

Modeling exposure to airborne metals using moss biomonitoring in cemeteries in two urban areas around Paris and Lyon in France

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Moss biomonitoring

In cemeteries of urban areas Lyon (n=51), Paris (n=77)

ICP-MS analysis 14 metals (cadmium, lead...)

+ land use data

Geographic information system Urban, agricultural, or forest areas; roads; altitude; etc. Publicly available data



+ land use regression modelling

Over 76x63km (Lyon) and 120x101km (Paris)

→ **Exposure surfaces** Satisfactory for metals emitted by human activities Plausible exposure surfaces To be linked with epidemiological data

Example: Cadmium, Paris region



- 1 Modeling exposure to airborne metals using moss biomonitoring in
- 2 cemeteries in two urban areas around Paris and Lyon in France.
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24 Abstract

Exposure of the general population to airborne metals remains poorly estimated 25 despite the potential health risks. Passive moss biomonitoring can proxy air quality at 26 27 fine resolution over large areas, mainly in rural areas. We adapted the technique to urban areas to develop fine concentration maps for several metals for Constances 28 cohort's participants. We sampled Grimmia pulvinata in 77 and 51 cemeteries within 29 ~50km of Paris and Lyon city centers, respectively. We developed land-use regression 30 models for 14 metals including cadmium, lead, and antimony; potential predictors 31 included the amount of urban, agricultural, forest, and water around cemeteries, 32 population density, altitude, and distance to major roads. We used both kriging with 33 external drift and land use regression followed by residual kriging when necessary to 34 derive concentration maps (500x500m) for each metal and region. Both approaches 35 led to similar results. The most frequent predictors were the amount of urban, 36 agricultural, or forest areas. Depending on the metal, the models explained part of 37 the spatial variability, from 6% for vanadium in Lyon to 84% for antimony in Paris, 38 but mostly between 20% and 60%, with better results for metals emitted by human 39 activities. Moss biomonitoring in cemeteries proves efficient for obtaining airborne 40 metal exposures in urban areas for the most common metals. 41

42

Keywords: air pollution; moss biomonitoring; cadmium; lead; exposure surface;
land-use regression

46 Introduction

As naturally occurring elements, metals abundantly occur in the lithosphere and 47 accumulate in the biosphere and atmosphere through processes including root 48 49 absorption and subsequent transfer through food webs, wind erosion, and human activities since the Bronze Age (Gall et al., 2015; Gnesin, 2013; Jaworowski et al., 50 1981). Some metals support life, yet all become toxic when exceeding thresholds 51 (Nordberg et al., 2007). Cadmium (Cd) and arsenic (As) for example are recognized 52 human carcinogens (International Agency for Research on Cancer, 2016), and, as 53 neurotoxicants, lead (Pb) and mercury (Hg) may also play a role in the development 54 and decline of cognitive functions (Genuis and Kelln, 2015; Grandjean and 55 Landrigan, 2014). As early as the 1960s it's been known that airborne metals are a 56 component of airborne particulate matter (PM) (Schroeder, 1968), and it is also 57 established that air pollution also affects health and cognition (Brauer et al., 2012; 58 Gatto et al., 2014). In Europe, toxic metals As, Cd, Pb, and nickel (Ni), have been 59 60 measured in PM (diameter <10µm or PM10) as enforced by Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management 61 62 and its updates. Yet these measurements are performed only at a few sites, providing 63 insufficient spatial coverage to allow for assessing the exposure of the general 64 population to these airborne metals. Further, the directive does not include other potentially harmful metals such as aluminum (Al), antimony (Sb), copper (Cu), or 65 66 zinc (Zn).

In France, a network of moss biomonitoring of atmospheric deposition of metals on
mosses (BRAMM) has recorded metal concentrations in mosses across 400-500
sampling sites over the rural and forested areas since 1996 (Lequy et al., 2016)
following the guidelines of the international program ICP-Vegetation (Schröder et al.,

2016). Briefly, this moss-biomonitoring technique, detailed in (Markert, 2007), relies 71 on mosses' lack of roots, making them dependent on atmospheric sources to get 72 water and nutrients (Bates, 1992; Tyler, 1990). Mosses combine a morphology of 73 leaves able to trap particulate metals (Bargagli, 2006) to a monolaver cell thickness 74 facilitating the accessibility of dissolved metals for the exchange sites in the cell walls 75 76 (Bates, 1992; Carballeira et al., 2008; González and Pokrovsky, 2014). Data obtained by this technique allowed for deriving concentration maps suitable for the French 77 rural and semi-urban populations, and was successfully used to estimate mortality 78 79 risks associated to airborne metal exposure (Lequy et al., 2019). However, most of the 80 French population lives in urban areas for which the above-mentioned concentration maps are not suitable. In fact, to the best of our knowledge, there are no available fine 81 concentration map for metals for urban populations. Moss biomonitoring was shown 82 83 to perform well in urban areas (Gallego-Cartagena et al., 2021; Jiang et al., 2018; 84 Zechmeister et al., 2005), capturing particles mostly within the inhalable fraction (Di Palma et al., 2017), and with a large influence of urban or traffic land use variables on 85 86 metal concentrations in mosses (De Nicola et al., 2013; Di Palma et al., 2017) but with 87 a negligible contribution of soil on metal concentrations (Jiang et al., 2018). Specific sources of metals are well known, such as non-exhaust traffic (e.g. brakes) for Cu, Sb 88 or Pb, or local or distant steel industry for Cd (Ledoux et al., 2017). For these reasons, 89 we aimed at adapting the moss biomonitoring technique to urban settings to derive 90 fine concentration maps by land use regression (LUR) modelling in two of the most 91 populated French regions, the greater Paris and Lyon areas. 92

