Aluminum geochemical characterization in agricultural soils: sequential chemical extraction combined with mineralogical analysis of the fine fraction

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Abstract. Understanding both the concentration and distribution of aluminum (Al) in agricultural soils is essential to provide a benchmark on the productivity of such soils. In this study, a combination of sequential chemical extraction and mineralogical investigation of the fine fraction was used in order to evaluate Al pools in agricultural soils in Galicia (NW Spain), an Atlantic European region where the wet climate favors leaching of soil basic cations. Determination of Al (soluble/exchangeable/specifically adsorbed, bound to manganese oxides, associated with amorphous compounds, bound to oxidizable organic matter, associated with crystalline iron oxides, and residual fraction) in the topsoil samples was performed to evaluate its potential environmental availability in the study area. Aluminum contents were determined by flame atomic absorption spectrophotometry and the mineralogy of the fine fraction of these soils was studied by X-ray diffraction (XRD). The results showed that Al is mainly in the residual phase, which represents Al incorporated in the lattice minerals, and consequently the threat of toxicity to plants and the environment is reduced. The XRD results showed the presence of hydroxy-Al interlayered vermiculites and kaolinite, accompanied by small amounts of goethite, mica, and quartz.

1. Introduction
Aluminum exists in the Earth’s crust as the most abundant metal representing 8% of its content in weight. It is a major element in soils and component of the solid phase, such as primary (e.g., feldspar, mica, amphibole, and pyroxene) and secondary minerals (e.g., kaolinite and Al-hydroxides, such as gibbsite and bayerite). Despite being ubiquitous and available during the life cycle of plants, Al has no specific biological function [1]. Apart from Al integrated into the structure of soil minerals (mainly silicates and also Al oxides), Al in the soil solution and Al reactive associated with solid phases also occurs, including exchangeable Al, weakly and strongly organically bound Al, forming non-crystalline minerals, and as interlayer hydroxy-aluminum polymers in clay minerals [2, 3]. The stability of the aluminum pool in the solid phase controls its facility to be released in the soil solution, Al integrated into the mineral structure being the most stable pool and therefore less likely to be released.
It is widely recognized that the total concentration of metals in soil is a poor indicator of toxicity to plants [4] since metals exist in different solid-phase forms that can vary greatly in terms of their bioavailability. Although the soil acts as a natural sink for lithogenic elements, such as Al, it could eventually turn into a source of potentially hazardous metals to plants in response to future land-use changes and biogeochemical alterations. Land use and agronomic practices can modify soil acidity and organic matter amount and composition, among other soil parameters, and consequently modify the Al pools [5-7], affecting the mobility of Al stored in the soil. Therefore, it is crucial to understand the degree of association of Al with various geochemical phases in soils, allowing us to assess its actual and potential environmental availability to biota in the terrestrial environment. Sequential chemical extraction provides information about Al forms that are more or less readily released into the soil solution.

In this study, a combination of sequential chemical extraction and mineralogical investigation of the fine fraction was used to evaluate Al pools in agricultural soils in Galicia (NW Spain), an Atlantic European region where the wet climate favors leaching of soil basic cations. This will contribute to understanding the current geochemical behavior of Al, as well as to predict both the geochemical behavior and environmental fate of this element in response to future land use scenarios and biogeochemical alterations of the soil environment.

2. Material and Methods
2.1. Description of the Study Area
The study soils are located in the province of A Coruña (Galicia, NW Spain) within the area of the geological formation known as “Schists of the Órdenes Complex” [8]. These soils are representative of a wide area of Galicia in terms of geology, soil types, land use, management practices, crops, and rainfall patterns. The climate is oceanic with an average annual rainfall of around 1200 mm and an average annual temperature of 13 ºC. The soil types are Umbrisols and Cambisols [9] developed from schists with a predominance of ferromagnesiamineral (biotite, chlorite, and amphiboles). The agricultural soils are mainly dedicated to grasslands and the cultivation of winter cereals and maize. Fertilization and liming practices are routinely applied to maintain or improve the crop yields of these soils.

