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Prediction of the concentration of chemical elements extracted by *aqua regia* in agricultural and grazing European soils using diffuse reflectance mid-infrared spectroscopy

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A B S T R A C T

The aim of this study was to develop partial least squares (PLS) models to predict the concentrations of 45 elements in soils extracted by the *aqua regia* (AR) method using diffuse reflectance Fourier Transform mid-infrared (MIR; 4000–500 cm^{-1}) spectroscopy. A total of 4130 soils from the GEMAS European soil sampling program (geochemical mapping of agricultural soils and grazing land of Europe) were selected. From the full soil set, 1000 samples were randomly selected to develop PLS models. Cross-validation was used for model training and the remaining 3130 samples used for model testing. According to the ratio of standard deviation to root mean square error (RPD) of the predictions, the elements were allocated into two main groups; Group 1 (successful calibrations, 30 elements), including those elements with RPD $\geqslant$ 1.5 (the coefficient of determination, R^2, also provided): Ca (3.3, 0.91), Mg (2.5, 0.84), Al (2.4, 0.83), Fe (2.2, 0.79), Ga (2.1, 0.78), Co (2.1, 0.77), Ni (2.0, 0.77), Sc (2.1, 0.76), Ti (2.0, 0.75), Li (1.9, 0.73), Sr (1.9, 0.72), K (1.8, 0.70), Cr (1.8, 0.70), Th (1.8, 0.69), Be (1.7, 0.66), S (1.7, 0.66), B (1.6, 0.63), Rb (1.6, 0.62), V (1.6, 0.62), Y (1.6, 0.61), Zn (1.6, 0.60), Zr (1.6, 0.59), Nb (1.5, 0.58), Ce (1.5, 0.58), Cs (1.5, 0.58), Na (1.5, 0.57), In (1.5, 0.57), Bi (1.5, 0.56), Cu (1.5, 0.55), and Mn (1.5, 0.54); and Group 2 for 15 elements with RPD values lower than 1.5: As (1.4, 0.52), Ba (1.4, 0.52), La (1.4, 0.52), Tl (1.4, 0.51), P (1.4, 0.46), U (1.4, 0.45), Sb (1.3, 0.46), Mo (1.3, 0.43), Pb (1.3, 0.42), Se (1.3, 0.40), Cd (1.3, 0.40), Sn (1.3, 0.38), Hg (1.2, 0.33), Ag (1.2, 0.32) and W (1.1, 0.19). The success of the PLS models was found to be dependent on their relationships (directly or indirectly) with MIR-active soil components.

1. Introduction

Detailed monitoring of elemental concentrations in soils is crucial in terms of risk assessment, nutritional status, land management, organic amendments, geological surveys and soil mapping. *Aqua regia* (AR) (3:1 [v/v] nitric acid [HNO_3] and hydrochloric acid [HCl]) has traditionally been used in soil chemistry in the determination of pseudo-total element concentrations in soils (ISO 11466:1995) for these purposes. Many environmental benchmark standards are based on AR metal concentrations (Kilbride et al., 2006), and it has been widely adopted in Europe and used by the Community Bureau of Reference of the Commission of the European Communities for the provision of reference soils (Ure, 1996). This analysis can provide an indication of the long-term potential toxicity effects of pollution as well as of long-term potential deficiency issues (Ure, 1996). The AR method does not provide an assessment of the total element concentration since the least acid-soluble components of soils, e.g. metal silicates, are not wholly digested (Kilbride et al., 2006). In addition it is time consuming and uses human and environmentally harmful extractants.

Visible–near infrared (vis–NIR; 25,000–4000 cm^{-1}) and mid-infrared (MIR; 4000–400 cm^{-1}) spectroscopy together with

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