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Spatial assessment of topsoil zinc concentrations in Europe

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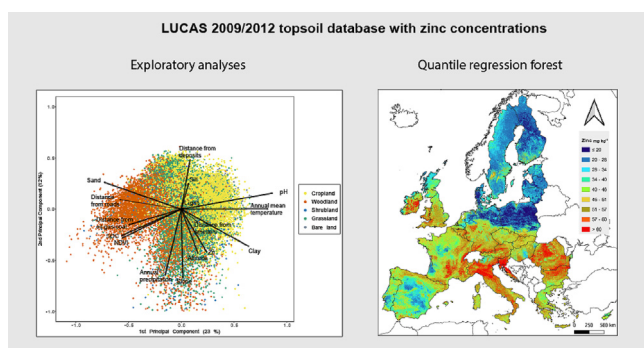
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HIGHLIGHTS

- A high resolution spatial assessment of topsoil Zn concentrations in Europe
- Mean Zn concentration in Europe is 47 mg kg⁻¹.
- One percent of all samples had concentrations above 167 mg kg⁻¹.
- Soil texture and pH are most important drivers for the variation in topsoil Zn.
- Highest Zn concentrations are found near Zn deposits, and in grasslands.

GRAPHICAL ABSTRACT



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ABSTRACT

Zinc (Zn) is essential to sustain crop production and human health, while it can be toxic when present in excess. In this manuscript, we applied a machine learning model on 21,682 soil samples from the Land Use and Coverage Area frame Survey (LUCAS) topsoil database of 2009/2012 to assess the spatial distribution in Europe of topsoil Zn concentrations measured by aqua regia extraction, and to identify the influence of natural drivers and anthropogenic sources on topsoil Zn concentrations. As a result, a map was produced showing topsoil Zn concentrations in Europe at a resolution of 250 m. The mean predicted Zn concentration in Europe was 41 mg kg⁻¹, with a root mean squared error of around 40 mg kg⁻¹ calculated for independent soil samples. We identified clay content as the most important factor explaining the overall distribution of soil Zn in Europe, with lower Zn concentrations in coarser soils. Next to texture, low Zn concentrations were found in soils with low pH (e.g. Podzols), as well as in soils with pH above 8 (i.e., Calcisols). The presence of deposits and mining activities mainly explained the occurrence of relatively high Zn concentrations above 167 mg kg⁻¹ (the one percentile highest concentrations) within 10 km from these sites. In addition, the relatively higher Zn levels found in grasslands in regions with high livestock density may point to manure as a significant source of Zn in these soils.

The map developed in this study can be used as a reference to assess the eco-toxicological risks associated with soil Zn concentrations in Europe and areas with Zn deficiency. In addition, it can provide a baseline for future policies in the context of pollution, soil health, human health, and crop nutrition.

1. Introduction

Zinc (Zn) plays a crucial role in various biological processes and is subsequently an essential micronutrient for living beings (Broadley et al., 2012; Brown et al., 1993; Wessells et al., 2012). Zinc can also be toxic

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when present in excess (Giller et al., 1998; Tyler et al., 1989). As a result, too low or too high soil Zn concentrations negatively affect soil functions and may harm animal and human health.

Zinc is ubiquitous in the environment and makes up 0.02 % by weight of the Earth's crust (Simon-Hettich et al., 2001; Wolf et al., 2022) with an estimated average concentration of 75 mg kg⁻¹ in the upper continental crust (Hu and Gao, 2008). In Europe, background levels of pseudo-total (Rodrigues et al., 2010) Zn concentrations in the topsoils have been reported to be around 45–50 mg kg⁻¹ (De Vos et al., 2006; Reimann et al., 2018). However, these concentrations can vary by more than a factor of 1000 (De Vos et al., 2006; Reimann et al., 2018) due to differences in parent material (De Vos et al., 2005, 2006) or due to anthropogenic inputs (Han et al., 2002; Keller and Schulin, 2003; Stemweis et al., 1988).

Parent material and geological features largely determine topsoil Zn concentrations (Alloway, 2008; Cicchella et al., 2015). Basic igneous rocks contain up to 240 mg kg⁻¹ Zn, generally higher than silica-rich igneous rocks that contain up to 140 mg kg⁻¹ (Nagajyoti et al., 2010). The Zn concentration in sedimentary rocks can range between 20 and 200 mg kg⁻¹, with the highest Zn concentrations in clays and shales (Alloway, 2008; Mertens and Smolders, 2013). At the local scale, relatively higher Zn concentrations can be found in Europe due to the presence of geological deposits rich in Zn, for example, in Ireland, Poland, Sardinia, Portugal, and Spain (Salminen et al., 2005).

From the late 19th century until now, Zn production has increased by a factor of 60 (Han et al., 2002). Zinc is a widely used metal, mainly for galvanizing steel products, brass products, or die casting (Graedel et al., 2005). The extraction and production of Zn are responsible for the largest amounts of Zn emissions into the atmosphere and its subsequent deposition to soils, followed by waste incineration and fossil fuel combustion (Stemweis et al., 1988). In addition, Zn originating from manufactured products can give rise to locally elevated concentrations. For example, corrosion of galvanized structures can result in elevated Zn concentrations in the soils underneath (Bertling et al., 2006). Zinc as part of the particulate matter emitted by brake linings or tyres was found to be responsible for increased Zn concentrations nearby traffic roads or in urban areas with dense road systems (Hjortenkrans et al., 2007; Yesilonis et al., 2008).

Agricultural inputs (e.g., mineral fertilizers, manure) can introduce unintended amounts of Zn. For example, mineral fertilizers containing trace elements introduce Zn in soils when applied to agricultural fields (Nziguheba and Smolders, 2008). Similarly, organic fertilizers such as sewage sludge or manure may contain significant amounts of Zn due to feed additives (Mantovi et al., 2003a).

The Zn inputs as mentioned above have led to soil contamination across Europe, as reported by several studies (Degryse et al., 2004, 2011; Douay et al., 2008; Kabala et al., 2020; Steinnes et al., 1997; Steinnes and Friedland, 2006). On the other hand, too low levels of Zn in European soils can limit crop production and lead to decreased crop nutritional quality (Sinclair and Edwards, 2008). Compared to Zn contamination and toxicity, less information is available about the occurrence of Zn deficiencies for crops and livestock in Europe and the potential implication for human health due to the associated lower nutritional quality (Moreno-Jiménez et al., 2022; Watson et al., 2012). One recent report states that micronutrient fertilizer use is growing in Europe, especially for elements like Zn (Global Monitor, 2020). It is unclear whether this is economically driven due to increased marketing of specialty fertilizers or whether this is the result of more knowledge, the application of precision agriculture, or an increased incidence of micronutrient deficiencies for crop production in Europe.

Soil mapping of geochemical properties is highly valuable for identifying geographical areas with potential environmental or health risks due to Zn contamination or deficiencies. Great efforts have been made to collect soil samples across Europe to establish soil databases, including Zn concentrations (Reimann et al., 2014a; Salminen et al., 2005). The Forum of European Geological Surveys (FOREGS) database consists of 1588 topsoil samples collected by geological surveys and related institutions from 26 Member States between 1998 and 2003 across Europe, including all land uses (Salminen et al., 2005). These data were used to map the distribution

of Zn in European topsoils by kriging (De Vos et al., 2006) and regression-kriging interpolation techniques (Lado et al., 2008). Based on the latter, Lado et al. (2008) found higher Zn concentrations in regions with increased urbanization approximated by the light intensity at night. Next to the FOREGS database, the Geochemical Mapping of Agricultural Soils (GEMAS) database consists of 4042 topsoil samples from 2008 to 2009 in agricultural and grazing fields across 33 European countries (Reimann et al., 2018). Point measurements were spatially interpolated to produce a map of Europe showing topsoil Zn concentrations (Reimann et al., 2014b). The authors concluded that parent material mainly explained Zn concentrations in agricultural soils and that anthropogenic inputs explained soil Zn concentrations in Central Europe to a minor extent. Our study builds on this work by using the more recent and more extensive 'Land Use and Coverage Area frame Survey' (LUCAS) topsoil database from 2009/2012 with Zn concentrations for almost 22,000 soil samples across Europe (Ballabio et al., 2018, 2021; Orgiazzi et al., 2018). Compared to FOREGS and GEMAS, LUCAS contains ten times more soil samples distributed over a larger variety of land uses, with detailed descriptions and analyses of various soil properties (Orgiazzi et al., 2018). We used LUCAS soil data to map topsoil Zn concentrations with machine learning algorithms. By doing so, we aimed (1) to gain better insights into the distribution of topsoil Zn concentrations in Europe, (2) to produce a map of topsoil Zn concentrations with higher resolution (i.e., 250 m) than previous products, (3) to quantify the influence of natural properties and anthropogenic sources on topsoil Zn concentrations and, (4) to discuss the risk of toxicities and deficiencies of topsoil Zn concentrations.

