



Asymmetric flow field-flow fractionation as a new approach to analyse iron-(hydr)oxide nanoparticles in soil extracts

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ABSTRACT

Iron-(hydr)oxide nanoparticles are important for the sequestration of organic carbon because of their small size and consequently large specific surface area. Therefore, there is an increasing interest in analytical techniques such as asymmetric flow field-flow fractionation (AF4) that allow for a direct measurement of the size distribution of nanoparticles (1–150 nm). We used AF4 coupled to high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) to analyse the size distribution and elemental composition of nanoparticles dispersed from three horizons of a podzol. We tested three extractants for the amount of dispersed Fe-(hydr)oxide nanoparticles. No Fe-(hydr)oxide nanoparticles were dispersed in 5 mM NaCl. In a 1 mM NaOH extraction (pH 9.0), the amount of Fe dispersed in the form of Fe-(hydr)oxide nanoparticles amounted to 0.2–0.8 g kg⁻¹, which corresponded to 2–13% of the Fe content as extracted with ammonium oxalate (Fe-ox). Pyrophosphate was found to be the most effective extractant for Fe-(hydr)oxide nanoparticles and extracted 1.0–4.7 g kg⁻¹ Fe as Fe-(hydr)oxide nanoparticles, corresponding to 16–47% of the Fe-ox content. These Fe-(hydr)oxide nanoparticles were 2–20 nm in size and maximum concentrations were found at a particle diameter of 5 nm. The dispersion of Fe-(hydr)oxide nanoparticles in pyrophosphate coincided with the extraction of a large fraction of the soil organic carbon content (55–69%) which shows that dispersion of organo-mineral aggregates results in the release of Fe-(hydr)oxide nanoparticles from the soil. The amount of Fe-(hydr)oxide nanoparticles extracted from the soil did not increase after ultrasonic treatment of the pyrophosphate suspension. Since not all Fe-(hydr)oxides can be dispersed from the soil as primary particles, AF4 cannot be used as a tool to analyse the specific surface area of the Fe-(hydr)oxides in the soil. Instead, AF4 should be considered as a complementary technique providing a direct measurement for the size of the Fe-(hydr)oxide nanoparticles in soil extracts.

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1. Introduction

Iron-(hydr)oxides are important soil constituents for the retention of soil organic matter (SOM) because of their large specific surface area (SSA) and their high density of surface groups (Hiemstra, 2013; Weng et al., 2008). Retention of SOM can occur via different mechanisms including sorption, co-precipitation and occlusion (Mikutta et al., 2006). The amount of SOM that can be sorptively protected by Fe-(hydr)oxides depends on the SSA of the Fe-(hydr)oxides in the soil (Eusterhues et al., 2005; Hiemstra et al., 2010). Eusterhues et al. (2005) determined the SSA of soils by N₂ gas adsorption and they derived a SSA of short-ranged ordered Fe-(hydr)oxides of ≈800 m² g⁻¹. Hiemstra et al. (2010) developed a new approach to estimate the SSA of Fe-(hydr)oxides based on the phosphate-buffering capacity of soils. They found that the SSA ranged between 200 and 1200 m² g⁻¹ for Fe-(hydr)oxides in large series of agricultural soils (Hiemstra et al.,

2010). Assuming a spherical particle geometry, the SSA of short-ranged ordered Fe-(hydr)oxides corresponds to equivalent particle diameters of 1 to 10 nm only (Hiemstra et al., 2010). This size is in agreement with other studies in which Fe-(hydr)oxide nanoparticles were detected using Mössbauer spectroscopy or transmission electron microscopy (TEM) (Penn et al., 2001; Van der Zee et al., 2005). However, spectroscopic techniques and surface area analyses give only an indirect measurement for the particle size of the Fe-(hydr)oxides. A direct measurement of the particle size-distribution in the small nano-range (<10 nm) is important because the SSA of the nanoparticles increases dramatically with a decrease in particle size for particles in this size-range. This calls for the application of an analytical approach that allows for fractionation and elemental analyses of nano-sized particles.

