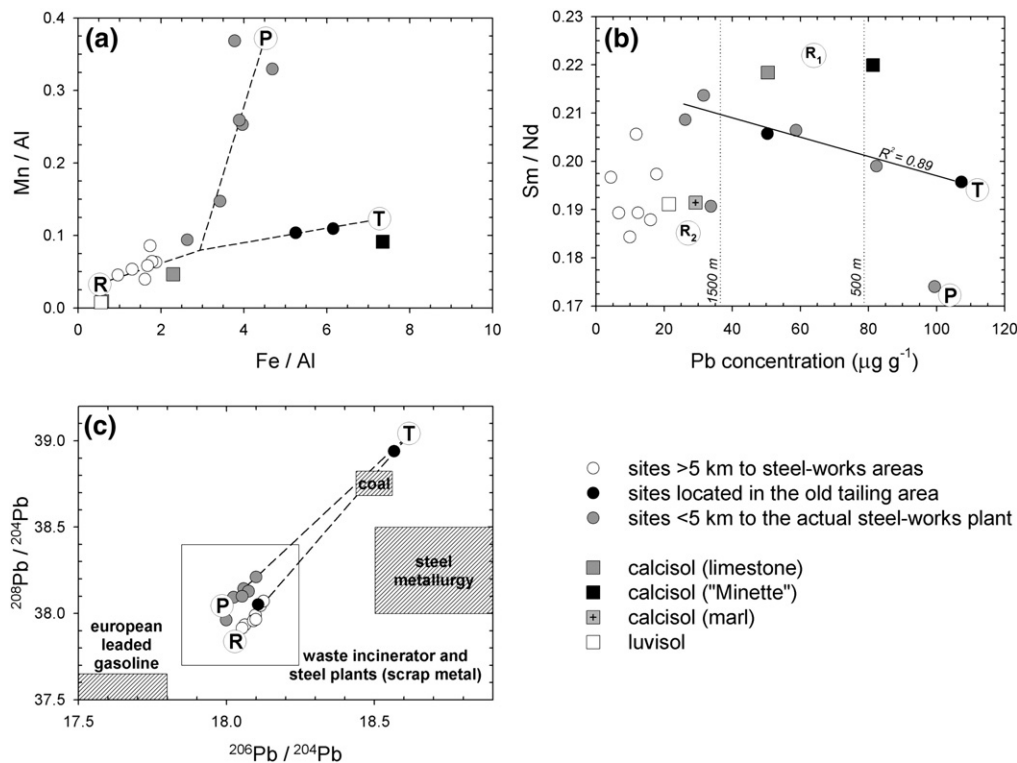


Fig. 2 – Origin of the atmospheric deposition in the south-western part of the Grand-Duchy of Luxembourg. Three potential sources of atmospheric emissions and depositions were identified—P (actual steel-work plant), T (old steel production tailing area) and R (remote areas)—using three independent tracers: (a) Mn/Al vs Fe/Al diagram for lichen samples and soils, (b) relationship of the Sm/Nd ratio to the Pb concentration measured in the lichen samples. This tracer allowed distinguishing between R₁ (soils located in the “Minette” ore area—southern part of the studied area) and R₂ (soils located in the luvisol and marl calcisol areas—northern part of the studied area). R² is the coefficient of determination of the relationship between lead concentrations and Sm/Nd ratios for lichens located at a distance <1500 m to the steel-work areas: $Sm/Nd = -0.002 [Pb] + 0.217$. Dashed lines indicate the distance to the steel-work areas, (c) ²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb ratios of lichens. The Pb isotopic compositions of the different possible sources are also reported: European leaded gasoline (Monna et al., 1997; Chiaradia and Cupelin, 2000), steel metallurgy plant (Véron et al., 1999), waste incinerators (Monna et al., 1997; Chiaradia and Cupelin, 2000; Carignan et al., 2005), and coal (Chiaradia and Cupelin, 2000).

enriched in both Mn (Mn/Al=0.35) and Fe (Fe/Al=3.5). The comparatively low concentrations in the lichen collected in the Sites 10 and 14 indicated that neither waste incinerator nor traffic emissions contain large quantities of Fe and Mn. This result is unusual at least for traffic pollution. Generally Mn and Fe contamination is related to industrial activities but in some studies road traffic was found to be the source of these elements (Zechmeister et al., 2005).