2. Material and methods

LUCAS topsoil 2009/2012 database was used for data analyses. All the data analyses were done in R software, version 4.2.1 (R Core Team and R Development Core Team, 2022) using Rstudio (RStudio Team, 2022), except for creating distance rasters for which we used using ArcGIS Pro (Esri, 2022). The specific packages and functions used for each of the analysis are mentioned further down in the text.

2.1. LUCAS soil samples

The LUCAS soil is part of the EUROSTAT LUCAS program and has resulted Europe's largest harmonized topsoil database (Orgiazzi et al., 2018). The 2009/2012 LUCAS topsoil database consists of 21,682 soil samples distributed over 27 European countries that have been analyzed for various physicochemical soil properties (Ballabio et al., 2016, 2019), including the concentrations of trace elements such as Zn (Orgiazzi et al., 2018; Tóth et al., 2016). The LUCAS 2009/2012 topsoil database consists of topsoil samples (0–20 cm) mainly taken in croplands and grasslands but also covering shrublands, woodlands, artificial land, wetlands, water areas, and bare lands (Eurostat, 2015; Tóth et al., 2013). The high number of soil samples that cover all the different land use classes differentiates the LUCAS topsoil database from previous European-scale soil information about trace elements (Imrie et al., 2008; Reimann et al., 2018).

The Zn concentrations in the LUCAS soil samples were initially measured for a subset of samples ($n = 500$) based on soil extraction with aqua regia (3 HCl: 1 HNO₃) for 16 h at room temperature, followed by an additional 2 h of boiling under reflux (ISO, 1995). This method was compared with measuring trace elements using aqua regia extraction with microwave heating (CEN, 2012). Since good correspondence between both methods was found, the more convenient microwave digestion method was used for measuring trace element contents in all LUCAS soil samples (Tóth et al., 2016). The Zn content in the soil extracts was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and the detection limit was 2.12 mg kg⁻¹ of Zn (Tóth et al., 2016). The 321 samples with Zn concentrations below this detection limit were not included in the analysis and were removed from the dataset. These samples were mainly located in Finland ($n = 36$), Sweden ($n = 17$), Germany ($n = 18$), Poland ($n = 114$), and France ($n = 114$). This removal led to a final dataset of 21,342 soil samples.

2.2. Exploratory analyses

Mean Zn concentrations per administrative region were calculated based on LUCAS topsoil samples. Boxplots were made of the soil Zn levels per country (Fig. 2) and land cover and use types (Figs. 3 and 4), and a biplot was constructed (Fig. 5) based on principal component analysis (PCA) using the soil Zn concentrations and the covariates which are explained in Section 2.3.1.

Next, the 21,342 soil samples were randomly divided into three different sets, namely training (60 %), validation (20 %), and test set (20 %). Using the *intersect* function of the *generics* package (Wickham et al., 2022), a check was done to ensure no overlap between the three different datasets.

2.3. Digital soil mapping

2.3.1. Covariates selection and pre-processing

A total of 18 covariates were used for mapping the soil Zn distribution over Europe. The covariates were chosen as they are expected to have an effect on soil Zn concentrations (De Vos et al., 2006; Hjortenkrans et al., 2007; Lado et al., 2008; Sauvé et al., 2000; Stemweis et al., 1988). These covariates can be divided into six main categories: climate (annual mean temperature, annual precipitation), topography (slope, altitude), lithology (parent material class, distance from Zn deposits and mines), soil properties (clay, sand, silt, pH, soil organic carbon, soil type), land cover (CORINE Land Cover, NDVI) and anthropogenic factors (distance from roads, distance from Zn smelters, distance from energy plants, distance from Zn deposits and mines, lights at night). An overview of the different covariates is given in Table S1, together with the corresponding reference and original spatial resolution.

To assess the influence of roads, smelters and energy plants on topsoil Zn concentrations, distance rasters were created. To include distance from roads as covariate, a weighted distance raster was created based on the different types of roads. The different types of roads were motorways, trunk roads, primary roads and secondary roads. For each type of road, an initial distance raster was created. The overall distance-from-roads raster was then calculated as the weighted sum of all these rasters, using the following weights: 1/4 for motorways, 2/4 for trunk roads, 3/4 for primary roads and 4/4 for secondary roads. With this approach, the most intensive used roads result in smaller distances and may contribute more to the Zn levels in soils. For the Zn deposits/mines, energy plants and smelters, no weights were used to calculate the overall distance raster.

Using the *gdalwarp* function from GDAL (GDAL/OGR Contributors, 2022), the extent, projection (EPSG:3035) and resolution was set the same for all covariate layers. A resolution of 250 m by 250 m was chosen as a compromise between the original resolutions of the different covariates used as input for the modeling (Table S1).

For the world reference base (WRB) soil type and parent material covariates, the number of levels of these qualitative variables exceeded the maximum number allowed for the machine learning algorithm (see next section). Therefore, these variables were converted to dummy variables using the *dummy_cols* function of the *fastDummies* package (Kaplan, 2020).

2.3.2. Machine learning algorithm

Random forest (RF) (Breiman, 2001), one of the most widely used algorithms for digital soil mapping of various properties and at various scales (Keshavarzi et al., 2022; Khaledian and Miller, 2020; Wadoux et al., 2020; Xiao et al., 2023), including Zn (Hengl et al., 2021; Shi et al., 2021; Taghizadeh-Mehrjardi et al., 2021). RF results only in the mean prediction, while quantile regression forest (QRF) estimates the probability distribution of the prediction (Meinshausen, 2006). The latter gives highly valuable information about the (spatial) uncertainty that is associated with the RF prediction, which is in turn relevant for the end-user of digital soil mapping products (Lark et al., 2022). We therefore used QRF for both predicting Zn concentrations (i.e. the conditional mean and median) and estimating the uncertainty of the predictions (Helfenstein et al., 2022; Poggio et al.,

2021). For QRF, the *ranger* (Wright and Ziegler, 2017) package was used in R with the *quantreg* argument in the function set to TRUE. We used the median prediction as the final predicted Zn concentration. The Zn concentrations were \log_{10} transformed prior to modeling because of their skewed distribution, but the distribution was still slightly skewed (median and mean of \log_{10} Zn concentrations in training set were respectively 1.60 and 1.56 mg kg^{-1}) with heavy tails and samples with relatively low and high concentrations. However, using median or mean prediction did not affect the predictions for the independent test set (Fig. S1).

It is known that RF can result in systematic bias in their predictions: small values are overestimated, and large values are underestimated (Liu et al., 2022). This was also the case for our Zn predictions when looking at the training dataset, but it was not the case when checking the residuals for the model predictions of the validation and test set. Therefore, we did not include bias correction in our analyses (Belitz and Stackelberg, 2021).

2.3.3. Hyperparameter selection

For the selection of hyperparameters, QRF models were built based on the training dataset. The possible number of trees ranged from 500 to 2000 with a step of 100, while the number of variables to possibly split at each node ranged between 5 and 15 and the minimum size of terminal nodes between 1 and 15. From all these 2640 possible combinations, a data frame was created and 1000 possible combinations were randomly selected given the computation time. The QRF that was built based on the training set with each combination of hyperparameters, was subsequently used to predict \log_{10} Zn concentrations for the validation set. The root mean squared error (RMSE, Eq. (1)) and correlation between measured and predicted (r , Eq. (2)) were each time calculated as follows:

$$RMSE = \sqrt{\frac{\sum (Zn^{OBS} - Zn^{QRF})^2}{\#samples}} \quad (1)$$

$$r = cor(\log Zn^{OBS}, \log Zn^{QRF}) \quad (2)$$

with Zn^{OBS} the observed Zn concentration, Zn^{QRF} the predicted Zn concentration by the QRF model. The combination of hyperparameters that resulted in the highest r for the predicted Zn concentrations of the validation set was selected. This selection of hyperparameters also resulted in the lowest RMSE. This set of hyperparameters was consequently used to fit the final QRF model using all samples in the training set.

