A Survey of Topsoil Arsenic and Mercury Concentrations Across France

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Abstract

Even at low concentrations, the presence of arsenic and mercury in soils can lead to ecological and health impacts. The recent European-wide LUCAS Topsoil Survey found that the arsenic concentration of a large proportion of French soils exceeded a threshold which indicated that further investigation was required. A much smaller proportion of soils exceeded the corresponding threshold for mercury but the impacts of mining and industrial activities on mercury concentrations are not well understood. We use samples from the French national soil monitoring network (RMQS: Réseau de Mesures de la Qualité des Sols) to explore the variation of topsoil arsenic and mercury concentrations across mainland France at a finer spatial resolution than was reported by LUCAS Topsoil. We use geostatistical methods to map the expected concentrations of these elements in the topsoil and the probabilities that the legislative thresholds are exceeded. We find that, with the exception of some areas where the geogenic concentrations and soil adsorption capacities are very low, arsenic concentrations are generally larger than the threshold which indicates that further assessment of the area is required. The lower of two other guideline values indicating risks to ecology or health is exceeded in fewer than 5% of RMQS samples. These exceedances occur in localised hot-spots primarily associated with mining and mineralization. The probabilities of mercury concentrations exceeding the further assessment threshold value are everywhere less than 0.01 and none of the RMQS samples exceed either of the ecological and health risk thresholds. However, there are some regions with elevated concentrations which can be related to volcanic material, natural mineralizations and industrial contamination. These regions are more diffuse than the hot-spots of arsenic reflecting the greater volatility of mercury and therefore the greater ease with which it can be transported and redeposited. The maps provide a baseline against which future phases of the RMQS can be compared and highlight regions where the threat of soil contamination and its impacts should be more closely monitored.

Keywords

Arsenic, mercury, topsoil, geostatistics, geogenic, contamination.

Introduction

Arsenic and mercury are toxic elements that can have negative effects on both ecosystems and human health. Their presence in soil can lead to the degradation of water quality, to negative impacts on the environment and to human health impacts through the contamination of water and food. In comparison to other trace metals and metalloids, arsenic and mercury are relatively mobile in the environment. Arsenic is susceptible to leaching in soil and although its vertical movements are rather slow it is known to lead to contamination of groundwater (Meharg and Rahman, 2003).

Mercury is subject to volatilization at ambient temperatures and is hence prone to atmospheric transport and deposition. Both metal(loid)s can be redistributed by erosion and accumulated in the food chain. In a recent study, Tóth et al. (2016) studied the distribution of what they referred to as heavy metal(loid)s in agricultural soils of the European Union. They compared the concentrations of these elements observed in the LUCAS Topsoil Survey (Tóth et al., 2013) to thresholds (Table 1) suggested by the Ministry of Environment of Finland (2007). Tóth et al. (2016) found a small proportion of samples exceeded the threshold for mercury which indicated that further assessment was required (0.5 mg/kg), and attributed these values to past gold mining activities. In contrast, they found that a large proportion of samples across Europe exceeded the corresponding threshold for arsenic (5 mg/kg). They therefore urged more focussed studies of the sources and distribution of topsoil arsenic particularly in Spain, Italy and France. The analyses of Tóth et al. (2016) primarily reported the metal(loid) concentrations at the scale of the European Union (EU) NUTS2 regions (Eurostat, 2015). These are considered to be the basic regions for the application of regional policies.

Riemann et al. (In Press) suggested that the findings of Tóth et al. (2016) were rather alarmist and noted that many of the threshold exceedances were as the result of the natural background variation of geochemicals rather than contamination. The results of the GEMAS survey (Geochemical Mapping of agricultural soils; Reimann et al., 2014) indicated that the continental-scale distribution of many trace elements including arsenic (Tarvainen et al., 2013) and mercury (Ottesen et al., 2013) were clearly dominated by geology. The dominant feature in maps of both elements was the southern boundary of the former glacial cover. Larger concentrations were evident in the area including France to the south of this line. Riemann et al. (In Press) therefore questioned whether thresholds derived for Finnish soils, where lower concentrations would be expected, were appropriate for the whole of Europe. For example, the soil action level for arsenic in agricultural soil in Belgium is 45 mg/kg and in Germany the value is 50 mg/kg in soils with temporarily reducing conditions and 200 mg/kg otherwise (Tarvainen el al., 2013). Similarly, Ottesen et al. (2013) noted that the mercury action levels for sensitive land use in various countries vary between 1 and 23 mg/kg.

In an inventory of trace element inputs to French agricultural soils, Belon et al. (2012) demonstrated that arsenic inputs from agricultural activities were not negligible. The inputs of mercury from such activities were much smaller but their distribution due to mining and industrial activities and atmospheric transport and deposition required investigation. Therefore, The French Agency for Energy and Sustainable Development (Ademe), requested an assessment of the distribution of these elements in mainland France, using the soil sample archive established by the French national soil monitoring network (RMQS; Réseau de Mesures de la Qualité des Sols; Figure 1).

Since the RMQS is based on a systematic rather than probabilistic design, the set of observations of each property cannot be treated as an independent sample and it is not possible to apply classical or design-based statistical methods when analysing the data (Brus and De Gruijter, 1997). Instead, we use model-based methods, specifically geostatistics, to model the spatial correlation between observations and to account for the systematic design. Standard geostatistical models (e.g. Webster and Oliver, 2007) include various assumptions about the observed data such that it is realized from a second order stationary multivariate Gaussian random function. In general, environmental properties do not conform to these assumptions. For example, the expected values of many soil trace elements are non-stationary – they vary according to the geological setting or the rate of deposition of the elements. Also, they are prone to extreme values or hot-spots that are inconsistent with the Gaussian assumption. Therefore, we employ the trans-Gaussian linear mixed model (Diggle and Ribeiro, 2007) to relax these assumptions and to produce reliable predictions of the spatial variation of the concentrations of arsenic and mercury, to quantify the uncertainty of these predictions and to determine the probability that the concentrations at each unobserved location exceed legislative thresholds.

The linear mixed model divides the variation of the property of interest into fixed and random effects. The fixed effects consist of a linear model relating the property to environmental covariates. Knowledge of the processes controlling the spatial variation of the property can be included in the model by selecting appropriate covariates. For example, we expect that the variation of arsenic and mercury concentrations in French soils are influenced by the geological setting, inputs from anthropogenic activities such as agriculture, industry and mining and the transport and deposition of these elements from these sources. Therefore, the covariates we include, namely a classification of parent material, a classification of land use, the average annual precipitation and the average annual potential evapotranspiration reflect these processes. Having estimated our model, we use statistical diagnostics to confirm that these covariates were indeed appropriate and significantly improved the fit of the model.

