# **Formation of soil geochemical anomalies by plant uptake of trace elements**

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## **Abstract**

Geochemical anomalies in surface soils may aid in exploration for buried mineral deposits. Most mechanisms proposed for the formation of surface soil geochemical anomalies are based on abiotic processes, but trace elements could also become locally enriched in soils above ore bodies as a result of uptake by plants and surface recycling. In this paper, we present a conceptual model of trace element biogeochemical cycling and use a simplified mass-balance calculation and calculations based in coupled first-order differential equations, both based on the conceptual model, to evaluate the possibility that soil anomalies form via plant uptake. The existence of soil geochemical anomalies depends on the balance between ecosystem net primary productivity and trace element losses through soil erosion and leaching. Mass-balance calculations predict that accumulation in soils should be favoured for more bioavailable elements. We suggest that soil geochemical anomalies are transient geological features, forming and dispersing as a result of the relative sizes of the accumulative and loss fluxes, and this is supported by our numerical model.

# **Key Words**

exploration; trace elements; geochemical anomalies; modelling; vegetation

# **Introduction**

In landscapes where basement rocks are covered by deep chemically weathered and/or transported regolith, soils present a key sampling medium for geochemical exploration (Rose *et al.,* 1979). The mechanisms by which anomalous concentrations of trace elements accumulate in transported regolith have been discussed in some detail from an abiotic perspective (Hamilton, 1998; Kelley *et al.,* 2006). Biological mechanisms for enrichment of surface soils with trace elements have been proposed (Butt, 1992), but these processes have not been considered in detail despite the historical and current use of plants as geochemical sampling media for exploration (e.g., Dunn, 1986).

The distribution of elements with depth in soils can be controlled by plant uptake and surface recycling, and characteristic biogenic depth distributions involving surface enrichment relative to depletion at depth are well-known for major elements such as potassium (Brantley *et al.,* 2007; Jobbagy and Jackson, 2001). In semiarid to arid climate zones, in particular, plants root to considerable depth (Canadell *et al.,* 1996) meaning that uptake of trace element ions from buried mineralisation is feasible (Rate, 2002).

The addition of trace elements to surface soils by vegetation must be considered together with losses of the same elements by other mechanisms. A detailed analysis of the biogeochemical fluxes of trace elements in terrestrial environments (Ma and Rate, 2009) suggests that the controlling processes are net primary productivity, soil erosion and soil solute transport; the fluxes relevant to these processes depend on the concentrations of trace elements in the vegetation, surface soil and soil pore-water reservoirs. An additional issue is that although the reservoir of trace elements in an ore body may be very large, the fraction of this reservoir (or its weathered dispersion halo) which is physically accessible and bioavailable to vegetation may be much smaller, and potentially subject to depletion by plant uptake and redistribution. The net accumulation of any trace element in surface soils via vegetation therefore will depend on the relative sizes of addition and depletion processes (Ma and Rate, 2009). Dilution, as a result of mixing with barren material (bioturbation and sediment deposition), will also affect measurable soil accumulation of trace elements but these processes will not be considered in this paper. The relative sizes of trace element fluxes will not be constant with time; for example, the plant uptake flux is expected to be a first-order process dependent on the concentration in the bioavailable reservoir, and therefore will decrease relative to other fluxes should the bioavailable reservoir be depleted. Surface soil anomalies may therefore be transient features as shown in Figure 1.



**Figure 1. Hypothetical forms of transient soil anomalies showing forming, mature and dispersed phases (redrawn from Ma and Rate, 2009).** 

#### **Methods**

#### *Mass balance calculations*

Estimation of net fluxes from buried mineralisation into surface soils were evaluated using a simple mass balance expression (Equation (1)):

$$
A = c_P \cdot \text{NPP} - (c_S \cdot f_S + c_W \cdot f_W) \tag{1}
$$

$$
^{(1)}
$$

where  $A = net accumulation in the soil,  $c_P = trace$  element content of plants, NPP = net primary productivity,$  $c_S$  = trace element content of soil,  $f_S$  = soil erosion flux,  $c_W$  = trace element content of soil solution, and  $f<sub>W</sub>$  = vertical water flux; all concentrations (mass/mass), all fluxes (mass/area/time)

## *Differential equation calculations*

All calculations were based on the assumption of first- or zero-order differential equations.

The vegetation reservoir dynamics were described by Equation (2):

$$
\frac{dc_p}{dt} = \left( (k_1 \cdot c_R + k_2 \cdot c_s - k_3 \cdot c_p) \cdot c_p \right) - \frac{(k_1 \cdot c_R + k_2 \cdot c_s - k_3 \cdot c_p) \cdot (c_p)^2}{c_p(\max)}\tag{2}
$$

where  $c_p$  is the concentration of the target element measured in vegetation,  $c_R$  is the concentration in the (deep) regolith source,  $c_s$  is the initial concentration of the soil reservoir,  $k_1$  is the rate constant for deep element uptake,  $k_2$  is the rate constant for shallow element uptake, and  $k_3$  is the rate constant for return of the target element to the soil reservoir. For simplicity, we assumed that the net plant return,  $k<sub>3</sub>$ , reflects the sum of the total element uptake, such that whatever is gained by the plant reservoir is returned to the soil. The concentration in the vegetation reservoir was constrained to a maximum value  $(c_{p \text{ (max)}})$ , and so the equation therefore takes on a logistic form shown by the fractional term at the right hand side of Equation (2).

