



Revisiting the K_f distribution coefficient concept through stringent geochemical modeling: Application to agronomical models under wastewater reclamation context



M. Pettenati*, N. Surdyk, L. Cary, W. Kloppmann

BRGM, 3 av. C. Guillemin, BP 36009, 45 060 Orléans, France

ARTICLE INFO

Article history:

Received 1 December 2014

Received in revised form 5 July 2015

Accepted 16 January 2016

Available online 5 February 2016

Keywords:

Wastewater reuse

Mobility of trace contaminants

Lead

Distribution coefficient

Sorption

PHREEQC model

Multi-parameter functions

ABSTRACT

The understanding of parameters controlling mobility of trace contaminants is a key topic in a world where groundwater resources for water supply are strongly exploited and consequently greater exposed to contamination risks. In the context of wastewater reuse as water saving option for irrigation, distribution coefficients for the partitioning of lead between Cretan soil and wastewater derived irrigation water are determined from laboratory experiments. In this study we use the stringent formulation of thermo-kinetic processes in the geochemical PHREEQC code to describe sorption isotherm functions generally used in agricultural water management models. PHREEQC modeling is performed to reproduce the sorption capacity of soil with a special attention to lead mobility. This model allows identifying geochemical key factors underlying K_f values. Multi-parameter functions of K_f are determined through statistical treatment of a large number of model runs with variable geochemical parameters.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The global GLASDOD survey, carried out by the United Nations in 1988–91, has demonstrated for the first time that human induced soil degradation is a vital problem in virtually all parts of the world (Oldeman et al., 1991; Sonneveld and Dent, 2009). One important aspect of soil degradation is the fixation and subsequent release of organic and inorganic pollutants, related to the extensive use of fertilizers, sewage sludge, manure, and to airborne contamination from industrial sources. Irrigation, pest control and fertigation schemes need to address mobility of trace contaminants to predict and prevent impacts on soil, surface- and groundwater and associated ecosystems. As the behavior and environmental fate of contaminants as well as the parameters controlling pollutant mobility in soils are still only partly understood, simplified approaches are widely used to predict the partitioning of organic or inorganic compounds between soil water, soil minerals and organic matter. The present study was conducted as part of the SAFIR project of the European 6th Framework Program aiming at providing new strategies and technologies for the reuse of domestic waste water in agriculture. Wastewater currently accounts for 2% of irrigation water in EU countries and 3.5% in the Mediterranean EU member states (Angelakis and Durham, 2008) and a strong increase of this proportion is expected due to the growing needs, decline of available resources and

to the fact that at present only one fifth of the available wastewater is reused in EU (Bixio et al., 2006, 2008) so that there is a strong potential for development. There is a direct link between the use of low quality water for irrigation and soil degradation. Studies of soils irrigated over several decades (up to 100 years) with the raw sewage of two megacities, Paris and Mexico city (Dere et al., 2006, 2007; Lucho-Constantino et al., 2005a,b) show significant heavy metal accumulation, especially in the uppermost soil zone.

The SAFIR project investigates the mean-term (3 years) effects on soil and crops of irrigation with wastewaters focusing on metals and pathogens. Contrarily to the precited studies these wastewaters underwent conventional primary, secondary and project-specific tertiary treatments (sand filter, membrane bioreactor, heavy metal removal, UV disinfection) so that the resulting water quality conforms to the prevailing regulation. One objective is to provide decision support to farmers who want to make use of non-conventional water resources through a decision support system integrating irrigation and fertigation strategy, water dynamics in soil, plant and soil quality and the associated risks and economy. When aiming at modeling heavy metal mobility in such a context, there is a need for a relatively straightforward and robust approach, able to include reactive transport of harmful compounds in decision support systems which have to be simple in use for the inexperienced user. Coupling of a geochemical code with a water and solute transport model will lead to a much higher degree of complexity of the resulting tool and would limit its use to specialists. In this paper, we develop a method to link geochemical models with agricultural water

* Corresponding author.

E-mail address: m.pettenati@brgm.fr (M. Pettenati).

management models through the derivation of sorption isotherm functions from a stringent thermo-kinetic model (PHREEQC, Parkhurst and Appelo, 1999) to be integrated in a soil–water–plant model (DAISY, Hansen et al., 1991).

Sorption isotherms can be used to describe the dependence of fixed (sorbed) concentrations of a given compound and its concentration in the liquid phase at thermodynamic equilibrium (synthesis in Limousin et al., 2007). Strictly spoken, the concept is limited to sorption–desorption processes but the typical experimental approach for determining partition coefficient values (batch experiments in which solutions with variable concentrations of the compound of interest are brought in contact with a given soil) will not distinguish the actual mechanisms of water–soil interactions. Sorption–desorption processes are predominant for organic compounds, even if biodegradation may play an important role, whereas for inorganic compounds, like heavy metals, other processes may prevail, in particular dissolution–precipitation reactions. Experimental determinations currently treat the water soil system as a black box: Within the liquid phase, only the total concentration of a given compound is taken into account, independently of the aqueous speciation, within the solid phase, no distinction of reactive mineral species is made. Nevertheless, the partitioning of a compound between the liquid and the solid phase is the result of a complex superposition of several competing reactions between aqueous species and mineral phases so that the derived sorption isotherms describe in fact not one single reaction but may result from a superposition of several of them. This may contribute to the extremely high variability observed for experimental partition coefficient values of heavy metals, depending on experimental conditions, key parameters as pH and organic matter content, and soil types (Forbes et al., 1976; Zhu, 2003; Carlon et al., 2004). The sorption isotherm approach has the advantage to be straightforward, relatively simply to implement in water and solute transport models, so that reactions with the solid phase can be taken into account to some degree, and is widely used in soil sciences, risk assessment and agronomy.

The basic idea of our approach is to start from a strict thermo-kinetic model of water–soil interaction and to perform aqueous–solid geochemical calculations using PHREEQC through a series of simulated batch experiments using data collected during irrigation experiments on Cretan soils. The PHREEQC experiments are backed up by laboratory batch experiments conducted in laboratory on the same soils. Those experiments take into account the kinetics of the water–soil reactions. They will, *in fine*, after equilibration of irrigation water with a given soil, under given pH, T, CEC... conditions, lead to partition functions between aqueous and the sum of different fixed forms of the investigated heavy metals.

In this study, after the first tests, concave isotherms, reaching a plateau or not, were privileged over linear relationships. They are described by the empirical Freundlich model:

$$A_i = K_f \cdot C_i^n \quad (1)$$

with A_i , the quantity of sorbed element i per unit weight of adsorbent; K_f , the distribution coefficient; C_i , the aqueous concentration of element i in equilibrium with sorbed concentration and n , a dimensionless non-linear sorption coefficient. A special case where $n = 1$ is the linear function K_d or “distribution coefficient” with 0 origin, an isotherm that is frequently used, due to its simplicity. In the following we will use the Freundlich isotherm as it represents the general case most widely encountered in experimental studies. This choice is also motivated by the analysis of the PHREEQC modeling results, indicating that for the investigated concentration range, a linear function (K_d) would have induced an oversimplification.

Starting from a stringent geochemical model describing the sum of ongoing water–soil reactions and coming up in the end with values for K_f and n is a form of simplification that is analogous to the experimental isotherm determination in batch experiments.

The aim of this study is to identify the geochemical key factors influencing K_f values taking into account the complex geochemical processes of water–soil interactions. PHREEQC geochemical model can be considered as an assemblage model combining thermodynamic models for inorganic speciation and mineral equilibria with separate models for ion binding to a large variety of reactive surfaces. Assemblage is powerful for the prediction of metal fate and transport in various environments (Groenberg and Lofts, 2014). Systematic variations of geochemical key parameters will then allow deriving multi-parameter functions of K_f that can be directly implemented in agronomical models. The method presented has been applied to the calculation of lead sorption on a Cretan soil.

2. Material and method

2.1. Field and soil sample characterization

The soil was sampled from the 0–30 cm horizon of an array of agricultural experimental plots in Crete near Chania, run by the NAGREF (National Agricultural Research Foundation of Greece). The soil is an alfisol with the following characteristics: the sandy fraction predominates (42–66%) together with a significant clay fraction (14–42%) and a loamy fraction of 14–26%. Calcite contents are homogeneously low, for the standards of the Chania area with 1.7 to 2.2%. Organic matter is concentrated in the uppermost 25 cm (0.6 to 1.47%); in the lower interval investigated (25 to 50 cm, the organic matter contents range from 0.27 to 0.74%. Porosity is around $36.4 \pm 1.6\%$. pH is close to neutral, and varies slightly around 6.5 (± 0.09). The sample is rich in silica, contained in by quartz and clays. It is also rich in aluminum and iron. The soil is more reddish in the eastern lower part of the array of plots with higher clay contents and a higher CEC (10 meq). The other parts are in contrast richer in sand and have a higher porosity and a lower CEC (5 meq).

2.2. Sorption isotherm

The soil was air-dried and passed through a 2-mm sieve. Prior to all batch experiments, the soil was kept at ambient temperature (18–20 °C) for 3 days. The target compound is lead but the experiment was designed to take into account the effects of competition between lead and other trace metal(oid)s (As, Cd, and Cu) that are found at variable concentrations in the secondary treated wastewater (STWW) provided by the municipal treatment plant of Chania city (Cary et al., 2015). The synthetic solution used for the batch experiments was realized from pure salts (CaCl₂, MgSO₄, MgCl₂, KCl, NaHCO₃, CdNO₃, CuNO₃, AsNO₃) and mimics the measured major and trace element composition of the irrigation water used at field scale (Table 1). For each run, pH, T, and the concentration of As, Cd and Cu were kept constant whereas Pb²⁺ concentration was incremented from 0.01 mg/l to 0.5 mg/l.

The sorption isotherm is obtained for each soil sample by equilibrating 5 g of soil with 50 ml of solution in PE flasks, containing constant concentrations of As (10 µg/l), Cu (40 µg/l) and Cd (2 µg/l) and variable concentrations of Pb.

Even if the tested range of 0.1 and 0.5 mg/l of lead is higher than the concentrations determined in domestic waste waters of the SAFIR sites (Cary et al., 2015; Surdyk et al., 2010), similar or higher concentrations have previously been tested for K_d measurements (Lions, 2004; Sauvé et al., 2000; Peters and Shem, 1992).

The flasks were cleaned by wetting with a solution of detergent TFD4 at 10% for one night followed by successive rinsing in demineralised water (2 times) then in MilliQ^R water (1 time).

Blank controls without soil were set up to check for contamination from the bottleware. Triplicates were made for each tested concentration. The tubes are isolated from the atmosphere and shaken end-over-end for 72 h at 18 °C and at 30 rpm. The suspensions are then centrifuged at 8000 rpm for 10 min, and the trace element concentration in

Download English Version:

<https://daneshyari.com/en/article/4573034>

Download Persian Version:

<https://daneshyari.com/article/4573034>

[Daneshyari.com](https://daneshyari.com)