Our objective is to assess how the concentrations of each element vary according to both natural factors and anthropogenic factors. In addition, we want to provide a baseline against which future phases of the RMQS can be compared and highlight regions where the threat of soil contamination should be more closely monitored.

Statistical Theory

Model-based geostatistics treats $\mathbf{z} = [z(x_1), z(x_2), \dots, z(x_n)]^{\mathrm{T}}$, the set of observations of a spatial variable made at locations x_i, as if it was realised from a random function $Z(x)$. For example, the $\mathbf{z}$ might be assumed to be realized from a linear mixed model *i.e.*:

$$\mathbf{z} = \mathbf{M}\boldsymbol{\beta} + \mathbf{r}, \tag{1}$$

where the $\mathbf{M}\boldsymbol{\beta}$ are the fixed effects and the $\mathbf{r}$ are the random or residual effects. Each column of the $n \times p$ matrix $\mathbf{M}$ contains the values of a covariate at each of the n locations and the $p \times 1$ vector $\boldsymbol{\beta}$ contains regression coefficients. Often, all of the elements of the first column of $\mathbf{M}$ are set equal to 1 so that the fixed effects include a constant. If a categorical property which classifies each location into one of c classes (e.g. parent material classes) is included in the fixed effects then $c - 1$ columns are added to $\mathbf{M}$. Each of these columns is a binary variable indicating the presence or absence of a particular class at each location. The presence or absence of the remaining class can be deduced from the presence or absence of these $c - 1$ classes. A continuous variable such as average annual precipitation can be included in a single column of $\mathbf{M}$. Thus, the fixed effects are a linear model of p covariates. The use of a linear mixed model is equivalent to the method referred to as kriging with external drift (e.g. Webster and Oliver, 2007).

The $n \times 1$ vector of random effects is realized from a multivariate Gaussian random function with mean zero and $n \times n$ covariance matrix $\mathbf{C}$. The elements of $\mathbf{C}$ are determined from an authorised variogram or covariance function $C(h)$ (Webster and Oliver, 2007) which describes how the expected squared difference between a pair of observations varies according to h, the distance separating the locations at which the observations were made. We use the nested nugget and Matérn covariance function:

$$C(h) = \begin{cases} c_0 + c_1 \text{ if } h = 0 \\ c_1 G(h) \text{ for } h > 0 \end{cases}, \tag{2}$$

where:

$$G(h) = \frac{1}{2^{\nu-1}\Gamma(\nu)}\left(\frac{2\sqrt{\nu}h}{a}\right)^{\nu} K_\nu\left(\frac{2\sqrt{\nu}h}{a}\right), \tag{3}$$

Γ is the Gamma function and K_ν is a modified Bessel function of the second kind of order ν. The random effects model parameters are c_0 the nugget, $c_1$the partial sill, a the distance parameter and ν the smoothness parameter. The inclusion of the smoothness parameter ν means that the Matérn function is flexible in terms of how $G(h)$ tends towards 1 for small h and it generalises some other commonly used covariance functions such as the exponential or Gaussian (Marchant and Lark, 2007).

Often, the assumption of Gaussian random effects is not consistent with observations of trace elements in soil because the data include extreme values which correspond to geogenic or anthropogenic hot-spots (e.g. Marchant et al., 2011a). Indeed, the RMQS observations of arsenic and mercury (Figure 2 and Table 2) were highly skewed. Such behaviour can be accommodated in the spatial model by applying a transformation to the observed data prior to estimating the linear mixed model. We apply the Box Cox transformation:

$$z_i = \begin{cases} \ln(y_i) & \text{if } \lambda = 0, \\ \dfrac{y_i^\lambda - 1}{\lambda} & \text{otherwise,} \end{cases} \tag{4}$$

where $y_i = y(x_i)$ is the observed concentration of the contaminant at location x_i, z_i is the corresponding transformed value which is assumed to be realized from the linear mixed model and λ is a parameter which gives the transformation some flexibility to ensure that the transformed values are consistent with a Gaussian distribution. Diggle and Ribeiro (2007) refer to such a model of a transformed variable as a trans-Gaussian model.

Our spatial model has p fixed effects parameters, four covariance function parameters and the Box Cox transformation parameter. Likelihood methods (Lark et al., 2006) can be used to fit all of these parameters to the observed data. A likelihood function quantifies the probability that the observed data would have been realized from a particular model with a specified set of parameters. The maximum likelihood estimator uses a numerical optimization procedure to find the set of parameter values that lead to the largest value of the likelihood.

The likelihood function can also be used to compare the suitability of different models. For example, we might wish to determine whether the inclusion of an additional covariate in the fixed effects leads to a worthwhile improvement in the fit of the model. The maximised likelihood from the extended model will be at least as large as the maximised likelihood from the original model. The Akaike Information Criterion (AIC; Akaike, 1973):

$$\text{AIC} = 2k - 2L,$$

weighs the quality of fit or maximised log-likelihood L against the complexity or number of parameters in the model k. The model with the smallest AIC is assumed to be the best compromise between quality of fit and model complexity.

For a linear mixed model, there is known to be a small bias in the maximum likelihood estimate of covariance parameters because the fixed effects parameters are treated as known rather than uncertain values. Patterson and Thompson (1971) minimized this bias by using a residual maximum likelihood (REML) estimator. The residual likelihood is not suitable for calculating the AIC.

Once the parameters have been estimated, the spatial model can be used to predict the expectation $\hat{Z}_t$ and variance $\tilde{Z}_t$ of the random function $Z(x_t)$ at any target location x_t where the fixed effect covariate information is available using the Best Linear Unbiased Predictor (BLUP). In the geostatistics literature the BLUP is often referred to as the kriging predictor (Webster and Oliver, 2007). The spatial model can be validated by omitting a set of observations from the data set and then using the remaining observations to predict the mean and variance of the random function at the locations of the omitted observations. Then diagnostics such as the standardised squared prediction error (SSPE):

$$\theta_t = \frac{\{z_t - \hat{Z}_t\}^2}{\tilde{Z}_t}, \tag{5}$$

can then be calculated at each omitted site. If the prediction errors are Gaussian then the θ will be realised from a standardised chi-squared distribution which has a mean of 1 and a median of 0.455 (Lark et al., 2006).