Asymmetric flow field-flow fractionation (AF4) is an analytical technique for size-fractionation of nanoparticles. The fractionation takes place in a thin water film and is driven by differences in diffusion coefficients, which can be related to the particle hydrodynamic diameter (Von der Kammer et al., 2011). Coupling of AF4 with high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) allows

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for size-fractionation and online analyses of the elemental composition of nanoparticles. The combination of AF4 with HR-ICP-MS has been applied successfully to study colloidal nanoparticles in environmental water samples (Lyvén et al., 2003; Regelink et al., 2013; Stolpe et al., 2013). However, so far only a few attempts have been done to use AF4 for analysis of soil nanoparticles (Baalousha et al., 2006; Plathe et al., 2010). A crucial step in AF4 analyses of soils is the dispersion of the primary nanoparticles into suspension as colloidal stable particles, which means that the nanoparticles are either electrostatically or sterically stabilized. However, knowledge on suitable extraction methods to disperse Fe-(hydr)oxide nanoparticles from the soil is limited, which, in turn, hampers the application of AF4 in soil analyses to characterize these nanoparticles.

A mild extractant, for example water or a dilute salt solution, can be used to mimic the soil pore-water (Koopmans and Groenenberg, 2011) and to disperse the potentially mobile soil nanoparticles (Kretzschmar and Sticher, 1997). However, Fe-(hydr)oxides in soils tend to associate with SOM (Baalousha, 2009) and these organo-mineral interactions need to be overcome to disperse the Fe-(hydr)oxide particles. Therefore, more Fe-(hydr)oxides may be dispersed when stronger extractants are used that can reduce the interactions between Fe-(hydr)oxides and SOM. For example, large amounts of SOM can be extracted in NaOH or pyrophosphate (Tatzber et al., 2007; Van Zomeren and Comans, 2007). The latter extractant is also commonly used to disperse soils for particle size fractionation (Pronk et al., 2011) and to extract Fe associated with SOM (Dümig et al., 2012; Jeanroy and Guillet, 1981). Following these classical extraction procedures however, Fe-(hydr)oxides may dissolve in the strong alkaline extractants, which is in conflict with our aim to extract the nanoparticles as intact particles for AF4-fractionation. Therefore, these extractants should be tested at a lower pH. In addition, ultrasonic energy can be used to disperse particles from the soil (An et al., 2010; Kaiser et al., 2012; Pronk et al., 2011). Ultrasonic treatment may however not release primary particles but small aggregates of particles (Calabi-Floody et al., 2011) which conflicts with our aim to measure the particle size of the primary Fe-(hydr)oxide nanoparticles. So far, our understanding of how extractant and ultrasonic treatment affects dispersion of Fe-(hydr)oxide nanoparticles is limited and no attempts have been done to analyse the released particles using AF4 coupled to HR-ICP-MS.

The objective of this study was to test three extractants for the dispersion of Fe-(hydr)oxide nanoparticles: (i) 5 mM NaCl, (ii) 1 mM NaOH and (iii) a 2 mM pyrophosphate solution. In addition to these three extractants, NaHCO₃ and pyrophosphate in combination with ultrasonic treatment were tested. The podzol was chosen because of the high Fe-(hydr)oxide content in the B horizon, where typically accumulation of Fe, Al, and OC occurs. We used AF4 coupled to an UV-analyser and HR-ICP-MS to analyse the size-distribution and elemental chemical composition of the dispersed nanoparticles. The results provide insight into (i) the size-distribution of Fe-(hydr)oxide nanoparticles and (ii) the role of organo-mineral interactions in dispersion of Fe-(hydr)oxide particles.

