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Aluminum fractionation and speciation in a coal mine dump: Twenty years of time-course evolution

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ABSTRACT

We study the time-course evolution of Al fractions and species in the solid and liquid phases of soils developed over spoil materials rich in sulfides, situated in the mine dump of As Pontes (NW Spain), over a twenty-year period. Three plots (CSA, CSP and P206), subjected to different reclamation practices, were monitored. Plot P206 was established by selecting spoil materials, trying to avoid pyrite oxidation by atmospheric contact, whereas in plots CSA and CSP spoils were placed randomly, CSA being richer in sulfides. Samples were taken at two depths (0–15 and 15–30 cm) in autumn 1992 and 2012. In 1992, plot CSA showed the lowest pH (2.8) and the highest SO_4^{2-} concentration (845 mg L^{-1}). This plot presented the lowest Al concentrations in the solid phase (corresponding to total non-crystalline Al, Al bound to organic matter, and inorganic non-crystalline Al), and the highest concentrations of total Al in solution. Most of this soluble Al was reactive Al, concretely labile Al, mainly represented by Al^{3+} (the most toxic species) and Al-SO_4. Contrary, plot P206 (where spoil material was selected) was the less acidic (pH 6.0), showed the lowest SO_4^{2-} concentration (17 mg L^{-1}) and the highest levels of Al in the solid phase, whereas Al in solution was very low. Twenty years later, no significant variations were found for pH in any of the plots, while there was a decrease of organo-aluminum complexes in the solid phase, as well as of SO_4^{2-}, total Al and labile Al in the liquid phase, and some new (previously undetected) soluble organo-aluminum forms were quantified. As regards the labile Al species, Al^{3+} and Al-SO_4 significantly decrease. However, plot CSA maintained the most acidic pH values and the highest SO_4^{2-}, total Al, reactive Al, labile Al, Al-SO_4 and Al^{3+} concentrations. The time-course evolution during the twenty-year period situated plots CSA and CSP in better conditions, closer to that of natural soils in the area.

1. Introduction

Open-cast mining is an anthropogenic activity that causes high environmental impact, especially in edaphic media, where it provokes a drastic alteration of biogeochemical cycles, including soil and water pollution and degradation (Conesa and Schulin, 2010).

The composition of the spoils derived from this kind of mining is highly variable, although large amounts of pyritic materials are frequently present. The pyritic materials were initially into unaltered rocky formations, in the deepest layers, but they suffer oxidation when exposed to the atmosphere, resulting in sulfuric acid generation. In fact, the strong acidity derived from sulfide oxidation is one of the most frequent problems in mine soils, (Kittrick et al., 1982; Hopkins et al., 2013) and it can favor mineral alteration, promoting dissolution of minerals and increasing ionic concentration in the soil solution and drainage waters. The presence of large concentrations of Al in the soil solution is especially important, due to its high bio-toxicity risk (Godbold and Hüttermann, 1994; Nogueirol et al., 2015).

Few studies have focused on Al speciation in environments affected by mining activities. However, some publications have demonstrated that the toxicity of dissolved Al varies in function of the species present, which is dependent on the pH of the medium (affecting to Al hydrolysis), and on organic carbon and sulfate concentrations (Pu et al., 2010; Waters and Webster-Brown, 2013).

Marques et al. (2010) indicate that Al^{3+} and Al-OH are the dominant species in acid drainage waters from mining areas. These acid drainage solutions from mining areas are frequently oversaturated for certain sulfate-aluminum minerals such as alunite, and for amorphous hydroxyl-aluminum minerals, which could decrease and be limiting of dissolved Al and sulfate concentrations (Marques et al., 2010; Pu et al., 2010).

In view of that all, acid mine spoils represent unbalanced geomorphologic systems, with physicochemical characteristics very different

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to that of natural soils, thus making difficult edaphogenic processes, revegetation and reclamation (Juwarkar et al., 2004; Kumar and Kumar, 2013; Sena et al., 2014).

The growing importance of Technosols, as well as their impact on environment are making evident in the convenience of promoting the study of their behavior and evolution (Jangorzo et al., 2013; Paradelo and Barral, 2013; Huot et al., 2014; Lilić et al., 2014). It has caused that a diversity of studies has focused on Technosols, some of them dealing with restoration of degraded areas (Tsolova et al., 2014; Zornoza et al., 2015).

Reclamation activities in these areas should focus on the use of appropriate techniques (as first step), properly selecting and managing mine spoils to allow or facilitate restoration of the original structure of the ecosystem (Zipper et al., 2011). As second step, it would be essential to carry out a follow up of the physicochemical characteristics of the spoils to assess the efficacy of the reclamation process with time.

The lignite opencast mine situated in As Pontes (A Coruña, Spain), has generated large amounts of mine spoil for more than 40 years, which have been disposed in a mine dump with a storage capacity of 700 Mm^3 and an upper surface of 1100 ha. During the 1980s the dump was divided in plots to be subjected to different reclamation tasks.

The objective of this work was to shed light on the time-course evolution of physicochemical characteristics of the solid and liquid phases, in three plots established in the As Pontes dump and subjected to different reclamation techniques. The study focused on Al forms and species in the solid and liquid phases of the soils in the plots, comparing data from two sampling years, 1992 and 2012.

