Use of soil properties and major element composition to predict background levels of trace elements in soils.

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INTRODUCTION
The usefulness of various soil parameters to predict naturally occurring levels of some metallic trace elements (MTE) in soils has been studied for some agricultural and forest soils of Southern Belgium. The driving factors of the content in Cu, Ni, Pb, and Zn were investigated through multi-scale comparisons (Colinet, 2003). This paper deals with multivariate and regression analysis of the results.

METHODS
Statistical analysis was performed on two datasets of soil profiles. The first is related to agricultural soils of the Belgian loess belt, while the second concerns soils of oak forests from diversified lithological environments. The agricultural soils are mainly luvisols and cambisols (WRB classification). The parent materials are quaternary loess and colluviums. The forest soils are acid cambisols (WRB) with the parent materials ranging from shale to coarse sandstones. Soil samples were collected on a soil-horizon basis. Due to strong modifications of the top soil layers by ploughing and agricultural management, the background values of MTE in agricultural soils were initially studied in relation to subsurface horizons. Subsurface model predictions were then compared with surface measured values. Regarding forest soils, the particle size distribution (PSD) was not determined on top Ah horizon due to high amounts of organic matter. Two statistical analyses were realized. The first included all the variables and subsurface horizons, and the second concerned all the variables (excluding PSD) and all the horizons.

Laboratory analyses
Soil parameters measured were pH (in water and KCl) at a soil:solution ratio of 2:5 (weight/volume), exchangeable acidity and aluminium using the Yuan Method for forest soils, total organic carbon (C – Springer-Klee Method), PSD following the chain hydrometer method with H₂O₂ and HCl pre-treatment, dispersion with Na-hexametaphosphate, and wet sieving at 50 µm, cationic exchange capacity (CEC – Metson Method) and base saturation of the exchange complex (V), and total Ca, Mg, K, Na, Al, Fe, Mn, Cu, Ni, Pb, and Zn (HNO₃+HF+HClO₄+HCl) by Flame Atomic Absorption Spectrometry.

Statistical analyses
Both datasets were analyzed in accordance with the following procedure: (i) classical statistical description, (ii) detection of outlier values, (iii) analysis of the correlation matrixes, (iv) PCA-based factorial analysis, (v) multivariate regression analysis. All the analyses have been performed with MINITAB 13.2. The performances of the regression models investigated, as well as other models from the literature, were evaluated on the basis of Mean Errors (ME) and Root Mean Square Errors (RMSE). The ME is an expression of the prediction bias while the RMSE is an indicator of the model precision, which is of frequent use.
RESULTS AND DISCUSSION

Factorial analysis
Although derived from varying lithologies and associated with different acidity levels agricultural and forest soils present similarities. In both cases, the first factor represents a gradient based on PSD. Fine fractions are linked to carrier phases while coarse fractions tend to dilute the MTE content. Cu, Ni, and Zn contents are clearly linked to total soil Fe, while Pb is influenced by clay and C content through soil CEC. An inverse relationship between pH and MTE content was found in forest soils, which may in part be explained by the fact that the most acidic soils were also associated with higher stoniness and thus present a higher content of MTE-bearing minerals in the coarse fractions.

Regression models
Various models for MTE prediction were obtained depending on the amount of available secondary information. The performance of these models is variable (Fig. 1). The results demonstrate the need for simplification to ensure a certain level of universality. The total soil Fe should be preferred to other parameters to predict MTE content because Fe and MTE are measured in the same extraction liquor. But in order to take advantage of existing databases for which the Fe content is lacking, the other explicative variables should not be discarded.

![Fig. 1. Relative precision of some of the tested regression models on an independent validation set. Root Mean Square Errors (RMSE) are divided by the RMSE obtained for the prediction with the mean.](image)

CONCLUSIONS
The driving factors of the soil MTE content have been studied through multivariate factorial analysis. The main driving factors are the PSD (for all the MTE), the Fe content (Cu, Ni, and Zn) and the CEC (Pb). Regression analysis has shown the difficulty to obtain universal models and also the interest to use the most simplified ones.

REFERENCES