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# A survey of topsoil arsenic and mercury concentrations across France

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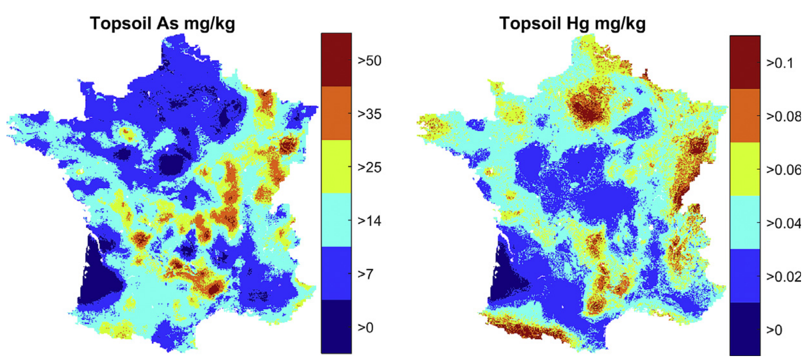
## HIGHLIGHTS

- Arsenic and Mercury are toxic elements that impact human health and the environment.
- We determine arsenic and mercury concentrations in over 2000 regularly spaced samples of French soil.
- Arsenic concentrations generally indicate that further investigation is required but do not exceed action levels.
- Mercury concentrations generally do not require further investigation.
- Both elements exhibit hot-spots caused by both geogenic and anthropogenic processes.

## GRAPHICAL ABSTRACT

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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

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phases of the RMQS can be compared and highlight regions where the threat of soil contamination and its impacts should be more closely monitored.



## 1. 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 volatilisation 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.

Reimann et al. (2016) 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. Reimann et al. (2016) 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 et 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.

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

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

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; Fig. 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

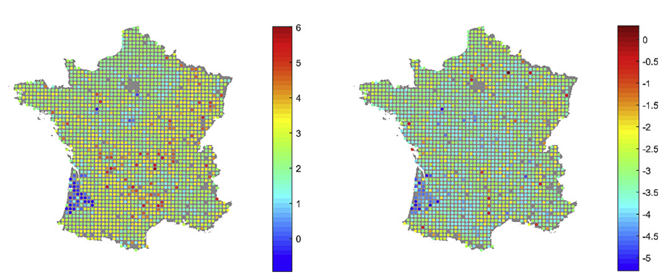


**Fig. 1.** (Left) Observed values of the natural logarithm of the arsenic concentration (log mg/kg) and (right) observed values of the natural logarithm of the mercury concentration (log mg/kg) superimposed on the prediction grid with spacing 2 km (grey).