The Box Cox transformation must be inverted to determine the corresponding properties of the random function of the observed concentration, $Y(x_t)$. If the inverse of Eqn. (4) is applied to a set of predicted values of the expectation of $Z(x_t)$ then the median of $Y(x_t)$ results. The median of $Y(x_t)$ is not equal to the mean because the distribution of the random function is not symmetric. The predicted mean of $Y(x_t)$ can be approximated by using the predicted mean and variance of $Z(x_t)$ to simulate a large number, e.g. 1000, realisations of $z(x_t)$. Then the inverse transformation is applied to each simulated value to yield a simulated sample of $Y(x_t)$ and the mean of the random function at this site can be predicted from the mean of this sample. The probability that $Y(x_t)$ exceeds a specified threshold at the target location can be approximated by the proportion of the 1000 back transformed simulated values which are larger than these threshold.

Further details regarding the estimation of and prediction from trans-Gaussian models are given by Diggle and Ribeiro (2007). These authors also provide R software to implement these methodologies (Ribeiro and Diggle, 2001).

Methods

The French National Soil Monitoring Network (RMQS)

The baseline survey of the RMQS (Arrouays et al., 2002) was completed in 2009. It consisted of measurements of 40 properties of soil samples collected from the 2 200 nodes of a 16-km square grid which covered the 550 000 km^2 French metropolitan territory (Figure 1). When factors such as urban areas, rivers or roads prevented sampling on a particular node, a nearby (within 1 km) cultivated or undisturbed location was sampled instead. When no such location was available, the node was omitted. Such omitted nodes are evident in Figure 1; particularly in urban areas where there is little bare soil.

At each sampled node, 25 individual soil cores were extracted according to an unaligned sampling design within an area of 20×20m. Each core consisted of soil from depths of 0-30 cm. These depths correspond to the layer of soil which in France is affected by ploughing. The individual cores were bulked to form a composite sample of around 7 kg. Approximately 0.4 kg of each sample was used to determine the 40 soil properties included in the initial protocol of the survey. The remainder of each sample was stored in a purpose-built archive facility at the INRA research station in Orléans, France.

Measurement of arsenic and mercury concentrations

The arsenic and mercury concentrations were measured for each sample where sufficient soil remained. The samples were prepared according to ISO 11464 (ISO, 2006). Each sample was dried at a temperature not exceeding 40°c, and a homogenized portion was then crushed in a 2mm sieve. A portion of this prepared soil sample was milled using a planetary ball mill machine. The subsample was then sieved to 250 µm. Arsenic and Mercury were determined on this milled subsample.

Arsenic was determined after mineralization with a mixture of hydrofluoric acid and perchloric acid, according to ISO 14869-1 (ISO, 2001). The mineralized solution was then analysed by mass spectrometry coupled to argon induced plasma, using hydrogen/helium collision cell technology to overcome interferences at mass 75. Dosages are performed on a Thermoscientific X series 2 ICPMS.

Mercury was analysed directly on the solid subsample, without preliminary mineralization, by a dry combustion method under oxygen flow (AMA 254 Mercury Analyser). After the drying and decomposition steps, the volatilized mercury was trapped and concentrated by a gold-based amalgam. The latter was then briefly heated to a high temperature to release the mercury for measurement by atomic absorption spectrometry. The test samples were between 20 and 200 mg depending on the mercury content of milled soil subsample.

The quantification limits were 0.0025 mg/kg for mercury and 0.1 mg/kg for Arsenic. The INRA soil analysis laboratory is accredited by COFRAC (the French accreditation committee) according to ISO 17025 (ISO, 2005).

Statistical Analyses

Trans-Gaussian linear mixed models were estimated for the spatial variation of arsenic and mercury across mainland France. We hypothesised that the local geology, land use and the rate of deposition were likely to be primary drivers of the variation in the concentrations of both elements. Therefore, we considered including a parent material classification, a land use or land cover classification and average annual precipitation as covariates in the fixed effects. Mean annual potential evapotranspiration was also considered since mercury is known to be particularly sensitive to volatilisation and strong evapotranspiration could reflect large mercury fluxes between the soil and atmosphere. The parent material and land cover classifications were categorical variables with nine and six classes respectively. Therefore, the inclusion of these covariates required a further 14 regression coefficients beyond the constant mean parameter which was also included. For each element, we used the maximum likelihood estimator to calibrate the 16 linear mixed models corresponding to the possible combinations of inclusion/exclusion of each of these four groups of covariates. The AIC was used to select the most parsimonious model. The most appropriate model for each element was then refitted using the REML estimator.

Leave-one-out cross-validation was performed for each fitted model and the resultant mean and median SSPEs were compared to their theoretical values. The REML estimated models and the BLUP were used to predict the concentrations of arsenic and mercury at each node of a 2-km square grid which covered mainland French. The probability that the concentration of these elements exceeded the thresholds proposed by the Ministry of Environment of Finland (2007) were also established. The three classes of threshold for each element are shown in Table 1. The 'threshold value' indicates the need for further assessment of the area. The 'guideline values' indicate concentrations which present ecological or health risks. The higher guideline value applies at industrial and transport sites whereas the lower guideline value applies elsewhere.

Covariate Information

The covariates considered for the fixed effects models are plotted in Figure 3 with a resolution of 1 km. The soil parent material information was extracted from the 1:1 000 000 scale soil database of Europe (King et al., 1995). The classes in this database were merged into the nine classes shown in Figure 3a. The land cover map was derived from the level three codes of the 2006 Corine land cover map (European Environment Agency, 2010). These codes were amalgamated into six classes as follows: 211-213 and 241-244 cropland; 231 grassland; 311-313 forest; 221-223 vineyard and orchard; 111-142 urban and 321-523 other. These broader classes reflected the variation in the natural content of geochemical trace elements (Atteia et al., 1994; Atteia et al., 1995; Baize, 1997; Baize, 2007; Baize, 2009). The average annual precipitation was extracted from the WorldClim dataset (http://www.worldclim.org/) and the average annual potential evapotranspiration was extracted from the SAFRAN database (Quintana-Segui et al., 2008; http://www.cnrm.meteo.fr/spip.php?article424).

