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“Lost in filtration”—The separation of soil colloids from larger particles

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ABSTRACT

Soil colloid science requires the separation of the colloids from larger particles in suspensions, which is frequently achieved by filtration. However, the results of filtration may be biased due to (i) pore clogging and (ii) the formation of a filter cake. In order to quantify these effects, we filtrated different volumes of soil suspensions containing mainly mineral (M), mainly organic (O) or mineral and organic (MO) colloids through 1.2 μm membranes. Turbidity and the concentrations of colloid-bound C, Si and Al were measured in the filtrates and, as a reference, in centrifugates of the suspensions. To exclude the influence of the filter cake and examine only pore clogging effects, we conducted the same filtration experiment with suspensions which have been pre-treated by a centrifugal elimination of particles >3 μm. Finally, we scanned a membrane after filtration with an electron microscope for the visualisation of possible pore clogging. Turbidity and concentrations of colloid-bound Al and Si in the filtrates of the pre-treated suspensions were one order of magnitude lower than in centrifugates. This discrepancy was most pronounced for M suspensions which indicates that filters preferentially remove mineral colloids. Microscope images revealed no sign for pore clogging and smaller filtrated suspension volumes did not lead to more colloid recovery in pre-treated filtrates. We assume that the colloids are retained within the thick, multilayered structure of the filter without clogging the main pores. When filter cakes are forming (experiment without previous centrifugation), turbidity and concentrations of colloid-bound Al, Si and C decrease with increasing filtration volume. However, the retaining effect of filter cakes seems negligible compared to the retaining effect within the filter. We conclude that the composition of soil colloidal suspensions depends significantly on the technique which is used to remove larger particles. Filtration underestimates the amount of colloids in suspension and centrifugation should be preferred as separation method at least for soils with colloids of similar density, either M or O.

1. Introduction

Colloids in soils are known as potential carriers for strongly sorbing substances, such as heavy metals and organic pollutants [1–3]. The examination of soil colloids requires the separation of the colloidal fraction from larger particles (usually >1 μm) in soil extracts. Different techniques are used for this purpose: some authors remove particles >1 μm by gravity [4,5] or by centrifugal force [6–11]. The size of the particles, which settle at a given relative centrifugal force (rcf) and time mainly depends on the particle density. The density of soil particles of one single soil sample may cover a wide range from <1.9 g/cm^3 (organic particles) [12] up to >5.0 g/cm^3 (iron oxides) [13]. For soil suspensions with a high diversity in particle density, it might be problematic to achieve a precise particle size separation for soil suspensions based on gravity and centrifugation methods.

A separation technique that is used to overcome this problem is filtration. Different types of filter material are available: e.g. cellulose nitrate filters, as used for example by Buykx et al. [14], Worrall et al. [15], Klitzke et al. [16] or Ziyang et al. [17], polycarbonate filters [18,19] or glass fibre filters [3]. The accuracy of filtration is high, if all particles bigger than the pores of the filters are retained, while all particles being smaller than the pores pass the filter without any retardation. Few studies show the suitability of special filter techniques like tangential ultra filtration for accurate size fractionation of colloids [20]. However, these techniques are only applicable at relatively low colloid concentration and high suspension volumes are needed. The accuracy of simple vacuum or pressure filtration may be limited due to clogging of membranes [21–25]. Karube et al. [26] recovered only 10% of the investigated kaolinite (100–300 nm particle size) passing a Nuclepore membrane filter of 200 nm pore diameter (polycarbonate, cylindrical pores), only 50% through 400 nm pores and 85% through 800 nm pores. Systematic studies of the effect of membrane clogging on soil colloid recovery in the filtrate and of the accuracy of different filtration and centrifugation methods are not available so far.

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Table 1
Basic characteristics of the studied soil samples.

Soil	pH (H_2O)	C_{org} content (%)	Texture	Parent material	Utilisation
M	5.1	4.3	Loamy silt	Volcanic ash	Hazelnut
MO	5.0	1.1	Sand	Sandy layer of the Pleistocene	Dry grassland, former sewage field
O	4.3	8.0	–	Fluvial sandy stream deposit of the Pleistocene	Former shooting range

Table 2
Applied separation technique and realised measurements for the different soil suspensions.

Separation technique	Measurement		
	Turbidity	Element concentrations	Particle size
Centrifugation	M, MO, O	M, MO, O	M, MO, O
Cellulose nitrate membrane filter (pre- and non-pre-treated)	M, MO, O	M, MO, O	MO, O (random samples)
Polycarbonate filter (pre- and non-pre-treated)	M, MO	n.d.	n.d.
Glass fibre filter (pre- and non-pre-treated)	M, MO	n.d.	M, MO

n.d. = not determined.