This study was carried out in twelve agricultural fields, where six surface layer soil samples (0-20 cm) were collected at each field in order to obtain a composite sample for analysis. The soil samples were air-dried and passed through a 2 mm nylon sieve to remove roots and large particles. The topsoils are characterized by moderately acidic pH, and organic matter content of about 6%, silt, and silty loam textures, low effective cation exchange capacity, low amount of exchangeable Al, the percentage of Al saturation in the exchange complex being highly variable, but low on average (about 30%). For a detailed discussion and more information about the study area, see [10-14].

2.2. Analytical methodology
In the selected soil samples Al fractionation was carried out by using a sequential extraction method [15] that allows extracting of six fractions defined operationally. Briefly, the reagents used were: a) F1–ammonium acetate for water-soluble/exchangeable/specifically adsorbed; b) F2–hydroxyamine hydrochloride for Al in Mn oxides; c) F3–ammonium oxalate in darkness for amorphous Al compounds and weak crystallinity compounds; d) F4–hydrogen peroxide 35% for Al bound to oxidizable organic matter; e) F5–ammonium oxalate under ultraviolet radiation for Al associated with crystalline Al and Fe oxides; and f) F6–hot mixed acid (HCl + HNO3 + HF) for Al within the crystal lattices of minerals (residual fraction). The Al concentrations were measured by flame atomic absorption spectrophotometry. Total Al was calculated as a sum of pools (F1 to F6).

The clay fraction (< 2 µm) was collected by siphoning after treating the soil/sediment samples with H2O2 followed by dispersion and agitation of the suspension. The mineralogy of the clay fraction was
estimated by X-ray diffraction using a Siemens D-500 diffractometer with Cu-Ka radiation, graphite monochromator, and Ni filter. Crystalline powder diagrams of samples without diversification and diffractograms of oriented aggregates of deferred samples were made. The deferred samples were saturated with Mg, ethylene glycol, K, and subjected to various thermal treatments.

3. Results and discussions

3.1. Mineralogical composition of the clay fraction

The mineralogical composition of the clay fraction of the topsoil samples is shown in table 1. The XRD results showed the presence of hydroxy-Al interlayered vermiculites and kaolinite as the most abundant minerals, accompanied by minors amounts of goethite, in addition to traces of mica and quartz in the topsoil.

Table 1. Mineralogical composition of the fine fraction of topsoil samples (<2 µm fraction).

| Mineral                             | Percentage |
|-------------------------------------|------------|
| Hydroxy-Al interlayered vermiculites | ≈           |
| Kaolinite                           | >           |
| Goethite                            | >           |
| Mica                                | ≈           |
| Quartz (traces)                     |            |

3.2. Aluminum fractionation

Aluminum is present in relatively low concentrations in the topsoils of the study area (25.58 g kg⁻¹ on average). This Al value is markedly lower than the mean that was proposed by [16] for the world’s soils (71 g kg⁻¹). Mean Al contents for each fraction of the sequential extraction and Al percentage distribution in the six extracted fractions are given in figure 1. Although the residual fraction represents the highest contribution to total Al content, variable amounts were obtained in the other fractions, the order of abundance for the average of all samples being as follows: residual fraction (78%) >>> oxalic acid/ammonium oxalate (in the dark) fraction (8%) = oxalic acid/ammonium oxalate (under ultraviolet) fraction (8%) > soluble/exchangeable/specifically adsorbed (3%) > Al bound to oxidizable organic matter (2%) ~ Al linked to Mn oxides (1.3%).

