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

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ABSTRACT

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

1. Introduction

As naturally occurring elements, metals abundantly occur in the lithosphere and accumulate in the biosphere and atmosphere through processes including root 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., 1981). Some metals support life, yet all become toxic when exceeding thresholds (Nordberg et al., 2007). Cadmium (Cd) and arsenic (As) for example are recognized human carcinogens (International Agency for Research on Cancer, 2016), and, as neurotoxicants, lead (Pb) and mercury (Hg) may also play a role in the development and decline of cognitive functions (Genuis and

Kelln, 2015; Grandjean and Landrigan, 2014). As early as the 1960s it's been known that airborne metals are a component of airborne particulate matter (PM) (Schroeder, 1968), and it is also established that air pollution also affects health and cognition (Brauer et al., 2012; Gatto et al., 2014). In Europe, toxic metals As, Cd, Pb, and nickel (Ni), have been measured in PM (diameter < 10 μm or PM10) as enforced by Council Directive 96/62/EC of September 27, 1996 on ambient air quality assessment and management and its updates. Yet these measurements are performed only at a few sites, providing insufficient spatial coverage to allow for assessing the exposure of the general population to these airborne metals. Further, the directive does not include other potentially harmful metals such as aluminum (Al),

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antimony (Sb), copper (Cu), or 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 on mosses' lack of roots, making them dependent on atmospheric sources to get water and nutrients (Bates, 1992; Tyler, 1990). Mosses combine a morphology of leaves able to trap particulate metals (Bargagli, 2006) to a monolayer cell thickness facilitating the accessibility of dissolved metals for the exchange sites in the cell walls (Bates, 1992; Carballeira et al., 2008; González and Pokrovsky, 2014). Data obtained by this technique allowed for deriving concentration maps suitable for the French rural and semi-urban populations, and was successfully used to estimate mortality risks associated to airborne metal exposure (Lequy et al., 2019). However, most of the 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 concentration map for metals for urban populations. Moss biomonitoring was shown to perform well in urban areas (Gallego-Cartagena et al., 2021; Jiang et al., 2018; 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 metal concentrations in mosses (De Nicola et al., 2013; Di Palma et al., 2017) but with 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 or Pb, or local or distant steel industry for Cd (Ledoux et al., 2017). For these reasons, we aimed at adapting the moss biomonitoring technique to urban settings to derive fine concentration maps by land use regression (LUR) modeling in two of the most populated French regions, the greater Paris and Lyon areas.

2. 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 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 municipalities are near sources of air pollutants such as roads while being relatively sheltered from direct contamination by humans or animals, and they offer homogeneous substrates such as concrete. In addition, opting for cemeteries allows for collecting mosses that grow in full light and can survive in contaminated environments. We selected a moss

living in cushion, *Grimmia pulvinata* (Hedw.) Sm., which performs well in biomonitoring airborne metals (Gallego-Cartagena et al., 2021), including in cemeteries (Natali et al., 2016).

2.1. 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 a concentration map, we proceeded as follows.

We developed a “target-style” gridded study design (Fig. 1), with concentric circles around the city center with increasing radii up to 49 km around Paris and 30 km around Lyon. These circles were crossed by transects starting from the center of the study site and passing through areas with the highest possible population density, while covering as many directions as possible. We classified population density into 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 études économiques (National Institute of Statistics and Economic Studies), 2016, 2021). For municipalities with less than 5000 inhabitants, the index is high, moderate, low, and very low population density, taking into account the surface actually inhabited. For municipalities with more than 5000 inhabitants, the index is residential, commercial or industrial areas, and recreational areas. In Fig. 1, to improve readability, the municipalities with less than 5000 inhabitants with high population density and the residential areas of municipalities with more than 5000 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 into a “low” population density category. In the areas around Paris and Lyon and their surrounding areas (referred to as Paris and Lyon for readability), population density decreases as the distance from city center increases, therefore reaching low values in the outer circles. The junctions between circles and transects defined different potential sampling sites. The absence of cemeteries at some junctions, the refusal of the town halls to collect mosses in cemeteries, the absence of concrete walls or tombstones, or the species of mosses have led to modify the initially selected 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.

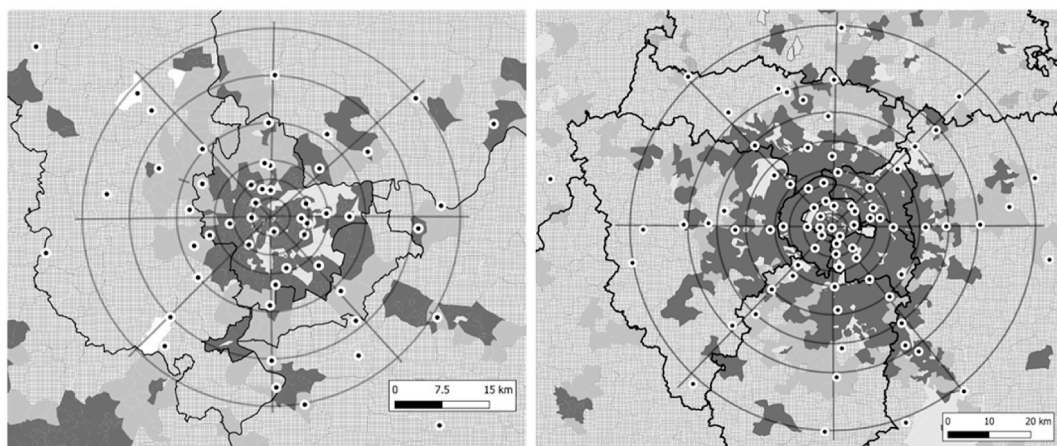


Fig. 1. Distribution of sampling sites (white-circled black dots) around Lyon (left) and Paris (right). Dark gray, medium gray, and gridded-gray areas indicate high, intermediate, and low population densities. Pale gray areas correspond to business or industry parks and to large uninhabited areas (forests, large parks, airports). Black lines indicate the borders of French départements.

