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Pb, Cu and Cr interactions with soil: Sorption experiments and modelling

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ABSTRACT

The objective of the study was to assess the extent of heavy metal contamination of a sandy soil submitted to long-term irrigation by effluent water. For this purpose, batch equilibrium technique on a sandy soil was adopted to investigate sorption of copper, chromium and lead at various pH and at ionic strength 0.01 M. Competitive sorption was evaluated as well for copper and chromium introduced at the same concentration. Batch experiments were carried out at 20 °C with the < 2 mm fraction of the soil, in suspension with 0.01 M $NaNO_3$ and at pH ranging from 2.0 to 9.0. Metallic ions under their nitrate salt form were introduced at the concentration at 6.10^{-4} M. The PHREEQC 2.12 hydrogeochemical interactive code was used to model experimental sorption data on the basis of heavy metal complexation at the interface soil/solution metallic onto proton exchanging sites. The experiments were described by double layer model and the surface complexation constants considering one type of exchangeable sites were determined by this discrete site model.

1. Introduction

Diffusion in natural porous media such as soil is still an important study to be made because it implies the fate and transport of contaminants in soils and groundwater. Indeed, among the different uptake pathways leading to the potential health risk of plants and people, uptake or mobility of heavy metals which are strongly dependent on soil pH are known to be very important. Soil represents complex mixture of components that could be involved into metal sorption processes: silica, clay, organic matter, iron and manganese oxides, etc. The sorption capacity of soil varies greatly according to its origin, its composition. The potential mobility of metals has to be elucidated on various porous systems in order to predict pollution in different conditions. Sandy soil is known to be very porous and then to facilitate the migration of metal ions towards the groundwater. It is then a particularly important system to be studied, especially in sensitive areas, potentially polluted.

Contaminant transport are commonly studied through sorption/desorption and kinetics experiments followed by modelling with geochemical codes. Indeed, contamination of groundwater depends on sorption processes on soil and consequently risk assessment has to be done to evaluate the various compartments subject to pollution. Many pollution problems at the field scale involve not only adsorption processes but also water flow, multicomponent solute transport, biogeochemical processes, etc. Models that integrate these processes can be efficient tools for studying and predicting the mobility of a wide range of inorganic and organic pollutants subject to various hydrologic and geochemical conditions. Indeed, fitting experimental sorption data with geochemical codes where conditions are controlled in batch reactors can help in selecting parameters and mechanisms responsible for pollutant transfer and quantifying their related, kinetic and hydrodynamic parameters.

Metals represent a known source of contamination because of industrial, agricultural and urban activities.

Cu is an essential micro-nutrient required in the growth of both plants and animals, but it becomes toxic over a certain concentration. As Cu is commonly used as fungicide in agricultural use, its content has to be monitored for risk assessment in the environment.

Among heavy metals, chromium has received little attention in comparison to Cd, Cu, Pb, Zn. Indeed, the dominant naturally occurring form of Cr is the trivalent oxide Chromite, a very stable spinel crystal structure. It is found in rocks, air, water, soil, and in volcanic dust and gases. It is slow to react and is considered essentially immobile in the environment, contrary to the highly mobile and toxic Cr(VI), whose occurrence is rare in nature. But, some investigated sites were found to present surface soil Cr contamination [1,2], which justify to study this element.

Lead is a significant environmental contaminant because it is toxic, persistent, and can be taken up and stored in biological tissues. This element is widely used in domestic and industrial applications and has a high probability to occur and accumulate in wastewater. Natural processes such as soil weathering and erosion, volcanoes and forest fires rarely result in elevated concentrations in the environment; and in fact, human activities are responsible for local serious contamination.

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Difficulty in the availability of fresh water to be used for irrigation in islands can be solved by using waste water after primary treatment such as activated sludge-type treatment plant followed by secondary purifying process such as lagoon. The long-term uses of such effluent water in agricultural lands can results in the build-up of metal levels in soils and groundwater [3]. Such a practice must be evaluated in term of pollution, included metal contamination. Indeed, the environmental impacts of municipal wastewater discharges are numerous and inputs of contaminants such as metals can cause toxicity to organisms in contact with these polluted waters.

In the present study, lagoon effluents generated by a municipal wastewater treatment plant were investigated in Porquerolles Island (South of France) to determine the environmental fate of trace metals in soil irrigated by such waters. For this purpose, we propose to evaluate the sorption capacity and binding strength of a sandy soil for copper(II), chromium(III) and lead(II). Because contaminated soils can contain more than one heavy metal species, the behaviour of a particular metal species in a soil system could be affected by the presence of other metals. In that context, competitive sorption between copper and lead was as well investigated in multi-element batch systems. The sorption was evaluated for three different depths of soil where intensive effluent water irrigation is taking place for 20 years on a peach tree field.

2. Experimental methods

2.1. Reagents

Reagents used in this study were of analytical grade or better. Milli-Q water used was from a Milli-Q deionizing system, Millipore, USA.

2.2. Study area

The soil samples were taken in Porquerolles Island (South of France) which is a particularly interesting area to study. Indeed, it suffers from lack of fresh water availability because the island cannot supply both agricultural and people needs, especially under touristy period, in summer time when the Mediterranean climate can impose up to six months of dryness in a row. In order to compensate this lack of fresh water, reuse of purified municipal waste water was found to be an alternative for agricultural supply in irrigation water. This effluent water (EW) is coming from lagoons, used as a secondary purifying process after a primary activated sludge treatment, and is supposed to be appropriate for irrigation.

2.3. Soil sample

The raw soil material was collected from a peach tree field irrigated for over 20 years by secondary effluent water (SEW) coming from lagoons. The soil samples were taken out at three different depths in duplicates on the irrigated soils (P_{20}, P_{40}, P_{60}) and the corresponding reference soils which were never irrigated (P_{ref20}, P_{ref40}, P_{ref60}). The soil is a sandy-type soil with about 80% silica, and is poor in organic matter content (between 0.5% and 1%). The organic matter content was evaluated by Total Carbon measurements on a Shimadzu-TOC V_{CSH}. The dried soil was sieved at 2 mm. The mineralogical composition was determined by X-ray diffraction (XRD) and revealed the presence of illite, smectite and vermiculite (between 3% and 6% depending on the depth). Quartz and K-spar peaks were also detected in agreement with the sandy texture of the soil. The surface area of the samples was determined by N_2 gas adsorption (BET method) and was estimated to 30 m^2/g.

2.4. Sorption experiments

2.4.1. As a function of pH

All the experiments were carried out at 20 °C ± 2 °C under atmospheric conditions, in polypropylene (PP) containers. The soil concentration was maintained at 50 g/L in electrolyte background concentration of 0.01 M $NaNO_3$. Metal ions were introduced at 6.10^{-4} M and their sorption was measured for a pH ranging from 2.0 to 9.0. Each depth of soil samples was compared to each other, for both the irrigated soil and its reference, to evaluate the eventual impact of irrigation and the organic matter content on metal retention properties of the soil. To investigate a potential sorption competition between copper and chromium, additional sorption isotherms were carried out, with 6.10^{-4} M concentrations for both metallic ions. In this case, Cr was introduced 24 h after Cu to allow Cu to complex first. The pHs were set up with increments of NaOH and HNO_3 0.1 M, and measured with a combination electrode (Hanna Instruments) after calibration with three buffers (4.01, 7.01 and 10.01 buffers from Hanna Instruments). The final volumes were adjusted with $NaNO_3$ 0.01 M to 20 mL. Kinetic study of the metal sorption indicated that the suspensions have to be stirred for 24 h to ensure complete sorption. The soil suspensions were then centrifuged at 2500 rpm for 20 min before metal analysis of the supernatant by AAS (FS95, Thermo Electron). The detection limit was 0.5 ppb and the analytical precision on metal concentration was between 1% and 3%. The supernatants were immediately acidified by 50 μL of HNO_3 72% before analysis. All samples were analysed three times and averaged. The metallic ions sorbed on the soil surface were calculated from the difference between the initial metal concentration introduced and free metal ions found in solution. All the samples were corrected from blank measurement and native soil content.

2.4.2. Precipitation isotherm

In order to discriminate sorption from precipitation, we performed, in the same conditions, isotherms according to the same protocol as above, but without any soil.

2.4.3. Desorption experiments

After sorption experiments, the solid is collected by centrifugation and 20 mL $CaCl_2$ 10^{-2} M are added. After 24 h stirring, the solid is collected another time by centrifugation. The procedure is repeated five times. These experiments were achieved for each metal and allowed us to check the reversibility of the metal complexes.

2.4.4. Kinetic

The kinetic experiments were conducted for a metal concentration of 6.10^{-4} M at fixed pH: 4.8 for Cu, 4.0 for Cr and 5.0 for Pb. The same procedure than sorption was followed, except that the contact time for each batch reactor was set to 0.5, 1, 2, 3, 6, 12 and 24 h, before centrifugation and AAS analysis.

2.5. Modelling

The formation of surface complexes at the soil/water interface can be described as a chemical reaction between an aqueous species and a surface functional group [4]. The calculation of the related equilibrium constants of the reactions taking place at the interface was performed using the hydrogeochemical code PHREEQC 2.12 [5].

The chemical speciation at equilibrium is defined by a set of equations representing the mass balance law for each chemical element and the electrical charge balance. The set of equilibrium equations is solved by the Newton–Raphson algorithm and the calculated data include the concentration of each chemical species in each phase. For a purely equilibrium calculation, each element in