We tested the hypothesis that the different filters used to filtrate soil colloidal suspensions get clogged by colloids and that this clogging decreases with decreasing load of filtrated colloids. Furthermore, we hypothesized that soil colloids are additionally retained by a filter cake forming on the filter along with filtration and consisting of particles >1 μm, and that the filter cake effect decreases with decreasing amount of particles >1 μm on the filter. In addition, we investigated the applicability of centrifugation to get suspensions of exact particle size separation from different soil samples.

2. Materials and methods

We mixed 30 g of three different soils (sieved to 2 mm) each with 300 ml deionised water (soil to water ratio of 1:10) in 500 ml polyethylene flasks: the Ah-horizon of a loamy-silty Andosol containing mainly **m**ineral colloids (allophane) (**M**[1]), a buried Oh-horizon of a Podzol containing mainly **o**rganic colloids (**O**[2]), and the Ah-horizon of a sandy Regosol with sewage field history and nearly equal amounts of **m**ineral **and o**rganic colloids (**MO**[3], Table 1). The suspensions were used for a batch experiment which we conducted with an end-over-end shaker for 16 h at a speed of 15 rounds per minute.

Aliquots of the soil suspensions of the three soils were treated in three different ways with three replicates each:

- One aliquot of the suspensions was centrifuged for 60 s to remove large particles which we expect to be responsible for filter cake formation. Rcf was 78 g. Particles with a density >2.0 g/cm^3 and a size >3 μm will settle under these conditions. 10 and 40 ml of the supernatants were filtrated by vacuum filtration through three types of filter material: 1.2 μm cellulose nitrate membrane filters (Sartorius Nr. 11303), 1.0 μm polycarbonate membrane filters (Cyclopore track etched membrane by Whatman) and 1.0 μm glass fibre filters (Pall, type A/E).
- The same filtration treatments were applied to the second aliquot of the suspensions, which, however, was not centrifuged prior to filtration.
- A third aliquot of the suspensions was exclusively centrifuged to a particle size of 1 μm, according to the equation by Stokes. We assumed a particle density of 1.5 cm^3/g for the O soil (10 min, rcf = 78), 2.4 cm^3/g for the M soil (3 min, same rcf) and an average density of 2.0 cm^3/g for the MO one (5 min, same rcf).

In the following, the three differently prepared sets of samples are called “pre-treated filtrates”, “non-pre-treated filtrates” and “centrifugates”.

Turbidity was taken as an indicator for the concentration of colloids and was measured in all filtrates and centrifugates with a turbidimeter (2100P ISO Turbidimeter, HACH). We also determined the particle size using light scattering (High Performance Particle Sizer, Malvern Instruments) to check the accuracy of the separation.

The centrifugates and, exemplarily, the pre- and non-pre-treated filtrates of the cellulose nitrate filter filtration (see Table 2) were ultracentrifuged for 1 h 17 min at 124,000 g (Beckman Coulter Optima L-90K Ultracentrifuge) to separate the dissolved part of the suspensions from the colloids. We analysed C, Al and Si concentrations of the supernatants to determine the concentrations of dissolved elements. Total element concentrations of the suspensions where directly determined by analysing non-ultracentrifuged suspensions. The difference between total element concentrations and concentrations of dissolved elements yielded the concentrations of colloid-bound elements. We quantified C with a Total Organic Carbon Analyser (TOC-5050A, Shimadzu) and Al as well as Si with flame AAS (1100B Atomic Absorption Spectrophotometer, Perkin Elmer). With regard to the environmental relevance of colloidal transport in soils, we also analysed Pb with a Varian SpectrAA 880Z Atomic Absorption Spectrometer in the filtrates and centrifugates.

In addition, we prepared scanning electron microscopy (SEM) images of the three filter types after prewashing with deionised water and the filtration of 1:10 diluted 10 ml Regosol suspension. The dried filters were analysed by SEM (Hitachi S-4000) after they had been surface sputtered with Au (~5 nm Au layer thickness).

3. Results and discussion

3.1. Permeability of filters for colloids

3.1.1. Quantity of the colloids

Colloid concentrations in the filtrates of both pre-treated soil extracts (M and MO) increased in the order: cellulose nitrate < polycarbonate < glass fibre filters. We attribute this to differently intensive retaining effects of the filters.

According to light scattering analysis, the particles of the M and O soils, which remained in suspension after centrifugation, were all smaller than 1000 nm. This indicates that centrifugation might be taken as a reliable method for an exact separation of colloids from larger particles. However, particles of the MO suspensions exhibited sizes also above 1000 nm. This seems obvious as an average density between organic and mineral particles had to be assumed

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[1] M: soil with mainly mineral colloids.

[2] O: soil with mainly organic colloids.

[3] MO: soil with a cross between mineral and organic colloids.