The use of empirical partition functions in the assessment and management of risks at polluted sites

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Abstract
To evaluate potential risks of contaminants to human health and ecosystems it is crucial to understand the main variables that control contaminants' fate within the soil matrix as well as the transfer of potentially toxic elements from soils to other environmental compartments.
This study focused on the use of soil chemical extractions to determine reactive and available pools of potentially toxic elements in soils. Freundlich-type empirical partition functions were applied to assess the biogeochemical reactivity of contaminants in soils and the soil⇒solution partition of potentially toxic elements. We observed that the variability of soil properties was able to effectively explain differences in the reactivity and chemical availability of contaminants. Case-studies from Portugal were analyzed.
In this presentation we will discuss the use of empirical functions to assess risks at polluted sites as well as to characterize the links between geochemical reactivity, chemical availability and water quality.

Introduction
Empirical models to estimate soil⇒solution partition relationships of elements in soils have been used recently to describe adsorption-desorption equilibria between reactive and available pools of potentially toxic elements (PTE's) in soils, taking into account soil properties (Römkens et al., 2009a; Rodrigues et al., 2010a). Empirical models were also used as an approximation of soil-plant transfer mechanisms and to correlate the metal availability to plants with soil properties (Römkens et al., 2009b).
This study will focus on advantages of the use of empirical partition functions in the assessment and management of risks of soil pollution to the terrestrial food chain as well as potential risks to water quality and aquatic biota. Case-studies from Portugal will be analyzed.

Materials and Methods
A total of 136 soils and 128 plants from different areas in Portugal were sampled. Sampling areas included both non-contaminated sites and contaminated soils affected by industrial activities or mining (Rodrigues et al., 2010b). Crops sampled included ryegrass (*Lolium perenne*), n=73; Italian ryegrass (*Lolium multiflorum*), n=9; orchard grass (*Dactilis glomerata*), n=12; collard greens (*Brassica oleracea*), n=23; and rye (*Secale cereale*), n=11.
Soil properties including pH_{CaCl2}, organic carbon (Org C), clay, and amorphous Fe and Al oxides contents (Fe_{ox} and Al_{ox}) were determined. Total pools of PTE's (As, Hg, Cu, Pb, Zn, Cd, Ni, Cr, Co, Ba, U, Fe, Mn, Al, Sb, Li, Be, Se, B and Mo) were analyzed in both soil and plant (shoots) samples. Furthermore, reactive pools (mimicked by an extraction 0.43 M HNO_3) and available pools (extraction with 0.01 M $CaCl_2$) were determined (Rodrigues et al., 2010a,b).

Results and discussion
Chemical availability
Freundlich-type empirical regression models based on element's reactive pools and soil properties (pH, Org C, clay) provided good estimations of available concentrations for As, Ba, Cd, Co, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn (r^2: 0.46–0.89) (Rodrigues et al., 2010a). As an example, Figure 1 shows the performance of Sb model. The soil⇒solution empirical function (r^2=0.82, S.E=0.30, p<0.001) obtained for this element was:

$$\log[Sb_{\text{available}}] = -1.0 - 0.75\times\log[\text{Org C}] + 0.65\times\log[\text{clay}] + 1.0*\log[Sb_{\text{reactive}}] \quad \textbf{(Eq. 1)}$$

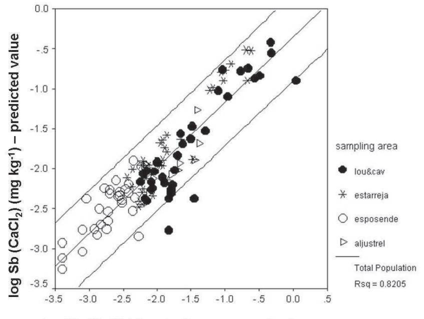

Figure 1. Performance of the empirical partition model for Sb in soils from Portugal.

For Cr and U the regression models did not provide a sufficiently good prediction of available PTE's levels.

Plant uptake and human exposure
An overview of plant concentrations of PTE's is shown in Table 1. Freundlich-type models were also derived to estimate plant contents of PTE's as a function of reactive element pools and soils properties. These

models were able to explain between 40 and 90 % of the variation of Cd, Zn, Pb, Cu, Hg, and Sb in feed crops (ryegrass and Italian ryegrass). Org C, pH and Al_{ox} were the main parameters explaining variability of PTE's concentrations in ryegrass.

Both soil⇒solution and soil⇒solution⇒crop partition relationships are essential to assess animal and human exposure to contaminants in soil. These can also be used in the calculation of threshold concentrations of PTE's in soils based on quality criteria for feed/ food crops or animal/ human acceptable daily intakes (ADI) of PTE's and soil characteristics.

Leaching to groundwater and surface water

Although the available pool measured by $CaCl_2$ is not entirely identical to *in situ* soil pore water concentrations, the levels measured by this extractant can be used as a first indicator for potential risk of contaminants' leaching from soils or water pollution. The concentrations of PTE's in $CaCl_2$ extracts were compared with the legal criteria for groundwater (to be used for water supply) in Portugal (Decreto-Lei 236/98, de 1-8-1998). Both the recommended and the admissible maximum values in groundwater for As, Ba, Cd, Cr, Cu, Hg, Pb, and Zn were exceeded in certain samples.

Soil⇒solution partition functions can be used to determine threshold soil concentrations from drinking water criteria or, as shown in Figure 2, from critical PTE's concentrations in surface water in view of impacts on aquatic biota.

Table 1. Ranges (min-max) of reactive pools of PTE's in soils and total shoot concentrations

	Concentration range (mg kg^{-1} dry weight)	
Element	Soil (reactive* pool)	Plants (shoot)
Hg	0.1-467**	0.006-5.4
Cd	0.03-1.4	0.01-5.0
Zn	1.8-519	11-432
Cu	1.2-1492	2.1-543
Pb	1.5-581	0.05-572
Ni	0.2-8.4	0.3-48
Co	0.07-14	0.04-3.4
As	0.04-384	0.1-56
U	0.04-4.1	0.01-0.2
Cr	0.07-8.9	0.8-110
Ba	2.3-208	1.4-80
Sb	0.006-1.4	0.2-15

*Given by soil extraction with 0.43 M HNO_3

**in μg kg^{-1}

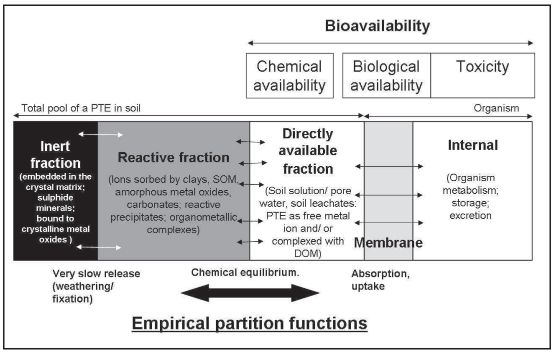

Figure 2. Evaluation of potential risks of soil contaminants to aquatic biota

Conclusions

Partition functions that link PTE reactivity and chemical availability are promising to assess animal or human exposure to soil contaminants as well as to derive soil threshold concentrations for a large array of PTE's. Mechanistic models may be necessary for Cr and U, for which poor relationships were obtained using this approach.

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