Supporting Information

Isotope Tracing of Atmospheric Mercury Sources in an Urban Area of Northeastern France

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21 pages (including title page)

7 Figures (SI-S1 to SI-S7)

2 Tables (SI-S1 and SI-S2)

Lichens sampling description

In order to assure homogeneity of the sample and to perform multiple elemental and isotopic analyses, between 3 and 25 g of lichens hanging on tree branches were collected. The quantity sampled depended upon the lichen abundance at the sampling site. The sampling area at a given site depended also upon the lichen abundance and ranged from $100m^2$ to around $1000m^2$. Lichens were sampled between ground level and 2 meters high.

Living lichens were sampled mainly on thin tree branches (2 to 5 years old depending on the tree). Hence, we estimated that the age of the lichens sampled at a site may range from 2 to 5 years. The sampling of a large amount of material was aimed to recover homogeneous age fractions of lichens at each site.

When available, different species were separated at a given site. Indeed, because lichens do not have the same behaviour regarding atmospheric air composition, the same species were not present at each sampling site. Some lichens are airborne pollution sensitive (e.g. Usnea species) whereas others are pollution tolerant (e.g. Xanthoria Parietina). Thus, depending on the sampling site and the lichen diversity and abundance, 4 fruticose species (Usnea sp (US), Ramalina farinacea (RF), Evernia prunastri (EP), Pseudevernia furfuracea (PF)) and 4 foliose species were sampled (Hypogymnia physodes (HP), Physcia tenella (PT), Xanthoria parietina and/or polycarpa (XP)). Furthermore, several fruticose species could have been mixed (Mix F) to satisfy a sufficient amount of matter for homogeneity and analytical issues.

Lichens were sampled with gloves and plastic tweezers in order to avoid contact and inclusion of tree bark (specifically in the case of foliose species sampling). Then, samples were put into polyethylene bags prior to sample proceeding.

For most of the sites, sampling was done over the years 2001, 2003, 2006, 2008 and 2009. In total, the Hg isotopic composition of lichens was investigated at 31 sampling sites (Figure SI-S1) corresponding to 51 lichen samples analyzed. 10 of the 31 sampling sites (corresponding to 19 of 51 lichen samples) were already presented in Carignan et al. (*33*). Information about type of lichen, sampling year and area, concentration and isotopic composition are given in Table SI-S1.

Sampling Sites Description

The region of study was divided into four major areas and one sub-area based (see Figure SI-S1) on quantitative criteria such as the inhabitant density, the presence or absence of industries, the proximity to anthropogenic emissions (road, commercial activities), the topography, the distance to the city of Metz, the density of forests and agricultural fields. Subdivisions identified were: rural area (RA), suburban area (SA), urban area (UA), industrial area (IV) and one sub-area located within the IV: industrial sites (I). In addition, one site with high Hg content measured in lichens drew our attention. Surroundings of this "contaminated point" (CP) located within the suburban area (Figure SI-S1) were sampled more intensively (SA/ACP). Descriptions of all these areas are given below.

Urban Area (UA, 5 sites). Sampling of the five lichen sites was done at the fringe of the historical centre, mainly because of the quantity of lichen available (distance from the city centre was less than 3 km). The population density within the urban area is 3000 inhab/km^2. Within this area, anthropogenic Hg sources may be multiple including domestic heating, urban traffic, one municipal waste incinerator, one coal and gas fired power plant.

Suburban Area (SA, 9 sites). This area is located between the rural area and the urban area (between 3 and 10 km from the city centre). With a density of inhabitants far less than in the urban area lichens were always sampled close to important roads or road connexions. Main anthropogenic Hg sources are a large coal fire power plant (500 MW) at the north of the city of Metz (in front of SA-12 sample, see Figure SI-S1), one waste combustor and domestic heating.

Rural Area (RA, 4 sites). This area comprised four sites sampled at a minimum of 12 Km from the city of Metz. Lichens were sampled at the edge of small woods surrounded by large cultivated fields and far from any roads, industrial activities or housing areas. Other than agricultural use (fertilizer, pesticides...), direct anthropogenic sources are scarce. Natural source emissions, such as soils or vegetation may be significant.

Industrial Valley (IV, 5 sites). The area covered in this study is the Southern part of the largest French industrial valley (Mosellan Valley), from Metz to Luxembourg. The studied area was located within the Orne Valley, which comprised an important number of iron mines and steel and iron factories. All the iron mines as well as many of the factories located within this valley were progressively closed during the 70-90's. Nevertheless, some large factories remain still active in the valley. Lichens IV-45 and IV-48 were sampled at the bottom of the valley (160 m elevation) whereas IV-46 and IV-47 were sampled at the top of the hills (250 and 350 m elevation respectively). IV-49 was sampled at a reconverted industrial site (now a large commercial mall).

Industrial sites (I, 2 sites). Two lichens were sampled at two different iron and steel factories still in operation at the time of the study, located within the industrial valley (IV). I-43 was sampled at the factory (steel industry and agglomerates) located in the town of Rombas (160 m elevation). Lichens were sampled just behind the fences of the factory on the west and south sides at around 50 to 100 meters of the stacks. I-44 was sampled at the factory (blast furnaces) located in the town of Gandrange (160 m elevation). Lichens were sampled just behind the fences of the factory on the south side from 50 to 200 meters of the stacks. For these two sites the foliose and fruticose lichen diversity was very low. Only two foliose lichen species were observed with a high abundance and identified as xantoria parietina and/or xantoria polycarpa (XP). Xanthoria parietina is known to be highly tolerant to airborne pollution such as acid rain and heavy metals and thus are characteristic lichens found in the polluted area.

Contaminated point (CP-27, Figure SI-S5, 1 site) and Suburban Area Around the Contaminated Point (SA/ACP, Figure SI-S5, 5 sites). This point is located in the suburban area as shown on the general map (see Figure SI-S1). The contaminated point (CP-27) was found next to an agricultural field, a small wood, several houses and a highway, including a service area about 1 km away (Figure SI-S5). Lichens from this site have Hg concentrations ranging between 350 and 450 $ng.g^{-1}$ over the years 2001 to 2008 (see Table SI-S1). In order to trace the dispersion of Hg around this site, five lichens were sampled covering an area of 2 km^2 (see Figure SI-S5).

Analytical Methods

All the lichens (other the ones reported in Carignan et al. (*33*)) were dried in the laboratory (105°C during at least 24 hours) or freeze-dried according to the method reported by Carignan and Gariépy (*13*). Between 0.5 and 1.5 g of dried matter was introduced into 6 ml of concentrated HNO_3 prior to achieve the high temperature and high pressure digestion method applied to the lichen reference material BCR-482 described in Estrade et al. (*37*).

