Sorption and mobility of Sb(V) in calcareous soils of Catalonia (NE Spain): Batch and column experiments

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ABSTRACT

The sorption of Sb(V) onto natural calcareous soils was studied in batch and column experiments as a function of physicochemical properties of the soil, namely: organic matter, the active fraction of Fe and Al and the pH of the soils. Batch experiments were performed in order to determine the sorption capacity and the kinetic rate of the sorption. Freundlich isotherm described properly the equilibrium experimental data and the kinetic results show that the sorption was very slow in all the soils studied (equilibrium after 7 days) when compared with literature data for Sb(V) sorption onto soils with higher iron content. Column experiments were carried out in order to determine the mobility of Sb(V) in the soils. The Thomas model can describe partially the breakthrough curves obtained for the Sb(V) sorption on the soils. The fitting of the model to the experimental data would indicate that transport and kinetic parameters also affected the dynamic sorption behavior. The experimental breakthrough curves can be properly described by the convective–dispersive equation (CDE) by using the CXTFIT code, and the parameters obtained by the model were in concordance to the sorption capacity reported in the column experiments. This study indicates that sorption of Sb(V) onto the soils is mainly affected in batch experiments by their 'active' Fe and Al content; while in column experiments organic matter content appeared as an important parameter. Desorption experiments resulted in a metalloid recovery above 90%, which indicates a fast and effective method to recover Sb(V) from calcareous soils and has implications for its geochemical behavior (vertical mobility in soil profiles) as a result of its relatively low Sb retention.

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1. Introduction

International environmental protection agencies consider antimony and its compounds as priority pollutants (Council of the European Communities, 1976; United States Environmental Protection Agency, 1979). The maximum antimony concentration in drinking waters established by the United States Environmental Protection Agency (2009) and the European Union (Council of the European Communities, 1998) is 6 µg dm^{-3}. Antimony is very toxic, affecting the human and animal health in different ways (Agency for Toxic Substances and Disease Registry, 1992; Elinder and Friberg, 1986; Gebel, 1997; Gebel et al., 1996, 1997; Ulrich, 1998).

There are different sources of antimony in natural waters, both natural and anthropogenic (Wilson et al., 2004; Steely et al., 2007; Ettler et al., 2007). In non-polluted waters its concentration is usually not higher than 1 µg dm^{-3}, but in the proximity of anthropogenic sources, antimony concentrations might be two orders of magnitude higher (Filella et al., 2002a).

According to thermodynamic equilibrium predictions, antimony exists as Sb(V) in oxic systems and as Sb(III) in anoxic systems (Filella et al., 2002b), however, even under reducing conditions, X-ray absorption studies on mine soil samples have shown that antimony is sorbed as Sb(V) instead of Sb(III) (Mitsunobu et al., 2005). Chemical speciation calculations show that in oxic conditions the predominant antimony species is the soluble Sb(OH)$_6^-$ (Filella et al., 2002b).

In spite of the identification of antimony as a toxic environmental pollutant, little is known about its environmental mobility and the antimony (V) interaction with mineral phases has not been studied in detail, yet. Iron oxides and iron hydroxides have a high affinity for antimony (Watkins et al., 2006; Nakamaru et al., 2006; Leuz et al., 2006; Tighe et al., 2005; Johnson et al., 2005; Scheinost et al., 2006; Martínez-Lladó et al., 2008) and the presence of these minerals seems to be responsible of the high sorption capacity of some soils (Nakamaru et al., 2006; Tighe et al., 2005; Lintschinger et al., 1998; Takaoka et al., 2005). However, there is still an evident lack of information on antimony retention on soils with low iron content. On the other hand, almost all the studies dealing with antimony sorption on soils are based on the determination of the antimony content in polluted soils compared to non-polluted soils and antimony distribution in plants (Murciego et al., 2007), this means that almost nothing

is known on the kinetics of the sorption process and the relation between sorption rate and soil composition.

In a previous work (Martínez-Lladó et al., 2008) a spatial distribution of fifteen trace elements potentially harmful for the human health and the ecosystem were studied in the soils of Catalonia, Spain. The antimony background and reference values proposed in this study were 1.36 and 4.33 mg kg^{-1}, respectively. In addition, the Sb concentration showed a high variability depending on the sample that was related to the influence of both geology of the soil and the possible antimony anthropogenic inputs (Martínez-Lladó et al., 2008). Around 40% of Catalan territory is disturbed by different anthropogenic activities like salt mining exploitation, agricultural activity and chemical, pharmaceutical and textile industry, which are the main sources of Sb, and other metalloids in the rivers and sediments of the central area of Catalonia (Casas et al., 2003).

In this context it is necessary to characterize the interaction (mobility) of Sb(V) with a non-contaminated soils of this region that can be strongly affected by the recently anthropogenic activity. The aim of this work is the study of the sorption of antimony (V) onto different non-polluted soils from the central area of Catalonia. For this purpose, batch and fixed bed experiments have been carried out in order to determine the sorption kinetics and the sorption capacity of the soils as well as the dynamic behavior (sorption and transport parameters) of antimony(V) on the soils.

In this sense, different isotherm and kinetic models have been used in order to characterize the sorption behavior in batch experiments and The CXTFIT code has been used to estimate the transport and sorption parameters of the convective–dispersive equation (CDE) by adjusting the model to the experimental breakthrough curves (BTC).