2.2. Moss sampling and metal concentrations

Details of the moss sampling are available in [Vieille et al. \(2021\)](#). Briefly, sampling in the Paris and Lyon regions took place in May and June 2018, respectively. In each sampling site, mosses were sampled with standardized methods by trained experts 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 on a total length of 15 m of top of wall, and using two different walls, to reduce the influence of any moss cushion potentially contaminated by the substrate. We chose concrete because of the low risk of potential contamination. Moreover, we avoided decorative metallic objects. Sampling collection in each site included a total of about 9600 cushions. Each cushion was validated with a magnifying glass (10× magnification). Samples were stored in a cooler before being brought back in the laboratory where they dried at room temperature before being manually cleaned, ground with an automatic non-polluting titanium grinder (Pulverisette 14, Fritsch, Germany), and sent for analyses. Sampling and preparation were conducted using nitril gloves and ceramic knives to avoid contamination. Mosses were analyzed by inductively coupled plasma mass spectrometry by the USRAVE laboratory (INRAE - Center de Bordeaux) (Agilent 7700x spectrometer) after drying at 40 °C and acid mineralization by HF/HNO₃/H₂O₂ (concentrations expressed at 103 °C after accounting for water loss on a subsample). For Hg, the moss powder is directly analyzed by Cold Vapour Atomic Fluorescence Spectrometry. Analyses provided concentrations of aluminum (Al), arsenic (As), calcium (Ca), cadmium (Cd), chromium (Cr), Cu, iron (Fe), mercury (Hg), sodium (Na), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V), and zinc (Zn). Analytical uncertainties are 20% for As, Cd, Cr, Cu, Na, Ni, Pb, Sb and V, 15% for Al and Fe and 10% for Ca, Hg and Zn.

2.3. Generating concentration maps

2.3.1. Source data for potential predictors

Corine Land Cover (2018, on <https://www.copernicus.eu/en>) was used to calculate the relative coverage of urban area, agricultural area, forest area, natural area, water within buffers of 500, 1000, 2500, and 5000 m radius around the sampling site (the subcategories used to define each category are detailed in the supplementary material). We used a minimal buffer radius of 500 m due to the resolution of Corine Land Cover (250 × 250 m). Data from the French geographic information system (GIS) database (Institut Géographique National) were used to calculate distance from major roads (defined as those classified level 1 and 2 i.e. corresponding to highways or equivalent, access roads, and 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 industry, we used the European pollutant release and transfer register for industrial 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 total annual emissions released by this site (in kg).

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 before starting developing the LUR models (Table 1).

All GIS processing and analyses were performed with R version using the packages “SP” ([Bivand et al., 2013](#)), “RASTER” ([Hijmans, 2020](#)), “GSTAT” ([Gräler et al., 2016](#)), and “AUTOMAP” ([Hiemstra et al., 2009](#)).

2.3.2. Developing land use regression models

LUR models were developed separately in each region. We aimed to find the most parsimonious models with the best goodness of fit between metal concentrations in mosses and spatial predictors, and applied the following steps. We natural log-transformed metal concentrations when the distribution was left-skewed, and checked for any outlier. We found

Table 1

List of variables and their description.

| Type | Variable | Buffer size (radius, m) | Code | N (%) or median [p25, p75] | | |
|---------------------|---|---------------------------|------------------------|----------------------------|------------------------|------------------------|
| | | | | Lyon (n = 51) | Paris (n = 77) | |
| Point | Substrate: wall or tombstone ^a | – | Substrate (Tombstones) | 9 (18%) | 58 (82%) | |
| | | | | Altitude (m) | – | altitude |
| | Population density (inhab/km ²) | – | density | 370 [166, 1979] | 1804 [247, 7997] | |
| | Distance to major roads (m) | – | dist_road | 525 [419, 1857] | 530 [210, 1334] | |
| | Buffer (%) | Agricultural area within: | 500 | agri_500 | 34 [0, 55] | 0 [0, 37] ^b |
| | | | 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] ^b | 0 [0, 5] ^b |
| | | | 1000 | forest_1000 | 0 [0, 12] ^b | 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] ^b | 0 [0, 0] ^b | |
| | | 1000 | water_1000 | 0 [0, 0] ^b | 0 [0, 0] ^b | |
| 2500 | | water_2500 | 0 [0, 4] ^b | 0 [0, 2] ^b | | |
| 5000 | | water_5000 | 2 [0, 4] | 1 [0, 3] | | |

p25 and p75 stand for the 25th and 75th percentiles.

^a Only concrete tombstones and top of walls.

^b 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.

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

Forward stepwise approach: 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 coefficient of determination (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 multivariable model.

Backward stepwise approach: for each metal, we included all the variables with a statistically significant Spearman correlation coefficient > 0.3. For both approaches, we subsequently removed one by one

any variable with a p -value > 0.05 . When all the remaining variables were significantly associated with the metal concentration, we handled nonlinear relationship as follows: when the predictor had more than 1 degree of freedom (i.e. a nonlinear relationship), and if the relationship visually did not deviate too much from linearity, we simply removed the spline function. If the relationship visually deviated from linearity, but was monotonic or transformable, we replaced the spline function by the most suitable function (power or natural 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 was in the expected direction. Finally, for each model we compared the models yielded by the forward and backward approaches and selected as final model the one with the best adjusted R^2 .

2.3.3. Deriving concentration maps

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

2.3.4. Quality of the models and of the concentration maps

To estimate the quality of each final model, in addition to the adjusted R^2 , we computed the Akaike Information Criterion (AIC) and the variance inflation factor (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-fold out validation (10-HOV). For each metal, separately in each study area, we first used 10 training sets (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. We then applied the coefficients and variograms to generate maps over the 500×500 m grid. We back-transformed the predicted values for all the natural log-transformed metals. Additionally, we developed variograms of the residuals from the LUR models using the training sets. We performed a 10-HOV first to evaluate the 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 coordinates of the validating sets (the remaining 10% of sites) and regressed these predicted values on the corresponding observed values to obtain a R^2 ; we also calculated the relative root mean square error (RRMSE). We categorized modeling quality scores: 1 (satisfactory final model (adjusted $R^2 > 0.45$) with satisfactory robustness (quantified by 10-HOV with an $R^2 > 0.3$)), 2 (satisfactory final model with poor robustness or conversely), and 3 (poor final model with poor robustness).