93 Material and Methods

To adapt the technique of moss biomonitoring used by BRAMM (Harmens, 2010) to
urban areas, we needed to find suitable sampling sites and moss species. Regarding

96 sampling sites, we opted for cemeteries for several reasons: at least one is located in most municipalities, they can shelter mosses (Natali et al., 2016), cemeteries in urban 97 municipalities are near sources of air pollutants such as roads while being relatively 98 sheltered from direct contamination by humans or animals, and they offer 99 homogeneous substrates such as concrete. In addition, opting for cemeteries allows 100 101 for collecting mosses that grow in full light and can survive in contaminated environments. We selected a moss living in cushion, Grimmia pulvinata (Hedw.) 102 Sm., which performs well in biomonitoring airborne metals (Gallego-Cartagena et al., 103 104 2021), including in cemeteries (Natali et al., 2016).

105

106 Study design

With the goal to provide concentration maps for urban populations for the general
population-based Constances cohort (Zins et al., 2015), the sampling strategy was
designed to cover the widest urban area where Constances participants were residing
and in which we could find cemeteries to sample mosses. To do so, and to obtain
sampling sites as evenly distributed as possible to subsequently develop an
concentration map, we proceeded as follows.

We developed a "target-style" gridded study design (Figure 1), with concentric circles 113 around the city center with increasing radii up to 49km around Paris and 30km 114 around Lyon. These circles were crossed by transects starting from the center of the 115 study site and passing through areas with the highest possible population density, 116 while covering as many directions as possible. We classified population density into 117 118 categories based on two indexes defined by the French institute for Statistics, according to the size of the municipality (Institut national de la statistique et des 119 études économiques (National Institute of Statistics and Economic Studies), n.d., 120 n.d.). For municipalities with less than 5000 inhabitants, the index is high, moderate, 121

low, and very low population density, taking into account the surface actually 122 inhabited. For municipalities with more than 5000 inhabitants, the index is 123 residential, commercial or industrial areas, and recreational areas. In Figure 1, to 124 improve readability, the municipalities with less than 5000 inhabitants with high 125 population density and the residential areas of municipalities with more than 5000 126 127 inhabitants were merged into a "high" population density category, and the low and very low population density areas of municipalities with less than 5000 inhabitants 128 into a "low" population density category. In the areas around Paris and Lyon and 129 their surrounding areas (referred to as Paris and Lyon for readability), population 130 density decreases as the distance from city center increases, therefore reaching low 131 values in the outer circles. The junctions between circles and transects defined 132 different potential sampling sites. The absence of cemeteries at some junctions, the 133 refusal of the town halls to collect mosses in cemeteries, the absence of concrete walls 134 or tombstones, or the species of mosses have led to modify the initially selected 135 136 sampling sites. Final sampling sites were chosen in the field among the potential candidates matching our criteria: 77 sites in Paris, 51 sites in Lyon. 137



138

139 Figure 1: distribution of sampling sites (white-circled black dots) around

140 Lyon (left) and Paris (right). Dark gray, medium gray, and gridded-gray areas

141 indicate high, intermediate, and low population densities. Pale gray areas correspond

to business or industry parks and to large uninhabited areas (forests, large parks,

143 airports). Black lines indicate the borders of French départements.