2.3.4. Mapping topsoil Zn concentrations

The calibrated QRF was used to predict the median (0.50 quantile), and 90 % prediction intervals bounded by the 0.05 quantile and 0.95 quantile, at every 250 m pixel in Europe. This was done using the *predict* function from the *ranger* package (Wright and Ziegler, 2017) and the *raster* package (Hijmans, 2022). The calculation of the two quantiles allowed an assessment of the spatial uncertainty of the final model (Helfenstein et al., 2022). Since the proportion of observations that fall into this prediction interval was around 90 % (Table 1), we concluded that the model is able to accurately quantify the uncertainty by this prediction interval (Helfenstein et al., 2022).

2.3.5. Map accuracy and residuals

Firstly, the soil samples from the test set were used as independent set to test map accuracy. To do so, the measured *versus* predicted concentrations were plotted, and accuracy metrics were calculated, namely the RMSE based on back-transformed concentrations (Eq. (1)), the r (Eq. (2)), the mean error (ME, Eq. (3)), the absolute mean error (MAE, Eq. (4)) and the Nash-Sutcliffe model efficiency coefficient (NSE, Eq. (5)):

$$ME = \frac{\sum (Zn^{OBS} - Zn^{QRF})}{\#samples} \quad (3)$$

$$MAE = \frac{\sum |Zn^{OBS} - Zn^{QRF}|}{\#samples} \quad (4)$$

Table 1

Accuracy metrics (Eqs. (1)–(5) in the main text) of the model for the training, validation and test dataset from the LUCAS soil samples, and for the GEMAS soil dataset. The RMSE, ME and MAE were calculated based on back-transformed concentrations.

	r	NSE	RMSE (mg kg ⁻¹)	ME (mg kg ⁻¹)	MAE (mg kg ⁻¹)	% of observations in 90 % prediction interval
Training (<i>n</i> = 12,669)	0.88	0.72	27	5	10	93
Validation (<i>n</i> = 4223)	0.55	0.30	47	7	20	91
Test (<i>n</i> = 4223)	0.55	0.30	36	7	19	91
GEMAS (<i>n</i> = 4313)	0.57	0.31	45	11	21	93

$$NSE = 1 - \frac{\sum(Zn^{OBS} - Zn^{QRF})^2}{\sum(Zn^{OBS} - \overline{Zn^{OBS}})^2} \quad (5)$$

with Zn^{OBS} the observed Zn concentration and Zn^{QRF} the predicted Zn concentration by the QRF model.

Secondly, the model residuals (measured – predicted) were calculated for the training set. The residuals were checked for spatial correlation by constructing a variogram, using the *variogram* function from the *gstat* package (Gräler et al., 2016). The variogram model was subsequently fitted using the *fit.variogram* function of the same package, and the model parameters were used to calculate the nugget-to-sill ratio. This ratio was subsequently used to assess the degree of spatial correlation of the model residuals (Kaya et al., 2022).

Finally, another external topsoil dataset was used to test map accuracy. This dataset consists of soil samples collected in 2008/2009 under the framework of the Geochemical Mapping of Agricultural and grazing land Soils (GEMAS) (Reimann et al., 2018). This soil set was collected outside the LUCAS soil survey, having a different sampling strategy (e.g., depth) and a slightly different method for measuring metal concentrations in aqua regia soil extraction. Thereby, this validation gives accuracy information for soil monitoring schemes outside the LUCAS survey, for example national monitoring schemes.

2.3.6. Variable importance

When fitting the QRF model with the *ranger* function, the variable importance was assessed based on the impurity measure (Wright and Ziegler, 2017) and plotted for the highest 16 ranked variables. This

Figure (Fig. 8) shows the general importance of each of the variables, based on the reduction in variance when using a particular variable at each split. For the most important variables, accumulated local effects (ALE) plots were constructed. These plots show the effect and corresponding direction of one variable on the predicted outcome while averaging the changes in the predictions by the other variables (Molnar, 2022). The ALEplots were created using the *explain* and *model_profile* functions from the *DALEX* package (Biecek, 2018).

3. Results

In the following sections, we will firstly present the results of exploratory statistical analyses, in which the LUCAS Zn concentrations were assessed by country, land use, and by means of multivariate analyses. Next, we will show the results of the RF model in terms of parameters and prediction accuracy. Finally, we will present the map of topsoil Zn concentrations and the variable importance for explaining the Zn distribution in Europe with the RF model.

3.1. Exploratory analyses of soil Zn concentrations

The spatial distribution of mean Zn concentrations per administrative region is shown in Fig. S2. Based on the LUCAS topsoil database, the mean Zn concentration in Europe was 47 mg kg⁻¹, and the median Zn concentration was 40 mg kg⁻¹. The majority (35 %) of samples had concentrations between 25 and 50 mg kg⁻¹, and 31 % had concentrations in the range between 50 and 100 mg kg⁻¹ (Fig. 1). Ninety-nine percent of all samples had concentrations below 167 mg kg⁻¹. The 1 % of samples that with

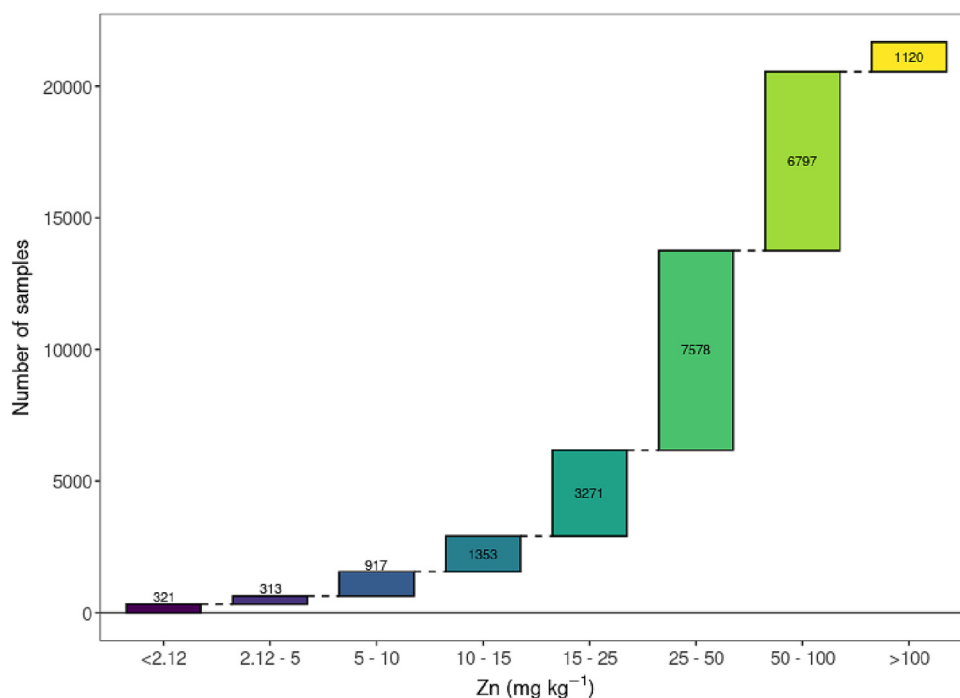


Fig. 1. The number of samples per Zn concentration category.

concentrations above 167 mg kg⁻¹ were mostly located in the UK, Ireland, Portugal, Slovenia, Italy, Germany and France (Fig. 2 and Fig. S3). Only 56 soil samples had concentrations higher than 300 mg kg⁻¹. The 321 or 1 % samples that had concentrations below 2.12 mg kg⁻¹ were mostly located in France and Poland, mostly present in cropland, followed by woodland and grasslands (Fig. S4).

Zinc concentrations varied between countries (Fig. 2), with the highest levels in Malta, Slovenia, Luxembourg, Bulgaria, Romania, and Belgium. The lowest mean concentrations were found in North-European countries, such as Poland, Finland, Lithuania, Latvia, Sweden, Estonia, and Denmark.

Topsoil Zn concentrations tended to be slightly higher in grasslands and bare lands than other land covers (Fig. 3). In line with these results, soils under agricultural use (mainly grasslands) generally contained the highest Zn concentrations based on median values and the number of samples with concentrations higher than 167 mg kg⁻¹, thereby belonging to the 1 % samples with the highest Zn concentrations (Fig. 4). However, it should be noted that agriculture is the dominant land use in the LUCAS database, representing 67 % of all soil samples. When looking at land use type, the occurrence of land used for transport, utilities, and residential area relatively increased when selecting only LUCAS samples with Zn concentrations

above 167 mg kg⁻¹ (Fig. 4). However, since these were only 15 samples, it is hard to draw strong conclusions based on this result.