Results

For arsenic, the best fitting model according to the AIC included parent material, land cover class, mean annual precipitation and mean annual evapotranspiration in the fixed effects (Table 3). The best fitting model for mercury included parent material, land cover class and mean annual precipitation in the fixed effects (Table 4). The inclusion of the parent material, land cover and precipitation covariates is consistent with our belief that there are both natural and anthropogenic sources of these elements and that they are subject to transport and deposition. We expected that the mean annual evapotranspiration was more like to be a driver of mercury variation than arsenic variation since mercury is more sensitive to volatilisation. The exclusion of the evapotranspiration term from the fixed effects of the mercury model possibly reflects that other confounding factors are concealing the effect of mercury volatilisation.

For both elements, the mean standardised squared prediction errors upon cross-validation were close to the theoretical value of 1.00. The median of the standardised squared prediction errors for the best fitting arsenic model was 0.36 and the corresponding value for mercury was 0.31. These values are reasonably close to the theoretical value of 0.45 and it appears that the models adequately fit the data.

The variograms (Figure 4) for both elements have a substantial nugget component of around 50% of the residual variance. The variograms differ in the effective range of spatial correlation. The effective range is defined as the lag distance at which the spatially correlated component of the variogram is equal to 95% of its sill variance. The arsenic variogram has an effective range of 238 km whereas the mercury one has an effective range of 466 km. This leads to the map of estimated arsenic concentrations having more localised hot-spots whereas regions of high mercury concentrations are more diffuse (Figures 5 and 6). The probabilities of the concentrations exceeding the Ministry of Environment of Finland thresholds are shown in Figure 7. In common with the results of the LUCAS Topsoil Survey (Tóth, 2016), the concentrations of arsenic were considerably more likely to exceed the threshold value than those of mercury. For much of France the probability of arsenic exceeding 5 mg/kg is greater than 0.9. The probability is slightly lower in the north of France and there are regions in the south west and central France where the probability is close to zero. Generally, the probability that the arsenic guideline values are exceeded (Figures 7c and 7d) are small except for relatively isolated hot-spots. The probability of the mercury concentration exceeding its threshold value is small across France only reaching 0.01 in hot-spots around Paris, along the border with Spain and in the north east of the country. The probabilities of exceeding the mercury guideline values (not shown) are negligible throughout France.

Discussion

The geographical regions and physical features of France referred to in this Discussion are shown in Figure 8.

Comparison with other surveys

The RMQS, LUCAS Topsoil and GEMAS surveys differ in terms of their site sampling protocol and the analytical methods used to determine arsenic and mercury concentrations. The LUCAS Topsoil survey is restricted to agricultural soils and the GEMAS survey is restricted to agricultural and grazing land (which are considered separately). The LUCAS Topsoil samples contain the top 20 cm of soil and are extracted from five points on a 4m × 4m cross. The GEMAS samples are down to 20 cm for agricultural land and 10 cm for grazing land and are the combination of five cores separated by about 10 m. The LUCAS Topsoil survey has an average sampling density of 1 site/ 200 km^2, each land use class in the GEMAS survey is sampled at a rate of 1 site/ 2500 km^2 whereas the 16 km grid of the RMQS corresponds to a rate of approximately 1 site/250 km^2. The analytical methods for LUCAS Topsoil and GEMAS were based on aqua regia extraction rather than the hydrofluoric acid extraction used by RMQS. Aqua Regia is known not to extract the total amount of metalloids especially those included in very resistant minerals. Therefore, we might have expected slightly higher concentrations in the RMQS survey. However, the shallower sampling depth of the LUCAS Topsoil and GEMAS surveys could be expected to lead to larger concentrations of mercury in regions where it has been deposited in the soil surface. The larger spatial support of the RMQS samples might lead to fewer extreme observations since very localised hot-spots will be more diluted.

The results of all three surveys indicate that for the majority of France there is a substantial probability that the Ministry of Environment of Finland (2007) threshold value for arsenic is exceeded. At the scale of the NUTS2 regions of the EU, between 30 and 90 % of the LUCAS Topsoil samples from each region exceed this threshold. Our analyses (Figure 7a) indicate that for RMQS samples the probabilities of exceedance are comparable and greater than 0.9 for a substantial portion of the country. There are also clearly discernible areas in Figure 7a where the probability is close to zero. These areas are not evident in the LUCAS Topsoil survey reporting at the NUTS2 scale. The results of Tóth et al. (2016) indicate that the proportion of LUCAS topsoil samples exceeding either the lower or upper guideline values for arsenic is less than 10 % in all of the NUTS2 regions. The RMQS results (Figures 7c and 7d) are consistent with these findings although more localised areas are evident where the probability of exceedance is up to 0.5.

The map of soil arsenic concentrations in Figure 6a is broadly similar to those derived by Tarvainen et al. (2013). Tarvainen et al. (2013) list 53 arsenic anomalies across Europe, eight of which occur in France. The French anomalies are primarily attributed to geology and mineralisation although mining activities within the Massif Central and the use of pesticides to the south west of this region are also cited. All of these anomalies are evident in Figure 6a apart from those associated with pesticides which we discuss in the next section.

The mean and median observed concentrations of topsoil arsenic in France of approximately 12 and 18 mg/kg respectively (Table 2) are slightly smaller than the corresponding values of 15 and 20 and mg/kg recorded in England and Wales (Rawlins et al., 2012) but larger than the median figure of 8 mg/kg reported by Reimann et al. (In Press) for the south of Europe. Although the results of our analysis do indicate that, according to the Finnish threshold, further monitoring of topsoil arsenic concentrations is required, it should be noted that that the largest RMQS measurements are substantially less than those recorded at severely impacted sites such as former industrial areas in the UK (Marchant et al. 2011b) and agricultural land neighboring industrial areas in China (Liao et al., 2005) or in Bangladesh paddy soils where arsenic in groundwater used for irrigation contains large amounts of arsenic (Meharg and Rahman, 2003).