144

145 Moss sampling and metal concentrations

Details of the moss sampling are available in Vieille et al (2021). Briefly, sampling in 146 the Paris and Lyon regions took place in May and June 2018, respectively. In each 147 148 sampling site, mosses were sampled with standardized methods by trained experts 149 only on concrete substrate, either on tombstones or on the top of walls, as follows: we collected an average of 75 moss colonies (minimum 50), on at least 10 tombstones or 150 on a total length of 15m of top of wall, and using two different walls, to reduce the 151 influence of any moss cushion potentially contaminated by the substrate. We chose 152 concrete because of the low risk of potential contamination. Moreover, we avoided 153 decorative metallic objects. Sampling collection in each site included a total of about 154 9600 cushions. Each cushion was validated with a magnifying glass (10x 155 156 magnification). Samples were stored in a cooler before being brought back in the laboratory where they dried at room temperature before being manually cleaned, 157 ground with an automatic non-polluting titanium grinder (Pulverisette 14, Fritsch, 158 Germany), and sent for analyses. Sampling and preparation were conducted using 159 160 nytril gloves and ceramic knives to avoid contamination. Mosses were analyzed by inductively coupled plasma mass spectrometry by the USRAVE laboratory (INRAE-161 Centre de Bordeaux) (Agilent 7700x spectrometer) after drying at 40°C and acid 162 163 mineralization by HF/HNO3/H2O2 (concentrations expressed at 103°C after 164 accounting for water loss on a subsample). For Hg, the moss powder is directly analyzed by Cold Vapour Atomic Fluorescence Spectrometry. Analyses provided 165 166 concentrations of aluminum (Al), arsenic (As), calcium (Ca), cadmium (Cd),

- 167 chromium (Cr), Cu, iron (Fe), mercury (Hg), sodium (Na), nickel (Ni), lead (Pb),
- 168 antimony (Sb), vanadium (V), and zinc (Zn). Analytical uncertainties are 20% for As,
- 169 Cd, Cr, Cu, Na, Ni, Pb, Sb and V, 15% for Al and Fe and 10% for Ca, Hg and Zn.
- 170

171 Generating concentration maps

172 Source data for potential predictors

Corine Land Cover (2018, on https://www.copernicus.eu/en) was used to calculate 173 the relative coverage of urban area, agricultural area, forest area, natural area, water 174 within buffers of 500, 1000, 2500, and 5000 m radius around the sampling site (the 175 subcategories used to define each category are detailed in the supplementary 176 material). We used a minimal buffer radius of 500m due to the resolution of Corine 177 Land Cover (250x250m). Sata from the French GIS database (Institut Géographique 178 National) were used to calculate distance from major roads (defined as those 179 classified level 1 and 2 i.e. corresponding to highways or equivalent, access roads, and 180 181 other busy roads - in m), the population density of each municipality (in inhabitant/km²), and the altitude (in m). To consider the potential influence of 182 industry, we used the European pollutant release and transfer register for industrial 183 184 emissions (in the air only and in 2018) to calculate, for each available metal (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) the distance to the closest industrial site (in m) and the 185 186 total annual emissions released by this site (in kg). 187 To use the most informative variables that did not risk to provide distorted estimates

- in the models, we removed any predictor containing more than 50% of null values
- 189 before starting developing the LUR models (Table 1).

- 190 All GIS processing and analyses were performed with R version using the packages
- 191 "SP"(Bivand et al., 2013), "RASTER"(Hijmans, 2020), "GSTAT"(Gräler et al., 2016),
- 192 and "AUTOMAP" (Hiemstra et al., 2008).
- 193

194 **Table 1: list of variables and their description.**

				N(%) or me	edian [p25, p75]
Type	Variable	Buffer size (radius,	Code	Lyon (n=51)	Paris (n=77)
		m)			
Point	Substrate: wall or tombstone*	-	Substrate(Tombst	9 (18%)	58 (82%)
			ones)		
	Altitude (m)	-	altitude	259 [216, 316]	78 [51, 110]
	Population density (inhab/km²)	-	density	370 [166, 1979]	1804 [247, 7997]
	Distance to major roads (m)	-	dist_road	925 [419, 1857]	530 [210, 1334]
Buffer	agricultural area within:	500	agri_500	34 [0, 55]	o [0, 37]**
(%)		1000	agri_1000	40 [6, 69]	10 [0, 47]
		2500	agri_2500	53[23,67]	15[0,53]
		5000	agri_5000	52 [24, 67]	19 [1, 52]
	forest area within:	500	forest_500	0 [0, 4]**	o [0, 5]**
		1000	forest_1000	$0[0,12]^{**}$	3[0, 20]
		2500	forest_2500	8 [0, 18]	9[0, 22]
		5000	forest_5000	10 [4, 15]	14 [1, 26]
	urban area within:	500	urb_500	63 [42, 91]	90 [49, 100]
		1000	urb_1000	50 [24, 86]	68 [28, 100]
		2500	urb_2500	33 [10, 73]	60 [16, 95]
		5000	urb_5000	28 [13, 69]	52 [17, 95]
	water area within:	500	water_500	0 [0, 0]**	0 [0, 0]**
		1000	water_1000	0 [0, 0]**	o [0, 0]**
		2500	water_2500	0 [0, 4]**	$0[0,2]^{**}$
		5000	water_5000	2 [0, 4]	1 [0, 3]

 $\ast:$ only concrete tombstones and top of walls

**: removed from dataset before developing the land use regression models. Natural area (see supplementary material for the details) buffer variables all included more than 50% of null values and were deleted from the dataset. p25 and p75 stand for the 25th and 75th percentiles.