Differences between soil Zn concentrations under different land covers could also be related to the differences in soil properties like pH and soil organic carbon and climatic factors like precipitation and temperature (Fig. 5). Based on PCA, we could explain 35 % of the variation in the data with the two first PCs. Generally, most of croplands were located in soils with higher pH and lower soil organic carbon compared with grasslands and forest soils. Based on the biplot shown in Fig. 5, Zn concentrations were mostly related to soil clay content than other soil properties. This result is a first indication of which covariates are most important for explaining soil Zn concentrations in Europe, which is elaborated on in Section 3.2.

3.2. QRF modeling results and accuracy

The final random forest model had relatively deep trees (minimal nodesize of 7) and a high number of variables that were randomly selected at each split (mtry of 12) (Table S2). The nugget-to-sill ratio of the model residuals of the training set was calculated to assess the spatial correlation. A ratio of 0.75–0.79 was obtained depending on the semivariogram model.

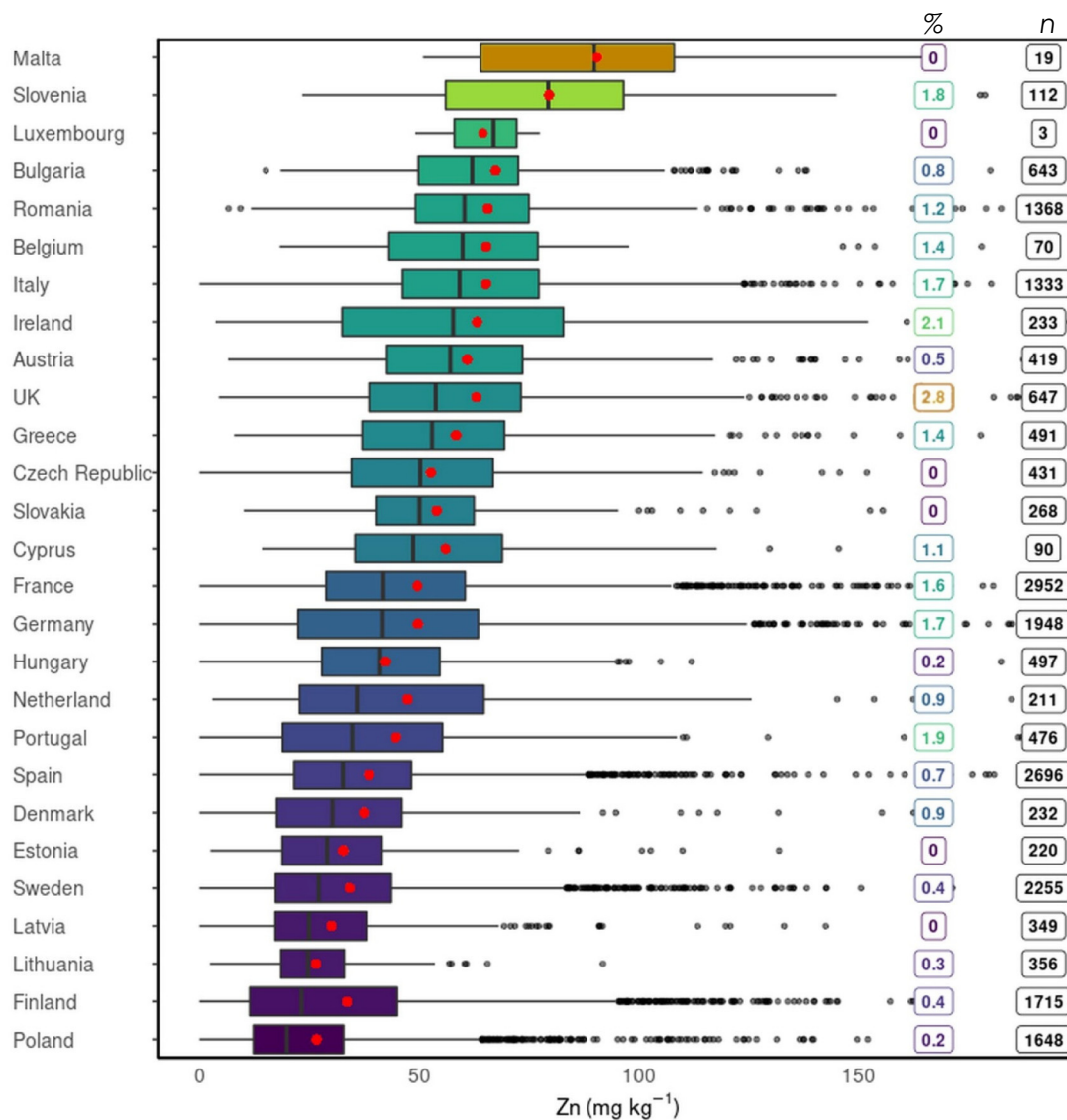


Fig. 2. Boxplots of Zn concentrations measured after aqua regia extraction in soils from different countries (EU26 + UK). Red markers show the mean concentrations for the countries, while the line within the boxplot represents the median. The lower and upper hinges correspond to the first and third quartiles, while the whiskers show the 1.5 inter-quartile range from the hinges. The numbers in the boxes in the right show the percentage of samples for that country that have concentrations higher 167 mg kg⁻¹, and the total number of samples for each country.

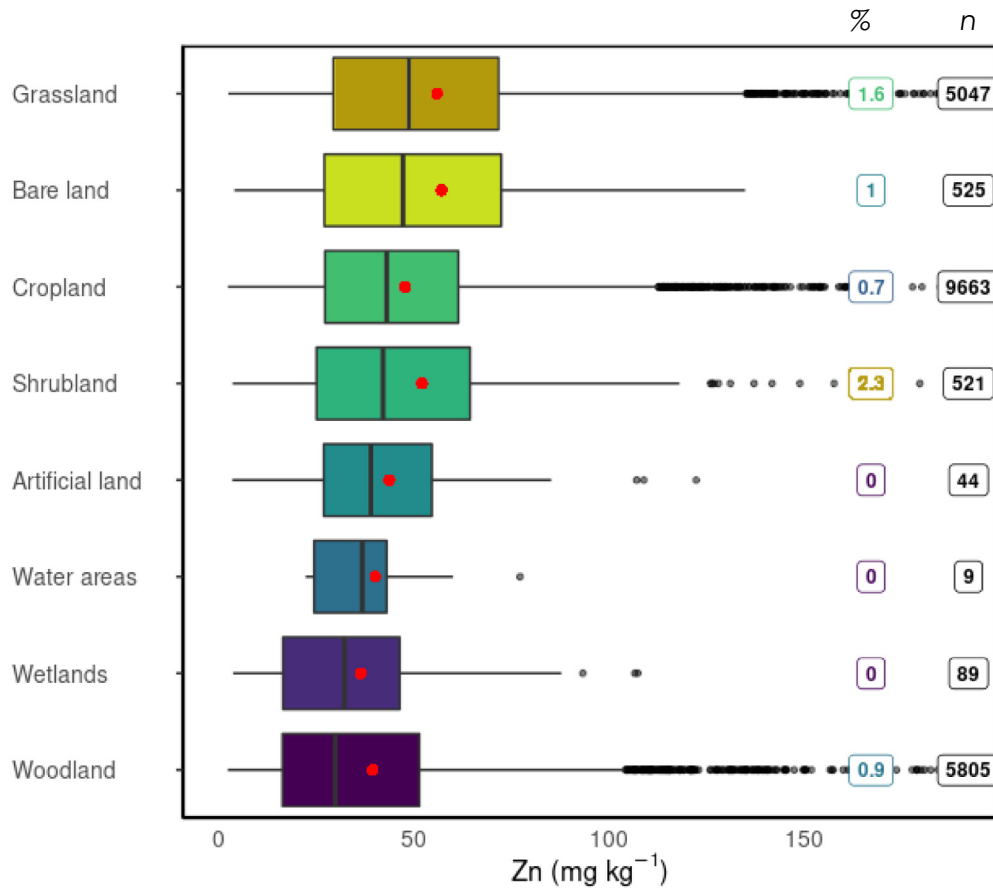


Fig. 3. Boxplots of Zn concentrations measured after aqua regia destruction in soils with different land covers. Red markers show the mean concentrations for the countries, while the line within the boxplot represents the median. The lower and upper hinges correspond to the first and third quartiles, while the whiskers show the 1.5 inter-quartile range from the hinges. The numbers in the boxes on the right show the percentage of samples for that country that have concentrations higher 167 mg kg⁻¹, and the total number of samples for land cover.