The Sm/Nd ratios appeared to be fractionated as a function of the distance from the steel-works as illustrated in the Sm/Nd vs Pb concentration diagram (Fig. 2b). In remote areas, the lichens had lower Pb concentrations and Sm/Nd ratios comparable to those of the corresponding soils. Sm/Nd ratios were close to calcisols (limestone and “Minette”—R₁) for Sites 2, 5, 6, 7 and 9 or close to calcisol (marl) and luvisol (R₂) for Sites 8, 10, 11, 12, 13, 14 and 15. Lichens collected closer to the waste incinerator appeared to have lower Sm/Nd ratios. The lichens collected in the R₁ area and close to the steel-work sites (P and T) showed decreasing Sm/Nd ratios in accordance with increasing Pb concentrations. Sm/Nd ratio and Pb define there a linear relationship ($Sm/Nd = -0.002 [Pb] + 0.217$; $R^2 = 0.89$, $n = 6$). Lichens at Site 3, closer to current steel

activities (P), showed a significant lower Sm/Nd ratio. This indicated, similar to a previous study (Lahd Geagea et al., 2007), that steel plants and the waste incinerator emitted larger quantities of Nd than of Sm (Fig. 2b).

The Pb isotopic ratios of the lichens were distributed between the three potential sources already characterized for the studied area (R, T and P—Fig. 2c) and were very similar to those of dust from waste incinerators given by Monna et al. (1997), Carignan et al. (2005) and steel-works according to Lahd Geagea et al. (2007). These ratios scattered in a relatively small area and were clearly distinguishable from less radiogenic leaded gasoline (Monna et al., 1997; Chiaradia and Cupelin, 2000) but also from more radiogenic steel-works (Véron et al., 1999). The largest variations in lead isotopic composition occurred in the most contaminated sites, which were collected close to the steel-work areas (grey and black symbols in Fig. 2c). The lichens were distributed along two lines, which met each other at the more radiogenic side. This intersection was represented by the old tailing area (Site 1), which contained a Pb isotopic signature similar to that of coal dust (Chiaradia and Cupelin, 2000). This Pb is derived from the older steel metallurgy using blast-furnace and coke combustion

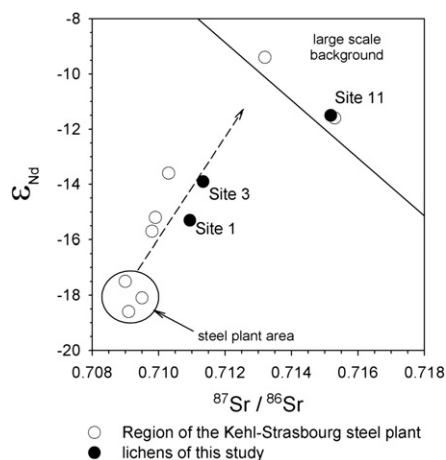


Fig. 3 – Comparison between industrial and geogenic Sr and Nd ($\epsilon_{Nd} = ((^{143}\text{Nd}/^{144}\text{Nd}/0.51264) - 1) \cdot 10^4$ —De Paolo and Wasserburg, 1976) isotopic compositions. The results of this study (sample nos. 1, 3 and 11) are compared to previous results obtained by Lahd Geagea et al. (2007) using tree bark in the vicinity of the Kehl–Strasbourg steel plant. The peri-urban samples are close to the regional trend. The Nd isotopic composition of the steel plants dust was very low suggesting that the Nd originated from Precambrian continental crust (e.g. banded iron formations). With increasing distance from the steel plant the Sr and Nd isotopic compositions increased and evolved to large-scale background values (dashed arrow).