3. Results

3.1. Metal concentrations

In both regions combined, metal concentrations ranged over several orders of magnitudes from Hg to Ca, between $0.10 \mu\text{g g}^{-1}$ [IQR: 0.21] for Hg and $1.7 \cdot 10^4 \mu\text{g g}^{-1}$ [IQR: $2.3 \cdot 10^4$] for Ca (Fig. 2). The magnitude was similar for each metal in the two regions, but still we found

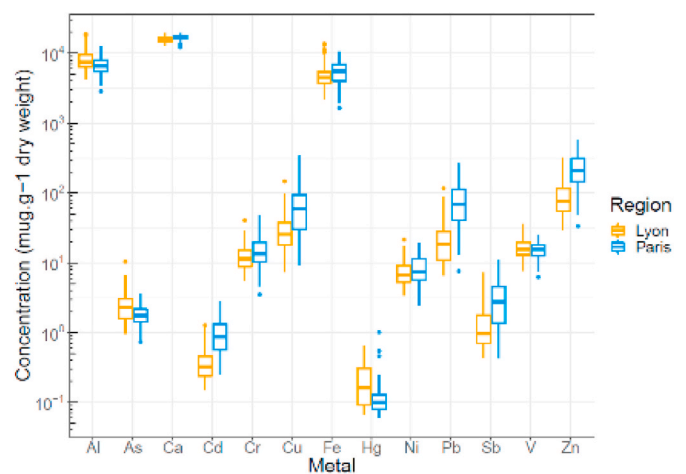


Fig. 2. Distribution (Y-axis on a log-10 scale) of the metal concentrations in mosses collected in the cemeteries of the regions of Lyon ($n = 51$) and Paris ($n = 77$) in 2018. See Table S1 for corresponding numeric data.

concentrations of Cd, Cu, Pb, Sb, and Zn at least twice as high in Paris as in Lyon.

3.2. Final models

Most final models were constructed based on the backward stepwise selection, which provided slightly higher adjusted R^2 for more than half of the metals in both regions (Table S2). Depending on the metal, and on the region, the models explained part of the spatial variability, from 6% for vanadium in Lyon to 84% for antimony in Paris, but mostly between 21% and 54% in Lyon and between 30 and 60% in Paris, with better results for metals emitted by human activities (Table 2). For each metal in both study regions, final models yielded lower AIC than intercept-only models (Table S3). The models yielded relationships in the expected direction for each included predictor (such as 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 variance in Paris, except for Al and As. Residuals were spatially autocorrelated only for Ca, Na, and Ni, in Lyon.

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).

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).

3.3. Comparing the mapping approaches in the two regions

The LUR approach needed a further step of residual kriging only for Ca, Na, and Ni, in the Lyon region. The 10-HOV indicated that this supplementary step increased the quality of the modeling for Ca and Ni, but not for Na. Using the same final models for both KED and LUR, the 10-HOV yielded similar R^2 for both approaches and most metals (Table 3). The HOV-10 R^2 ranged from 0.03 to 0.74, and the RRMSE ranged between 0.08 and 0.88. Comparing the adjusted R^2 of the final models to those of the 10-HOV, we calculated lower absolute values of percentage change in Paris (median 14%, IQR 6–40) than in Lyon (median 38%, IQR 12–45) and therefore varying robustness across metals and areas. Combining this estimation of robustness and the

Table 2

Final land-use regression models for each metal in each region, including the transformation of the metal distribution, the formula used for the linear regression, and the adjusted coefficient of determination (R2).

| Region | Metal | Transformation | Model formula | R2 |
|--------|-------|----------------|--|------|
| Lyon | Al | natural log | $6.9 + \text{forest_2500} \times -1.4 + I(\text{dist_road}^{-0.05}) \times 2.7 + \text{altitude} \times 0.0013$ | 0.26 |
| Paris | Al | none | $7600 + \text{forest_5000} \times -5800$ | 0.24 |
| Lyon | As | natural log | $0.51 + \text{forest_2500} \times -2.9 + \text{altitude} \times 0.0023$ | 0.37 |
| Paris | As | none | $2.1 + \text{forest_5000} \times -1.8$ | 0.25 |
| Lyon | Ca | none | $15000 + \text{urb_1000} \times 1700$ | 0.14 |
| Paris | Ca | none | $17000 + \text{agri_5000} \times -1700 + \text{density} \times 0.06 + \text{forest_1000:I}(\text{forest_1000} < 0.25) \times -690 + \text{forest_1000:I}(\text{forest_1000} \geq 0.25) \times 7400$ | 0.28 |
| Lyon | Cd | natural log | $-1 + \text{urb_1000} \times 0.59 + I(\text{forest_5000}^{0.3}) \times -0.93 + \text{Substrate (Tombstones)} \times 0.38$ | 0.58 |
| Paris | Cd | natural log | $-1 + \text{urb_5000} \times 0.87 + \text{density} \times 2e-5 + \text{Substrate (Tombstones)} \times 0.34$ | 0.67 |
| Lyon | Cr | natural log | $2.7 + \text{forest_2500} \times -2.1$ | 0.31 |
| Paris | Cr | natural log | $2.8 + \text{altitude} \times -0.0033 + \text{urb_5000} \times 0.44 + \text{forest_2500} \times -1.1$ | 0.63 |
| Lyon | Cu | natural log | $3.1 + \text{urb_1000} \times 0.9 + \text{forest_2500} \times -2.1$ | 0.55 |
| Paris | Cu | natural log | $3 + \text{urb_5000} \times 1.6 + \text{water_5000} \times 7.2$ | 0.67 |
| Lyon | Fe | natural log | $8.7 + \text{forest_2500} \times -1.7$ | 0.20 |
| Paris | Fe | none | $1700 + \text{altitude} \times -13 + \text{urb_5000} \times 6500 + \text{agri_5000} \times 5000$ | 0.50 |
| Lyon | Hg | natural log | $-2.3 + \text{urb_1000} \times 0.99$ | 0.23 |
| Paris | Hg | natural log | $-2.9 + \text{altitude} \times -0.0025 + \text{urb_2500} \times 0.95 + \text{agri_5000} \times 0.81 + \text{Substrate (Tombstones)} \times 0.2$ | 0.34 |
| Lyon | Na | natural log | $7 + \text{forest_2500} \times -1.8$ | 0.12 |
| Paris | Na | natural log | $6.5 + \text{forest_2500} \times -1.1 + \text{agri_2500} \times 0.33$ | 0.29 |
| Lyon | Ni | natural log | $1.9 + \text{urb_1000} \times 0.38 + \text{forest_2500} \times -1.3$ | 0.32 |
| Paris | Ni | natural log | $2.1 + \text{altitude} \times -0.0031 + \text{urb_500} \times 0.27 + \text{forest_2500} \times -1.1 + \text{density} \times 1.5e-05 + \text{Substrate (Tombstones)} \times 0.16$ | 0.69 |
| Lyon | Pb | natural log | $2.1 + \text{urb_500} \times 1.1 + \text{Substrate (Tombstones)} \times 0.72$ | 0.49 |
| Paris | Pb | natural log | $3.4 + \text{forest_1000} \times -1.2 + \text{density} \times 3.7e-05 + \text{Substrate (Tombstones)} \times 0.91$ | 0.59 |
| Lyon | Sb | natural log | $1.5 + \text{agri_1000} \times -0.75 + I(\text{forest_5000}^{0.2}) \times -1.8$ | 0.62 |
| Paris | Sb | natural log | $0.16 + \text{urb_5000} \times 1.6 + \text{forest_1000} \times -1.2$ | 0.84 |
| Lyon | V | natural log | $2.9 + \text{forest_5000} \times -0.88$ | 0.06 |
| Paris | V | none | $-0.75 + \text{urb_5000} \times 15 + \text{agri_5000} \times 15 + I(\text{altitude}^{-0.5}) \times 34$ | 0.43 |
| Lyon | Zn | natural log | $6.5 + I(\text{forest_5000}^{0.3}) \times -2.2 + \text{agri_500} \times -0.92 + \log(\text{density}) \times -0.12$ | 0.65 |
| Paris | Zn | natural log | $4.5 + \text{urb_5000} \times 0.61 + \text{density} \times 2.8e-05 + \text{Substrate (Tombstones)} \times 0.47$ | 0.56 |