This high ratio indicates a weak spatial correlation, so no further modifications of the model were done to produce the final map (Kaya et al., 2022).

The accuracy of the final model was calculated based on various accuracy metrics (Table 1) for the independent test set of the LUCAS data (Fig. 6) and for an external dataset, namely the GEMAS dataset (Reimann et al., 2018). The final model resulted in an RMSE of 36–47 mg kg⁻¹ for soil samples not used for model calibration, a mean error of about 7–11 mg kg⁻¹, and an MAE of about 20 mg kg⁻¹ of Zn. The correlation coefficient was 0.55. As can be seen in Fig. 6, the predicted values cover a smaller range than the actual Zn concentrations measured in the LUCAS topsoil samples.

3.3. Distribution of topsoil Zn in Europe

Fig. 7 shows the distribution of topsoil Zn concentrations based on QRF modeling. The uncertainty of the map of topsoil Zn concentrations is shown in Fig. S5 as the difference between the 0.95 and 0.05 quantiles.

Based on RF modeling, clay content was the most important variable explaining topsoil Zn concentrations in Europe (Fig. 8), followed by sand and pH. Topsoil Zn concentrations increased with increasing clay and decreasing sand content (Fig. S6). Zinc concentrations increased with higher soil pH but decreased with increasing pH above 7–8.

4. Discussion

4.1. Natural drivers explain topsoil Zn concentrations in Europe

The mean topsoil Zn concentration of 41 mg kg⁻¹ predicted by our model aligns with findings from previous sampling campaigns (De Vos

et al., 2006; Reimann et al., 2018). The variability in Zn concentrations was large, with apparent differences between EU countries (Fig. 2) and regions (Fig. 7 and Fig. S2). The lowest concentrations were found in Northern European countries, such as Poland, Finland, Lithuania, Latvia, Sweden, Estonia, and Denmark, with median concentrations below 30 mg kg⁻¹. The highest concentrations were found in Malta, Slovenia, Luxembourg, Bulgaria, Romania, and Belgium. The national concentrations ranges of Zn based on LUCAS topsoil database were in line with national inventories (Bini et al., 1988; Noulas et al., 2018).

To gain insights into the spatial distribution of topsoil Zn concentrations in Europe and the underlying drivers, we applied quantile regression forests (Meinshausen, 2006) as a digital soil mapping algorithm using LUCAS topsoil database. Based on this model, we were able to produce a dataset showing Zn distribution across Europe at 250 m resolution (Fig. 7) that will be publicly available at the European Soil Data Centre (ESDAC) of the Joint Research Centre (Panagos et al., 2022b) and for which the underlying drivers were quantitatively assessed. The fine resolution and the evaluation metrics obtained in this study showed an improvement compared to previous attempts to map topsoil Zn concentrations across Europe based on regression kriging (Lado et al., 2008; Noulas et al., 2018). The evaluation metrics are in line with what has been already found when mapping trace elements at the continental scale, e.g., for mercury based on LUCAS topsoil database (Ballabio et al., 2021) and for nutrients and trace elements on the African continent (Hengl et al., 2017). The quantitative assessment of the underlying drivers presented in this manuscript (Fig. 8), both natural and anthropogenic, are novel results compared to previous publications and products on topsoil Zn concentrations in Europe (Lado et al., 2008; Reimann et al., 2018).

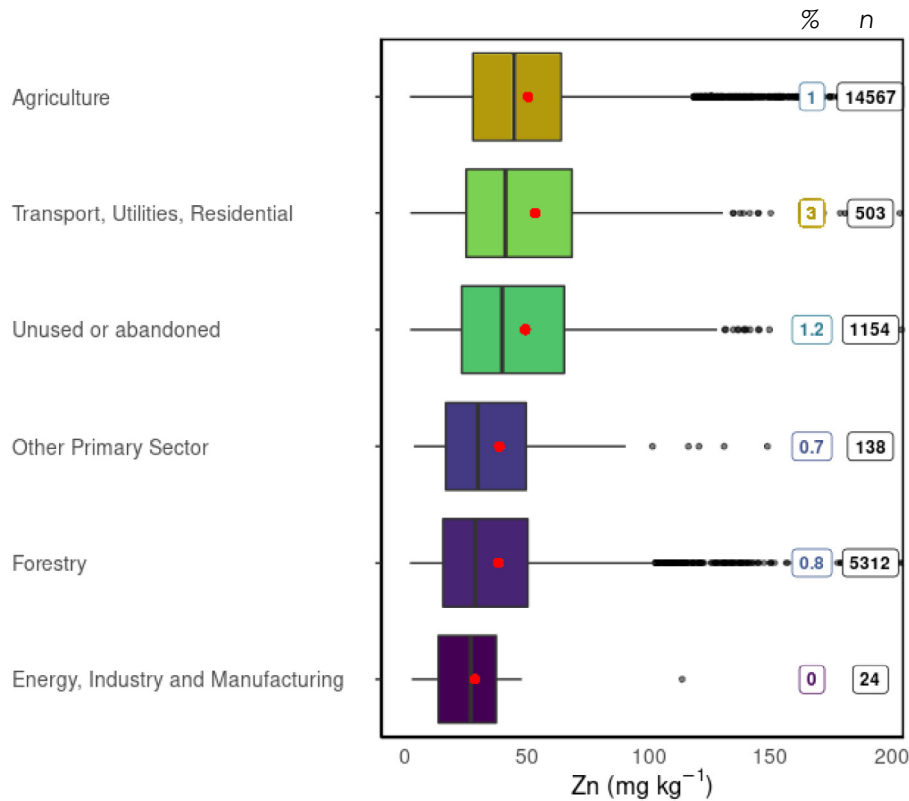


Fig. 4. Boxplots of Zn concentrations measured after aqua regia destruction in soils under different land uses. Red markers show the mean concentrations for the countries, while the line within the boxplot represents the median. The lower and upper hinges correspond to the first and third quartiles, while the whiskers show the 1.5 inter-quartile range from the hinges. The numbers in the boxes on the right show the percentage of samples for that country that have concentrations higher 167 mg kg⁻¹, and the total number of samples for each land use.

Looking at the spatial distribution of topsoil Zn concentrations, the first and utmost important observation was the difference between North and Southern Europe, with predominantly higher concentrations in Southern Europe (Fig. 7). This North-South border follows the southernmost limit of the last glaciation (De Vos et al., 2006). Northern Europe is characterized by coarse-grained soils compared to Southern Europe, and clay content in European soils follows the same North-South border as found here for Zn (Ballabio et al., 2016). The northern boundary of loess distribution in Europe also follows the same North-South border on the European mainland (Haase et al., 2007). Consequently, clay content was the most crucial variable for explaining the distribution of Zn in European topsoils selected by random forest modeling (Fig. 8). The clay textural class comprises a wide variety of soil minerals, which are generally not the most relevant soil surfaces for Zn adsorption except at extremely low pH values below 4 (Dijkstra et al., 2004). By contrast, Zn adsorption processes in soils are dominated by the adsorption to carboxylic and phenolic functional groups of soil organic matter (Groenenberg et al., 2017; Van Eynde et al., 2022a), while metal (hydr)oxides become more important with increasing pH (Van Eynde et al., 2022a, 2022b). However, in this study, we were not looking only at the labile Zn concentrations in soils, which is the fraction distributed over the solid and solution phase by adsorption processes (Groenenberg et al., 2017). Instead, we modeled the distribution of the pseudo-total Zn content measured after aqua regia destruction, which comprises additional Zn that is inert. This inert Zn pool is occluded within the mineral soil matrix, and becomes only available for organisms by slow weathering processes (Rodrigues et al., 2010). Rock types that result in clayey soils upon weathering contain the highest Zn content (Alloway, 2008; Mertens and Smolders, 2013), explaining the higher Zn levels in clay soils compared to sandy soils found in Europe with our model.