2. Material and methods

2.1. Soil sampling

The sampling area is located in the Lysina catchment, situated in the mountainous region of the Slavkov Forest Protected Landscape Area in the western part of the Czech Republic. The soil profile is characterized as a Folic Albic Podzol and a photograph of the soil profile is available in Appendix A. Samples were taken from seven distinct soil horizons, i.e., AE, E, Bh₁, Bh₂, Bs, BC, and C. More information about the chemistry and hydrology of the Lysina catchment can be found in previous papers (Krám et al., 2009, 2012). The Lysina catchment has been studied by the Czech Geological Survey since 1988. The Lysina catchment is part of the Czech network of forest catchments

(Global Earth Observation and Monitoring of the Atmosphere, with the acronym GEOMON) and in four international networks ([i] International Cooperative Programme [ICP]—Waters, [ii] ICP—Integrated Monitoring, [iii] International Long Term Ecological Research (ILTER), and [iv] Soil Transformations in European Catchments [SoilTrEC]).

2.2. General soil analyses

Soil samples were dried at 40 °C and sieved over 2 mm prior to analyses. The pH was measured in a soil–water suspension at a soil solution ratio (SSR) of 0.4 kg l⁻¹. The soil organic carbon (SOC) content was measured by dry combustion using an elemental analyser (Carlo Erba Nitrogen Analyzer). The cation exchange capacity (CEC) and exchangeable cations were determined using the unbuffered BaCl₂ method (Pansu and Gautheyrou, 2006) and cation concentrations were measured by inductively coupled plasma atomic emission spectrometer (ICP-AES; Varian Vista Pro). The clay content was determined by the pipette-method after dispersion of the soil samples in a 0.4 M pyrophosphate solution (Ashworth et al., 2001). The amount of Fe and Al extractable in acid ammonium oxalate was determined according to the extraction method of Schwertmann (1973). Shortly, soil suspensions at a SSR of 0.05 kg l⁻¹ were prepared using 0.2 M ammonium oxalate solution at pH 3 and shaken for 2 h in the dark. The supernatants were analysed for Fe (Fe-ox) and Al (Al-ox) by ICP-AES. In addition to short-ranged ordered Fe- and Al-(hydr)oxides, acid ammonium oxalate can also dissolve some micro-goethite, allophane and imogolite and extracts monomeric Fe and Al (Pansu and Gautheyrou, 2006; Parfitt and Childs, 1988; Schwertmann, 1973). Total Fe-(hydr)oxide soil content, which includes both short-ranged ordered Fe-(hydr)oxides and goethite, was measured using the dithionite-citrate-bicarbonate (Fe-DCB) method of Holmgren (1967). Shortly, 1 g of soil was extracted using 30 ml of 0.66 M citrate and 0.11 M sodium-bicarbonate solution and 1 g of dithionite. Soil suspensions were shaken for 16 h at room temperature, followed by centrifugation. After centrifugation, Fe concentrations in the supernatants were measured by ICP-AES.

2.3. Extraction of soil nanoparticles

Soil samples from three distinct horizons, the Bh₁, Bh₂ and Bs, were selected for the extraction of soil nanoparticles because of their high Fe-ox and Al-ox contents.

2.3.1. NaCl

Soil suspensions were prepared using a 5 mM NaCl solution at a SSR of 0.1 kg l⁻¹. The final pH values of the suspensions ranged between pH 4.0 and 4.5.

2.3.2. NaOH

Soil suspensions were prepared using a 1 mM NaOH solution at a SSR of 0.002 kg l⁻¹. The final pH values of the suspensions were between 9.4 and 9.7. A low SSR was chosen to increase the fraction of dispersed nanoparticles from the soil. The NaOH concentration was low compared to the concentration used in the classical method (Van Zomeren and Comans, 2007) because a higher concentration and thus a higher pH could result in dissolution of Fe- and Al-(hydr)oxides.

2.3.3. Pyrophosphate

Soil suspensions were prepared using a 2 mM pyrophosphate (Na₄P₂O₇) solution at a SSR of 0.002 kg l⁻¹. Prior to the addition to the soil, the pH of the pyrophosphate solution was lowered to pH 9.0 using concentrated HCl to prevent dissolution of Fe- and Al-(hydr)oxides (Kaiser and Zech, 1996). The final pH values of the suspensions after shaking were between 7.7 and 8.8. The classical pyrophosphate extraction method uses a concentration of 0.1 M pyrophosphate (Jeanroy and Guillet, 1981). We used a lower

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