amount of explained spatial variation by the final models, we broadly classified three types of modeling quality: satisfactory adjusted R2 of the final model with satisfactory robustness (eg Zn in Lyon), satisfactory adjusted R2 of the final model with poor robustness (eg Pb in Paris) or poor adjusted R2 of the final model with satisfactory robustness (eg As in Lyon), and poor adjusted R2 of the final model with poor robustness (eg Na in Lyon) (Table 3).

3.4. Final concentration maps by metal and by region

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 favoured for most metals in both regions. The predicted concentration maps clearly showed a gradual decline on concentration away from the city center. This pattern is driven by the urban and natural predictor variables entering in most models (Fig. 3, Figure S2).

4. Discussion

Biomonitoring of mosses in cemeteries together with geostatistical modeling 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 modeling yielded similar results but with generally better robustness for LUR.

To date, only few other methods allow attributing airborne metal exposures to populations. CHIMERE, a chemistry-dispersion model, provides concentrations of PM and PM components regionally (Mailler et al., 2017; Menut et al., 2013) and showed some agreement in the predicted concentrations of atmospheric Cd and measured concentrations of Cd in mosses, with Kendall correlations generally above 0.5 in Paris and 0.4 in Lyon (Vieille et al., 2021). LUR models have been developed 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 industrial sources (Coudon et al., 2019), but only from industrial sources and not yet for other metals. A study using field X-Ray analysis on epiphytic mosses to measure Cu, Pb, and Zn, also produced LUR maps in a study area in the USA but for three metals (Messenger et al., 2021). Studies comparing or combining these predicted exposures would help better estimate exposure to airborne metals. There were not 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 measuring sites or alternative measurement techniques.

This study is based on passive moss biomonitoring, whose concentration values show strong relationships with modelled metal emission or deposition in rural areas at least for Cd and Pb (Harmens et al., 2012), and of Cd in Paris and Lyon (Vieille et al., 2021). This moss biomonitoring technique, which therefore can proxy atmospheric concentrations, allowed for (i) rapid collection of sufficient moss samples to cover large urban areas and (ii) measuring many metals or potential other components (e.g. persistent organic pollutants, platinoids) with high cost-effectiveness. Cemeteries – at least in France – offer a regular sampling frame and choice of possible sampling sites that will most likely shelter *Grimmia pulvinata*, or, at least, a single moss 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 debris of different substrates, we sampled only concrete surface. Regarding the modeling process, all the predictors used to build the final models were readily available and open source, with regular updates so that the predictor data generally matched the moss sampling periods. The sets of final predictors were quite similar in both regions even though population density entered more frequently in the Paris models, probably due to the high percentages of urban coverage and the high 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 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, probably because they were too far from the sampling sites in both regions with at least a few kilometres from the closest site. The final models explained a large amount of the spatial variability of metals mainly emitted by

Table 3

Coefficient of determination (R2) and relative root mean square error (RRMSE, unitless) of the HOV-10 validation for the KED and LUR approaches, and final approach chosen as the one providing the higher R2.

