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Geochemical indices and regression tree models for estimation of ambient background concentrations of copper, chromium, nickel and zinc in soil

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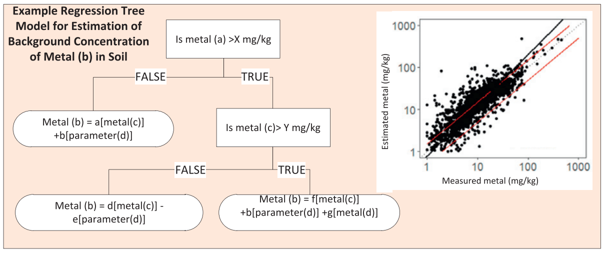
HIGHLIGHTS

- Estimation of ambient background Cr using normalization with Fe.
- Quantification of Cu contamination by normalization with Ni.
- Regression tree model provided for estimation of background Ni in soils.
- Geochemical indices not suitable for estimation of background Zn in urban surface soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Geochemical ratios between elements of environmental concern and Fe have been recommended for estimation of “background” concentrations of Cr, Cu, Ni and Zn in soil. However, little research has occurred to assess the consistency of geochemical ratios across soils developed in different environments. Broad application of generic geochemical ratios could result in under or over estimation of anthropogenic impacts to soil and subsequent inaccurate assessment of risk to the environment. A soil survey was undertaken in Victoria, Australia, including collection of samples (n = 622) from surface (0–0.1 m below ground level) and sub-surface (0.3–0.6 m below ground level) soils, overlying Tertiary-Quaternary basalt, Tertiary sediments and Silurian siltstones and sandstones. Samples were analyzed for metals and soil physical and chemical properties (particle size, cation exchange capacity, organic matter and pH). Geochemical correlations between elements in soils from different parent materials and environments were compared against geochemical relationships reported in Australia and internationally. Ratios of Cr and Fe were relatively consistent across parent materials, and comparable to published models for estimation of background Cr. Conversely, ratios between Cu, Ni, and Zn with Fe, were variable between soils developed in different weathering environments and/or soil depths. Alternative regression equations and rule based regression tree models were developed as an improved means for prediction of ambient background Cu, Ni and Zn concentrations in soil. Ambient background concentrations of Ni and

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Cr were predictable across parent materials and depths, allowing these models to be extended to soils across Australia and potentially internationally.

1. Introduction

Assessment of ambient background metal concentrations represents an important component of environmental risk assessment and contaminated land management. However, it is often difficult to distinguish areas of contamination from areas of natural enrichment due to the broad extent of human disturbance to the environment and the high natural variability of metal concentrations in soil (Appleton et al., 2008; Ander et al., 2013).

Several authors have identified strong positive correlation between background (geogenic) metal concentrations and earth metals such as Fe in soil (Hamon et al., 2004; Myers and Thorbjornsen, 2004; Aide, 2005). Hamon et al. (2004) proposed that generic linear regression models, based on correlation between Cr, Cu, Ni, and Zn and Fe can be used for estimation of background metal concentrations in soil. Subsequently, geochemical ratios, proposed by Hamon et al. (2004), were incorporated into national government guidance for estimation of ambient background metal concentrations in Australian soils, for derivation of site specific ecological risk criteria (NEPC, 2013). However, the accuracy of application of generic geochemical indices for estimation of ambient background metal concentrations across soils developed in different geochemical environments has not been assessed in the peer-reviewed literature.

Positive correlation between metals and Fe in soil has been attributed to the high metal binding capacity of Fe oxides and sequestration of metals with Fe oxides during soil formation (Singh and Gilkes, 1992). However, it is expected that metal to Fe ratios would be altered by environmental conditions that result in dissolution of minerals (for example reducing conditions) and/or conditions which influence Fe and Mn oxide formation (Liu et al., 2002; Štyriaková et al., 2016). The influence of changing environmental conditions on the accuracy of estimation of ambient background metal concentrations using geochemical normalization with Fe has not been assessed.

Geochemical ratios of metals in soil are typically based on chemical and mineralogical associations in the natural environment (i.e. natural geochemical or pedological processes) (Goldschmidt, 1937; Aide, 2005). Due to broad low level diffuse contamination associated with anthropogenic activities, metal concentrations in surface soils collected from urban and regional areas (at sites away from point sources of contamination) are considered representative of “ambient background” rather than “geogenic background” (Rosman et al., 1993; De Deckker et al., 2010; Stromsoe et al., 2013). However, given the generally low level of diffuse contamination expected to be present in the environment, compared to geogenic variability (Fabian et al., 2017), it is hypothesized that geochemical ratios can be applied in urban areas for distinguishing added point source contamination from ambient background concentrations.

Where geochemical variability cannot be captured by simple linear geochemical regression equations, (for example in the form of $\text{Log}\,[Cr] = a\,[Fe] + b$) multiple regression techniques including regression tree models may provide improved estimation of ambient background concentrations of metals (Meersmans et al., 2008; Wilford et al., 2015). Regression tree models use rules to separate data into subgroups with similar characteristics (e.g. soils with different pH or texture) and then provide multivariate linear regression equations for each sub-group (Breiman, 1984). Recently, regression tree methods, utilizing spatial variables (e.g. vegetation cover, elevation, topography) have been applied for the purpose of mapping expected soil conditions (Bou Kheir et al., 2014; Wilford et al., 2015). However, data for spatial variables typically has limited resolution, for example resolution of 100 m × 100 m (Gallant and Dowling, 2003; Gallant and Austin, 2012a; b), which may not be suitable for distinguishing the presence of added contamination from natural variation, at the scale of environmental site assessments (i.e. within one paddock or property allotment). To our knowledge, regression tree models using geochemical variables (rather than spatial variables) have not previously been applied for estimation of ambient background metal concentrations in soil. We proposed to test the suitability of regression tree models, developed using geochemical variables, for prediction of background metal concentrations in specific soil samples and quantification of added contamination.

Nickel and Cr have been reported to be naturally enriched in soils of Victoria, Australia (Mikkonen et al., 2017) and therefore geochemical methods for distinguishing natural enrichment from added contamination of these metals is of key interest for environmental practitioners. The objectives of this study were to develop geochemical regression models for prediction of ambient background concentrations of Cu, Cr, Ni and Zn in soils from varied geochemical environments and parent materials and to identify environmental or geochemical factors that change expected geochemical ratios.

2. Method

2.1. Soil survey

A background soil survey was undertaken across Greater Melbourne, Mitchell, Ballarat and Greater Geelong, of Victoria, Australia (Fig. 1). Surface (0.0–0.1 m) and sub-surface samples (within the interval 0.3–0.6 m) were collected from 314 locations ($n = 622$). The sample collection methodology is further described by Mikkonen et al. (2018b). Within the targeted regions, samples were grouped based on the mapped underlying bedrock; Tertiary-Quaternary basalt of the Newer Volcanics (basalt); Tertiary sediments including the Brighton Group (sediments) and Silurian siltstone and sandstone (siltstone and sandstone) (VandenBerg, 1997). Sample locations targeted areas of least environmental disturbance away from point sources of contamination including roads, buildings and industrial areas (Darnley, 1995).

The pH of soils in the assessment area ranged from 3.2 pH units to 8.6 pH units and was typically acidic with a median of 4.7 pH units and 5.25 pH units in surface and sub-surface soils, respectively. Median organic matter content in assessed soils was 7.1% and 1.3% in surface and sub-surface soils, respectively. Soils included sands (predominantly overlying sediments) to heavy clays overlying weathered basalt.

The extent of weathering of a soil can provide an indication of paleo-geochemical conditions and the degree of metal leaching