195

- 197 Developing land use regression models
- 198 LUR models were developed separately in each region. We aimed to find the most
- 199 parsimonious models with the best goodness of fit between metal concentrations in
- 200 mosses and spatial predictors, and applied the following steps. We natural log-

transformed metal concentrations when the distribution was left-skewed, and 201 checked for any outlier. We found only one outlier, for Hg in the Paris region, with an 202 unlikely value of 1 µg.g⁻¹, which we excluded. After computing univariate Spearman 203 correlations between each metal concentration and all spatial predictors, we pre-204 selected only variables with a Spearman correlation coefficient>0.3. We used 205 206 supervised modeling to choose the final predictors, after conducting both forward and backward stepwise approaches. At first, we used generalized additive modeling to 207 account for any possible nonlinear relationship by including spline functions for all 208 209 continuous variables.

<u>Forward stepwise approach</u>: for each metal, we included potential predictors one by
one in a generalized additive model. Starting from the predictor yielding the
univariate model with the highest R2, followed by the next highest in turn. At each
iteration we kept the newly included predictor only if the variable increased the
adjusted R2 of the multivariate model.

Backward stepwise approach: for each metal, we included all the variables with a 215 statistically significant Spearman correlation coefficient>0.3. For both approaches, 216 we subsequently removed one by one any variable with a p-value>0.05. When all the 217 remaining variables were significantly associated with the metal concentration, we 218 handled nonlinear relationship as follows: when the predictor had more than 1 degree 219 of freedom (i.e. a nonlinear relationship), and if the relationship visually did not 220 deviate too much from linearity, we simply removed the spline function. If the 221 relationship visually deviated from linearity, but was monotonic or transformable, we 222 replaced the spline function by the most suitable function (power or natural 223 224 logarithm). In the case of a non-monotonic and not easily transformable relationship, we removed the variable from the model. We also checked whether the relationship 225 was in the expected direction. Finally, for each model we compared the models 226

yielded by the forward and backward approaches and selected as final model the onewith the best adjusted R2.

229

230 Deriving concentration maps

We created a 500x500m resolution grid covering each region and computed all the 231 predictors used by the final models for each metal on each mesh of these grids to 232 generate the concentration maps. We then applied, on each 500x500m mesh of these 233 grids, the final models based on two methods, to generate concentration maps: 234 kriging with external drift (KED) or land use regression (LUR) followed by residual 235 kriging when necessary. Regarding KED, for each metal in each region, a variogram 236 was computed, based on the site geocodes, the metal concentration (log-transformed 237 when necessary), and the predictors included in the final model (Figure S1). Using 238 this modelled variogram, universal kriging was performed over the 500m pixels. 239 Regarding LUR with kriging of the residuals, for each metal in each region, we 240 applied the final model over the 500x500m grid. Then, when the residuals of the final 241 model showed a statistically significant spatial autocorrelation based on Moran's I 242 test (Bivand et al., 2013), we performed ordinary kriging over the 500x500m grid and 243 added these values to those obtained after applying the LUR model. 244

245

246 Quality of the models and of the concentration maps.

To estimate the quality of each final model, in addition to the adjusted R2, we

248 computed the Akaike Information Criterion (AIC) and the variance inflation factor

249 (VIF) of each variable of each model. We considered multicollinearity for VIF larger

than 10. We assessed the quality of KED and LUR by 10-hold out validation (10-

HOV). For each metal, separately in each study area, we first used 10 training sets

252 (each set is a random selection of 90% of the sites) to derive regression coefficients

for both approaches, and to obtain variograms for all metals in the KED approach. 253 We then applied the coefficients and variograms to generate maps over the 254 500x500m grid. We back-transformed the predicted values for all the natural log-255 transformed metals. Additionally, we developed variograms of the residuals from the 256 LUR models using the training sets. We performed a 10-HOV first to evaluate the 257 258 robustness of the final model, and another 10-HOV to evaluate the robustness of the variogram for the residual kriging. Finally, we extracted the predicted values at the 259 260 coordinates of the validating sets (the remaining 10% of sites) and regressed these predicted values on the corresponding observed values to obtain a R2; we also 261 262 calculated the relative root mean square error (RRMSE). We categorized modeling 263 quality scores: 1 (satisfactory final model (adjusted R2>0.45) with satisfactory robustness (quantified by 10-HOV with an R2>0.3)), 2 (satisfactory final model with 264 265 poor robustness or conversely), and 3 (poor final model with poor robustness). 266

267 Results

268 Metal concentrations

In both regions combined, metal concentrations ranged over several orders of
magnitudes from Hg to Ca, between 0.10 µg.g⁻¹ [IQR: 0.21] for Hg and 1.7 10⁴ µg.g⁻¹
¹ [IQR: 2.3 10⁴] for Ca (Figure 2). The magnitude was similar for each metal in the
two regions, but still we found concentrations of Cd, Cu, Pb, Sb, and Zn at least twice
as high in Paris as in Lyon.