| Metal | Region | R2 | | RRMSE | | Final approach | Model quality |
|-------|--------|------------|------------|------------|------------|----------------|---------------|
| | | HOV10, KED | HOV10, LUR | HOV10, KED | HOV10, LUR | | |
| | | | Model | Kriging | | | |
| Al | Lyon | 0.05 | 0.20 | | | LUR | 3 |
| Al | Paris | 0.18 | 0.22 | | | LUR | 3 |
| As | Lyon | 0.39 | 0.28 | | | KED | 2 |
| As | Paris | 0.17 | 0.20 | | | LUR | 3 |
| Ca | Lyon | 0.10 | 0.05 | 0.08 | | KED | 3 |
| Ca | Paris | 0.09 | 0.12 | | | LUR | 3 |
| Cd | Lyon | 0.31 | 0.34 | | | LUR | 1 |
| Cd | Paris | 0.33 | 0.36 | | | LUR | 1 |
| Cr | Lyon | 0.20 | 0.21 | | | LUR | 3 |
| Cr | Paris | 0.60 | 0.62 | | | LUR | 1 |
| Cu | Lyon | 0.30 | 0.30 | | | LUR | 1 |
| Cu | Paris | 0.50 | 0.52 | | | LUR | 1 |
| Fe | Lyon | 0.14 | 0.17 | | | LUR | 3 |
| Fe | Paris | 0.47 | 0.46 | | | KED | 1 |
| Hg | Lyon | 0.17 | 0.15 | | | KED | 3 |
| Hg | Paris | 0.22 | 0.41 | | | LUR | 2 |
| Na | Lyon | 0.04 | 0.07 | 0.02 | | KED | 3 |
| Na | Paris | 0.06 | 0.08 | | | LUR | 3 |
| Ni | Lyon | 0.38 | 0.26 | 0.35 | | KED | 2 |
| Ni | Paris | 0.63 | 0.64 | | | LUR | 1 |
| Pb | Lyon | 0.03 | 0.08 | | | LUR | 2 |
| Pb | Paris | 0.17 | 0.20 | | | LUR | 2 |
| Sb | Lyon | 0.27 | 0.31 | | | LUR | 1 |
| Sb | Paris | 0.71 | 0.74 | | | LUR | 1 |
| V | Lyon | 0.03 | 0.03 | | | LUR | 3 |
| V | Paris | 0.51 | 0.53 | | | LUR | 2 |
| Zn | Lyon | 0.47 | 0.48 | | | LUR | 1 |
| Zn | Paris | 0.29 | 0.34 | | | 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).

human activities except Hg, with between 40 and 82% explained for Ni in Lyon or Sb in Paris, respectively. At ambient temperature Hg can exist in gaseous form, and this high volatility may have disturbed the spatial distribution of Hg concentrations in mosses collected during late spring. During the sampling, temperatures were as high as 27.2 °C and 28.6 °C in Paris and Lyon (data from the French meteorological agency Météo-France) – without considering the likely higher temperature on the concrete substrate. For metals mostly emitted by natural sources, the models explained a lesser amount of spatial 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 forest variables, which were negatively correlated. However, multicollinearity does not affect the models' predictive accuracy.

The present result showed largely higher moss concentrations in urban areas than those previously found in rural areas since 1996 (Lequy et al., 2017), up to a factor 12 for Cu for example, in Paris. These urban and rural results seem consistent and plausible, given the positive relationships of metals with relative urban area or negative relationships with its opposite, i.e. greenspace areas, and a strong gradient from the city center to the rural outskirts of Lyon and Paris, and in line with other studies. Indeed, despite the methods are not the same and therefore the estimates are not straightforwardly comparable, the relationships we found between metal concentrations and land use variables, such as traffic, were of the same direction as those found in studies using field measurements on epiphytic mosses in the USA (Messenger et al., 2021), or using other biomonitoring techniques using moss bags or epiphytes in Italy (Capozzi et al., 2016; Di Palma et al., 2017; De Nicola et al., 2013). All of these techniques were able to capture spatial variations of metals from either urban or rural sources, thereby reinforcing the plausibility of our results. In our dataset, forest and agricultural variables were

negatively correlated with urban variables and may better capture the variability of some metals in mosses in cemeteries.

This study presents the limits inherent to passive moss bio-monitoring, including the uncertainty on the period of exposure they represent. However, it is usually estimated that mosses accumulate metals over their lifespan of several years. Mosses, being living organisms, are affected by meteorological conditions in particular drought periods since mosses rely on water even more than other plants (Markert, 2007). But since they accumulate over several years, we took the hypothesis, as in the BRAMM network and the ICP-Vegetation program, that the concentrations in mosses are able to reflect spatial variations in air quality when compared across sampling sites for the same date. Several possible disturbances may either disturb mosses' physiology and 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 tombstones, which cannot be easily retrieved, or the use of herbicides or other products by cemeteries. During the sampling, data on the use of herbicides or other products proved difficult to collect, with information available for 55% and 80% of the sampled cemeteries in the regions of Paris and Lyon, respectively. Of those, 29% and 47% had information while 26% and 33% declared they used no treatment, in the respective study areas. We could not assess the local effect of wind-blown particles of cemeteries' topsoil, possibly contaminated by metals (Neckel et al., 2016); yet the spatial patterns of metal concentrations, and their relationships with the land use variables included in the final models, suggest that any local topsoil effect would be negligible. The fact that *Grimmia pulvinata* develops preferentially on concrete does not allow the use of cemeteries or tombstones built in a material other than concrete (e.g. granite). This was not an issue in Paris or Lyon but it may be the case in other regions in France or in the world,