2. Materials and methods

2.1. Study area

The study was carried out at the dumping site of the opencast lignite mine of As Pontes (A Coruña, NW Spain) (Fig. 1), where lignite exploitation ended in 2007. The coordinates of the dumping site are 43° 27′ 40″ N and 7° 57′ 17″ W. Its surface area is 11,000,000 m^2 (1100 ha), and its storage capacity is 700 Mm^3.

The local climate is temperate-humid, with an average annual rainfall of 1500 mm, and its mean annual temperature is 13 °C, with marked fluctuations throughout the year.

The spoil material consists in tertiary sediments (originally situated between layers of the exploited coal), as well as phyllites that were placed at the edge of the sedimentary basin. Part of this material contains high amounts of pyrite.

2.2. Sampling and analysis

The dumping site was divided in different plots, taking into account the age, the kind of spoil material, and the reclamation treatment applied. In this study, three plots were used (called CSP, CSA and P206, retaining the nomenclature given in their construction), that were monitored since 1992 (Monterroso and Macías, 1998).

Reclamation tasks of these Technosols started in 1980, and have been previously described by Val et al. (1988) and Gil et al. (1990). Plots CSP (2.6 ha) and CSA (2.9 ha) were established in 1972, when very heterogeneous spoil materials were dumped without previous design or reclamation criteria.

The dominant materials in plot CSA were tertiary sediments, very rich in carbonaceous clays with a high content of pyrite. In plot CSP, the spoil material consisted in a mixture of tertiary sediments (with variable contents in carbonaceous clays), quaternary sediments from alluvium or colluvium origin, and remaining materials derived from natural soils of the area.

In 1980, plantation of the tree species *Pinus radiata* D. Don, and *Castanea sativa* Miller, was initiated in plot CSP, whereas plantation of *Betula pubescens* Ehrh, and *Eucalyptus spp.* was initiated in plot CSA.

In 1983, both plots were added with the following materials: 20 cm of topsoil (2000 m^3 ha^{-1}), lime amendment (3 t ha^{-1}), and inorganic fertilization of nitrogen, phosphorus and potassium (NPK, 8-15-15, dosing 0.7 t ha^{-1}).

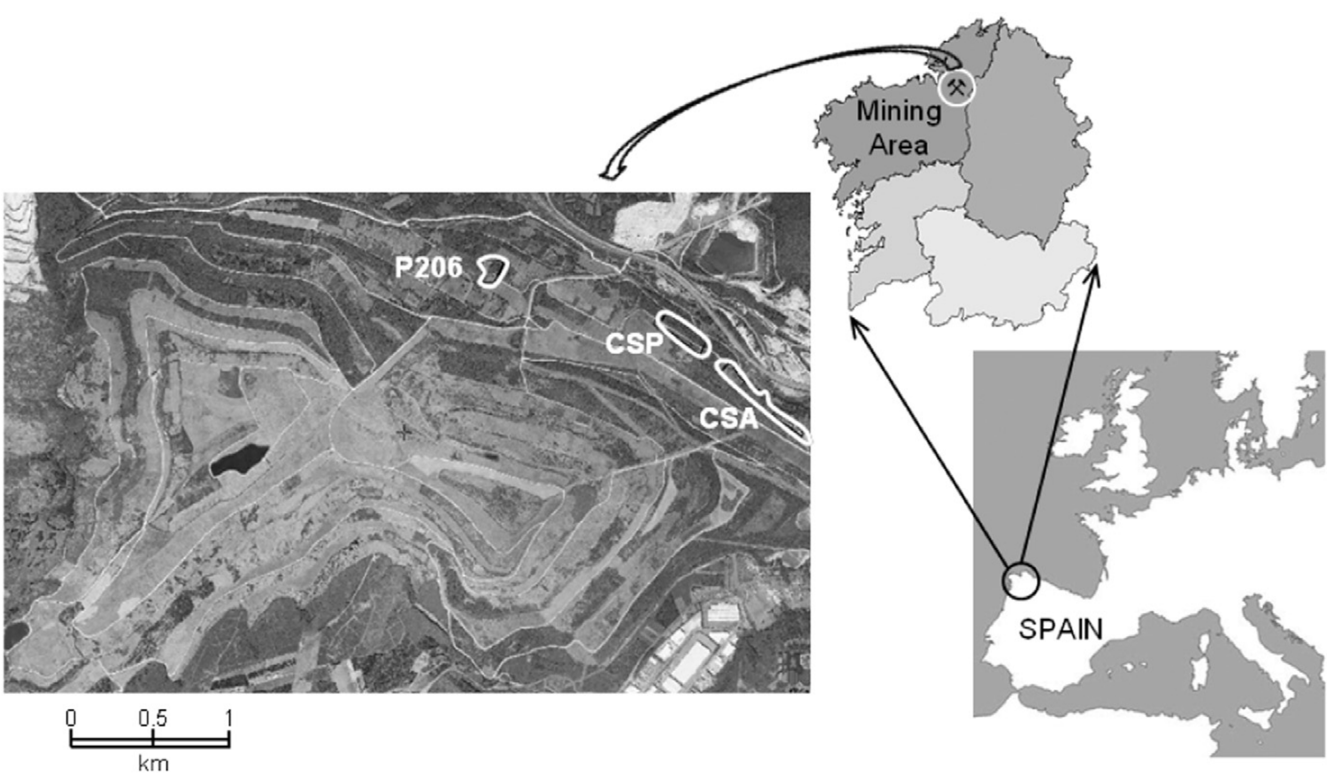

Fig 1. Localization of the three plots (P206, CSP and CSA) in the coal mine dump of As Pontes (NW Spain).