The results of the LUCAS Topsoil and RMQS surveys agree that the probability that the soil mercury concentration exceeds its threshold value is less than 0.1 across France. Tóth et al. (2016) do state that “some soil samples with Hg above the higher guideline value (5 mg/kg) were still found on agricultural land of France, Germany, Italy and Spain”. Such concentrations are substantially larger than 1.37 mg/kg, the maximum value recorded in the RMQS. Such large values were not readily apparent in the pictorial representations of the LUCAS Topsoil data in Tóth et al. (2016) where (in agreement with Figure 6b) the mercury concentrations appear to be mostly in the range of 0.02-0.3 mg/kg. Therefore, these extreme values can be interpreted as localised outliers, perhaps caused by localised soil contamination within the smaller spatial support of the LUCAS Topsoil samples. Ottesen et al. (2013), reported that only 15 of the 4000 GEMAS samples returned mercury concentrations greater than 1 mg/kg. They identified three mercury anomalies in France, namely contamination from Paris, possible contamination from WW1 battlefields in Verdun and mineralisation or contamination in the Vosges. The Paris and Vosges anomalies are evident in Figure 6b. The Verdun anomaly appears to be more localised although one elevated concentration in the region is evident in Figure 1 (right). The RMQS median mercury concentration of 0.04 mg/kg is similar to the corresponding GEMAS values for French agricultural and grassland displayed in Figure 4 of Ottesen et al. (2013). The Ottesen et al. (2013) maps of mercury concentrations across France are broadly similar to Figure 6b although our results do appear to have a finer spatial resolution reflecting the larger sampling density.

The spatial variation of topsoil arsenic concentrations across France

In Figures 5a and 6a we see that particularly small concentrations of topsoil arsenic are predicted in sandy acidic soils such as in Landes, Sologne and North of the Vosges. These soils are developed on deposits mainly composed of quartz, and the low concentrations result from very low geogenic arsenic contents and very low adsorption capacities of the soils. There are also rather low concentrations in the Paris Basin and more generally on the north-western part of France which is characterized by the presence of quaternary eolian deposits (Arrouays et al., 2011). On a continental scale, Tóth et al. (2016) found that areas of quaternary origin in the north of Europe have substantially lower topsoil arsenic concentrations than most other regions. Moreover, most of these soils developed on these deposits are luvisols characterized by a strong impoverishment of the topsoil in clay and iron oxides. Shallow soils developed on chalk (Charentes, Champagne) also exhibit rather low arsenic concentrations which might be attributable to the effects of high soil pH on arsenic adsorption (Ghosh et al, 2006).

There are some localized arsenic hotspots (Vosges, Limousin, Cévennes, and borders of the Massif Central). Previously, Bossya et al. (2012) commented on arsenic contamination within the Massif Central. Some of these hotspots are correlated with well-known mining areas (e.g. the Limousin and the Cévennes) and they are all places of intense geochemical mineralization. Since the majority of the topsoil arsenic is contained in such hotspots there is a danger that the 16 km grid of the RMQS is too coarse to fully capture the distribution of arsenic across France and some features might be missed. For example, we observe quite large arsenic concentrations attributable to metallurgy and coal mining in the north east (Lorraine) but we do not see the equivalent pattern in the north of France, which has the same industrial history. Also, arsenic contamination might be expected in the wine growing regions due to historic use of pesticides containing lead and arsenic. This pollution is not evident in the predicted maps and might have been diluted by deep ploughing in the vineyards.

The spatial variation of topsoil mercury concentrations

There appear to be various natural and anthropogenic sources of mercury. The predicted maps (Figures 5b and 6b) contain evidence of various geogenic effects linked to volcanic materials (centre of the Massif Central) and some natural mineralizations in mountainous regions (Pyrénées, Jura, Vosges, northern Alps and Massif Central). This effect may be amplified by the high levels of carbon in these areas because mercury is strongly bound to organic matter (Ottesen et al., 2013; Wang et al., 2015). Indeed, in Figure 9 we see that the lower bound on the mercury concentration within RMQS samples does appear to increase with the concentration of soil organic carbon. These carbon effects could also be leading to relatively high mercury concentrations in Brittany and Normandy for instance.

There is a clear mercury contamination around Paris, that could be due to industrial smelting and use of metals, waste burning, coal combustion for heating, and organic waste disposal on soil. One hot spot in the north west of Paris almost exactly corresponds to the location of the biggest waste water treatment plant in Europe and the second largest in the world. We might suspect that at this site there has been a long history of organic waste spreading on the surrounding soils and that historically the mercury contents in these wastes were not as well controlled as they are now (Journal Officiel, 1980). There is also a smooth gradient of mercury towards the north and north-east which is consistent with mercury transport by prevailing winds followed by re-deposition. This transported mercury may directly come from historical industrial emissions or from volatilization from soils surrounding old industries or having received contaminated urban sludge. Also, in the extreme north of France, there is contamination that is attributable to the metallurgic industry. Previous studies (e.g. Saby et al., 2011) have shown this region to be contaminated by cadmium, lead and zinc and the residuals of coal burning. Finally, some hotspots of mercury in the Massif Central region correspond to historical mining for gold.

Conclusions

National-scale soil monitoring networks are required to determined where soil functionality is threatened and remediation or changes in land management practices might be required. It is not always possible to anticipate the soil indicators that will be of interest to land managers and policy makers. There are many threats to soil functionality such as erosion, decline in organic matter, decline in biodiversity, contamination, sealing, landslides, salinization and compaction and the priorities of stakeholders might change over time. Therefore, it is vital that soil samples are archived so that different properties can be measured in the future. The RMQS archived a portion of soil from each of the 2200 sites. This permitted us to measure the concentration of arsenic and mercury in these samples, to determine the average concentrations of each element across France and to map their spatial variation. Using linear mixed models and expert interpretation, we were able to identify different origins of these metal(loid)s. Such relationships could not have been so easily discerned had the modelling been restricted to a larger scale such as the EU NUTS2 regions. Arsenic came principally from geogenic sources linked both to broad categories of soil parent material and to more located mineralization sources or mining activities. Mercury exhibited gradients linked to human sources of diffuse contamination in addition to the effects of natural mineralization and mining. Future phases of the RMQS will be compared to these baselines to determine whether and where the concentrations of these toxic elements are increasing in French topsoils.

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Figures

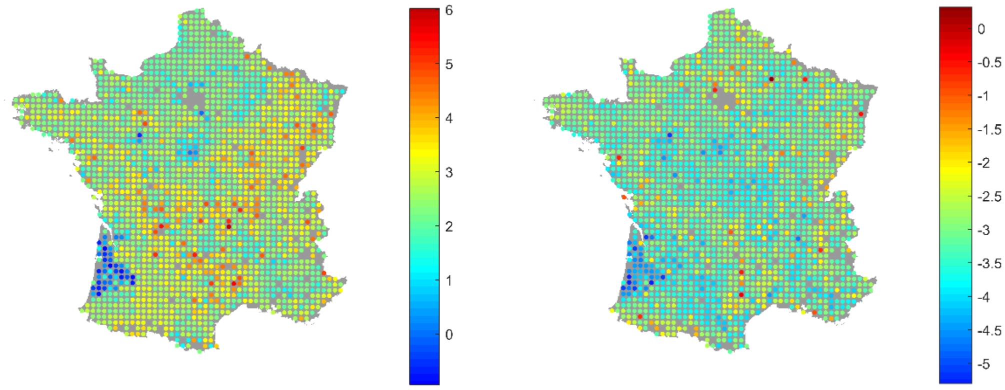

Figure 1: (Left) Observed values of the natural logarithm of the arsenic concentration (log mg/kg) and (right) observed values of the natural logarithm of the mercury concentration (log mg/kg) superimposed on the prediction grid with spacing 2 km (grey).