The increase in Zn concentrations with increasing SOC and pH (Fig. S6), can be explained by adsorption processes. Soil organic matter is the most

important reactive surface for Zn adsorption (Sauvé et al., 2000), and it is known that Zn adsorption increases with high pH (Van Eynde et al., 2022a).

However, the pH did not have a linear and constant effect on Zn concentrations in topsoils (Fig. S6). Zn concentrations increased with increasing pH but decreased with increasing pH when pH was higher than 7–8. In soils with such high pH values, Zn speciation of the labile fraction may not be dominated by adsorption processes but by the precipitation of minerals (Duffner et al., 2014). These minerals may be less extractable with aqua regia destruction, resulting in relatively lower concentrations. This dual effect of soil pH on topsoil Zn concentrations can explain the lower Zn concentrations in some regions in Southern Europe. For example, regions with soil pH above eight and relatively lower Zn concentrations were found in Spain near Cadiz and Jaen, Southwest of Madrid and near Palencia (Fig. 7).

On the other hand, lower Zn concentrations were found in regions with lower pH values, for example, in the South of Bordeaux and Orléans. According to the soil type map of Europe, these areas are characterized by Podzols (Panagos et al., 2022b). In this type of soil, higher Zn losses by leaching are expected due to the presence of organic matter chelates and the low pH (Warwick et al., 1999). Similarly, in Denmark and the North of Germany and Poland, higher Zn levels were found in those areas with relatively higher pH than surroundings. In Hungary, the two regions with relatively lower Zn concentrations (Fig. 7) were not related to soil pH but to lower clay content.

The maps of soil type and parent material (Panagos et al., 2022b) used as covariates in our QRF model were not important for explaining topsoil Zn concentrations (Fig. 8). However, these maps are coarser than the maps of soil physico-chemical properties (Table S1) based on LUCAS soil data (Ballabio et al., 2016, 2019), which can explain why soil properties were more important for explaining topsoil Zn concentrations in the RF model than soil and parent material classes.

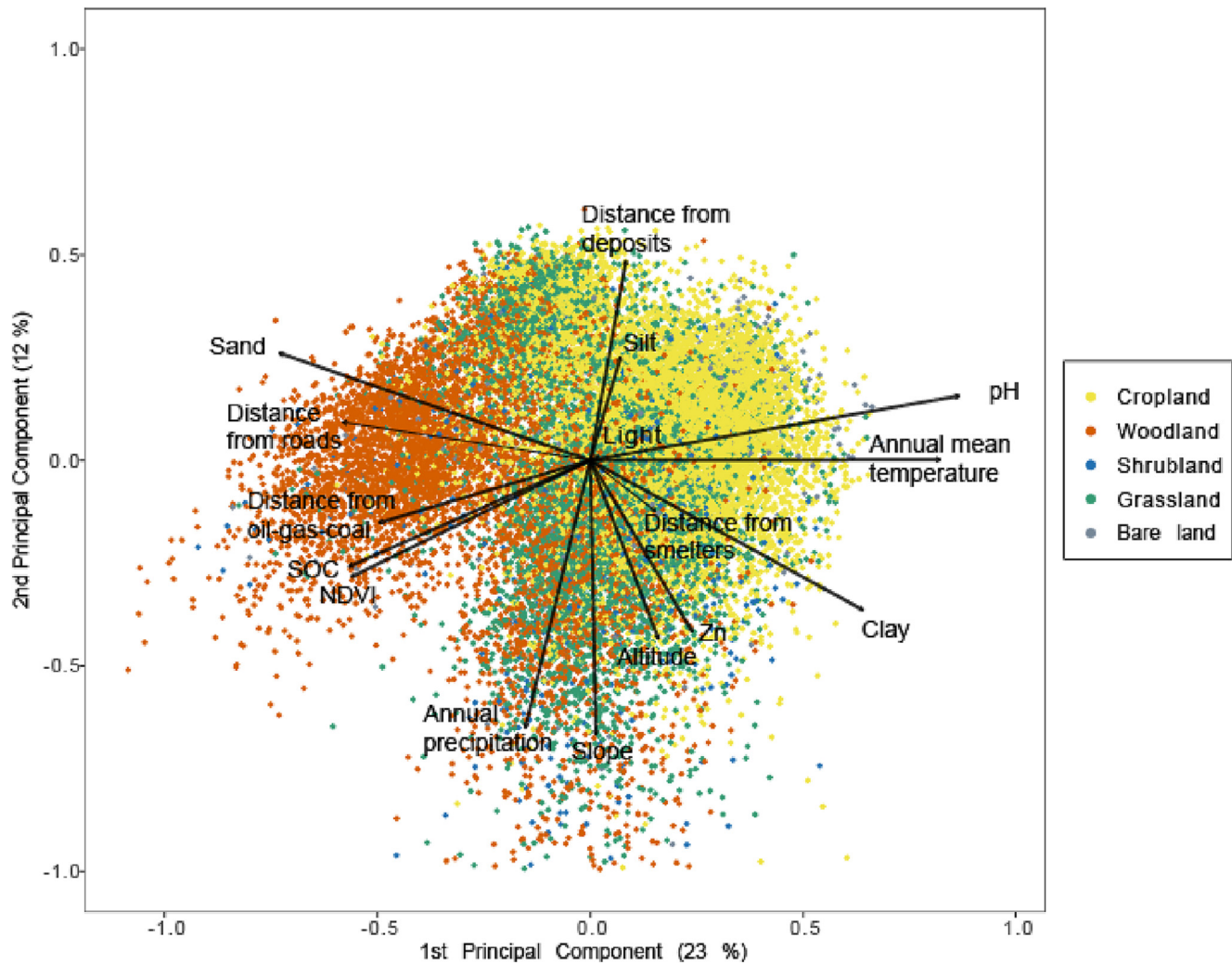


Fig. 5. Biplot showing the results of the principal component analysis. Point markers show the samples for the different land covers based on the LUCAS survey. The arrows represent the different numeric covariates in modeling soil Zn concentrations. The % given in the x- and y-axis shows the variation explained in the data by the respective principal component.

In addition to soil properties, climatic variables as mean annual temperature were important for explaining topsoil Zn concentrations in Europe. According to our QRF model, topsoil Zn concentrations increased with increasing temperature until $\pm 10^\circ\text{C}$, after which the topsoil Zn concentrations decreased (Fig. S6). The effect of precipitation on Zn concentrations showed a similar trend, albeit less important for the overall prediction than temperature (Fig. S6). The importance of temperature and precipitation for mapping nutrients, specifically Zn, at the continental scale, was previously found for Africa (Hengl et al., 2017, 2021) and at the global scale (Moreno-Jiménez et al., 2023). Moreno-Jiménez et al. (2023) found that the concentrations of micronutrients, including Zn, are lowest in regions with low temperature and high temperature, with an inflection point around 13°C . Our results align with these findings, albeit with a slightly lower inflection point than. The authors argued that this temperature effect is due to the occurrence of minerals and associated weathering rate and the decomposition of soil organic matter (Moreno-Jiménez et al., 2023), both important sources of micronutrients such as Zn in soils (Alloway, 2008).

4.2. Importance of Zn deposits and mining for high Zn concentrations

The distance from natural Zn deposits or Zn mines was the most important variable to explain Zn concentration in Europe, after soil, climatic, and landscape features (Fig. 8). With increasing distance, the Zn concentrations in European topsoils decreased (Fig. S6). The effect was especially relevant

within a range of 10 km. When looking at the distribution of LUCAS topsoil samples with concentrations higher than 167 mg kg^{-1} , i.e., the 1% samples with the highest concentrations, the distribution of Zn deposits and mines in Europe explained the intensity of samples with high Zn concentrations found in some regions (Fig. S3). For example, in Spain, France, Portugal, Sweden, Romania, and Slovenia, 1% of LUCAS samples with high Zn concentrations often coincided with Zn deposits and mines (Fig. S5). Previous studies have already reported high soil Zn concentrations in these regions due to natural deposits, current or past mining activities, and nearby smelters (Big et al., 2012; Escarré et al., 2000; Freitas et al., 2004; Monterroso et al., 2014; Vreča et al., 2001).