The surface soil reservoir dynamics were described by Equation (3):

$$
\frac{dc_s}{dt} = k_3 \cdot c_p - k_2 \cdot c_s - k_4 \cdot c_s - k_5 \cdot c_s \tag{3}
$$

where  $k_3$  is the rate constant for plant return to soil  $(y^{-1})$ ;  $k_4$  is the rate constant for erosional loss from soil  $(y<sup>-1</sup>)$ , and  $k_5$  is the rate constant for leaching (deep drainage) loss from soil  $(y<sup>-1</sup>)$ .

Rate constants for deep (regolith source) and shallow (surface recycling) plant uptake were defined by Equations (4) and:

$$
k_1 = a \cdot (\text{NPP} \cdot c_{\text{R}}) / \mathcal{E}
$$
 (4)

$$
k_2 = (\text{NPP} \cdot c_s) / \mathcal{E}
$$
 (5)

where *a* is the ratio between the rate constants for deep  $(k_1)$  and the shallow  $(k_2)$  element uptake flux (based on work on phreatic/soil water use ratios and deep/shallow root biomass ratios, and taking values between

0.02-0.05) and  $\zeta$  is the vegetation standing biomass. Rate constants for other processes were selected to represent realistic rates based on literature values for litter fall, soil erosion, and leaching.

# **Results**

Results of mass balances for a range of elements are summarised in Figure 2, which shows values of NPP/erosion for different elements which reduce net surface soil accumulation to zero, plotted at set values of erosion or NPP. In this instance, critical values of erosion rates are plotted in the bottom two curves at set NPP values of 5000 kg/ha/y (square symbols) and at 500 kg/ha/y (circular symbols). Values of NPP at which net element accumulation is zero are plotted in the top curve (triangular symbols), at a fixed erosion rate of 500 kg/ha/y. The plant: soil concentration ratio in Figure 2 represents an index of bioavailability. For example, for the readily bioavailable trace element, Zn, for a large NPP value of 5000 kg/ha/yr, the critical erosion rate at which net loss will occur from the soil pool (1000 kg/ha/yr) is high relative to other less bioavailable elements. For net surface soil accumulation of less bioavailable Cr to occur, soil erosion must be negligible. The likelihood of forming a surface soil anomaly via vegetation uptake decreases in the order Zn>Cu>Au>Ni>Cr>As>Co for Ni/Cr-poor (felsic) soil environments and in the order Zn>Cu>Au >As>Co≈Ni>Cr for Ni/Cr-rich (mafic-ultramafic) soil environments.



**Figure 2. Critical values for soil anomaly formation plotted against realistic plant/soil concentration ratios for the elements considered (re-drawn from Ma and Rate, 2009).** 

The dynamics of surface soil accumulation described by differential equation calculations were highly dependent on the input parameters. For example, for gold, with  $NPP = 2000$  kg/ha/y, the regolith concentration of Au needs to be at least 20 ppm for significant anomalism (soil response >5 times background) to occur, even in the absence of erosional losses. Such results do not always match field observations in landscapes with transported regolith, and do not agree with the mass balance presented above or with published studies (e.g., Lintern *et al.,* 1997), where sometimes significant accumulation in the soil and vegetation reservoirs occurs over <1 ppm of source Au.

In a simulation parameterised for copper (Figure 3), at a low erosion rate of 10 kg/ha/y, the loss from the soil produces a peak in accumulation and eventual decline in the soil reservoir. The vegetation concentration also shows a gradual decline from a maximum concentration (the constrained concentration) due to the feedback loop into the vegetation reservoir as the shallow uptake flux from the soil reduces (Figure 6 2 (a)). Increasing the erosion rate to 25 kg/ha/y produces a sharper peak in both the soil and vegetation reservoirs (Figure 6 2 (b)). Thus, the higher the erosional loss from soil, the more rapidly the biogeochemical anomaly declines. Anomalism measured by the soil response ratio for Cu is low, as Cu is an abundant element in the surface environment, and therefore the background is relatively high compared to the peak input from the deep source.

For some elements (*e.g*., Cu, As and Au; see Figure 3 for Cu), some depletion in the surface soil occurs initially (through erosion and shallow uptake by the vegetation), since there is a lag time  $({\sim}10^5$  y) for elements taken up from depth to accumulate in the surface soil (small deep uptake rates).



**Figure 3. Calculated Cu concentrations in the source, vegetation and soil reservoirs. (Input parameters: biomass=15 t/ha; NPP=2000 kg/ha/y; erosion =10 kg/ha/y; initial soil concentration= 2.2 mg/kg; initial source Concentration**[2] 42 (mg/kg); initial vegetation concentration 10 mg/kg. Rate constants: deep uptake  $(k_1)$ 3.0×10<sup>-7</sup> y<sup>-1</sup>; shallow uptake  $(k_2)$  2.9×10<sup>-6</sup> y<sup>-1</sup>; plant return  $(k_3)$  3.6×10<sup>-7</sup> y<sup>-1</sup>; soil erosion  $(k_4)$  1.3×10<sup>-7</sup> y<sup>-1</sup>. Leaching **was not considered in this calculation.)** 

## **Conclusion**

Our analysis of the potential for vegetation uptake to generate surface soil geochemical anomalies for trace elements has shown that this mechanism is feasible and should be considered in exploration models. The extent of surface soil accumulation by plant uptake is strongly dependent on the balance between deep uptake and recycling, net primary productivity and soil erosion with a minor contribution from leaching. Our modelling also suggests that biogenic surface soil anomalies will be transient geological features.

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