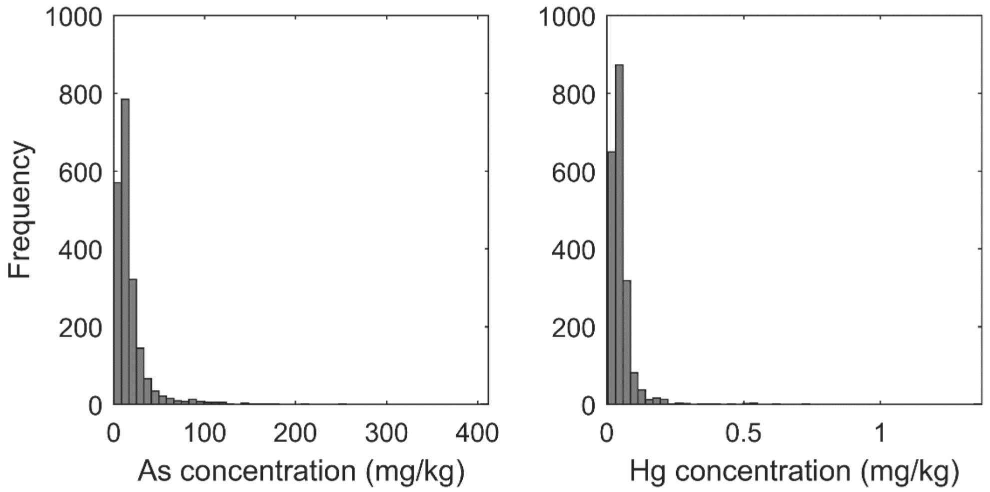

Figure 2: (left) Histogram of observed arsenic concentrations (mg/kg); (right) histogram of observed mercury concentrations (mg/kg).

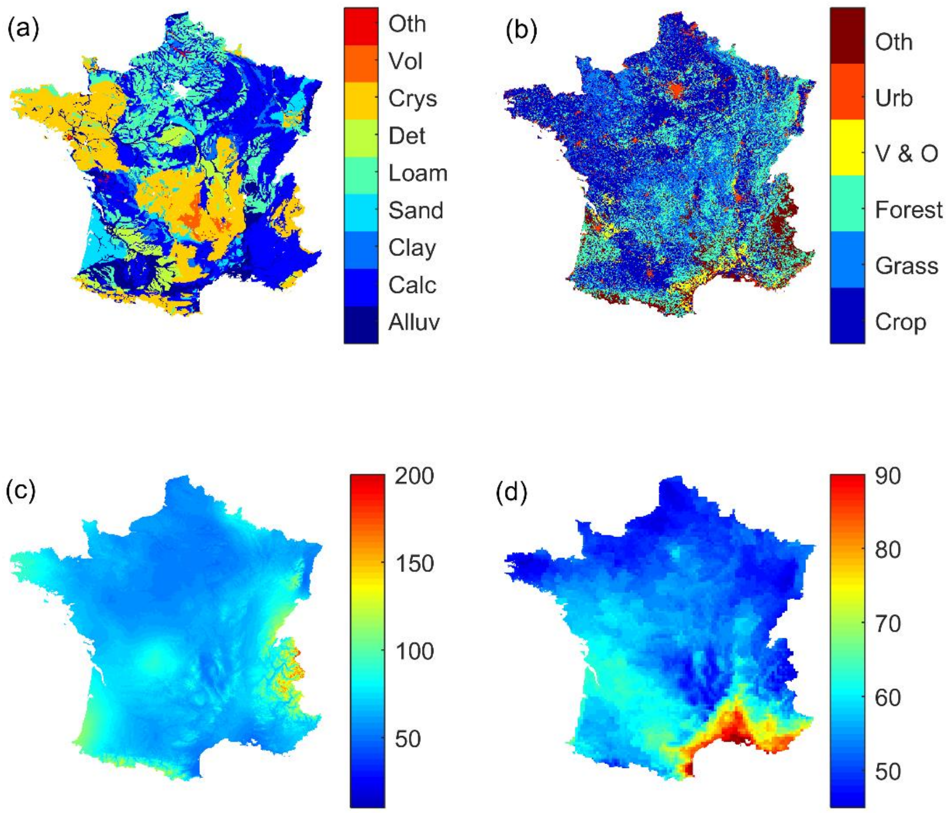

Figure 3: The spatial covariates included in the linear mixed model. (a) Parent material classes: “undifferentiated alluvial deposits or glacial deposits” (alluv); “calcareous rocks” (calc); “Clayey materials” (clay); “sandy materials” (sand); “loamy materials” (loam); “detrital formations” (det); “crystalline rocks and migmatites” (crys); “volcanic rocks” (vol) and “other rocks” (oth). (b) Land cover classes derived from the 2006 Corine land cover map: “cropland” (crop); “grassland” (grass); “forest” (forest); “vineyards and orchards” (V & O); “urban” (urb); “other” (oth). (c) Average annual precipitation (cm/year). (d) average annual potential evapotranspiration (cm/year).