With increasing distance from smelters and roads, the Zn concentrations decreased (Fig. S6). However, the effect is smaller than what was found for Zn deposits and mines. The effect of roads on topsoil Zn concentrations was unclear at smaller distances (Fig. S6). This unclear effect of roads on topsoil Zn concentrations may be because we assigned arbitrary weights to the different road types. However, it should be noted that Zn contamination near roads is relatively local, with higher Zn levels found only a few meters from the road (Bodar et al., 2005). This fine resolution of a few meters does not align with the scale of topsoil Zn concentrations modeled in this study. The relative increase of sites under land use 'transport, utilities and residential area' when selecting only LUCAS samples with Zn concentrations above 167 mg kg^{-1} (Fig. 4) may suggest the importance of transport for high Zn concentrations.

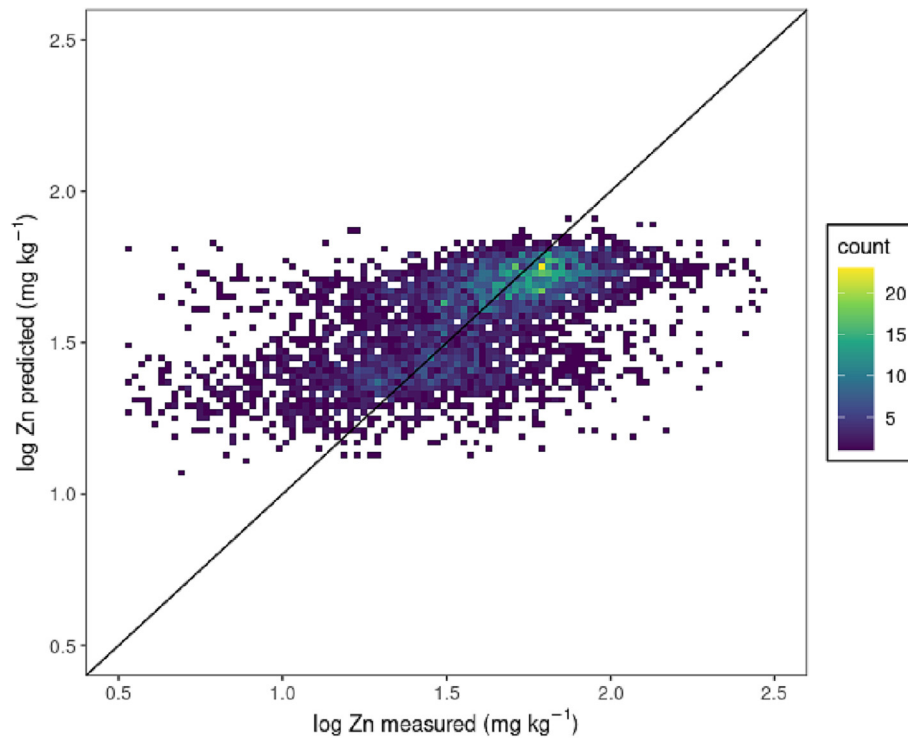


Fig. 6. Validation plot showing the comparison between the measured Zn concentrations in LUCAS soil samples after aqua regia destruction, and the predicted Zn concentrations based on random forest modeling. The color gradient shows the number of points around the 1:1 line. The comparison is shown for the test set of 4223 LUCAS soil samples which is an independent set not used for model calibration nor hyperparameter selection.

4.3. The effect of agricultural management on Zn concentrations

Previous studies have shown that agricultural inputs (e.g., mineral fertilizers, manure) contain Zn, and application may lead to unintended Zn inputs to soils. Mineral fertilizers contain various trace elements (Nziguheba and Smolders, 2008). Recent studies have shown that Zn concentrations in phosphate fertilizers distributed in Europe can reach up to 500 mg kg⁻¹ (Verbeeck et al., 2020), while Zn concentrations in animal manure due to feed additives can be even higher (Sager, 2007). The latter may explain the occurrence of soils with high Zn levels in areas with high livestock densities with high manure production and application (Panagos et al., 2022a), such as the Netherlands, Germany, Northern Italy, the UK and, Ireland (Fig. S3). Previous studies have found elevated soil Zn concentrations due to manure application in these regions (Mantovi et al., 2003b; Nicholson et al., 2003; Schipper et al., 2008). When selecting the LUCAS samples with Zn concentrations above 167 mg kg⁻¹, the relative frequency of grassland soils increased (Fig. S7 and Fig. 3). Grasslands represented 37 % of these high Zn soils, which may point to additional Zn sources from manure, which is shown to be relatively more important in grassland than in cropland soils (Imseng et al., 2019; Keller and Schulin, 2003). The inclusion of spatial data on fertilizer and manure inputs may improve the modeling of topsoil Zn concentrations in Europe. However, such data is currently unavailable at a fine spatial scale (Panagos et al., 2022a).

4.4. Risk assessment

Threshold values used to assess Zn contamination in European soils differ across Member States (Mininni et al., 2015) and can vary between 60 and 450 mg kg⁻¹ (Bauer et al., 2020; Collivignarelli et al., 2019; Mininni et al., 2015). For some Northern European countries (e.g., Denmark, Sweden, Poland), these threshold values are relatively low (i.e., around 100 mg kg⁻¹), in line with the lower Zn concentrations in our study. Given the distribution of Zn concentrations in European topsoils based on LUCAS soil data, we can conclude that Zn contamination in soils is rare

since 95 % of soil samples had concentrations below the lowest soil Zn threshold (i.e. 100 mg kg⁻¹) values across Europe.

There have been concerns about the differences in these threshold levels across Member States to assess metal contamination. Some have raised the need for harmonized threshold levels and monitoring schemes (Mizutani et al., 2015; Morvan et al., 2008; Theocharopoulos et al., 2001). The variety among limit values can be partly explained by the fact that these limit values are based on aqua regia soil destructions, which are measurements of the pseudo-total concentrations. These concentrations are not directly linked to metal availability and thus possible (eco-)toxicological risks (Nolan et al., 2003). The large variety among countries can, therefore, potentially reflect the large variety in soil properties that determine the eco-toxicological risk of pseudo-total heavy metal concentrations. However, the variety within countries of these soil properties is already quite large (Ballabio et al., 2016, 2019). Only a few countries consider soil properties like texture and pH to define Zn thresholds for soil contamination (Mininni et al., 2015). Studies have shown that these soil properties affect the availability of pseudo-total metal concentrations in soils towards plants and organisms (de Vries et al., 2007, 2011; Groenenberg et al., 2010; Tipping et al., 2003) and the associated risk (Nolan et al., 2003).

Similarly, assessing regions at risk of Zn deficiencies for crop production is challenging based on the analysis of aqua regia concentrations. However, soils with low total Zn contents are more likely to result in crop Zn deficiencies (Alloway, 2009). Based on our results, Northern European countries and, for example, the calcareous soils in Spain, may therefore impose challenges related to micronutrient deficiencies (Moreno-Jiménez et al., 2022; Sánchez-Rodríguez et al., 2021; Sinclair and Edwards, 2008). The total Zn levels in these regions can be considered low, i.e., in the range of 10–30 mg kg⁻¹ (Lindsay, 1972). These low soil Zn levels possibly affect the crop nutritional quality and human health (Mensink et al., 2013). Further research can be useful to better understand the associated risks in agricultural areas in with low topsoil Zn concentrations that our model identified.