Hg concentrations of lichens sampled from 2001 to 2008 were analysed after digestion using Gas chromatography-isotope-dilution coupled to Thermo-Finnigan X2 ICP-MS (Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (IPREM) in Pau) according to the method described in Montperrus et al. In order to assure 100% digestion yield, multiple digestions of the lichen reference material BCR-482 were performed as well as digestion of lichens already analysed in Carignan et al. (33) (e.g. RA-10, RA-35) and duplicate of digestion (RA-01) (see Table S1). Hg concentrations of lichens sampled in 2009 were determined on dry material by using the mercury analyser Milestone DMA-80®. Here, multiple digestions of the BCR-482 were also done as well as digestion duplicate (e.g. IV-47). Digestion yields were directly measured comparing the intensity of the sample relative to the reference material NIST 3133 in the same acidic matrix on the MC-ICP-MS before the isotopic analysis.

The isotopic compositions of lichens were analyzed by using a cold-vapor generation system (home-made gas-liquid separator, see Estrade et al. (*37*)) coupled to a Nu Plasma HR (Nu Instruments, UK) MC-ICP-MS at the IPREM/LCABIE in Pau, as described in Estrade et al. (37). Digested lichens as well as the NIST SRM 3133 reference material "delta zero" were diluted in a similar acidic matrix (between 10 and 20% HNO_3 v/v) to appropriate Hg concentrations (3 to 5 μg.L^{-1}) and Hg(II) was reduced on line with 3% w/v $SnCl_2$ (Alfa Aesar NormaPur) in 1 mol.L^{-1} supra pur HCl. The instrumental mass bias drift was monitored by using the standard-sample-standard bracketing method and NIST SRM 997 Thallium as the internal reference and corrected with the exponential mass fractionation law. The Thallium was continuously introduced using a desolvation unit (DSN). Mixing with Hg^0 was done into the ICP-MS torch using a double input torch. Additional descriptions are provided in Estrade et al. (*37*).

Variations in Hg isotopic composition are expressed relative to the standard reference material NIST SRM 3133, using the delta notation and following recent recommendations for Hg isotope measurement (Blum and Bergquist (*38*)):

$$\delta^{X/198}(\text{‰})_{\text{sample/NIST3133}} = \left(\frac{^{X/198}\text{Hg}_{\text{sample}}}{^{X/198}\text{Hg}_{\text{NIST3133}}} - 1\right) \times 1000.$$

where X represents Hg isotopes other than 198. Mass Independent Fractionation (MIF) are expressed as described in Blum and Bergquist (*38*)

$$\Delta^{199}Hg = \delta^{199}Hg_{measured} - 0.252 \times \delta^{202}Hg_{measured}$$

$$\Delta^{200}Hg = \delta^{200}Hg_{measured} - 0.502 \times \delta^{202}Hg_{measured}$$

$$\Delta^{201}Hg = \delta^{201}Hg_{measured} - 0.752 \times \delta^{202}Hg_{measured}$$

$$\Delta^{204}Hg = \delta^{204}Hg_{measured} - 1.493 \times \delta^{202}Hg_{measured}$$

For this study the long term external reproducibility of the method was determined by repeated analyses of the secondary mono-elemental reference material CRPG-RL24H for which our results were compared to published values in Estrade et al. (*37*). The external reproducibility of unknown samples was calculated as 2 standard errors (2SE) of the mean value (from different brackets of the sample), except when this value was lower than the external reproducibility of the method. The isotopic composition of multiple digestions (n=5) of the lichen reference material BCR-482 was in agreement with the value determined in Estrade et al. (*37*). Added to these reference materials, we started to run during the last analysis session the well-characterized UM-Almaden material that showed also results in agreement with the published values (Blum and Bergquist (*38*)). All the results are reported in Table SI-S2.

Statistical calculations

All statistical analyses were undertaken with STATISTICA software, version 5.5 (StatSoft, USA). The mercury concentrations, δ^{202}Hg, Δ^{199}Hg and Δ^{201}Hg were tested by one-way analysis of variance (ANOVA) in order to investigate the effects of sampling areas on the concentration and isotopic results in lichens (degree of freedom =3). Significant differences between paired means were determined by Tukey HSD for unequal N (Spjotvol Stoline). Prior to analysis, homoscedasticity was assessed by Brown-Forsythe test. For all statistical analysis, the significance level was set at $\alpha = 0.05$. The dataset tested included geographical areas UA, SA, RA and IV. Area I was not taken into account because only two samples were available to perform statistical tests.

Additional comments on data points removed from calculations

In order to define average isotopic compositions for each individual area, SA-12 was removed from calculations because of its non-homogeneity between 2003 and 2008. Indeed, its concentration decreased two fold and the Δ^{199}Hg values changed also drastically between these two years. This change in concentration and isotopic composition indicated either a bias in the sampling (e.g. sampling of dead or young lichens) or variation in Hg atmospheric fallout for this given site. In addition, the point IV-49 was removed from calculations because Δ^{199}Hg measured (-0.39 ± 0.05‰) at this point contrasted with the average defined by other sampling sites in the industrial valley (-0.27‰). In fact, point IV-49 was sampled above a slag heap, while are all other sites represent converted industrial sites into commercial and recreational areas since 15 years. Point IV-49 was thus considered as more representative of the suburban area than of the industrial valley.

Additional comments on the Contaminated point (CP-27) and Suburban Area Around the Contaminated Point (SA/ACP). This study is located in the suburban area as showed on Figure SI-S1. The contaminated point was found throughout the years to display an average [Hg] of 400 ng.g^{-1} and a δ^{202}Hg, averaging at +1.38 ± 0.19 ‰ associated with a Δ^{199}Hg of -0.49 ± 0.12 ‰ (CP-27, 2SE n=4, Tab. SI-S1). The lichen SA/ACP-42 was sampled in front of CP-27 on the other side of the highway at c.a. 200 meters away and presents Hg concentration of 196 ng.g^{-1} also, high regarding all others lichens of this area (see Table SI-S1 and Figure SI-S6). Furthermore, this lichen displays a δ^{202}Hg +0.46 ± 0.19 ‰ that is lighter than CP-27, but heavier than all other lichens from suburban area. It shows a similar Δ^{199}Hg (-0.42 ± 0.05 ‰) to SA/ACP lichens (see Fig SI-S7). Lichens SA/ACP 38-39-40-41 were sampled over 200m away from CP-27 and show Hg concentrations in the average determined for all others lichens of the study (80-130 ng.g^{-1}, Table SI-S1 and Figure SI-S6) with isotopic compositions in the range determined for the suburban area ($\delta^{202}Hg$ = -1.14 ± 0.12‰; $\Delta^{199}Hg$ = -0.42 ± 0.05‰ and $\Delta^{201}Hg$ = -0.46 ± 0.06 ‰, 2SE, n=4). Figure SI-S7 presents the $\Delta^{199}Hg$ versus the $\delta^{202}Hg$ of the contaminated point (CP-27) and lichens sampled in the surrounding area. It clearly shows that this contamination source has a small-scale impact, probably limited to a few hundred meters.