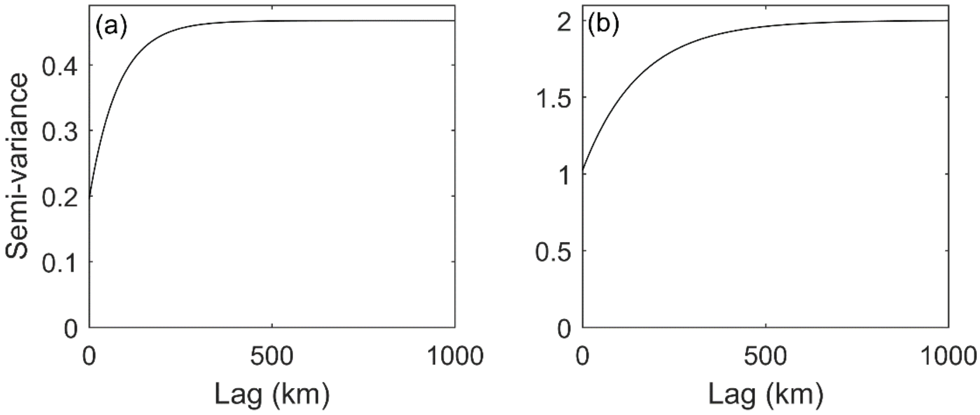

Figure 4: (a) estimated variogram of random effects from the linear mixed model of transformed arsenic concentrations; (b) estimated variogram of random effects from the linear mixed model of transformed mercury concentrations.

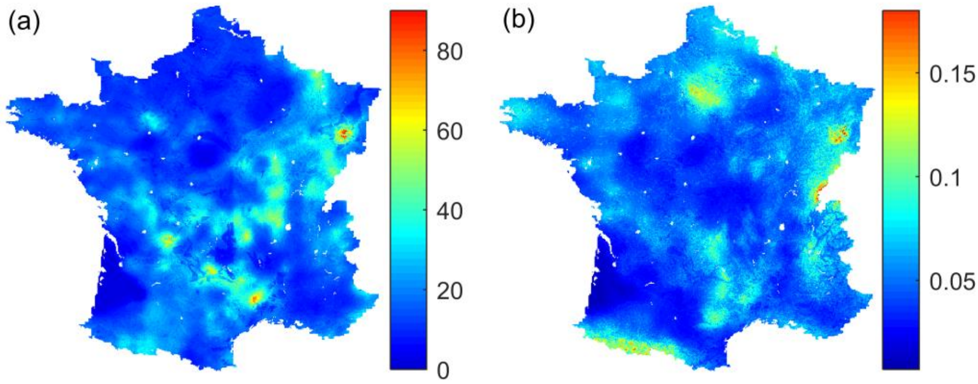

Figure 5: (a) predicted map of expected arsenic concentrations; (b) predicted map of expected mercury concentrations.

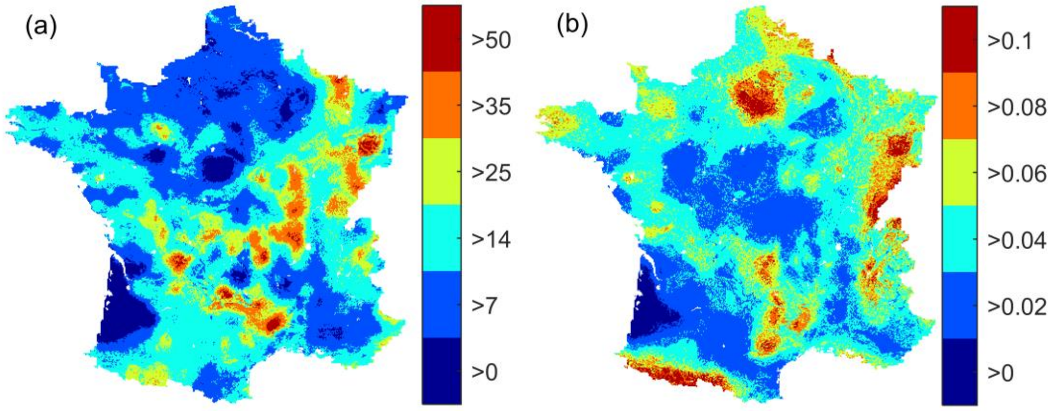

Figure 6: (a) categorical predicted map of expected arsenic concentrations (mg/kg); (b) categorical predicted map of expected mercury concentrations (mg/kg).