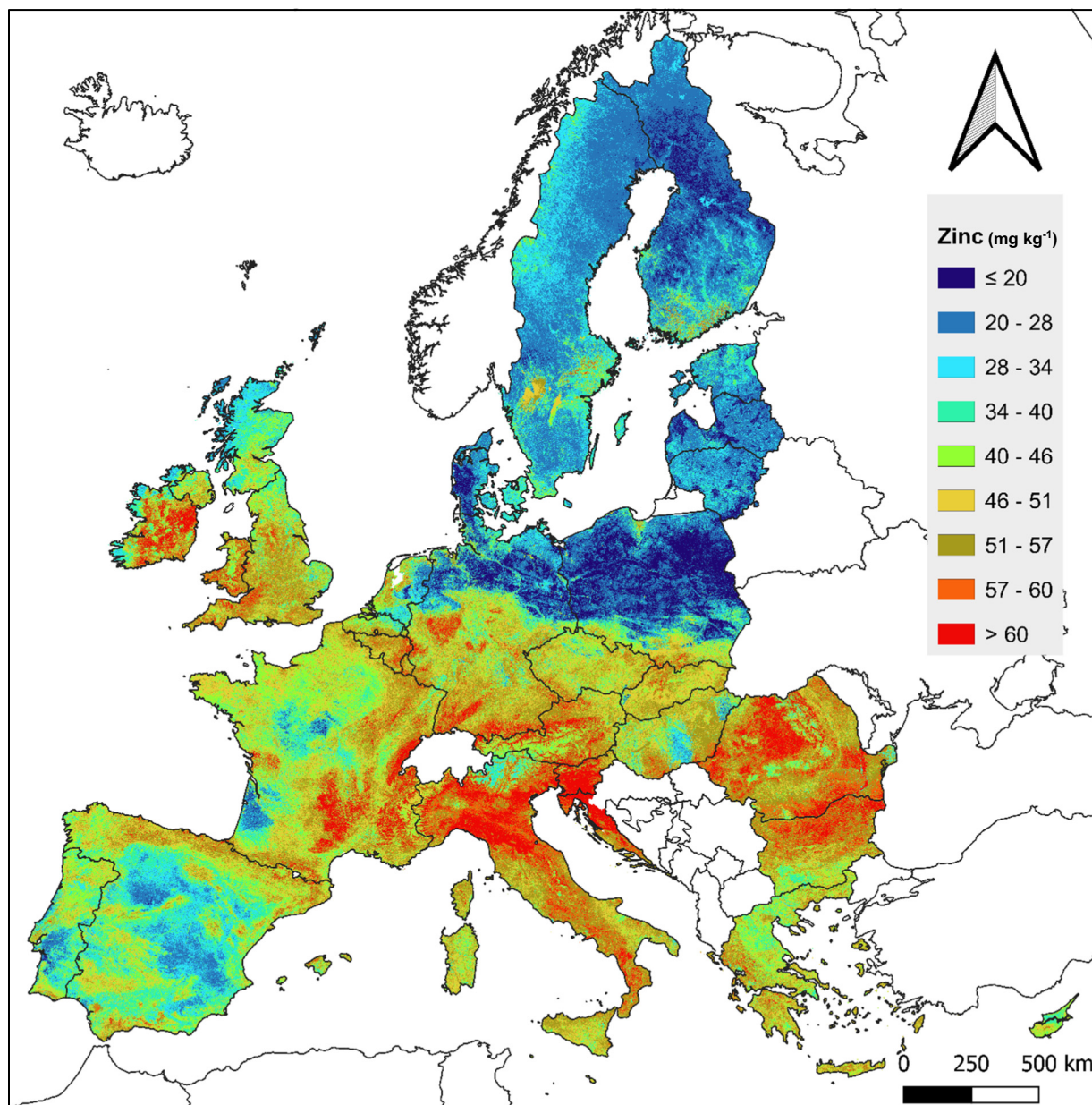


Fig. 7. The Zn concentration (mg kg^{-1}) in European topsoils as predicted by the quantile regression forest. The resolution of this map is 250 m by 250 m.

4.5. Policy and application

Policy actions and sector initiatives (Harvest Plus, 2021; International Zinc Association, 2022) at national, regional, and global scales have addressed the issues related to Zn deficiencies and pollution. On the global scale, the United Nations adopted the Sustainable Development Goals (SDGs). Among these 17 SDGs, Zn plays a crucial role in several ones. As an essential micronutrient for animals and crops, Zn is important in reaching zero hunger (SDG 2). As an essential micronutrient for humans, and an element that can be toxic in excess, it is an important element to consider to reach good health and well-being (SDG 3) and to preserve life below water (SDG 14) and on land (SDG 15).

The European Commission recently proposed the EU Green Deal to make Europe the first climate-neutral continent by 2050, with a significant role of soils for reaching this ambition (Montanarella and Panagos, 2021). As part of the EU Green Deal, the Farm to Fork Strategy aims to ensure sustainable food security and food security, emphasizing nutritious food for which Zn can be a key element to be considered. In addition, the Zero Pollution Action Plan (European Commission, 2020) aims to prevent, control,

and remediate soil, water, and air pollution by pollutants such as heavy metals like Zn.

This assessment contributes to establishing a baseline of Zn concentrations in European topsoils to run outlook scenarios and future projections. This assessment can contribute to the identification of diffuse pollution and contamination sources across Europe. In addition, it can serve to evaluate existing threshold levels based on aqua regia soil destruction concerning the background levels. Finally, the map of topsoil Zn concentrations produced in this study can be used as input into applications for translating pseudo-total Zn concentrations into other soil fractions, which are more related to bioavailability and consequently to eco-toxicological or deficiency risks (de Vries et al., 2007).

5. Conclusions

The LUCAS topsoil database offers the opportunity to assess the spatial distribution of topsoil physical, chemical, and biological properties across Europe. The output maps represent important soil property baselines for policy regulations and soil monitoring in the European Union.

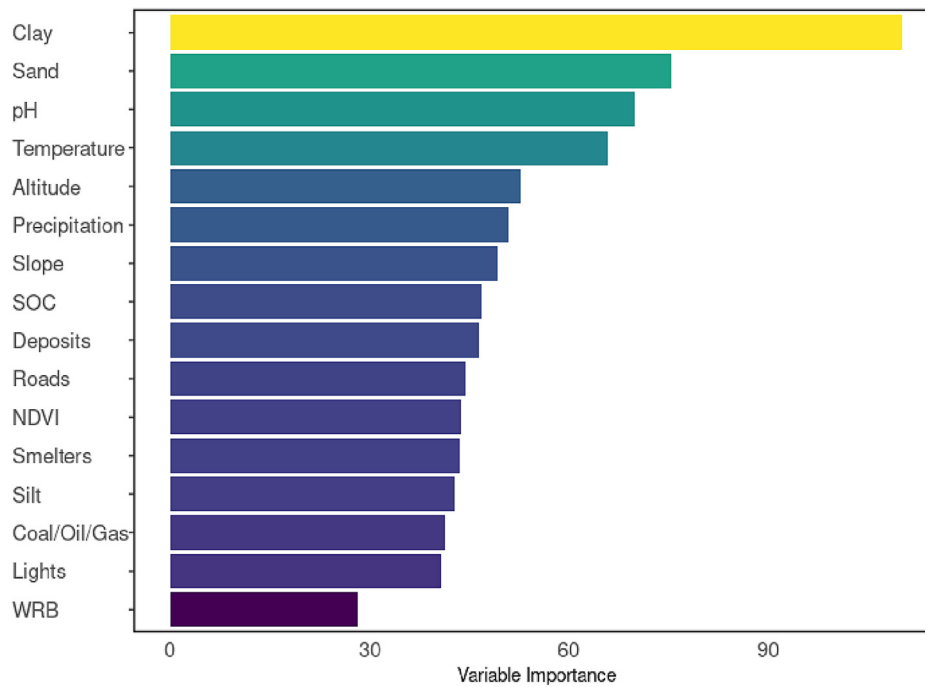


Fig. 8. The ordered importance of the covariates in the random forest model for Zn concentrations in European topsoils. The importance is only shown for the 16 most important covariates (i.e. excluding parent material and land cover). The x-axis shows the variable importance based on the variance reduction at each split when the particular variable is used. The effects of each variable on the predicted Zn concentrations are shown in Fig. S5 in the supplementary information.

This study presented the spatial distribution of topsoil Zn concentrations across Europe. We identified topsoil clay content as the most important predictor for Zn concentrations, with higher concentrations in soils with higher clay content. As such, natural soil properties related to parent material were most important for the Zn distribution in Europe. This difference in parent material and soil texture explained the considerable difference in Zn levels between North and Southern Europe. In addition, soils with relatively low and high pH values (i.e. Calcisols and Podzols) were identified as regions with relatively low Zn levels.

Based on our analyses, we identified two possible natural and anthropogenic drivers for high Zn levels in soils. One was the natural mineral deposits and anthropogenic mining activities. Samples close to these locations (i.e. 10 km) had the highest Zn concentrations, often above 167 mg kg^{-1} , representing only 1 % of all LUCAS soil samples. In addition, we found that soils under grassland contribute primarily to the soils with the highest Zn concentrations. This could be due to additional Zn inputs by manure, which contains elevated Zn levels due to Zn additives given to livestock.

CRediT authorship contribution statement

Elise Van Eynde: Conceptualization, Methodology, Software, Visualization, Writing original draft and revision, Formal Analysis, Validation, Investigation.

Arthur Nicolaus Fendrich: Methodology, Software, Revision.

Cristiano Ballabio: Methodology, Software, Revision.

Panos Panagos: Conceptualization, Revision.

Data availability

The authors do not have permission to share data.

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.scitotenv.2023.164512>.

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