methods and becomes strongly remobilized with wind. The diagram pointed to at least two additional sources with distinct isotopic compositions. The lichens collected in the vicinity of the old tailing area and in the remote areas defined the mixing line R-T with less radiogenic Pb isotopic compositions than those situated close to the steel-works. We assumed that the second end-member of the R-T line corresponded to a regional background isotopic Pb composition (R in Fig. 2c). These sites showed a homogenous isotopic composition with an average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.159. It is interesting to note that the sites located close to the waste incinerator plotted on this R-T mixing line with a $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratio (37.9) similar to that of the Strasbourg waste incinerator (37.8) but lower than the $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratios determined for the steel plants (>37.9) (Lahd Geagea et al., 2008a,b). The lichens collected close to the steel-works (<5 km) were located on the line P-T with sites being more radiogenic in Pb. They were similar to those found in aerosols of a steel-works using an electric arc furnace unit to melt scrap material in the vicinity of Strasbourg City (France): $^{208}\text{Pb}/^{204}\text{Pb} = 37.9$ – 38.1 and $^{206}\text{Pb}/^{204}\text{Pb} = 17.98$ – 18.01 (Lahd Geagea et al., 2007, 2008a,b).

Isotopic compositions of Sr and Nd were determined in only three lichen samples, which corresponded to Site 1 (old steel tailings area), Site 3 (current steel-work) and Site 11 (remote area). The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of the sites 1 and 3 were much lower (0.7109 and 0.7113) than the atmospheric $^{87}\text{Sr}/^{86}\text{Sr}$ baseline composition (0.719–0.725) determined for the neighbouring Vosges mountains and the Rhine Valley

(Lahd Geagea et al., 2008a,b); but they were only slightly more radiogenic than an aerosol sample collected close to the steel-works NE of Strasbourg City (0.7098—Lahd Geagea et al., 2007). Site 11 from the remote area had a Sr isotopic composition close to that of the baseline composition found in the Vosges Mountains (Stille et al., 2006). The $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios have also been determined for the three sites. The lowest ϵ_{Nd} values of -13.9 and -15.3 have been found for Sites 1 and 3, from the steel-work areas (Fig. 3). Such low Nd isotopic ratios are not typical for rocks from Western Central Europe but are characteristic of old Precambrian basement rocks or for argillites of Precambrian banded iron formations (Stille and Clauer, 1986). Thus, these low ϵ_{Nd} values might suggest that iron used for old steel production originated from the Precambrian continental crust. The values were similar to those found close to the steel factory situated in the urban environment of Strasbourg–Kehl (-17.5 ; Lahd Geagea et al., 2007). Fig. 3 includes not only the three lichens of this study but also tree bark samples collected in the urban area of Strasbourg–Kehl and from its peri-urban environment. $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} values were similar to those found previously for the Strasbourg–Kehl environment and suggested comparable Sr and Nd isotopic signatures for the steel-works and the natural large-scale background.

4. Summary and conclusions

The investigated area of the Grand-Duchy of Luxembourg is one of the oldest European industrial sites of steel production. Nevertheless, its impact on the regional air contamination has never been studied in detail. On the other hand, it was a perfect location to support recent results concerning the tracing of industrial activities using concentrations and isotopic ratios of REE.

In this study, different isotope and elementary ratios have been used to identify the most important pollutant sources. The Mn/Al vs. Fe/Al diagram and Pb isotopic ratios were useful tools to distinguish between historical (blast-furnace units) and actual (electric arc furnace unit) steel production as well as remote areas. Further investigation might help us to determine the evolution of trace metal contamination due to these two different steel production processes. With the help of the Sm/Nd ratios and Pb concentrations in the lichens, it was possible to identify the local background composition controlled by the corresponding soil signatures. Moreover, the interaction of the steel-works emissions with the local background atmospheric component appeared to become important at distances <1.5 km from these industrial sites.

The Sr and Nd isotope data appear correlated with each other and occur in between values of the local background and of the filter dust from the steel-works situated in the Rhine valley. This indicated that the Sr–Nd isotope system may characterize factories using electric arc furnace and scrap metal (including cars) for the steel production. The Nd isotopic compositions detected in the lichens close to the industrial sites were very low compared to crustal rocks of Western Central Europe, which makes the Nd isotope ratio a powerful tool to trace steel-works' atmospheric emissions.

Further study with larger sample sizes and field replicates would allow hypothesis testing of these findings using significance tests.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2008.05.029.

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