Figure 1. Left: Mean Al contents in the topsoils for each fraction of the sequential extraction (g kg⁻¹); Right: Al percentage distribution in the six extracted fractions

The pool extracted by ammonium acetate (F1) corresponds to soluble, exchangeable, and specifically adsorbed Al since no carbonate minerals were identified. This fraction corresponds to the most labile pool and may become available for the plants with simple changes in the ionic strength of the medium. In this pool, Al constituted a low percentage: 3% of the total. In terms of concentration, it represents high levels (0.8 g kg⁻¹) and therefore involves a high risk of biotoxicity, but it should be noted that negative effects on the plants were not observed in our soils probably due to the presence of organo-Al complexes, which limit their toxicity to plants [17].
The Al pool bound to oxyhydroxides can be mobilized with the increase or reduction of oxidizing conditions in the environment. The less important pools were linked to the Mn oxides (F2) and linked to the organic matter (F4), which only reached 1.68 y 1.25% respectively of Al in the study soils, which means a concentration of the order of 0.35 g kg⁻¹ in each of these pools. The low value of Al bound to the oxidizable organic matter could be due to the fact that a part of organically complexed Al has already been extracted in F3 (oxalic-oxalate in the dark fraction). The organic fraction released under oxidizing conditions is not considered to be mobile and bioavailability; metals are incorporated into stable high molecular mass humic substances, which release a small amount of metal over a long time [18].

A mean of 2.12 g kg⁻¹ was obtained in the pool extracted with oxalic-oxalate in the dark, which is considered to represent the sum of amorphous Al (and/or weakly crystalline) in organic complexes and inorganic compounds. This fraction is more reactive than the one bound to the crystalline oxides (mean concentration was 2.04 g kg⁻¹). Each of these fractions contributes to 8% of the total Al. Likely, a portion of the Al pool extracted with oxalic-oxalate in the dark comes from the hydroxy-Al polymers in interlayer positions of vermiculates as was reported by [19], among others. The pool of Al in the crystalline oxides probably arises in part from Al substituting Fe in goethite [20] since this mineral is the only crystalline oxyhydroxide present (in small quantities) in the clay fraction of these soils. But in addition to goethite, this pool can include other fractions, such as hydroxy-Al from the interlayer region of the vermiculates as was reported by [21].

Aluminum is an element little affected by weathering processes and this implies its abundance in the residual fraction (non-extractable Al) in which it comprises a mean concentration of 19.87 g kg⁻¹, i.e., Al predominance in this fraction (77.68%) agrees with the geochemical behavior of this element. The residual fraction is extremely stable and does not represent Al mobilization hazard, as associated Al is retained within crystal lattices of layer silicates and well-crystallized oxide minerals. Aluminum, tied up in silicate phases or poorly soluble mineral phases, is only released after destruction of the matrix [22].

According to sequential chemical extraction results, Al is mainly in the most resistant phases (based on the sum of the last three fractions) as crystalline Fe oxides, associated with oxidizable organic matter, and silicates. Al in so-called more soluble soil phases (sum of the first three fractions), i.e., in the phases having high probabilities of being environmentally available, constitutes 12.67% (about 3 g kg⁻¹) of the total Al in the topsoils of the study area, suggesting very low bioavailability of this element in these agricultural soils, and consequently, the toxicity hazard is reduced.

4. Conclusions
The sequential extraction study revealed that the potentially bioavailable fraction of Al in the agricultural soils of the study area is low, therefore, the risk of this element for the plants and the environment is minimal under the environmental conditions currently prevailing. The majority of aluminum extracted from the soils is concentrated in the residual fraction, which is extremely stable and does not represent the Al mobilization hazard. The results of the Al fractionation and the mineralogical investigation of the fine fraction of these agricultural soils suggests that the Al pools extracted with both oxalic-oxalate in the dark and oxalic acid/ammonium oxalate under ultraviolet can be partially attributed to the hydroxy-Al interlayered vermiculates.
Acknowledgments
This paper is a contribution to the Project CGL2014-56907-R of the National Program of Research, Development and Innovation Oriented to the Challenges of Society, which was funded by the Spanish Ministry of Economy and Competitiveness. M. L. Rodríguez-Blanco has been awarded a postdoctoral research contract (Juan de la Cierva Programme), which was funded by the Spanish Ministry of Economy and Competitiveness.

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