274

Figure 2: distribution (Y-axis on a log-10 scale) of the metal

concentrations in mosses collected in the cemeteries of the regions of
Lyon (n=51) and Paris (n=77) in 2018. See Table S1 for corresponding numeric
data.

279

280 Final models

281 Most final models were constructed based on the backward stepwise selection, which provided slightly higher adjusted R2 for more than half of the metals in both regions 282 (Table S2). Depending on the metal, and on the region, the models explained part of 283 the spatial variability, from 6% for vanadium in Lyon to 84% for antimony in Paris, 284 but mostly between 21%-54% in Lyon and 30-60% in Paris, with better results for 285 286 metals emitted by human activities (Table 2). For each metal in both study regions, 287 final models vielded lower AIC than intercept-only models (Table S3). The models 288 yielded relationships in the expected direction for each included predictor (such as 289 higher concentrations of metals with higher coverage of urban areas, population density, or closer to major roads) (Table 2). The final models typically explained more 290

variance in Paris, except for Al and As. Residuals were spatially autocorrelated only

292 for Ca, Na, and Ni in Lyon.

- 293 In each final model, the VIF of most predictors was lower than two, with only some
- values larger than six but overall indicating no multicollinearity (Table S4).
- 295
- 296 Table 2: final models for each metal in each region, including the
- 297 transformation of the metal distribution, the formula used for the linear
- 298 regression, and the adjusted R2.
- 299

9				
Region	Metal	Transformation	Model formula	R2
Lyon	Al	natural log	6.9 + forest_2500 x -1.4 + I(dist_road^-0.05) x 2.7 + altitude x 0.0013	0.26
Paris	Al	none	7600 + forest_5000 x -5800	0.24
Lyon	As	natural log	0.51 + forest_2500 x -2.9 + altitude x 0.0023	0.37
Paris	As	none	2.1 + forest_5000 x -1.8	0.25
Lyon	Ca	none	15000 + urb_1000 x 1700	0.14
Paris	Ca	none	17000 + agri_5000 x -1700 + density x 0.06 +	0.28
			forest_1000:I(forest_1000 < 0.25) x -690 + forest_1000:I(forest_1000 ≥ 0.25) x 7400	
Lyon	Cd	natural log	-1 + urb_1000x0.59 + I(forest_5000^0.3) x -0.93 + Substrate(Tombstones) x 0.38	0.58
Paris	Cd	natural log	-1 + urb_5000 x 0.87 + density x 2e-5 + Substrate(Tombstones) x 0.34	0.67
Lyon	Cr	natural log	2.7 + forest_2500 x -2.1	0.31
Paris	Cr	natural log	2.8 + altitude x -0.0033 + urb_5000 x 0.44 + forest_2500 x -1.1	0.63
Lyon	Cu	natural log	3.1 + urb_1000 x 0.9 + forest_2500 x -2.1	0.55
Paris	Cu	natural log	3 + urb_5000 x 1.6 + water_5000 x 7.2	0.67
Lyon	Fe	natural log	8.7 + forest_2500 x -1.7	0.20
Paris	Fe	none	1700 + altitude x -13 + urb_5000 x 6500 + agri_5000 x 5000	0.50
Lyon	Hg	natural log	-2.3 + urb_1000 x 0.99	0.23
Paris	Hg	natural log	-2.9 + altitude x -0.0025 + urb_2500 x 0.95 + agri_5000 x 0.81 + Substrate(Tombstones) x 0.2	0.34
Lyon	Na	natural log	7 + forest_2500 x -1.8	0.12

Paris	Na	natural log	6.5 + forest_2500 x -1.1 + agri_2500 x 0.33	0.29
Lyon	Ni	natural log	1.9 + urb_1000 x 0.38 + forest_2500 x -1.3	0.32
Paris	Ni	natural log	2.1 + altitude x -0.0031 + urb_500 x 0.27 +	0.69
			forest_2500 x -1.1 + density x 1.5e-05 +	
			Substrate(Tombstones) x 0.16	
Lyon	Pb	natural log	2.1 + urb_500 x 1.1 + Substrate(Tombstones) x 0.72	0.49
Paris	Pb	natural log	3.4 + forest_1000 x -1.2 + density x 3.7e-05 +	0.59
			Substrate(Tombstones) x 0.91	
Lyon	\mathbf{Sb}	natural log	1.5 + agri_1000 x -0.75 + I(forest_5000^0.2) x -1.8	0.62
Paris	\mathbf{Sb}	natural log	0.16 + urb_5000 x 1.6 + forest_1000 x -1.2	0.84
Lyon	V	natural log	2.9 + forest_5000 x -0.88	0.06
Paris	V	none	-0.75 + urb_5000 x 15 + agri_5000 x 15 +	0.43
			I(altitude^-0.5) x 34	
Lyon	Zn	natural log	6.5 + I(forest_5000^0.3) x -2.2 + agri_500 x -0.92 +	0.65
			log(density) x -0.12	
Paris	Zn	natural log	4.5 + urb_5000 x 0.61 + density x 2.8e-05 +	0.56
			Substrate(Tombstones) x 0.47	