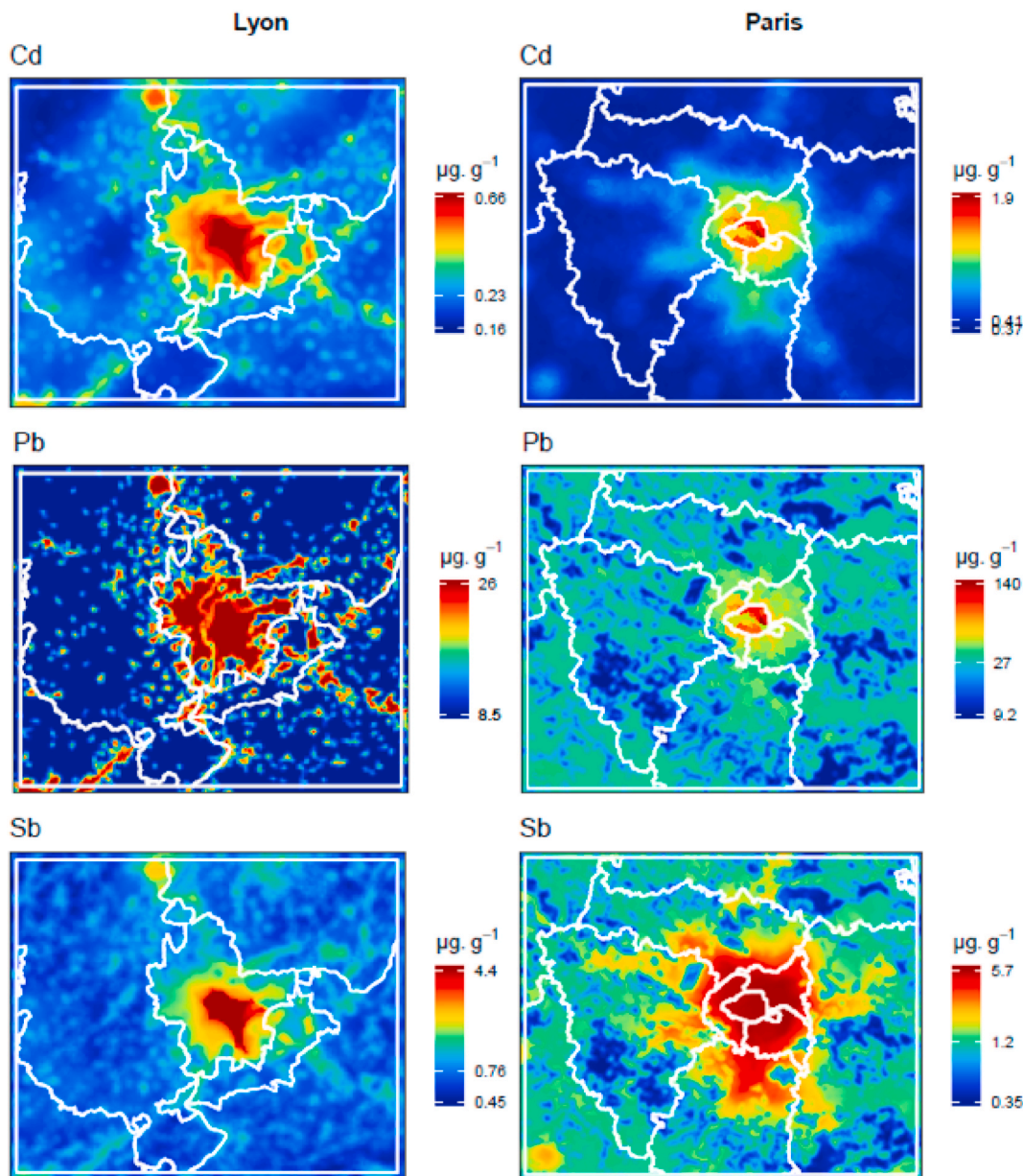


Fig. 3. Final concentration maps of Cd, Pb, and Sb in Lyon (left) and Paris (right). The legends display the minimum, median and maximum values on a log-10 scale for readability. These maps have the same extents as those in Fig. 1. White lines represent the borders of French départements.

for which it would be mandatory to find a more suitable moss species. As expected, KED and LUR provided similar maps of similar quality; KED may be used as an alternative for air pollutants when using LUR does 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.

5. 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.

Credit author 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; Marcel Goldberg: Funding acquisition, Writing – review & editing; Marie Zins: Funding acquisition, Writing – review & editing; Sébastien Leblond: Resources, Methodology; Funding acquisition, Writing – review & editing, Kees de Hoogh: Conceptualization, Supervision, Writing – review & editing, Bénédicte Jacquemin: Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2022.119097>.

References

- Bargagli, R., 2006. *Antarctic Ecosystems: Environmental Contamination, Climate Change, and Human Impact*. Springer Science & Business Media.
- Bates, J.W., 1992. Mineral nutrient acquisition and retention by bryophytes. *J. Bryolog.* 17, 223–240. <https://doi.org/10.1179/jbr.1992.17.2.223>.
- Bivand, R.S., Pebesma, E., Gomez-Rubio, V., 2013. *Applied Spatial Data Analysis with R*, second ed. Springer, NY.
- Brauer, M., Amann, M., Burnett, R.T., Cohen, A., Dentener, F., Ezzati, M., Henderson, S. B., Krzyzanowski, M., Martin, R.V., Van Dingenen, R., van Donkelaar, A., Thurston, G.D., 2012. Exposure assessment for estimation of the global burden of disease attributable to outdoor air pollution. *Environ. Sci. Technol.* 46, 652–660. <https://doi.org/10.1021/es2025752>.
- Capozzi, F., Giordano, S., Di Palma, A., Spagnuolo, V., De Nicola, F., Adamo, P., 2016. Biomonitoring of atmospheric pollution by moss bags: discriminating urban-rural structure in a fragmented landscape. *Chemosphere* 149, 211–218. <https://doi.org/10.1016/j.chemosphere.2016.01.065>.
- Carballeira, C.B., Aboal, J.R., Fernández, J.A., Carballeira, A., 2008. Comparison of the accumulation of elements in two terrestrial moss species. *Atmos. Environ.* 42, 4904–4917. <https://doi.org/10.1016/j.atmosenv.2008.02.028>.
- Chen, J., de Hoogh, K., Gulliver, J., Hoffmann, B., Hertel, O., Ketzler, M., Weinmayr, G., Bauwelinck, M., van Donkelaar, A., Hvidtfeldt, U.A., Atkinson, R., Janssen, N.A.H., Martin, R.V., Samoli, E., Andersen, Z.J., Oftedal, B.M., Stafoggia, M., Bellander, T., Strak, M., Wolf, K., Vienneau, D., Brunekreef, B., Hoek, G., 2020. Development of Europe-wide models for particle elemental composition using supervised linear regression and random forest. *Environ. Sci. Technol.* 54, 15698–15709. <https://doi.org/10.1021/acs.est.0c06595>.
- Coudon, T., Danjou, A.M.N., Faure, E., Praud, D., Severi, G., Mancini, F.R., Salizzoni, P., Fervers, B., 2019. Development and performance evaluation of a GIS-based metric to assess exposure to airborne pollutant emissions from industrial sources. *Environ. Health* 18, 8. <https://doi.org/10.1186/s12940-019-0446-x>.
- De Nicola, F., Spagnuolo, V., Baldantoni, D., Sessa, L., Alfani, A., Bargagli, R., Monaci, F., Terracciano, S., Giordano, S., 2013. Improved biomonitoring of airborne contaminants by combined use of holm oak leaves and epiphytic moss. *Chemosphere* 92, 1224–1230. <https://doi.org/10.1016/j.chemosphere.2013.04.050>.
- Di Palma, A., Capozzi, F., Spagnuolo, V., Giordano, S., Adamo, P., 2017. Atmospheric particulate matter intercepted by moss-bags: relations to moss trace element uptake and land use. *Chemosphere* 176, 361–368. <https://doi.org/10.1016/j.chemosphere.2017.02.120>.
- Gall, J.E., Boyd, R.S., Rajakaruna, N., 2015. Transfer of heavy metals through terrestrial food webs: a review. *Environ. Monit. Assess.* 187, 201. <https://doi.org/10.1007/s10661-015-4436-3>.
- Gallego-Cartagena, E., Morillas, H., Carrero, J.A., Madariaga, J.M., Maguregui, M., 2021. Naturally growing graminaceae family mosses as passive biomonitors of heavy metals pollution in urban-industrial atmospheres from the Bilbao Metropolitan area. *Chemosphere* 263, 128190. <https://doi.org/10.1016/j.chemosphere.2020.128190>.
- Gatto, N.M., Henderson, V.W., Hodis, H.N., St John, J.A., Lurmann, F., Chen, J.-C., Mack, W.J., 2014. Components of air pollution and cognitive function in middle-aged and older adults in Los Angeles. *Neurotoxicology* 40, 1–7. <https://doi.org/10.1016/j.neuro.2013.09.004>.
- Genius, S.J., Kelln, K.L., 2015. Toxicant exposure and bioaccumulation: a common and potentially reversible cause of cognitive dysfunction and dementia. *Behav. Neurol.* 2015, e620143. <https://doi.org/10.1155/2015/620143>.
- Gnesin, G.G., 2013. On the origin of metallurgical technologies in the Bronze Age. *Powder Metall. Met. Ceram.* 52, 477–488. <https://doi.org/10.1007/s11106-013-9550-6>.
- González, A.G., Pokrovsky, O.S., 2014. Metal adsorption on mosses: toward a universal adsorption model. *J. Colloid Interface Sci.* 415, 169–178. <https://doi.org/10.1016/j.jcis.2013.10.028>.
- Gräler, B., Pebesma, E., Heuvelink, G., 2016. Spatio-Temporal Interpolation using gstat. *R J.* 8, 204–218.
- Grandjean, P., Landrigan, P.J., 2014. Neurobehavioural effects of developmental toxicity. *Lancet Neurol.* 13, 330–338. [https://doi.org/10.1016/S1474-4422\(13\)70278-3](https://doi.org/10.1016/S1474-4422(13)70278-3).
- Harmens, H., 2010. Monitoring of atmospheric deposition of heavy metals, nitrogen and POPs in Europe using bryophytes. monitoring manual. International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops.
- Harmens, H., Ilyin, I., Mills, G., Aboal, J.R., Alber, R., Blum, O., Coşkun, M., De Temmerman, L., Fernández, J.A., Figueira, R., Frontasyeva, M., Godzik, B., Goltsova, N., Jeran, Z., Korzekwa, S., Kubin, E., Kviatkovs, K., Leblond, S., Liiv, S., Magnússon, S.H., Maňková, B., Nikodemus, O., Pesch, R., Poikolainen, J., Radnovic, D., Rühling, A., Santamaria, J.M., Schröder, W., Spiric, Z., Stafilov, T., Steinnes, E., Suchara, I., Tabors, G., Thöni, L., Turcsányi, G., Yurukova, L., Zechmeister, H.G., 2012. Country-specific correlations across Europe between modelled atmospheric cadmium and lead deposition and concentrations in mosses. *Environ. Pollut.* 166, 1–9. <https://doi.org/10.1016/j.envpol.2012.02.013>.
- Hiemstra, P.H., Pebesma, E.J., Twenhöfel, C.J.W., Heuvelink, G.B.M., 2009. Real-time automatic interpolation of ambient gamma dose rates from the Dutch Radioactivity Monitoring Network. *Comput. Geosci.* 35 (8), 1711–1721. <https://doi.org/10.1016/j.cageo.2008.10.011>.
- Hijmans, R.J., 2020. *Raster: Geographic Data Analysis and Modeling*. Institut national de la statistique et des études économiques (National Institute of Statistics and Economic Studies), 2016. Definition - IRIS | Insee [WWW Document]. <https://www.insee.fr/en/metadonnees/definition/c1523>. (Accessed 9 July 2021).
- Institut national de la statistique et des études économiques (National Institute of Statistics and Economic Studies), 2021. La grille communale de densité | Insee [WWW Document]. <https://www.insee.fr/fr/information/2114627>. (Accessed 9 July 2021).
- International Agency for Research on Cancer, 2016. *IARC MONOGRAPHS ON THE EVALUATION OF CARCINOGENIC RISKS TO HUMANS*, vol. 109 (Lyon).
- Jaworowski, Z., Bysiek, M., Kownacka, L., 1981. Flow of metals into the global atmosphere. *Geochem. Cosmochim. Acta* 45, 2185–2199. [https://doi.org/10.1016/0016-7037\(81\)90071-5](https://doi.org/10.1016/0016-7037(81)90071-5).
- Jiang, Y., Fan, M., Hu, R., Zhao, J., Wu, Y., 2018. Mosses are better than leaves of vascular plants in monitoring atmospheric heavy metal pollution in urban areas. *Int. J. Environ. Res. Publ. Health* 15, 1105. <https://doi.org/10.3390/ijerph15061105>.
- Ledoux, F., Kfoury, A., Delmaire, G., Roussel, G., El Zein, A., Courcot, D., 2017. Contributions of local and regional anthropogenic sources of metals in PM_{2.5} at an urban site in northern France. *Chemosphere* 181, 713–724. <https://doi.org/10.1016/j.chemosphere.2017.04.128>.
- Lequy, E., Dubos, N., Witté, I., Pascaud, A., Sauvage, S., Leblond, S., 2017. Assessing temporal trends of trace metal concentrations in mosses over France between 1996 and 2011: a flexible and robust method to account for heterogeneous sampling strategies. *Environ. Pollut.* 220, 828–836. <https://doi.org/10.1016/j.envpol.2016.10.065>. Part B.
- Lequy, E., Sauvage, S., Laffray, X., Gombert-Courvoisier, S., Pascaud, A., Galsomies, L., Leblond, S., 2016. Assessment of the uncertainty of trace metal and nitrogen concentrations in mosses due to sampling, sample preparation and chemical analysis based on the French contribution to ICP-Vegetation. *Ecol. Indic.* 71, 20–31. <https://doi.org/10.1016/j.ecolind.2016.06.046>.
- Lequy, E., Siemiatycki, J., Leblond, S., Meyer, C., Zhivin, S., Vienneau, D., de Hoogh, K., Goldberg, M., Zins, M., Jacquemin, B., 2019. Long-term exposure to atmospheric metals assessed by mosses and mortality in France. *Environ. Int.* 129, 145–153. <https://doi.org/10.1016/j.envint.2019.05.004>.
- Mailler, S., Menut, L., Khvorostyanov, D., Valari, M., Couvidat, F., Siour, G., Turquet, S., Briant, R., Tuccella, P., Bessagnet, B., Colette, A., Létinois, L., Markakis, K., Meleux, F., 2017. CHIMERE-2017: from urban to hemispheric chemistry-transport modeling. *Geosci. Model Dev. (GMD)* 10, 2397–2423. <https://doi.org/10.5194/gmd-10-2397-2017>.
- Markert, B., 2007. Definitions and principles for bioindication and biomonitoring of trace metals in the environment. *Journal of Trace Elements in Medicine and Biology, Third International Symposium/Federation of European Societies on Trace Elements and Minerals (FESTEM)* 21 (Suppl. 1), 77–82. <https://doi.org/10.1016/j.jtmb.2007.09.015>.
- Menut, L., Bessagnet, B., Khvorostyanov, D., Beekmann, M., Blond, N., Colette, A., Coll, I., Curci, G., Foret, G., Hodzic, A., Mailler, S., Meleux, F., Monge, J.-L., Pison, I., Siour, G., Turquet, S., Valari, M., Vautard, R., Vivanco, M.G., 2013. Chimere 2013: a model for regional atmospheric composition modelling. *Geosci. Model Dev. (GMD)* 6, 981–1028. <https://doi.org/10.5194/gmd-6-981-2013>.
- Messenger, M.L., Davies, I.P., Levin, P.S., 2021. Low-cost biomonitoring and high-resolution, scalable models of urban metal pollution. *Sci. Total Environ.* 767, 144280. <https://doi.org/10.1016/j.scitotenv.2020.144280>.
- Natali, M., Zanella, A., Rankovic, A., Banas, D., Cantaluppi, C., Abbadi, L., Lata, J.-C., 2016. Assessment of trace metal air pollution in Paris using slurry-TXRF analysis on cemetery mosses. *Environ. Sci. Pollut. Res.* 23, 23496–23510. <https://doi.org/10.1007/s11356-016-7445-z>.
- Neckel, A., Júnior, A.C.G., Ribeiro, L.A., Silva, C.C.O. de A., Cardoso, G.T., 2016. Cemeteries heavy metals concentration analysis of soils and the contamination risk for the surrounding resident population. *Int. J. Eng. Res. Appl.* 6, 30–35.

- Nordberg, G.F., Fowler, B.A., Nordberg, M. (Eds.), 2007. Handbook on the Toxicology of Metals. Elsevier. <https://doi.org/10.1016/B978-0-12-369413-3.X5052-6>.
- Schröder, W., Nickel, S., Schönrock, S., Meyer, M., Wosniok, W., Harmens, H., Frontasyeva, M.V., Alber, R., Aleksiyenak, J., Barandovski, L., Carballeira, A., Danielsson, H., Temmermann de, L., Godzik, B., Jeran, Z., Karlsson, G.P., Lazo, P., Leblond, S., Lindroos, A.-J., Liiv, S., Magnússon, S.H., Mankovska, B., Martínez-Abaigar, J., Piispanen, J., Poikolainen, J., Popescu, I.V., Qarri, F., Santamaria, J.M., Skudnik, M., Špirić, Z., Stafilov, T., Steinnes, E., Stihl, C., Thöni, L., Uggerud, H.T., Zechmeister, H.G., 2016. Spatially valid data of atmospheric deposition of heavy metals and nitrogen derived by moss surveys for pollution risk assessments of ecosystems. *Environ. Sci. Pollut. Res.* 23, 10457–10476. <https://doi.org/10.1007/s11356-016-6577-5>.
- Schroeder, H.A., 1968. Airborne metals. *Sci. Citiz.* 10, 83–88. <https://doi.org/10.1080/21551278.1968.9957619>.
- Tripathy, S., Tunno, B.J., Michanowicz, D.R., Kinnee, E., Shmool, J.L.C., Gillooly, S., Clougherty, J.E., 2019. Hybrid land use regression modeling for estimating spatio-temporal exposures to PM2.5, BC, and metal components across a metropolitan area of complex terrain and industrial sources. *Sci. Total Environ.* 673, 54–63. <https://doi.org/10.1016/j.scitotenv.2019.03.453>.
- Tyler, G., 1990. Bryophytes and heavy metals: a literature review. *Bot. J. Linn. Soc.* 104, 231–253. <https://doi.org/10.1111/j.1095-8339.1990.tb02220.x>.
- Vieille, B., Albert, I., Leblond, S., Couvidat, F., Parent, É., Meyer, C., 2021. Are Grimmia mosses good biomonitors for urban atmospheric metallic pollution? Preliminary evidence from a French case study on cadmium. *Atmosphere* 12, 491. <https://doi.org/10.3390/atmos12040491>.
- Zechmeister, H.G., Hohenwallner, D., Riss, A., Hanus-Ilmar, A., 2005. Estimation of element deposition derived from road traffic sources by using mosses. *Environ. Pollut.* 138, 238–249. <https://doi.org/10.1016/j.envpol.2005.04.005>.
- Zins, M., Goldberg, M., Team, C., 2015. The French CONSTANCES population-based cohort: design, inclusion and follow-up. *Eur. J. Epidemiol.* 30, 1317–1328. <https://doi.org/10.1007/s10654-015-0096-4>.