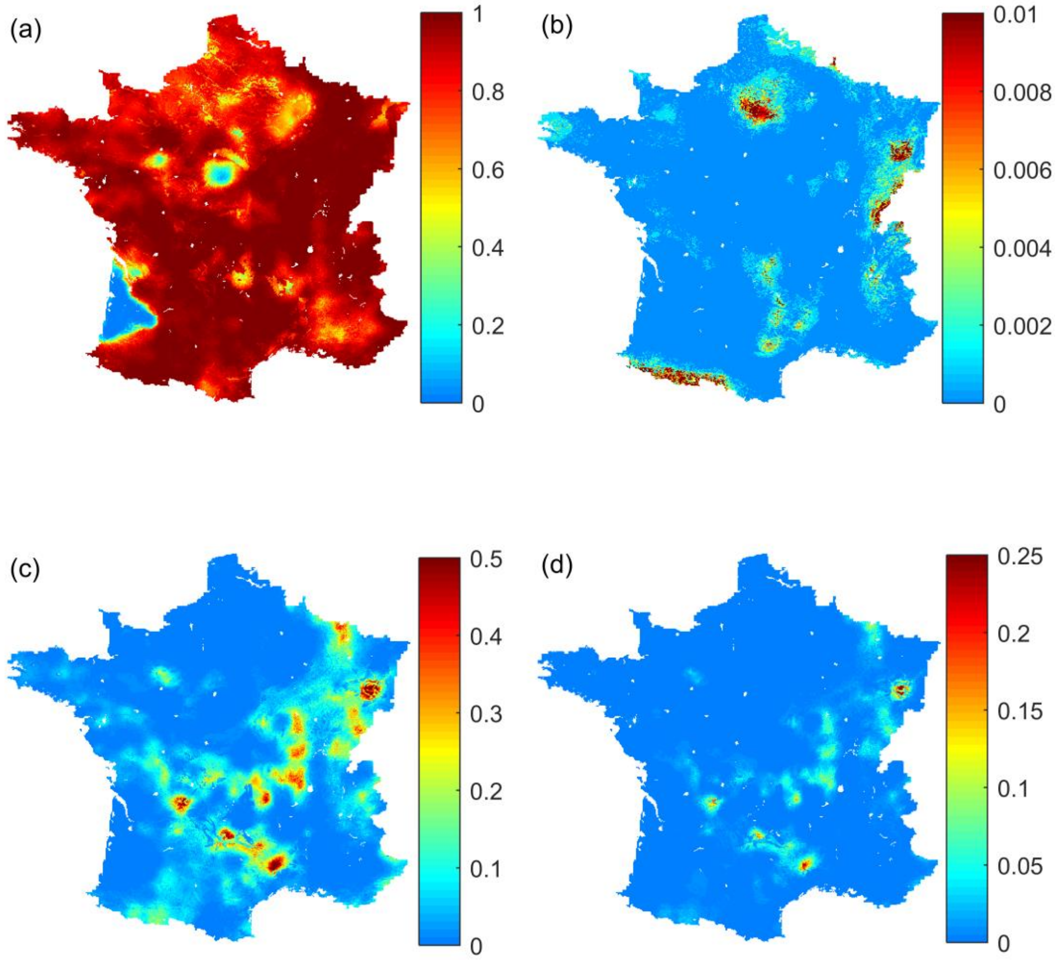

Figure 7: Predicted probabilities of exceedance of the Ministry of Environment of Finland (2007) threshold and guidance values for metal/metalloids in soil. (a) arsenic concentration exceeding the threshold value of 2 mg/kg; (b) mercury exceeding the threshold value of 0.5 mg/kg; (c) arsenic exceeding the lower guideline value of 50 mg/kg; (d) arsenic exceeding the higher guideline value of 100 mg/kg.

Figure 8: Relevant physical and geographical features in France.

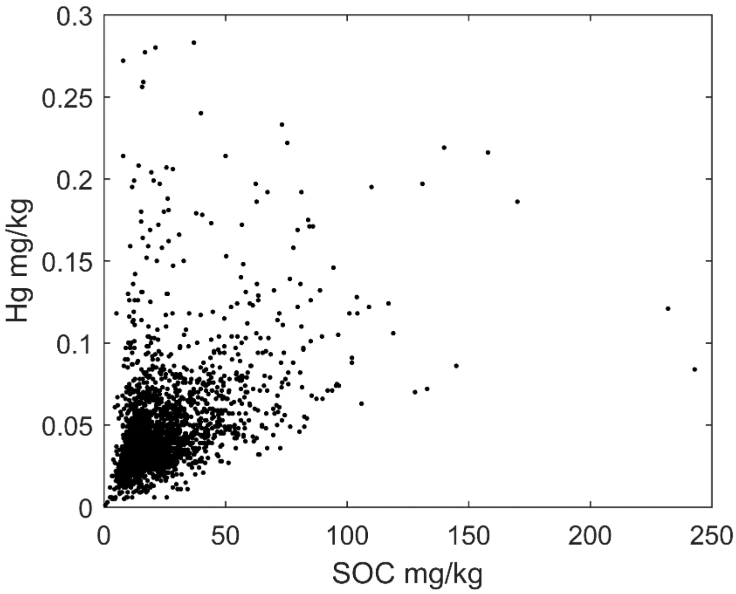

Figure 9: Relationship between soil organic carbon and mercury concentrations (mg/kg) for RMQS samples with mercury concentration less than 0.3 mg/kg.

Tables

Element	Threshold mg/kg	Lower guideline mg/kg	Higher guideline mg/kg
Arsenic	5	50	100
Mercury	0.5	2	5

Table 1: Ministry of Environment of Finland (2007) threshold and guideline concentrations for arsenic and mercury in soils.

Element	*n*	Mean mg/kg	Median mg/kg	Min mg/kg	Max mg/kg	Skewness
Arsenic	2017	17.93	12.20	0.39	412.00	6.42
Mercury	2017	0.052	0.041	0.005	1.370	10.55

Table 2: Number of observations, *n*, and summary statistics for arsenic and mercury concentrations in the RMQS survey.

Covariates	-L	No. of parameters	AIC	Mean (SSPE)	Median (SSPE)
c	0	6	12	1.00	0.32
c, pm	-29.9	14	-31.8	1.01	0.31
c, lu	-16.9	11	-11.7	1.00	0.30
c, pr	0.0	7	14.0	1.00	0.32
c, evt	-1.7	7	10.5	1.00	0.32
c, pm, lu	-44.1	19	-50.2	1.01	0.30
c, pm, pr	-30.0	15	-30.0	1.01	0.31
c, pm, evt	-31.1	15	-32.2	1.01	0.31
c, lu, pr	-17.6	12	-11.26	1.00	0.30
c, lu, evt	-17.6	12	-11.26	1.00	0.31
c, pr, evt	-1.9	8	12.2	1.00	0.32
c, pm, lu, pr	-45.3	20	-50.6	1.01	0.31
c, pm, lu, evt	-44.7	20	-49.3	1.01	0.30
c, pm, pr, evt	-31.6	16	-31.1	1.01	0.31
c, lu, pr, evt	-19.2	13	-12.4	1.00	0.30
c, pm, lu, pr, evt	**-46.7**	**21**	**-51.3**	**1.01**	**0.31**

Table 3: Statistics for estimated linear mixed models of arsenic. Covariates are constant (lu), parent material (pm), land use (lu), precipitation (pr), potential evapotranspiration (evt). Best fitting model is shown in bold. A constant has been added to the log-likelihood values such that the constant model has zero log-likelihood.

Covariates	-L	No. of parameters	AIC	Mean (SSPE)	Median (SSPE)
c	0	6	12.0	1.00	0.36
c, pm	-10.7	14	6.7	1.01	0.38
c, lu	-38.1	11	-54.1	1.00	0.36
c, pr	-11.6	7	-9.1	1.00	0.37
c, evt	-4.0	7	6.0	1.00	0.36
c, pm, lu	-50.4	19	--62.7	1.01	0.37
c, pm, pr	-20.9	15	-11.8	1.01	0.38
c, pm, evt	-13.6	15	2.8	1.01	0.38
c, lu, pr	-51.0	12	-78.0	1.01	0.36
c, lu, evt	-41.9	12	-59.7	1.01	0.36
c, pr, evt	-12.0	8	-8.1	1.00	0.37
c, pm, lu, pr	**-62.1**	**20**	**-84.3**	**1.01**	**0.36**
c, pm, lu, evt	-53.2	20	-66.5	1.01	0.36
c, pm, pr, evt	-21.3	16	-10.5	0.97	0.34
c, lu, pr, evt	-51.3	13	-76.6	1.01	0.35
c, pm, lu, pr, evt	-62.4	21	-82.8	1.01	0.36

Table 4: Statistics for estimated linear mixed models of mercury. Covariates are constant (c), parent material (pm), land use (lu), precipitation (pr), potential evapotranspiration (evt). Best fitting model is shown in bold. A constant has been added to the log-likelihood values such that the constant model has zero log-likelihood.