300

On average, the final models included approximately three predictor variables in
Paris and two in Lyon (Table S5). In both regions, the most frequent covariables were
forest and urban land use – they occurred even more frequently in Lyon than in
Paris; population density entered more frequently in the Paris models (Table 1). The
large majority of predictors had linear relationships with metal concentrations and
did not need transformation, with a few exceptions such as forest and population
density for Zn in Lyon (Table 2).

308

309 Comparing the mapping approaches in the two regions

310 The LUR approach needed a further step of residual kriging only for Ca, Na, and Ni in

311 the Lyon region. The 10-HOV indicated that this supplementary step increased the

312 quality of the modelling for Ca and Ni, but not for Na. Using the same final models

313 for both KED and LUR, the 10-HOV yielded similar R2 for both approaches and most

metals (Table 3). The HOV-10 R2 ranged from 0.03 to 0.74, and the RRMSE ranged

between 0.08 to 0.88. Comparing the adjusted R2 of the final models to those of the

316 10-HOV, we calculated lower absolute values of percentage change in Paris (median

317	14%, IQR 6-40) than in Lyon (median 38%, IQR 12-45) and therefore varying
318	robustness across metals and areas. Combining this estimation of robustness and the
319	amount of explained spatial variation by the final models, we broadly classified three
320	types of modelling quality: satisfactory adjusted R2 of the final model with
321	satisfactory robustness (eg Zn in Lyon), satisfactory adjusted R2 of the final model
322	with poor robustness (eg Pb in Paris) or poor adjusted R2 of the final model with
323	satisfactory robustness (eg As in Lyon), and poor adjusted R2 of the final model with
324	poor robustness (eg Na in Lyon) (Table 3).

325

326 Table 3: R2 and RRMSE (unitless) of the HOV-10 validation for the KED

327 and LUR approaches, and final approach chosen as the one providing the

328 higher R2.

Metal	Region	R2		RRMSE		Final approach	Model quality	
		HOV10,	HOV10),	HOV10,	HOV10,		
		KED	LUR		KED	LUR		
			Model	Kriging				
Al	Lyon	0.05	0.20		0.46	0.41	LUR	3
Al	Paris	0.18	0.22		0.20	0.20	LUR	3
As	Lyon	0.39	0.28		0.43	0.47	KED	2
As	Paris	0.17	0.20		0.28	0.28	LUR	3
Ca	Lyon	0.10	0.05	0.08	0.09	0.09	KED	3
Ca	Paris	0.09	0.12		0.08	0.08	LUR	3
Cd	Lyon	0.31	0.34		0.51	0.46	LUR	1
Cd	Paris	0.33	0.36		0.56	0.54	LUR	1
Cr	Lyon	0.20	0.21		0.52	0.52	LUR	3
Cr	Paris	0.60	0.62		0.27	0.26	LUR	1
Cu	Lyon	0.30	0.30		0.71	0.71	LUR	1
Cu	Paris	0.50	0.52		0.46	0.44	LUR	1
Fe	Lyon	0.14	0.17		0.50	0.49	LUR	3
Fe	Paris	0.47	0.46		0.25	0.25	KED	1
Hg	Lyon	0.17	0.15		0.67	0.67	KED	3
Hg	Paris	0.22	0.41		0.31	0.22	LUR	2
Na	Lyon	0.04	0.07	0.02	0.80	0.81	KED	3
Na	Paris	0.06	0.08		0.31	0.3	LUR	3
Ni	Lyon	0.38	0.26	0.35	0.41	0.42	KED	2
Ni	Paris	0.63	0.64		0.34	0.34	LUR	1

Pb	Lyon	0.03	0.08	0.88	0.83	LUR	2
Pb	Paris	0.17	0.20	0.75	0.76	LUR	2
Sb	Lyon	0.27	0.31	0.87	0.81	LUR	1
\mathbf{Sb}	Paris	0.71	0.74	0.37	0.36	LUR	1
V	Lyon	0.03	0.03	0.41	0.41	LUR	3
V	Paris	0.51	0.53	0.16	0.16	LUR	2
Zn	Lyon	0.47	0.48	0.54	0.52	LUR	1
Zn	Paris	0.29	0.34	0.53	0.54	LUR	1

HOV: hold-out validation; LUR: land use regression ; KED: kriging with external drift. For the LUR approach, metals Ca, Na, and Ni required an extra step of residual kriging since the residuals of the regression had a significant positive spatial autocorrelation. Modeling quality scores: 1 (satisfactory final model (adjusted R2>0.45) with satisfactory robustness (quantified by 10-HOV with an R2>0.3)), 2 (satisfactory final model with poor robustness or conversely), and 3 (poor final model with poor robustness).