Literature cited

Monperrus, M.; Tessier, E.; Veschambre, S.; Amouroux, D.; Donard, O., Simultaneous speciation of mercury and butyltin compounds in natural waters and snow by propylation and species-specific isotope dilution mass spectrometry analysis. *Anal. Bioanal. Chem.* **2005,** *381*, (4), 854-862.

TABLES

TABLE SI-S1: Summary of sampling year, type of lichens, Hg concentrations and mercury isotope compositions of lichens sampled on the different geographical areas of the study

Sample Name	Year	Lichen specie	Hg (ng g^{-1})	RSD (%)[a)]	n[b)]	Study[c)]	δ^{199}Hg	2SE	δ^{200}Hg	2SE	δ^{201}Hg	2SE	δ^{202}Hg	2SE	δ^{204}Hg	2SE	Δ^{199}Hg	2SE	Δ^{200}Hg	2SE	Δ^{201}Hg	2SE	Δ^{204}Hg	2SE	Δ^{199}Hg/ Δ^{201}Hg
Urban Area (UA)																									
UA-21A	2001	HP	88		1	A	-0.57		-0.64		-1.37		-1.42				-0.22		0.07		-0.30				0.71
UA-21	2006	HP	91		1	A	-0.57		-0.52		-1.33		-1.30				-0.24		0.13		-0.35				0.68
UA-21			**90**	**2**			**-0.57**	**0.01**	**-0.58**	**0.18**	**-1.35**	**0.07**	**-1.36**	**0.18**			**-0.23**	**0.03**	**0.10**	**0.09**	**-0.33**	**0.07**			**0.69**
UA-17	2008	EP	**134**	**13**	2	B	**-0.56**	**0.07**	**-0.49**	**0.09**	**-1.15**	**0.13**	**-0.99**	**0.19**	**-1.55**	**0.29**	**-0.31**	**0.05**	**0.01**	**0.06**	**-0.41**	**0.07**	**-0.08**	**0.15**	**0.76**
UA-18	2003	HP	97		1	A	-0.62		-0.50		-1.33		-1.11				-0.34		0.06		-0.49				0.69
UA-18a	2006	EP	93		1	A	-0.51		-0.36		-0.98		-0.75				-0.32		0.02		-0.41				0.77
UA-18	2008	Us+EP	86		1	B	-0.52	0.07	-0.44	0.09	-1.14	0.13	-0.97	0.19	-1.33	0.29	-0.28	0.05	0.05	0.06	-0.41	0.07	0.11	0.15	0.67
UA-18			**92**	**6**			**-0.55**	**0.07**	**-0.43**	**0.09**	**-1.15**	**0.20**	**-0.94**	**0.21**	**-1.33**	**0.29**	**-0.31**	**0.05**	**0.04**	**0.06**	**-0.44**	**0.07**	**0.11**	**0.15**	**0.71**
UA-16	2008	EP	**151**	**15**	2	B	**-0.43**	**0.07**	**-0.28**	**0.09**	**-0.85**	**0.13**	**-0.65**	**0.19**	**-1.04**	**0.29**	**-0.26**	**0.05**	**0.04**	**0.06**	**-0.36**	**0.07**	**-0.07**	**0.15**	**0.74**
UA-15	2008	EP	**125**	**13**	1	B	**-0.40**	**0.07**	**-0.16**	**0.09**	**-0.69**	**0.13**	**-0.42**	**0.19**	**-0.72**	**0.29**	**-0.29**	**0.05**	**0.05**	**0.06**	**-0.37**	**0.07**	**-0.09**	**0.15**	**0.79**
Suburb Area (SA)																									
SA-07	2003	EP	110		1	A	-0.71		-0.51		-1.32		-1.10				-0.43		0.04		-0.49				0.88
SA-07	2006	EP	93		1	A	-0.67		-0.39		-1.19		-0.92				-0.44		0.07		-0.50				0.88
SA-07	2008	EP	78		2	B	-0.48	0.12	-0.32	0.13	-0.94	0.20	-0.79	0.27	-1.33	0.29	-0.28	0.05	0.07	0.06	-0.35	0.07	-0.15	0.15	0.80
SA-07			**94**	**17**			**-0.62**	**0.17**	**-0.41**	**0.13**	**-1.15**	**0.27**	**-0.94**	**0.22**	**-1.33**	**0.29**	**-0.38**	**0.13**	**0.06**	**0.06**	**-0.44**	**0.12**	**-0.15**	**0.15**	**0.85**
SA-12B	2003	HP	163		1	A	-0.77		-0.73		-1.71		-1.61				-0.36		0.08		-0.50				0.73
SA-12	2008	HP	83		1	B	-0.61	0.07	-0.73	0.09	-1.45	0.13	-1.58	0.19	-2.42	0.29	-0.21	0.05	0.06	0.06	-0.27	0.07	-0.06	0.15	0.79
SA-12			**123**	**46**			**-0.69**	**0.07**	**-0.73**	**0.09**	**-1.58**	**0.13**	**-1.59**	**0.19**	**-2.42**	**0.29**	**-0.29**	**0.15**	**0.07**	**0.06**	**-0.38**	**0.23**	**-0.06**	**0.15**	**0.76**
SA-13	2008	EP	**91**	**9**	1	B	**-0.55**	**0.07**	**-0.30**	**0.09**	**-0.99**	**0.13**	**-0.67**	**0.19**	**-0.94**	**0.29**	**-0.38**	**0.05**	**0.04**	**0.06**	**-0.49**	**0.07**	**0.07**	**0.15**	**0.78**

Sample Name	Year	Lichen specie	Hg (ng g^{-1})	RSD (%)[a)]	n[b)]	Study[c)]	δ^{199}Hg	2SE	δ^{200}Hg	2SE	δ^{201}Hg	2SE	δ^{202}Hg	2SE	δ^{204}Hg	2SE	Δ^{199}Hg	2SE	Δ^{200}Hg	2SE	Δ^{201}Hg	2SE	Δ^{204}Hg	2SE	Δ^{199}Hg/Δ^{201}Hg
SA-14a	2001	HP	105		1	A	-0.71		-0.56		-1.43		-1.21				-0.41		0.04		-0.52				0.79
SA-14a	2003	HP	111		1	A	-0.74		-0.58		-1.38		-1.23				-0.43		0.04		-0.46				0.93
SA-14	2008	EP, PF	136		1	B	-0.61	0.07	-0.39	0.09	-1.07	0.13	-0.79	0.19	-1.38	0.29	-0.41	0.05	0.01	0.06	-0.47	0.07	-0.21	0.15	0.87
SA-14			**117**	**14**			**-0.69**	**0.08**	**-0.51**	**0.12**	**-1.29**	**0.23**	**-1.07**	**0.29**	**-1.38**	**0.29**	**-0.42**	**0.05**	**0.03**	**0.06**	**-0.48**	**0.07**	**-0.21**	**0.15**	**0.86**
SA-23	2008	EP	**101**	**10**	2	B	**-0.55**	**0.08**	**-0.28**	**0.12**	**-0.87**	**0.22**	**-0.62**	**0.24**	**-0.96**	**0.30**	**-0.40**	**0.05**	**0.03**	**0.06**	**-0.40**	**0.07**	**-0.04**	**0.15**	**0.99**
SA-29	2001	RF	118		1	A	-0.62		-0.36		-1.11		-0.87				-0.40		0.08		-0.46				0.87
SA-29	2003	HP	118		1	A	-0.68		-0.62		-1.40		-1.35				-0.34		0.05		-0.39				0.88
SA-29a	2006	EP	130		1	A	-0.65		-0.47		-1.19		-1.01				-0.39		0.04		-0.42				0.92
SA-29			**122**	**6**			**-0.65**	**0.04**	**-0.48**	**0.15**	**-1.23**	**0.17**	**-1.08**	**0.28**			**-0.38**	**0.06**	**0.06**	**0.04**	**-0.42**	**0.07**			**0.89**
SA-37	2008	Mix F	**121**	**12**	1	B	**-0.60**	**0.07**	**-0.46**	**0.09**	**-1.20**	**0.13**	**-0.95**	**0.19**	**-1.51**	**0.29**	**-0.36**	**0.05**	**0.02**	**0.06**	**-0.48**	**0.07**	**-0.08**	**0.15**	**0.75**
SA-24	2006	EP	76		1	A	-0.68		-0.52		-1.34		-1.09				-0.41		0.03		-0.51				0.79
SA-24	2008	EP	90		1	B	-0.69	0.07	-0.58	0.09	-1.27	0.13	-1.14	0.19	-1.71	0.29	-0.41	0.05	-0.01	0.06	-0.41	0.07	0.00	0.15	0.98
SA-24			**83**	**12**			**-0.69**	**0.07**	**-0.55**	**0.09**	**-1.30**	**0.13**	**-1.12**	**0.19**	**-1.71**	**0.29**	**-0.41**	**0.05**	**0.01**	**0.06**	**-0.46**	**0.07**	**0.00**	**0.15**	**0.89**
SA-19	2008	Mix F	**108**	**11**	1	B	**-0.74**	**0.07**	**-0.60**	**0.09**	**-1.48**	**0.13**	**-1.26**	**0.19**	**-1.94**	**0.29**	**-0.42**	**0.05**	**0.04**	**0.06**	**-0.53**	**0.07**	**-0.06**	**0.15**	**0.80**
Rural Area (RA)																									
RA-10A	2003	EP, PF	85		1	A	-0.99		-0.88		-1.89		-1.74				-0.55		0.00		-0.59				0.94
RA-10	2003	EP, PF	88		1	B	-0.82	0.07	-0.69	0.09	-1.61	0.13	-1.49	0.19	-2.11	0.29	-0.44	0.05	0.06	0.06	-0.49	0.07	0.11	0.15	0.91
RA-10			**87**	**2**			**-0.90**	**0.17**	**-0.78**	**0.19**	**-1.75**	**0.28**	**-1.61**	**0.25**	**-2.11**	**0.29**	**-0.50**	**0.11**	**0.03**	**0.07**	**-0.54**	**0.10**	**0.11**	**0.15**	**0.92**
RA-35	2001	EP, PF	140		2	B	-0.69	0.16	-0.40	0.17	-1.22	0.19	-0.89	0.22	-1.33	0.46	-0.46	0.10	0.04	0.06	-0.55	0.03	0.00	0.13	0.85
RA-35	2003	EP, PF	130		1	A	-0.84		-0.41		-1.33		-0.90				-0.61		0.04		-0.65				0.93
RA-35	2003	EP, PF	177		1	B	-0.82	0.07	-0.47	0.09	-1.40	0.13	-1.07	0.19	-1.68	0.29	-0.55	0.05	0.07	0.06	-0.60	0.07	-0.08	0.15	0.92
RA-35B	2006	US	97		1	A	-0.82		-0.61		-1.47		-1.21				-0.51		0.00		-0.56				0.91
RA-35			**136**	**24**			**-0.79**	**0.07**	**-0.47**	**0.09**	**-1.35**	**0.13**	**-1.02**	**0.19**	**-1.50**	**0.29**	**-0.53**	**0.06**	**0.04**	**0.06**	**-0.59**	**0.07**	**-0.04**	**0.15**	**0.90**

Sample Name	Year	Lichen specie	Hg (ng g^{-1})	RSD (%)[a]	n[b]	Study[c]	δ^{199}Hg	2SE	δ^{200}Hg	2SE	δ^{201}Hg	2SE	δ^{202}Hg	2SE	δ^{204}Hg	2SE	Δ^{199}Hg	2SE	Δ^{200}Hg	2SE	Δ^{201}Hg	2SE	Δ^{204}Hg	2SE	Δ^{199}Hg/ Δ^{201}Hg
RA-03	2008	Mix F	**98**	**10**	2	B	**-0.72**	**0.07**	**-0.43**	**0.09**	**-1.23**	**0.13**	**-0.99**	**0.19**	**-1.49**	**0.29**	**-0.47**	**0.05**	**0.06**	**0.06**	**-0.49**	**0.07**	**-0.02**	**0.15**	**0.96**
RA-01	2008	EP	77		1	B	-0.77	0.07	-0.70	0.09	-1.53	0.13	-1.49	0.19	-2.17	0.29	-0.40	0.05	0.05	0.06	-0.41	0.07	0.05	0.15	0.97
RA-01	2008	RF	78		2	B	-0.94	0.07	-0.82	0.09	-1.78	0.13	-1.64	0.19	-2.41	0.29	-0.53	0.05	0.00	0.06	-0.55	0.07	0.04	0.15	0.97
RA-01			**77**	**1**			**-0.86**	**0.07**	**-0.76**	**0.09**	**-1.66**	**0.13**	**-1.57**	**0.19**	**-2.29**	**0.29**	**-0.46**	**0.13**	**0.02**	**0.07**	**-0.48**	**0.14**	**0.05**	**0.02**	**0.97**
Industrial Sites (I)																									
I-43	2009	XP	**78**	**8**	1	B	**-0.64**	**0.07**	**-0.93**	**0.09**	**-1.61**	**0.13**	**-1.90**	**0.19**	**-2.91**	**0.29**	**-0.16**	**0.05**	**0.02**	**0.06**	**-0.18**	**0.07**	**-0.07**	**0.15**	**0.90**
I-44	2009	XP	**115**	**12**	2	B	**-0.60**	**0.07**	**-0.90**	**0.09**	**-1.55**	**0.13**	**-1.89**	**0.19**	**-2.94**	**0.29**	**-0.13**	**0.05**	**0.04**	**0.06**	**-0.13**	**0.07**	**-0.13**	**0.15**	**0.96**
Industrial Valley (IV)																									
IV-45	2009	HP, PT	**82**	**8**	2	B	**-0.67**	**0.07**	**-0.83**	**0.09**	**-1.59**	**0.13**	**-1.75**	**0.19**	**-2.72**	**0.29**	**-0.23**	**0.05**	**0.05**	**0.06**	**-0.27**	**0.07**	**-0.11**	**0.15**	**0.84**
IV-46	2009	HP, PT	**148**	**15**	1	B	**-0.83**	**0.07**	**-1.11**	**0.09**	**-1.99**	**0.13**	**-2.22**	**0.19**	**-3.34**	**0.29**	**-0.27**	**0.05**	**0.01**	**0.06**	**-0.32**	**0.07**	**-0.03**	**0.15**	**0.83**
IV-47	2009	HP, PT	107		2	B	-0.85	0.07	-1.06	0.09	-1.93	0.13	-2.19	0.19	-3.31	0.29	-0.30	0.05	0.04	0.06	-0.28	0.07	-0.04	0.15	1.06
IV-47	2009	HP, PT	107		1	B	-0.81	0.07	-1.04	0.09	-1.90	0.13	-2.13	0.19	-3.26	0.29	-0.28	0.05	0.03	0.06	-0.30	0.07	-0.08	0.15	0.93
IV-47			**107**	**11**			**-0.83**	**0.07**	**-1.05**	**0.09**	**-1.91**	**0.13**	**-2.16**	**0.19**	**-3.28**	**0.29**	**-0.29**	**0.05**	**0.04**	**0.06**	**-0.29**	**0.07**	**-0.06**	**0.15**	**0.99**
IV-48	2009	HP, PT	**98**	**10**	2	B	**-0.81**	**0.07**	**-1.02**	**0.09**	**-1.89**	**0.13**	**-2.07**	**0.19**	**-3.16**	**0.29**	**-0.29**	**0.05**	**0.03**	**0.06**	**-0.33**	**0.07**	**-0.06**	**0.15**	**0.87**
IV-49	2009	HP, PT	**120**	**12**	2	B	**-0.88**	**0.04**	**-0.94**	**0.08**	**-1.87**	**0.08**	**-1.94**	**0.25**	**-2.89**	**0.37**	**-0.39**	**0.05**	**0.04**	**0.06**	**-0.41**	**0.11**	**0.01**	**0.00**	**0.96**
Contaminated point (CP)																									
CP-27	2001	EP	338		2	A	-0.32		0.63		0.30		1.24				-0.64		0.00		-0.63				1.01
CP-27	2003	Mix F	350		2	A	-0.05		0.69		0.65		1.40				-0.40		-0.01		-0.40				0.99
CP-27	2006	EP	450		2	A	-0.16		0.72		0.58		1.50				-0.54		-0.03		-0.54				0.99
CP-27	2008	HP	424		2	B	-0.03	0.07	0.69	0.09	0.69	0.13	1.37	0.19	2.00	0.29	-0.38	0.05	0.00	0.06	-0.34	0.07	-0.04	0.15	1.12
CP-27			**391**	**14**			**-0.14**	**0.13**	**0.68**	**0.09**	**0.56**	**0.17**	**1.38**	**0.19**	**2.00**	**0.29**	**-0.49**	**0.12**	**-0.01**	**0.06**	**-0.48**	**0.13**	**-0.04**	**0.15**	**1.03**

Sample Name	Year	Lichen specie	Hg (ng g^{-1})	RSD (%)[a)]	n[b)]	Study[c)]	$\delta^{199}Hg$	2SE	$\delta^{200}Hg$	2SE	$\delta^{201}Hg$	2SE	$\delta^{202}Hg$	2SE	$\delta^{204}Hg$	2SE	$\Delta^{199}Hg$	2SE	$\Delta^{200}Hg$	2SE	$\Delta^{201}Hg$	2SE	$\Delta^{204}Hg$	2SE	$\Delta^{199}Hg/\Delta^{201}Hg$
Suburb Area Around Contaminated Point (SA/ACP)																									
SA/ACP-38	2009	RF,EP	**88**	**9**	1	B	**-0.67**	**0.07**	**-0.43**	**0.09**	**-1.21**	**0.13**	**-0.99**	**0.19**	**-1.55**	**0.29**	**-0.42**	**0.05**	**0.07**	**0.06**	**-0.46**	**0.07**	**-0.06**	**0.15**	**0.90**
SA/ACP-39	2009	RF,EP	**81**	**8**	2	B	**-0.66**	**0.07**	**-0.54**	**0.09**	**-1.29**	**0.13**	**-1.21**	**0.19**	**-1.98**	**0.29**	**-0.36**	**0.05**	**0.06**	**0.06**	**-0.38**	**0.07**	**-0.18**	**0.15**	**0.94**
SA/ACP-40	2009	RF,EP	**133**	**13**	1	B	**-0.77**	**0.07**	**-0.49**	**0.09**	**-1.32**	**0.13**	**-1.11**	**0.19**	**-1.88**	**0.29**	**-0.49**	**0.05**	**0.07**	**0.06**	**-0.49**	**0.07**	**-0.23**	**0.15**	**0.99**
SA/ACP-41	2009	RF,EP	**92**	**9**	1	B	**-0.73**	**0.07**	**-0.56**	**0.09**	**-1.46**	**0.13**	**-1.25**	**0.19**	**-1.88**	**0.29**	**-0.42**	**0.05**	**0.07**	**0.06**	**-0.52**	**0.07**	**-0.01**	**0.15**	**0.79**
SA/ACP-42	2008	RF,EP	**196**	**20**	1	B	**-0.30**	**0.07**	**0.24**	**0.09**	**-0.10**	**0.13**	**0.46**	**0.19**	**0.54**	**0.29**	**-0.42**	**0.05**	**0.01**	**0.06**	**-0.44**	**0.07**	**-0.15**	**0.15**	**0.94**

a) Relative standard deviation indicated except if only one sample was analyzed. In this case, a SD of 10% was reported
b) number of measurements
c)A: Carignan et al. 2009; B: This study

TABLE SI-S2: Isotopic compositions of reference material CRPG RL24H, BCR-482 and UM-Almaden

Sample	n[a)]	$\delta^{199}Hg$	2SD	$\delta^{200}Hg$	2SD	$\delta^{201}Hg$	2SD	$\delta^{202}Hg$	2SD	$\delta^{204}Hg$	2SD	$\Delta^{199}Hg$	2SD	$\Delta^{200}Hg$	2SD	$\Delta^{201}Hg$	2SD	$\Delta^{204}Hg$	2SD
CRPG-RL24H	28	0.60	0.07	1.29	0.09	1.89	0.13	2.58	0.19	3.87	0.29	-0.05	0.05	-0.01	0.06	-0.05	0.07	0.02	0.15
BCR-482	10	-0.98	0.09	-0.75	0.11	-1.86	0.16	-1.68	0.26	-2.62	0.32	-0.56	0.07	0.09	0.06	-0.60	0.05	-0.11	0.10
UM-Almaden	5	-0.18	0.03	-0.32	0.01	-0.48	0.07	-0.61	0.14	-0.94	0.23	-0.03	0.02	-0.02	0.06	-0.02	0.03	-0.03	0.10

a) number of measurements

FIGURES

FIGURE SI-S1: General map of the sampling locations and sampling points in Rural Area (RA), Suburban Area (SA), Urban Area (UA), Industrial Site (I), Industrial Valley (IV) and inside Industrial site (I). The magnitude of anomalies ($\Delta^{199}Hg$) found in lichens for each geographical area over the nine years of sampling is represented as a function of the size of the circle.

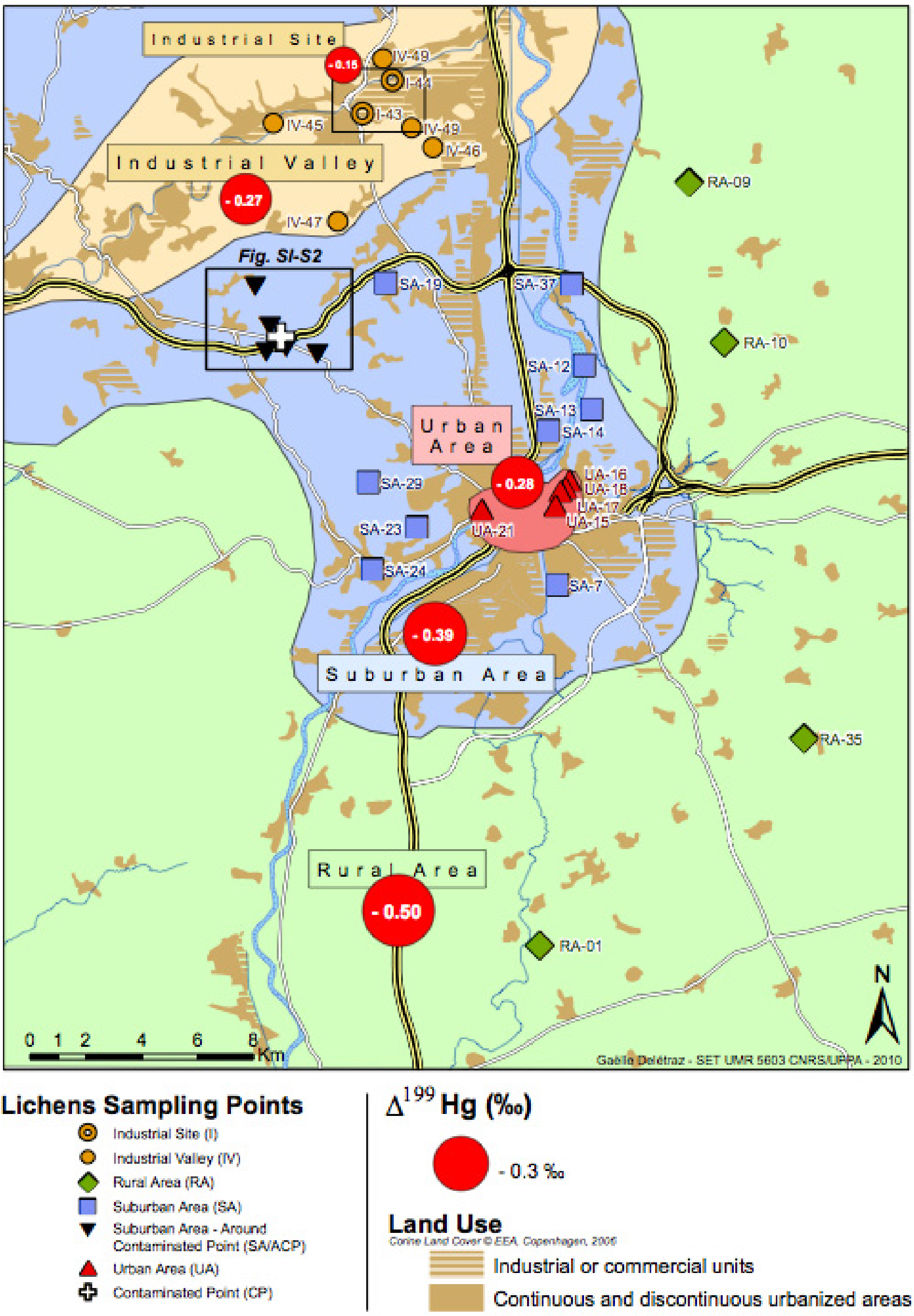

FIGURE SI-S2: Mercury concentrations for each point sampled in Urban Area (UA), Suburban Area (SA), Rural Area (RA), Industrial Valley (IV) ar

Industrial Sites (I) for the years 2001, 2003, 2006, 2008 and 2009. Lichens species are indicated for each sampling point (see nomenclature in the te:

above). The horizontal black line and the doted rectangle represent respectively the average Hg concentration and the standard deviation (SD) on tl

average within each area.

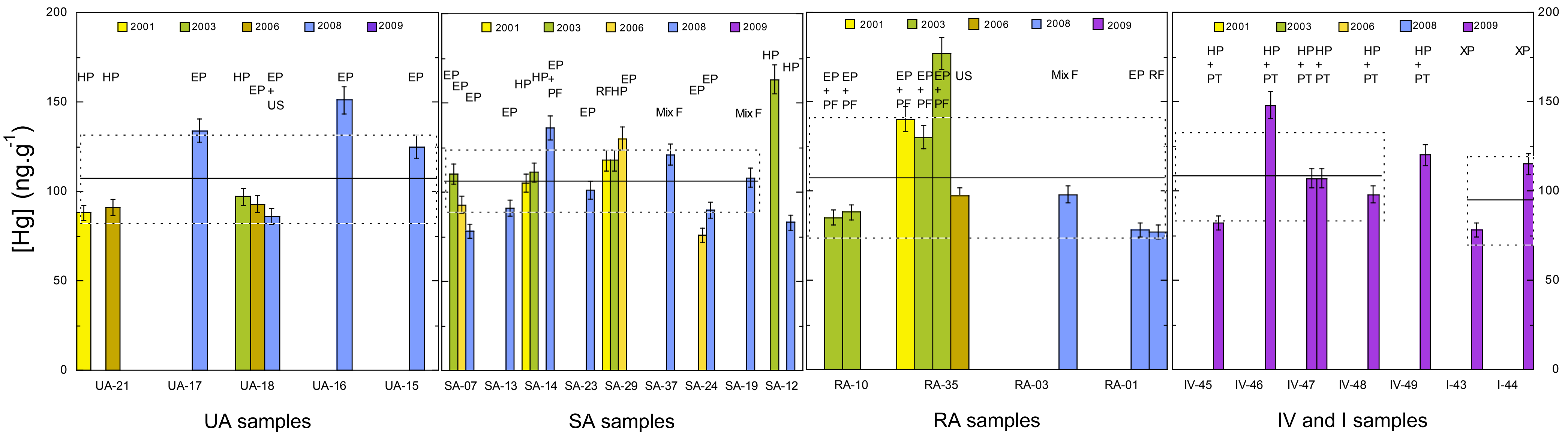

FIGURE SI-S3: δ^{202}Hg (‰) for each point sampled in Urban Area (UA), Suburban Area (SA), Rural Area (RA), Industrial Valley (IV) and Industrial Sites (I) for the years 2001, 2003, 2006, 2008 and 2009. Lichens species are indicated for each sampling point (see nomenclature in the text above). The horizontal black line and the doted rectangle represent respectively the average δ^{202}Hg and the 2SE on the average within each area.

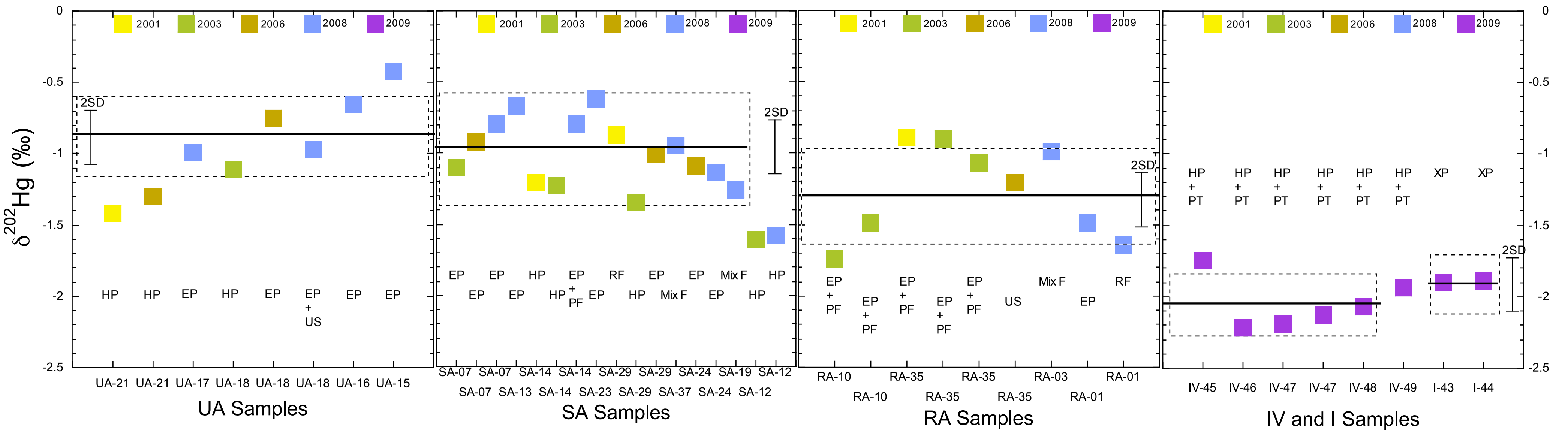

FIGURE SI-S4: $\Delta^{199}Hg$ (‰) for each point sampled in Urban Area (UA), Suburban Area (SA), Rural Area (RA), Industrial Valley (IV) and Industrial Site

the years 2001, 2003, 2006, 2008 and 2009. Lichens species are indicated for each sampling point (see nomenclature in the text above). The horizontal bla

and the doted rectangle represent respectively the average $\Delta^{199}Hg$ and the 2SE on the average within each area.

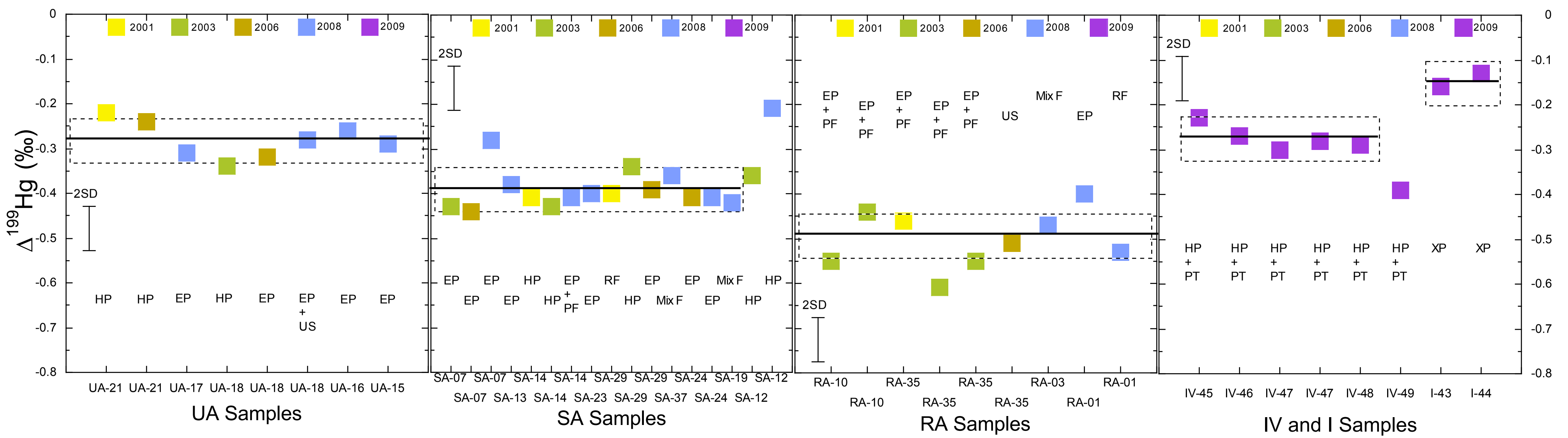

FIGURE SI-S5: Location of the studied area around the contaminated point CP-27

(www.geoportail.fr © 2008 - IGN)

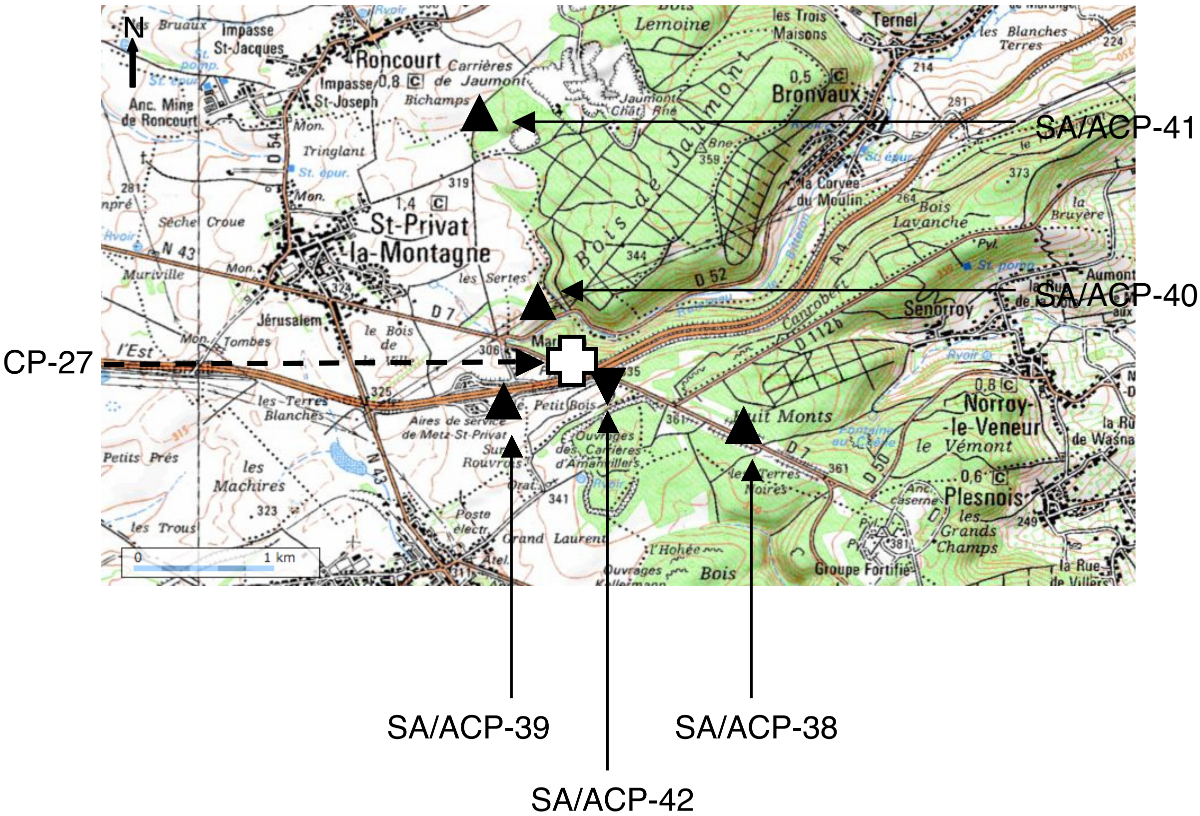

FIGURE SI-S6: Average mercury concentrations (years 2001, 2003, 2006, 2008 and 2009) for the lichen sampled at the contaminated point (CP-27, empty cross). Lichens sampled around CP-27 (SA/ACP, filled black triangles) are in the Hg concentrations range of all other lichens of the study. Lichen sampled at around 200 meters of CP-27 (inverse filled black triangle) display an intermediate Hg concentration of 200 $ng.g^{-1}$.

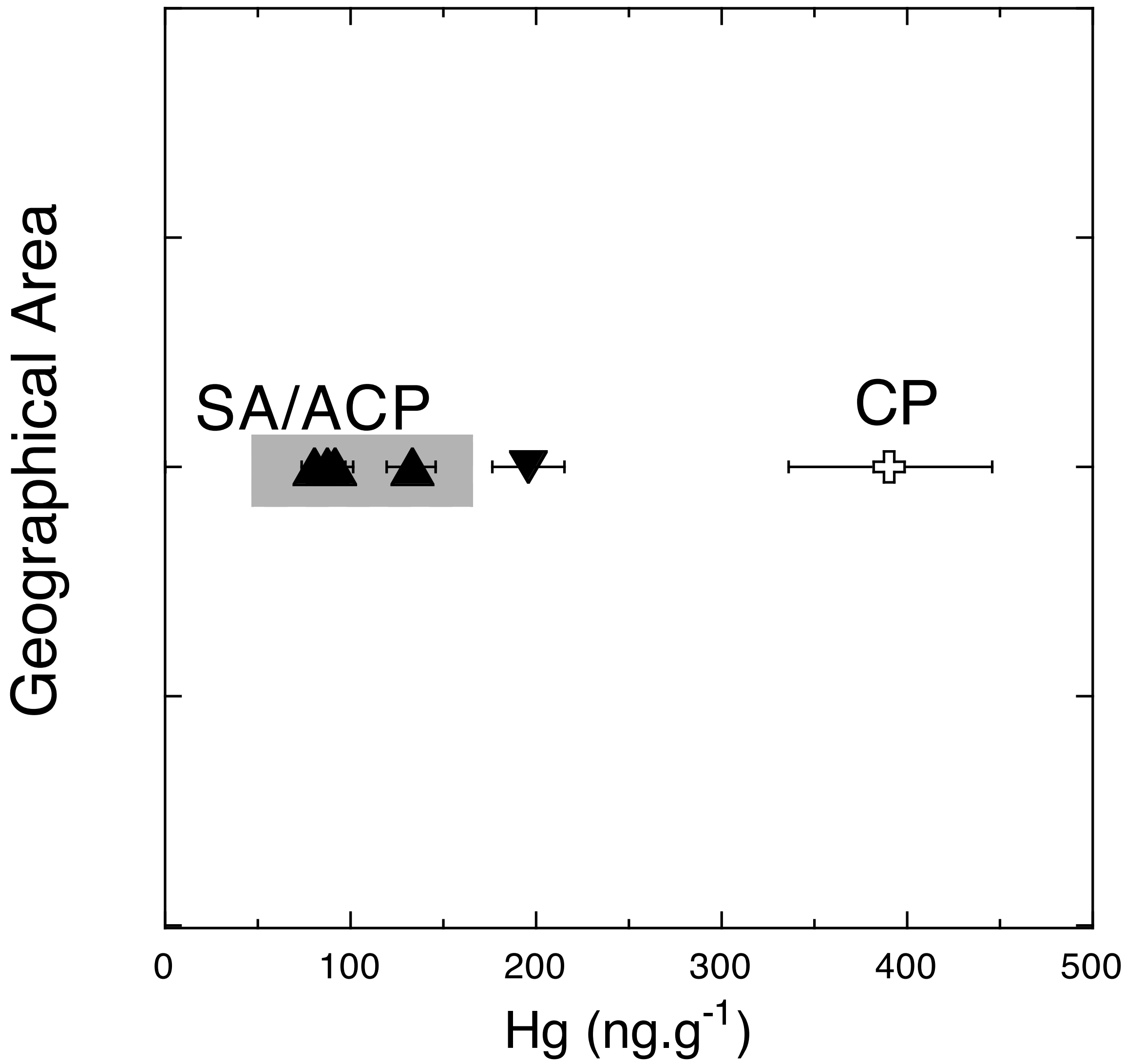

FIGURE SI-S7: $\Delta^{199}Hg$ versus $\delta^{202}Hg$ for the lichens sampled at the contaminated point (CP-27, empty cross) in suburban area around the contaminated point (SA/ACP 38-39-40-41, filled black triangles) and at 200 meter of CP-27 (SA/ACP 42, inverse filled black triangles).