2. Experimental

2.1. Characterization of soils

Catalonia is located in the western Mediterranean, and makes up the NE part of the Iberian Peninsula. Covering an area of 32,000 km^2, its territory has a significant physiographic diversity, which implies a wide range of soil types. The central area of Catalonia is a depressed region that defines the eastern sector of the Ebro Basin. This central depression is infilled by sediments derived from the uplift and erosion of the Pyrenees and the Catalan Coastal Ranges (located in the east of Catalonia) since Paleogene times (Puigdefàbregas et al., 1992). The soils used in this work come from the Bages region and they were not altered by any anthropogenic activity. Samples of 8 different soils representative of the different geological environments in the region were taken (see Fig. 1). These calcareous soils were selected because they presented relatively high pH values and low iron content.

Soils were dried at 35–40 °C, and the fraction with particle size<2 mm was chosen for the experiments. The mineral phases present in the column fillings were identified with a BRUKER D5005 X-Ray Diffractometer (XRD), with Cu K-alpha radiation. Calcite (CaCO$_3$) and dolomite (CaMg(CO$_3$)$_2$) were identified in all samples with the exception of soils 1 and 8, which only showed calcite peaks (data not shown).

The pH of the soils was determined by an electrometric method, equilibrating 10 g of the soil with 10 cm^3 of a 0.01 mol dm^{-3} CaCl$_2$ and measuring the pH of the solution with a commercial electrode (Crison 52 04) (Thomas, 1996).

Total carbonate content was determined following the methodology described by Loeppert and Suarez (1996), based on the CO$_2$ released by the carbonates decomposition after reaction with HCl.

Water content was determined by measuring the weight loss of the soil after drying at 104 °C (Nelson and Sommers, 1996).

Organic matter content was estimated using the methodology described by Nelson and Sommers (1996), based on the weight loss of the soils after heating at 400 °C.

The content on 'active' iron and aluminum was determined by extraction with ammonium oxalate (Loeppert and Inskeep, 1996). The values obtained for the aforementioned parameters and the background Sb(V) concentration on the soils are shown in Table 1.

2.2. Batch experiments methodology

Antimony (V) solutions were prepared from KSb(OH)$_6$. Ionic strength was kept constant at 0.01 mol dm^{-3} in all the experiments by means of NaClO$_4$·H$_2$O addition. Experiments were carried out at 25.0 ± 0.1 °C as previously described Martínez-Lladó et al. (2008). Samples were filtered by using 0.45 μm cellulose filters before analysis. pH of the samples was monitored by a combined electrode (Crison 52 02). Antimony concentration in solution was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Agilent 7500cx after microwave-assisted dissolution. Soils were decomposed in closed Teflon vessels with Merck Suprapur Quality HNO$_3$ and HF acids following EPA guidelines (United States Environmental Protection Agency, 2003). Dissolved soils were diluted with 1% HNO$_3$. In order to validate the method used, a certified reference soil (NCS DC73319 LGC Promochem) was analyzed 7 times using the previously described method. The detection method for Sb(V) was 0.1 mg kg^{-1}. The experimental and certified values were 1.36 ± 0.06 and 0.90 mg kg^{-1}, respectively. Sb 121 and Sb 123 isotopes were monitored in order to check for possible interferences. Discrepancies observed between the certified and measured value could be due to variability in the extraction procedures of Sb from the soil solution. Although the manufacturer of the reference material did not give any reference, it is possible than the extraction procedure used in this work could mobilize more analyte to the liquid phase than the one used to certify the material. Ultrapure Quality 1000 mg dm^{-3} standards (Scharlau, Germany) were used to prepare standards ranging from 1 to 100 ppb. Aliquots of a 1000 mg dm^{-3} Rh standard were added to achieve a final concentration of 10 ppb in samples and calibration standards as internal standard. The limit of detection of the method was calculated as three times the standard deviation of 7 blanks.

Equilibrium isotherms were carried out with batch experiments at room temperature (25 ± 0.1 °C). Samples of 0.5 g of soil were put in contact with 20 cm^3 of an aqueous solution of Sb(V) (initial concentrations ranging from 10^{-6} to10^{-2} mol dm^{-3}) in polyethylene tubes and stirred until equilibrium was achieved. Initial concentration rang was determined by the detection limit of Sb(V) and from the low solubility of KSb(OH)$_6$.

Kinetic experiments were performed in order to determine sorption as a function of time, dynamic contacts were carried out in polyethylene tubes, one tube for each contact time. In these experiments, samples of 0.5 g of soil were putted in contact to a 10^{-5} mol dm^{-3} Sb(V) aqueous initial concentration and stirred until equilibrium was achieved. Sampling was performed from several hours to 7 days.

The equilibrium pH in batch experiments were ranged from 7.4 to 7.9 and differed in less than 0.2 units from the samples pH of each soil.

2.3. Column experiments methodology

The hydraulic properties of the column were determined by pumping a tracer through the column. In the case of non-reactive tracers, the convective–dispersive equation can be expressed to (Fonseca et al., 2009; van Genuchten, 1980):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{1}$$

where C is the flux average or resident concentration (mol dm^{-3}), m is the average pore water velocity (m s^{-1}), D is the dispersion coefficient (m^2 s^{-1}), x is distance (m), and t is time (s).