329

330 Final concentration map by metal and by region

331 The final concentration map for each metal and each region is the one with the higher

adjusted R2 and lower RRMSE after 10-HOV (Table 3). The LUR approach was

333 favoured for most metals in both regions. The predicted concentration maps clearly

334 show the gradual decline on concentration away from the city center. This pattern is

driven by the urban and natural predictor variables entering in most models (Figure

336 3, Figure S2).



338 Figure 3: final concentration maps of Cd, Pb, and Sb in Lyon (left) and



- 340 log-10 scale for readability. These maps have the same extents as those in Figure 1.
- 341 White lines represent the borders of French départements.

342 Discussion

Biomonitoring of mosses in cemeteries together with geostatistical modelling proved
an efficient method to generate concentration maps in urban areas, with satisfactory
quality for metals emitted by human sources, such as Cd and Cu, but with lesser
quality for metals emitted by natural sources, such as Ca and Na. The final models
were parsimonious. In most cases, KED and LUR modelling yielded similar results
but with generally better robustness for LUR.

349

To date, only few other methods allow attributing airborne metal exposures to 350 populations. CHIMERE, a chemistry-dispersion model, provides concentrations of 351 PM and PM components regionally (Mailler et al., 2017; Menut et al., 2013) and 352 showed some agreement in the predicted concentrations of atmospheric Cd and 353 measured concentrations of Cd in mosses, with Kendall correlations generally above 354 0.5 in Paris and 0.4 in Lyon (Vieille et al., 2021). LUR models have been developed 355 356 for some metals included in PM2.5 in Western Europe (Chen et al., 2020), and in Pittsburgh, USA (Tripathy et al., 2019). A GIS-based tool provides Cd exposure from 357 industrial sources (Coudon et al., 2019), but only from industrial sources and not yet 358 359 for other metals. A study using field X-Ray analysis on epiphytic mosses to measure 360 Cu, Pb, and Zn, also produced LUR maps in a study area in the USA but for three metals (Messager et al., 2021). Studies comparing or combining these predicted 361 exposures would help better estimate exposure to airborne metals. There were not 362 363 enough monitoring sites of concentrations of metals (As, Cd, Ni, Pb) in PM10 to allow for a comparison with our exposure assessment, again advocating for more 364 365 measuring sites or alternative measurement techniques.

366

This study is based on passive moss biomonitoring, whose concentration values show 367 strong relationships with modelled metal emission or deposition in rural areas at 368 least for Cd and Pb (Harmens et al., 2012), and of Cd in Paris and Lyon (Vieille et al., 369 2021). This moss biomonitoring technique, which therefore can proxy atmospheric 370 concentrations, allowed for (i) rapid collection of sufficient moss samples to cover 371 372 large urban areas and (ii) measuring many metals or potential other components (e.g. persistent organic pollutants, platinoids) with high cost-effectiveness. Cemeteries -373 at least in France – offer a regular sampling frame and choice of possible sampling 374 sites that will most likely shelter Grimmia pulvinata, or, at least, a single moss 375 376 species that will not risk to confound the spatial variability of the measured concentrations. For the sake of homogeneity and to avoid potential contamination by 377 debris of different substrates, we sampled only concrete surface. Regarding the 378 379 modeling process, all the predictors used to build the final models were readily 380 available and open source, with regular updates so that the predictor data generally 381 matched the moss sampling periods. The sets of final predictors were quite similar in 382 both regions even though population density entered more frequently in the Paris 383 models, probably due to the high percentages of urban coverage and the high 384 variability in population density in Paris. However, for each metal both variables and coefficients differed between the two regions; more data in other regions is needed to 385 386 explore the possibility to pool the data to obtain a single model to be applied to several unsampled regions. None of the models used the data on industrial sites, 387 probably because they were too far from the sampling sites in both regions with at 388 389 least a few kilometres from the closest site. The final models explained a large 390 amount of the spatial variability of metals mainly emitted by human activities except Hg, with between 40 and 82% explained for Ni in Lyon or Sb in Paris, respectively. At 391 ambient temperature Hg can exist in gaseous form, and this high volatility may have 392

disturbed the spatial distribution of Hg concentrations in mosses collected during 393 late spring. During the sampling, temperatures were as high as 27.2°C and 28.6°C in 394 Paris and Lyon (data from the French meteorological agency MeteoFrance) - without 395 considering the likely higher temperature on the concrete substrate. For metals 396 mostly emitted by natural sources, the models explained a lesser amount of spatial 397 398 variability. We did not detect strong multicollinearity in the final models. Some VIF values larger than 6 occurred in models including both urban and agriculture or 399 forest variables, which were negatively correlated. However, multicollinearity does 400 401 not affect the models' predictive accuracy.

The present result showed largely higher moss concentrations in urban areas than 402 those previously found in rural areas since 1996 (Lequy et al., 2017), up to a factor 12 403 for Cu for example, in Paris. These urban and rural results seem consistent and 404 plausible, given the positive relationships of metals with relative urban area or 405 negative relationships with its opposite, i.e. greenspace areas, and a strong gradient 406 from the city center to the rural outskirts of Lyon and Paris, and in line with other 407 studies. Indeed, despite the methods are not the same and therefore the estimates are 408 not straightforwardly comparable, the relationships we found between metal 409 concentrations and land used variables, such as traffic, were of the same direction as 410 those found in studies using field measurements on epiphytic mosses in the USA 411 (Messager et al., 2021), or using other biomonitoring techniques using moss bags or 412 epiphytes in Italy (Capozzi et al., 2016; Di Palma et al., 2017). All of these techniques 413 were able to capture spatial variations of metals from either urban or rural sources, 414 thereby reinforcing the plausibility of our results. In our dataset, forest and 415 416 agricultural variables were negatively correlated with urban variables and may better capture the variability of some metals in mosses in cemeteries. 417

418

This study presents the limits inherent to passive moss biomonitoring, including the 419 uncertainty on the period of exposure they represent. However, it is usually estimated 420 that mosses accumulate metals over their lifespan of several years. Mosses, being 421 living organisms, are affected by meteorological conditions in particular drought 422 periods since mosses rely on water even more than other plants (Markert, 2007). But 423 since they accumulate over several years, we took the hypothesis, as in the BRAMM 424 network and the ICP-Vegetation program, that the concentrations in mosses are able 425 to reflect spatial variations in air quality when compared across sampling sites for the 426 same date. Several possible disturbances may either disturb mosses' physiology and 427 428 their ability to biomonitor metals, or contaminate mosses with metals: the use of bleach or surfactants to clean tombstones, or the (former) paintings on some 429 tombstones, which cannot be easily retrieved, or the use of herbicides or other 430 products by cemeteries. During the sampling, data on the use of herbicides or other 431 products proved difficult to collect, with information available for 55% and 80% of 432 the sampled cemeteries in the regions of Paris and Lyon, respectively. Of those, 29% 433 and 47% had information while 26% and 33% declared they used no treatment, in the 434 respective study areas. We could not assess the local effect of wind-blown particles of 435 436 cemeteries' topsoil, possibly contaminated by metals (Neckel et al., 2016); yet the spatial patterns of metal concentrations, and their relationships with the land use 437 variables included in the final models, suggest that any local topsoil effect would be 438 negligible. The fact that Grimmia pulvinata develops preferentially on concrete does 439 not allow the use of cemeteries or tombstones built in a material other than concrete 440 (e.g. granite). This was not an issue in Paris or Lyon but it may be the case in other 441 regions in France or in the world, for which it would be mandatory to find a more 442 suitable moss species. As expected, KED and LUR provided similar maps of similar 443 quality; KED may be used as an alternative for air pollutants when using LUR does 444

not provide satisfactory outputs. The 10-HOV indicated that some models lack
robustness but the concentration maps presented in this study showed plausible
spatial patterns, at least for metals emitted by human activities. Such concentration
maps seem to provide a sufficient geographical contrast in concentrations across each
study area, for a future use as exposure data at individual level in epidemiological
studies.

451 Conclusion

Moss biomonitoring in cemeteries offers a practical alternative for rapid estimation of
exposure to airborne metals in urban areas, and land-use regression provided
satisfactory concentration maps for airborne metals emitted by human sources.
Further research to compare these results with more conventional techniques should
refine exposure assessment for airborne metals such as Cd, Hg, or Pb, but also for
other potentially harmful metals and other pollutants.

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467

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Airborne metal measures remain scarce to derive exposure for large urban populations We measured metals in mosses to derive exposure surfaces in two large French cities We applied land use regression modeling and obtained surfaces for 13 metals Models were satisfactory and robust particularly for cadmium and antimony

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CRediT authorship contribution statement

Emeline Lequy: Conceptualization, Data Curation, Methodology, Software, Formal analysis, Writing - Original Draft, Writing - Review & Editing;

Caroline Meyer: Resources, Data Curation, Methodology, Writing - Review & Editing;

Danielle Vienneau: Methodology, Writing - Review & Editing

Claudine Berr: Funding acquisition, Writing - Review & Editing;

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Kees de Hoogh: Conceptualization, Supervision, Writing - Review & Editing

Bénédicte Jacquemin: Conceptualization, Funding acquisition, Supervision, Writing - Review & Editing

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: