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## Comparison of preconcentration methods of the colloidal phase of a uranium-containing soil suspension

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### Abstract

Three methods of membrane separation by dead-end, tangential, and centrifugal ultrafiltration (UF) were considered in order to understand the physicochemical phenomena occurring during the preconcentration of the colloidal phase of soil water. The analytical approach used involved dynamic light scattering (DLS), transmission electron microscopy (TEM), determination of total organic carbon (TOC-metry) and mass spectrometry (ICP-MS). The mass amounts of the major components of the colloidal phase, i.e. Al, Fe and total organic carbon (TOC), as well as the mass amount of uranium considered as a trace element of environmental interest, were determined, both in soil water, and in the concentrates (i.e. retentates) and filtrates of this water obtained by the 3 methods tested.

Dead-end ultrafiltration led to an enlargement of the size distribution towards larger sizes because of agglomeration/aggregation phenomena. This method also generated enrichment of concentrates, in particular in organic matter. The consequence was that large structures were observed coating or embedding the particles initially present individually dispersed in the test sample. The mass amounts of elements and TOC increased more importantly than expected, which confirmed the enrichment of the concentrates from the dissolved phase probably by sorption on colloidal objects. To a lesser extent similar effects were observed after tangential ultrafiltration. Such phenomena were not observed after centrifugal ultrafiltration. From a practical point of view, both tangential and centrifugal ultrafiltration proved to be both the most practical and the best suited for the preconcentration of soil water sample. Finally, centrifugal ultrafiltration has proved to be the best compromise given the preservation of colloidal particles and method practicality.

**Key words:** colloidal characterization; sample preparation; nanoanalytics;

## 1. Introduction

Because of their size from about 1 nm to 1  $\mu\text{m}$ , and therefore their low mass, colloidal objects are mainly subjected to Brownian motion and not to Earth's gravity [1]. As a result, colloidal objects can remain in suspension for long periods of time and over long distances. They are important components in waters, at the dissolved-particulate interface [2]. Especially, the presence of ligands in colloidal form is likely to significantly affect the mobility of pollutants in natural environments. Therefore, the sorption/desorption processes of the colloidal objects from soil and their mobilization dynamics in (sub) surface waters have received a large attention the last few years [2–4]. In particular, the ability of colloidal objects to increase pollutant transport depends on their size, structure, chemical composition, as well as their stability and reactivity with the pollutants according to the chemical characteristics of the surrounding environment [5,6].

The ubiquity of colloidal objects is due to the fact that they are continuously generated at the interface between a porous solid phase, typically a soil, and an aqueous phase, for example groundwater [6,7]. Therefore, even if colloidal objects are found in low concentration in a punctual water sample from an environment of interest, they can play a major role in contaminant transport in this environment. Thus, whatever the colloidal concentration, the determination of the physical and chemical characteristics of the colloidal phase is required to improve the understanding of the mechanisms of colloid transport.

To decrease any change in both physical and chemical characteristics of the colloidal objects, and ensure the reliability of analytical results, a special attention has to be paid to the sample preparation step [8–11]. Indeed, the preparation method can induce profound changes, in particular the size and structure of colloidal objects. Structure refers to the object as a whole, as well as the crystalline state of the material(s). Consequently the dissolution of the colloidal objects as well as their sorption capability can be affected [12,13]. Such changes can particularly occur during the preconcentration of colloidal phases, where the concentration factor can range from about ten to several hundred times [14]. Two major preconcentration strategies can be used, based on centrifugation and membrane separation (filtration). Ultracentrifugation was used sequentially to prepare soil samples [15]. However, because soil colloidal objects are extremely polydisperse and due to their wide density range, ultracentrifugation does not enable the colloidal phase to be completely recovered. In particular, the fraction of size less than a few nanometers up to a few tens of nanometers is difficult to recover because of the great gravitational force that must be applied. In addition,

agglomeration/aggregation or shearing of colloidal objects may occur, leading to structural modifications of the colloidal phase [16,17]. Membrane separation is the most commonly used concentration methods. It can be implemented in different ways depending on the force applied to pass the water sample through the membrane [18–21]: either a pressure differential (by pressing, or vacuum suction) or a centrifugal force. The pressure gradient can be frontal (most often named dead-end in the literature, and also below) or tangential. Clogging of the membrane pores is one of the well-known major drawbacks of membrane separation processes [22–24]. Formation of a filter cake or occurrence of membrane polarization is frequently mentioned in the literature [25,26]. The characteristics of the colloidal phase may be affected by such phenomena. Thus, recent works have focused on these different phenomena, and/or on the possible enhancement of the filtration process [27–30]. For example, it was possible to limit the development of filter cake in dead-end mode by stirring the solution at the filter [8]. However, despite the common use of these methods and the interest in evaluating, understanding and solving of the problems inherent in filtration, the impact of the filtration process on a colloidal phase during concentration step is still poorly known.

The aim of this investigation was to understand the physicochemical phenomena occurring during membrane separation implemented in order to preconcentrate the colloidal phase. For that purpose, three different ultrafiltration methods (dead-end, tangential and centrifugal) were considered and used with the same concentration factor, on the same soil water sample taken as a reference sample. Physico-chemical characteristics of the colloidal phase of the reference sample and the concentrated and filtered phases of this sample were determined and compared. In addition, the practicality of the ultrafiltration methods was evaluated. Indeed, this point is essential in view of the investigation strategy of water collected on site in future applications.

## **2. Materials and methods**

### *2.1. Soil*

Samples of podzol soil from the wetlands of Landes Gascony (France) were taken from a study site previously described [31,32] and now well documented with regard to the physico-chemistry of soils and waters, and uranium distribution. This soil, previously characterized, was selected with the idea to obtain reference soil colloidal suspension that can be used as a test sample. Soil

was sampled from the upper horizon E, where uranium is present as a result of ancient deposits of solid fragments on the soil surface [32]. Previous studies demonstrated the presence of uranium in dissolved and colloidal phases in the interstitial waters of this horizon especially. In the colloidal phase, uranium could be both constitutive of colloidal objects or associated with colloidal objects [32–34]. The soil collected was dried, homogenized, sieved to 1mm and stored at room temperature in the dark until use.

## *2.2. Chemicals*

Ultra-high quality 69% nitric acid (GT Baker) was used for the preparation of the mass spectrometry analysis. Polystyrene sulfonate and polyethylene oxide standards with molar masses ranging from 697 to 960000 g mol<sup>-1</sup> used for the assessment of the effective cut-off of the membrane were from Polymer laboratories Ltd. (Bloomberg, UK). Polystyrene standards (PSS) hydrodynamic diameters of 20, 80, 200 and 400 nm used for the size calibration process came from Duke Scientific Corp (Microgenics Corporation, Fremont, CA, USA). The Total Organic Carbon (TOC) analyzer was calibrated using solutions of sodium hydrogen carbonate for the inorganic carbon measurements and using solutions of potassium hydrogen phthalate for the total carbon measurements (Nacalai Tesque, Kyoto, Japan).

## *2.3. Sample preparation*

Reference soil colloidal suspension was obtained by using a static leaching method: A soil aliquot was mixed with milli-Q water using a rotary shaker with a solid/liquid ratio of 1/50. This ratio was chosen after preliminary tests (ratios tested between 1 and 100). These tests showed that the colloidal phase of the soil water obtained with this ratio had characteristics similar to those of the waters taken from the field [33]. After 48 hours shaking, the soil water sample was kept at  $(4.0 \pm 0.5)^{\circ}\text{C}$  and sheltered from the light for 48 hours in order to settle the largest suspended particles down. The supernatant was then recovered and passed through a PolyEtherSulfone (PES) filter of 0.45 $\mu\text{m}$ . This filter membrane was chosen because (i) the PES material did not generate any observable interaction with the sample, nor any significant change in its chemical composition and zeta potential, (ii) the 0.45  $\mu\text{m}$  cut-off agreed with the dimensional characteristics of the colloidal fraction carrying the majority of the uranium (85 % of U was found below 450 nm). The soil colloidal suspension obtained proved to be stable at

least over a period of several months. Moreover, the leaching process was repeatable (i.e. the generated samples had similar physico-chemical characteristics). The obtained suspension was expected to be a mixture of Al / Fe oxides-containing particles and humic compounds [32,34]. Therefore, the soil colloidal suspension sample could serve as test sample and its colloidal phase was taken as a reference sample for the concentration tests.

#### *2.4. Membrane separation*

Three different methods were applied on the test sample, based on dead-end, tangential, and centrifugal ultrafiltration (UF) respectively. The devices chosen for the concentration experiments were a polycarbonate filter holder (16510 serie, Sartorius), a Minimate™ TFF System (Pall Corporation) and a Pierce™ Protein Concentrator (Thermo Scientific) respectively. The membrane material selected was PES, according to the preliminary tests above-mentioned. The smallest cut-off available for the three ultrafiltration systems tested was 10kDa. Thus, this membrane was selected. Preliminarily, its effective cut-off was experimentally evaluated. It was found to correspond to hydrodynamic diameters of  $(2.06 \pm 0.15)$  nm. The UF methods were applied with a concentration factor of 10, corresponding to the low threshold of the concentration range usually used [14]. This concentration factor was chosen in order to be able to apprehend any impact from a low concentration constraint (i.e. possible agglomeration/aggregation and change in the elemental distribution between the dissolved colloidal phases), knowing that a greater constraint would likely increase this impact. Both the concentrate (i.e. the retentate) and the filtrate of the test sample were collected and analyzed. The concentrate was expected to contain the colloidal phase with objects of hydrodynamic diameters over about 2 nm (simply called “colloidal phase” hereinafter), and a part of the dissolved phase. The filtrate was expected to contain dissolved species and objects smaller than about 2 nm (simply called “dissolved phase” hereinafter).

From the test sample, each concentration method was triplicated. All three methods need a rinse step of their membrane and their filtration module prior to use. For each UF method, the duration necessary to obtain the desired concentration factor was noted. In addition, membranes were chemically analyzed, and system and membrane blanks performed.

### *2.5. Colloidal and concentrated phase characterization*

The analytical investigation strategy was defined as described below preliminary to the characterization of the colloidal phase of the test sample and the concentrated phases of the three ultrafiltered samples.

Investigation strategy. A set of physicochemical characteristics was defined to serve as comparison indicators between the concentrated samples (hereinafter referred to as concentrates) and the test sample whose colloidal phase was taken as a reference (soil suspension). The intrinsic parameters considered in this study for nano-objects were size, shape, structure, and chemical composition, because all the properties enabling the behavior and fate of the nano-objects to be known depend on these parameters [35]. The analytical strategy was constructed in order to be able to determine these parameters with sufficient precision for a comparison. Thus, the size distribution of the colloidal population was evaluated by dynamic light scattering (DLS); the shape and structure of the objects (in terms of texture including the possible structural organization within the object) in the bulk suspension and the concentrates were obtained by transmission electronic microscopy (TEM); the elemental chemical composition (major and trace) of the suspension where the colloidal population was determined by atomic mass spectrometry (ICPMS) and the total organic carbon content (TOC) measured by TOC meter. Such a multi-technique strategy enables all the analyses (or the preparation making it possible to fix the sample before analysis in the case of microscopy) to be carried out almost simultaneously for all the concentrates generated. Therefore, the possible biases induced by temporality can be limited.

Size distribution. Dynamic light scattering (DLS) analysis was performed using a DynaPro NanoStar (Wyatt) with a laser at 658 nm and a photodiode detector with a 90° detection angle. An external calibration with the polystyrene standards was carried out preliminary. For that a set of autocorrelation curves was obtained from 20 to 400 nm. This calibration was useful (i) to verify that the hydrodynamic radius values given by the instrument correspond to those of the analyzed size standards, (ii) to find the most accurate fitting of the autocorrelation curve of each sample analyzed by those of the standards. For a polydisperse sample in particular, it is known that its autocorrelation curve has a lower slope smaller than that of a monodisperse sample. This curve is therefore between the curves of two monodisperse size standards, which

define the minimum, maximum and the range of sizes of the polydisperse sample. In addition, the size distribution can be qualitatively estimated by examining the intersection of the autocorrelation curve of this polydisperse sample with the curves of the different monodisperse standards used for the calibration. It is thus possible to verify and validate the relevance of each size distribution built by the DLS instrument. All samples (i.e. both the test sample, and concentrates and filtrates, all replicated) were analyzed three times, each time with 15 replicates. Hydrodynamic radii were obtained using a scattering intensity weighted autocorrelation function.

Shape and texture. Samples were examined with a transmission electronic microscope (TEM) Talos F200S device (ThermoFisher). For this TEM analysis, the samples were prepared as described by Baalousha et al. (2005) [35]: a drop of each sample suspension was deposited onto a TEM grid covered by a copper membrane. After drying on filter paper, the grids were rinsed with milliQ water 2 times, dried before their analysis by TEM. TEM parameters were optimized to preserve the texture of the colloids and to avoid contamination through the few molecules present into the microscope column. Typically, an accelerating voltage of 200keV, an emission of 1 upon a scale of 6, and a C2 aperture of 100  $\mu\text{m}$  were used. Apparent objective aperture selected was a 40  $\mu\text{m}$  in bright field mode (BF) while Selection apertures for Selective Area Electron Diffraction mode (SAED) were 70 or 10  $\mu\text{m}$  ones.

Elementary composition, and total organic carbon content (TOC). The concentrations of major elements (aluminum and iron) and the trace element of interest (uranium) were obtained for all the samples (i.e. both the test sample, and concentrates and filtrates) by mass spectrometry analysis (ICP-MS). An ICPMS 7900ce model (Agilent Technology, Tokyo, Japan) was used, equipped with a concentric nebulizer (MicroMist), an ultra-high matrix introduction (UHMI) spray chamber model cooled to 2°C and a Collision Reaction Cell (CRC). The operating conditions were the following: nickel sample and skimmer cones; argon plasma and make up gas; plasma gas flow rate, 1 L min<sup>-1</sup>; make up gas flow rate, 0.15 L min<sup>-1</sup>. The different stable isotopes monitored were <sup>27</sup>Al, <sup>57</sup>Fe and <sup>238</sup>U. Prior to the analyses, a 5% nitric acid solution containing two internal standards (Yttrium and Bismuth) were added to compensate any instrumental sensitivity variation. A range of separate standards of known concentrations of Al, Fe and U was used for external calibration. TOC concentrations for both the test sample and the concentrates and filtrates were obtained from a total organic carbon analyzer (TOC-Vws, Shimadzu). For all elemental and TOC analyzes, concentration blanks (i.e. filtrates, concentrates and filters) were performed.



### 3. Results and discussion

#### 3.1. Size distribution of the colloidal phases

The colloidal phase of the reference suspension (Figure 1A) showed a Gaussian-like distribution with hydrodynamic radii of approximately 65 to 155 nm (range of  $90\pm 3$  nm), and a mean radius of  $104\pm 2$  nm. Such a size continuum was expected because the colloidal phase of the same type of sample previously characterized had similar dimensional characteristics; it is typical of a natural soil colloidal phase distribution [34,36,37].

Concerning the three concentrated samples, no object was detected in the corresponding filtrates. For all concentrates, a lower DLS laser power than the reference was observed during measurement. Knowing that the laser power is automatically reduced when the colloidal concentration is too high, this observation qualitatively confirms the colloidal phases were more concentrated than the reference. The size distributions of the colloidal phases of the concentrates are presented in Figure 1B to D. To facilitate comparison with the reference, the latter is superimposed on each distribution (black dotted line). The distributions differed more or less from the reference depending on the UF method:

- The dead-end UF caused a significant broadening of the size distribution of colloidal objects ( $140\pm 4$  nm versus  $90\pm 3$  nm for the reference), with a pronounced positive skewness corresponding to sizes up to about 200 nm. No modification of the distribution for small sizes is visible. This suggests a significant redistribution due to agglomeration/aggregation phenomena.
- The tangential UF also led to a significant slight positive skewness with no apparent modification of the distribution for small sizes as for dead-end UF. Thus, a size range of  $110\pm 4$  nm was consistently observed for the three replicated concentrates. This also suggests partial size redistribution probably due to limited agglomeration/aggregation phenomena since the sizes did not exceed approximately 170 nm.
- The centrifugal UF did not lead to a significant size distribution broadening (size range of  $95\pm 3$  nm). No positive skewness was seen either. The overall shape of the distribution suggests this method had a limited impact on size distribution.

### *3.2. Microscopic texture of the objects from the test sample and the concentrates*

The TEM images from the bulk suspension and the concentrated phases are shown in Figure 2. For the reference suspension, three main types of components can be highlighted (first see the numbered black circles in images 1 and 2, in Figure 2A):

(1) Organic matter whose structure suggests that it is mainly humic-like in a more or less network organization. This is in agreement with a previous characterization carried out on this soil [31];

(2) Particles from a few nanometers to a few ten of nanometers, rather spherical shaped, and appearing mainly individually dispersed. They could be either inorganic and / or globular organic nanomaterials (from the condensation of humic substances) [35,38,39]. In addition to these particles, crystalline polygonal shaped objects of approximately 100-400 nm are also observed (image 4 in Figure 2A). Additional analysis by X-ray diffraction showed the presence of aluminum-containing crystalline nanominerals, which confirms the inorganic nature of the observed particles in these images. The presence of inorganic particles is also in agreement with what was expected given the knowledge of the colloidal phase of this soil [32,34].

(3) Mixed assemblies of particles and humic substances. These assemblies appear in a network organization, organic matter seeming to encompass the particles. Previous studies identified these textures as inorganic particles coated by diffuse humic-acid like organic matter [40,41]. Other spheroid mixed assemblies, individually dispersed, can be also seen in image 3 (Figure 2A).

The size ranges of the particles (images 2-4 in Figure 2A) and some organic structures visualized (image 1) are consistent with the size range determined by DLS. This is not the case for most assemblies involving organic matter, and in particular for all mixed assemblies ((3) in image 2). These structures were likely a consequence of sample preparation prior to TEM analysis (grid deposition and drying) since no size corresponding to these structures appears in the size distribution. These structures were therefore probably not representative of the initial colloidal phase; it can be assumed they give an indication of the ability of organic matter to agglomerate/aggregate when its concentration in solution increased.

For the concentrates (Figure 2, B-D), more material was observed, which confirms the concentration effectiveness after the use of any of the three methods tested. However, there

were some changes in both the texture and the organization of the components of the concentrates compared to the reference. Indeed, while both organic matter and particles were still present in the three concentrates, their distribution changed according to the UF method used. Thus, after dead-end and tangential ultrafiltration, on the one hand, organic structures and mixed assemblies appeared denser and more compact (as seen in the dark parts indicated by dotted arrows in the images 1 to 3 in Figures 2B and 2C, respectively; in these areas the particles with their net outline can be distinguished from the organic matter whose contour is more diffuse). At the same time, no single particles were observed, while the network structures in which particles were encompassed were also more expanded (See diffuse grey parts indicated punctually by dark arrows, also in Figures 1 to 3 of Figures 2B and 2C). Thus, as for the bulk of the test sample, the structures observed by TEM were larger than the DLS size range (more than 500 nanometers in diameter). On the other hand, particle agglomerates/aggregates appeared as illustrated by the images 4 in Figures 2B and 2C. This is consistent with a redistribution of the colloidal particles during both dead-end and tangential ultrafiltration, as suggested by the DLS size distributions discussed above. In summary, from an initial state in the reference where both individually dispersed particles and organic assemblies were present, these two UF methods led to agglomeration/aggregation phenomena in the concentrates, with concentration of particles within assemblies; these assemblies, in particular the organic ones were also probably agglomerated/aggregated between them during the drying step of the concentrates prior to their observation by TEM.

In contrast, after centrifugal UF, more particles can be seen individually dispersed than in the reference sample (images 1 to 3 in Figure 2D, highlighted by a dotted circle in the image 1), which was expected. In addition, possibly crystallized objects as initially seen (image 4 in Figure 2D compared to image 4 in 2A) were also present. Diffuse organic matter could be also observed (diffuse grey parts in images 1 to 3 in Figure 2D) but it seemed sparser than in the reference. No mixed assembly could be observed as in dead-end and tangential ultrafiltration.

### *3.3. Concentrate / filtrate chemical distributions*

At this stage of the investigation, the analytical determination for comparison of the chemical species in the dissolved and colloidal phases of both the reference sample and the concentrates did not seem to be relevant. Indeed, such a determination would have implied

that the dissolved and colloidal phases of the reference sample were separated before analysis; and this separation step would have necessarily been a source of bias. Therefore, the chemical species (Al, Fe, U and TOC) were determined by chemical analysis in the bulk of the reference sample, and the filtrates and concentrates obtained by the different UF methods. These species were also determined in the filters of the ultrafiltration systems in order to achieve the most complete mass balance possible. The results obtained are first presented in Figure 3. They are expressed in amounts relative to the amounts in the bulk of the reference sample in order to facilitate the comparison between the different UF methods. The colloidal mass amounts (Figure 3B) were then calculated on the basis of a mass balance assuming that (i) the dissolved mass of a species was distributed as 9/10 in the filtrate and 1/10 in the concentrate, in agreement with the overall mass concentration factor applied, and (ii) the colloidal mass was the difference between the total mass and the dissolved mass in the concentrate. In addition, the absolute mass amounts found in the bulk of the reference sample and in the concentrates are reported in Figure 4 in order to (i) get an idea of their order of magnitude, (ii) evaluate behavior of elements and TOC, as well as colloidal components in relation to the nature and organization of these components, as discussed above.

The recoveries are shown in Figure 3 A. The differences in recoveries do not seem globally significant in view of the associated uncertainties. However, elementary recoveries always exhibited the same trend, which means that the observed differences were not only due to random error. Thus, Al, Fe and U recoveries were always about 100% for centrifugal and dead-end ultrafiltration. Tangential UF seems to induce elementary losses (recoveries around 85%); it is likely that the circulation of the sample to be concentrated all along the tubing favored the elemental sorption. Another cause of loss, which could be identified and therefore considered in the recovery evaluation, is that inherent to the interactions with the filter membrane. This phenomenon represented up to 16% of the mass balances for TOC, and no more than 4% for Al, Fe and U in the case of tangential UF. The result concerning the elements was expected since this method would minimize fouling of the membrane and adsorption of inorganic components on the filter surface. However, it seems difficult to conclude regarding analyte losses on filters, never appearing systematically larger for one method than for another.

Concentrate / filtrate chemical distributions are presented in Figure 3 B. Whatever the species considered the same trend is observed. Thus, and despite the same concentration factor of the volume of the suspension, analyte masses in the concentrate increased according to:

centrifugal <tangential <dead-end UF, and analyte masses in the filtrate followed the opposite trend i.e. dead-end <tangential <centrifugal UF. The increase in the amount of chemical species in the concentrate may be inversely correlated with the motion of the suspension and the shear forces induced during the filtration process according to the method used. This suggests that sorption phenomena of the dissolved or colloidal species on the colloidal objects would be favored in suspension left in static state as was previously observed during dead-end filtration without stirring [8]. On the contrary, centrifugal ultrafiltration could minimize these phenomena. This method could also minimize agglomeration/aggregation phenomena especially by preventing the formation of assemblies such as those between particles and humic-like substances, and / or induce the loss of physical integrity of the most fragile colloidal assemblies. These last two hypotheses are consistent with TEM images (images 1 to 4 in Figure 2D) and DLS size distribution, which revealed neither mixed assembly nor loss of integrity of the nanoparticle components in the concentrate obtained after centrifugal UF. Concerning TOC, mass amount was lower in the concentrates obtained by centrifugal ultrafiltration than those from the other methods. This is also in agreement with the TEM images where few humic-like substances were observed in the centrifugal concentrate as in the reference. Given the set of TEM images of both the reference and concentrates, this suggests that the dead-end and tangential UF methods could lead to enrichment of the concentrates by initially dissolved species. This is in agreement with the above discussion about mass amount increase. This is also relevant given the motion of the suspension and the possible membrane clogging. Indeed, it was expected that this phenomenon is favored during dead-end UF, minimized in tangential UF and minimal in centrifugal UF.

Examining the absolute mass amounts of species in the concentrates, in addition with their respective colloidal mass amounts enables these observations to be refined and quantified. From Figure 4, all mass amounts of species were above the minimum theoretical concentration, i.e. (U, Al), (U, Fe) and (U, COT) were above the black dot, and outside the grey area in Figure 4 (see explanations in the legend), except (U, COT) after centrifugal UF (see below). The elemental and TOC mass amounts in the concentrates with respect to this minimum theoretical concentration were thus 5 to 7 times greater after dead-end UF, 3 to 4 times after tangential UF and 1.2 to 1.8 times (except TOC) after centrifugal UF. Given the results discussed above, this could be the overall expected consequence of an effective concentration of the colloidal phase. But this could also come from an enrichment of this phase, in particular organic matter, during dead-end and tangential UF, as illustrated by

Figure 2B and C. This enrichment is especially visualized in Figure 4 where (U, COT) is located very to the right of the dotted line for dead-end and tangential UF. The same trend is observed for iron, and to a lesser extent for aluminum. The location on the right also suggests either a less visible mass increase for the trace element U than for the major species, or a slight loss in this element. The overall enrichment of concentrates is also confirmed by the comparison between the UF methods: the mass amounts of Fe, Al and TOC in the concentrates were approximately 2 times higher after dead-end UF than after tangential UF; they were 4 times higher after dead-end UF than after centrifugal UF, except for the TOC for which the mass was 14 times higher after UFF than after UFC. The calculated colloidal mass amounts of Fe, Al and TOC in the concentrates were approximately 2 to 3 times higher after dead-end UF than after centrifugal UF; they were approximately 4 to 5 times higher after dead-end UF than after centrifugal UF, except for the TOC for which the mass amount was about 600 times higher after UFF than after UFC. The enrichment of the colloidal phase was more important than the overall enrichment of the concentrate. It concerned both elements and TOC. However, after centrifugal UF the TOC mass amount appeared to increase comparatively much less than that of Al and Fe; the positioning to the left of the minimum theoretical concentration even suggests a loss of organic matter.

These results are consistent with the knowledge acquired from previous studies on suspensions of this same soil: on the one hand Fe as TOC were found to be mainly in the dissolved phase, whereas Al was mainly in the colloidal phase. On the other hand Al and Fe were constitutive of the colloidal particles, Al being approximately 10 times more concentrated than Fe in the colloidal phase; U could be both constitutive of and sorbed on colloidal objects [32,42]. This set of observations firstly highlights that the nature of the organic matter gives it the ability to easily form (sub) micrometric assemblies depending on the surrounding physicochemical conditions, as observed by TEM after dead-end and tangential UF (Figures 2B and C). For these two methods in particular, there are both less physical constraints and probably more physicochemical interactions with the filter, these interactions limiting the transfer of species through it. Thus, in the concentrate, there was not only concentration of the colloidal phase due to the decrease in the volume of solution, but also enrichment, mainly of it, in organic matter and in initially dissolved elements, which limited the impact on the size distribution of this phase. However, element enrichment remained moderate after tangential UF: mass amounts of Al, Fe and U were approximately 1.5 times higher than those found after centrifugal UF. Knowing that the colloidal particles

were also effectively concentrated after centrifugal UF, this last method probably did not generate enrichment in elements initially dissolved in the concentrate; a decrease in TOC in the concentrate was even observed. This suggests that the organic matter was mainly in the dissolved phase passing through the filter and / or in the form of colloidal assemblies involving weak interactions, labile under the ultrafiltration conditions applied in centrifugal UF. The fate of the elements complexed with the organic matter was then the same as that of the organic matter, remaining or (re) passing in the dissolved phase of the filtrate. In the case of uranium, a loss in this element due to partial desorption from the colloidal carriers, in particular the inorganic particles, is also possible. If it existed, it remained moderate, tangential and centrifugal UF leading to colloidal U mass amounts relatively close, as observed in Figure 3B (9 and 5% of the total mass, respectively).

### *3.4. Evaluation of the method convenience*

In order to complete the evaluation and comparison of the methods, and regardless of their ability to preserve the colloidal phase, their practicality was also considered. In Table 1 are listed the different criteria for convenience evaluation for each of the three UF methods.

Dead-end UF was widely longer to use due to a filtration rate lower than centrifugal and tangential UF. Moreover, its very low filtration rate could have increased the risk of modifying the composition of the sample, in particular because of the biological activity. When large volumes had to be concentrated, tangential UF appeared the best suited. In addition, and for future applications, a tangential system is space saving, lightweight, simple and rapid to use so that it is also well suited for on-site field analyses, once the membrane previously cleaned. When relatively small volumes could be filtered, centrifugal UF was also well suited. In the perspective of future applications, centrifugal ultrafiltration is preferentially carried out in the laboratory. It could also to be considered on site, although this was not tested in this study. Indeed, portable systems are commercially available.

## **4. Conclusion**

The comparative evaluation of the intrinsic parameters characterizing the colloidal populations of the concentrates obtained after ultrafiltration of soil water enabled the physicochemical phenomena occurring during membrane separation and so the effects of the

3 tested methods to be highlighted. The concentration appeared to be effective for the 3 methods, with more colloidal material. However, the filtration used to concentrate also led to:

(i) A change in the size distribution, especially for dead-end UF with a significant agglomeration/aggregation, and in a lesser extent for tangential UF. Given the importance of this structural parameter on the mobility of colloidal objects and therefore of associated trace elements as uranium, it is therefore important to identify the method generating the least change in size, namely centrifugal UF. Indeed, at the submicrometric scale, small differences in size can have large behavioral impacts [43].

(ii) An enrichment in both inorganic and especially organic matter of the concentrate after dead-end UF. In a lesser extent, tangential UF also led to enrichment in organic matter. It probably contributed to the agglomeration/aggregation of particles, which were then observed embedded in organic clusters. Given the importance of organic matter as a carrier of pollutants, and particularly uranium, and in the perspective of environmental studies, any enrichment of the colloidal phase must be ideally avoided. This appears especially critical using dead-end UF. Such enrichment was not found after centrifugal UF, objects observed at the nanoscale and at the population level appearing identical before and after ultrafiltration. It is also desirable to avoid any loss of chemical species by loss of integrity of the colloidal assemblies. Such a phenomenon remains possible especially during centrifugal UF. However, element mass amount in the concentrates after tangential and centrifugal UF were found to be of the same order of magnitude.

From a practical point of view, both tangential and centrifugal ultrafiltration appeared well adapted to the concentration of waters. Given all the results obtained, centrifugal UF appears the best preconcentration compromise in terms of preservation of colloidal particles and practicality. The joint use of tangential and centrifugal ultrafiltration for the characterization of the colloidal phase could be interesting. Indeed, such strategy could provide a better understanding of the behavior of the colloidal phase comprising more or less labile assemblies, as well as associated trace elements.

To conclude, all the results obtained in the present study highlight that the behavior of the colloidal phase including sorption and agglomeration/aggregation phenomena depends not only on the chemical changes but also on the physical solicitations occurring during filtration. In other words, the preconcentration of the colloidal phase, and more generally its preparation



or even the conditions under which this phase is studied can only be operational. The present study led to a first assessment of the impact of this “operationality”.

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## Caption of Figures

Figure 1: Size distribution of the colloidal phase of the concentrates from A) Reference, B) Dead-end, C) Tangential and D) Centrifugal ultrafiltration. In black dotted line, for comparison: size distribution of the colloidal reference.

Figure 2: Microscopic images from the colloidal phase of the reference sample (A) and concentrated phases (Dead-End (B), Tangential (C) and Centrifugal ultrafiltration (D)). Black circles and arrows highlight areas of interest.

Figure 3: Mass balances for Al, Fe, U and TOC after dead-end (UFF), tangential (UFT) and centrifugal (UFC) ultrafiltration. A) Recoveries calculated from the masses in both concentrate and filtrate, and in the filter, compared to the bulk sample (reference), and B) Corresponding relative mass distribution between filtrate and concentrate obtained after ultrafiltration.

Figure 4: Uranium according to the major components in the concentrates obtained after dead-end (UFF), tangential (UFT) and centrifugal (UFC) ultrafiltration, and originally in the soil water sample (BULK). Mass amounts are given for 1L of initial suspension.

*The black dashed line formalizes a minimal theoretical reduction of the masses in the retentate in the case where only dissolved species would be present; the black dot corresponds to a reduction of 1/10 of the masses in the bulk with reference to the concentration factor equal to 10 used in this study. It is therefore expected that pairs of mass amounts (U, Al), (U, Fe) and (U, COT) are located both above and to the right of the black dot (i.e. outside the grey area) after preconcentration of the colloidal phase.*

## Caption of Table

Table 1. Criteria of convenience evaluation of concentration methods

*The operating values indicated in the first three columns refer to conditions used in this study. They may change if the filter cut-off and/or the device model are different.*

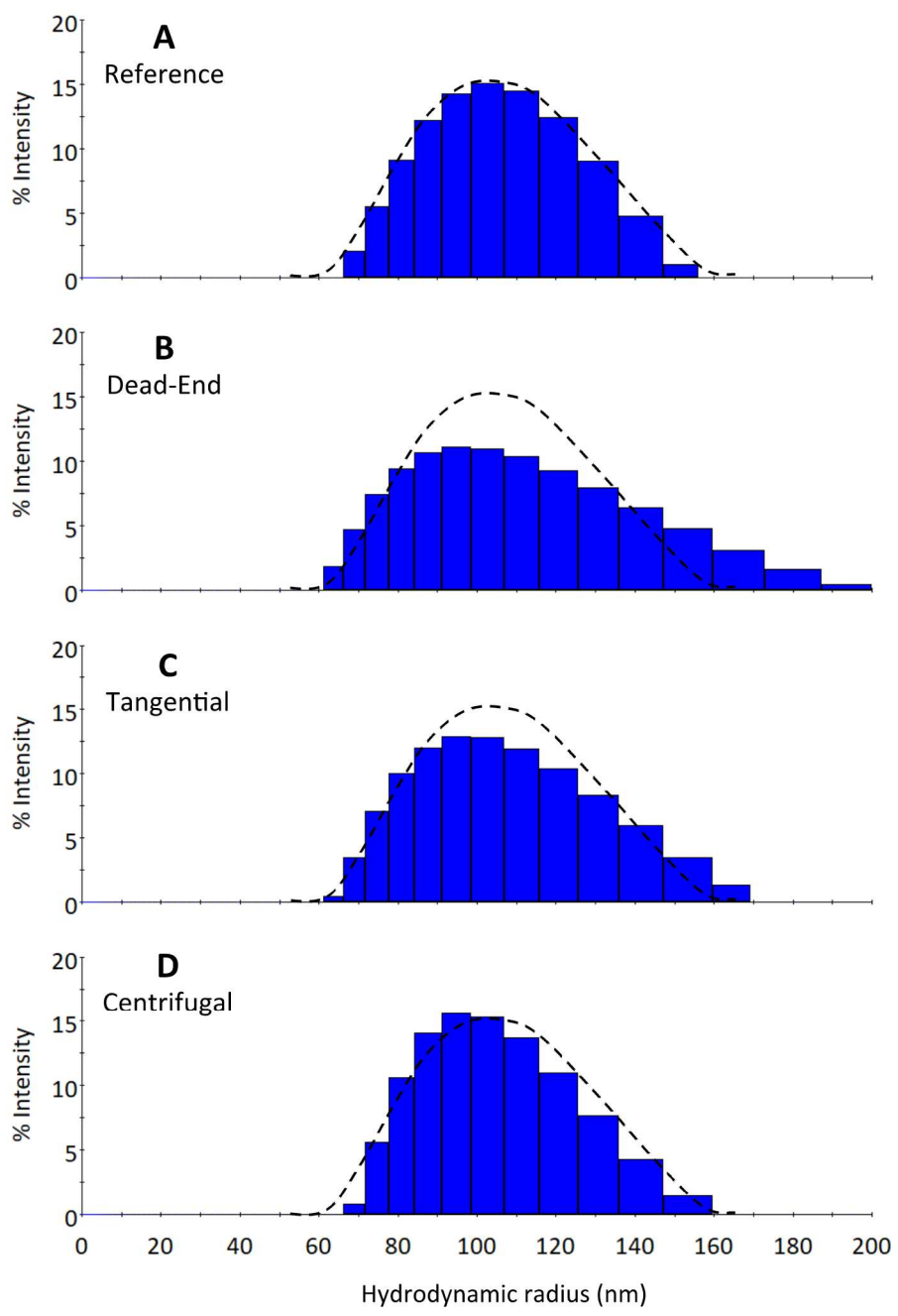


Figure 1

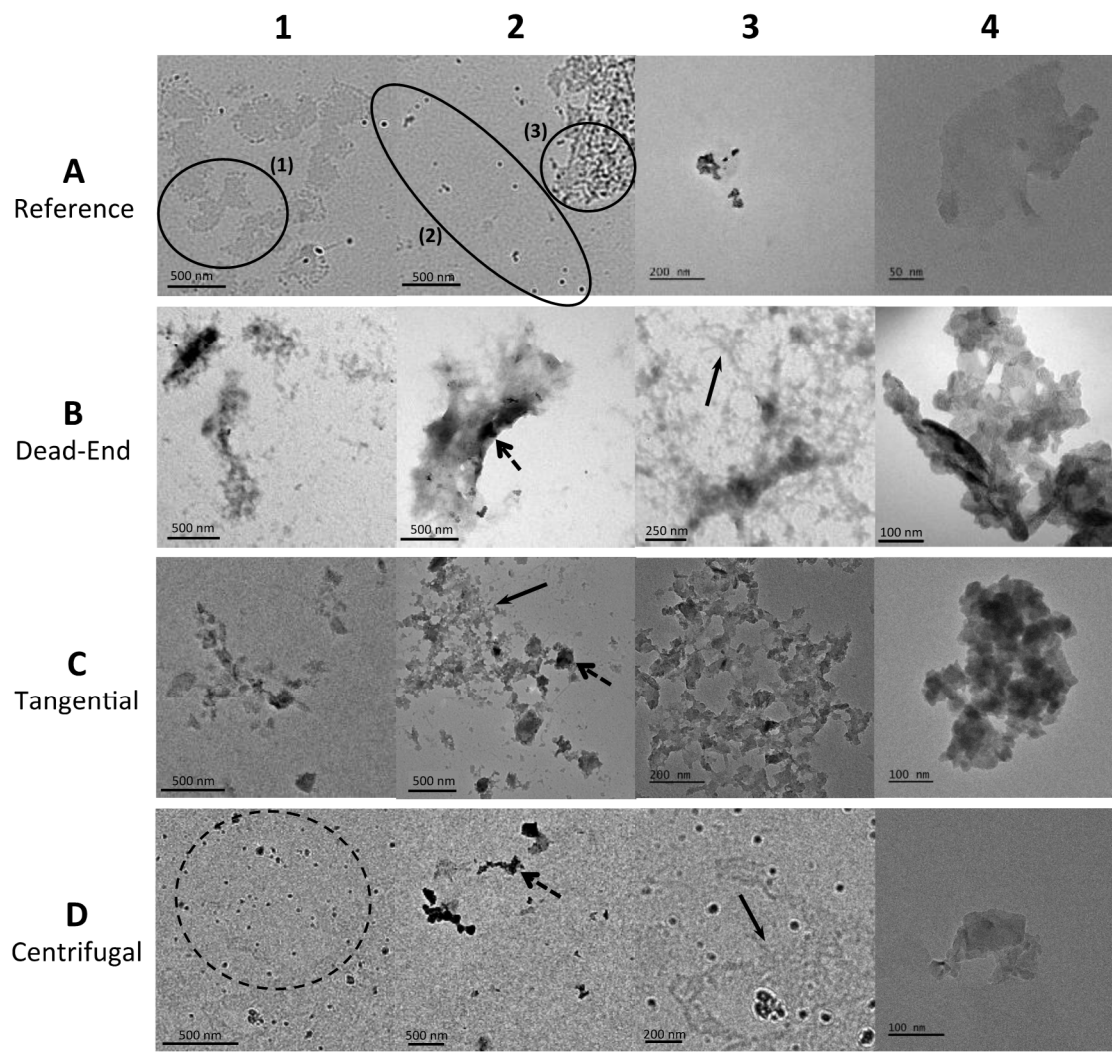


Figure 2

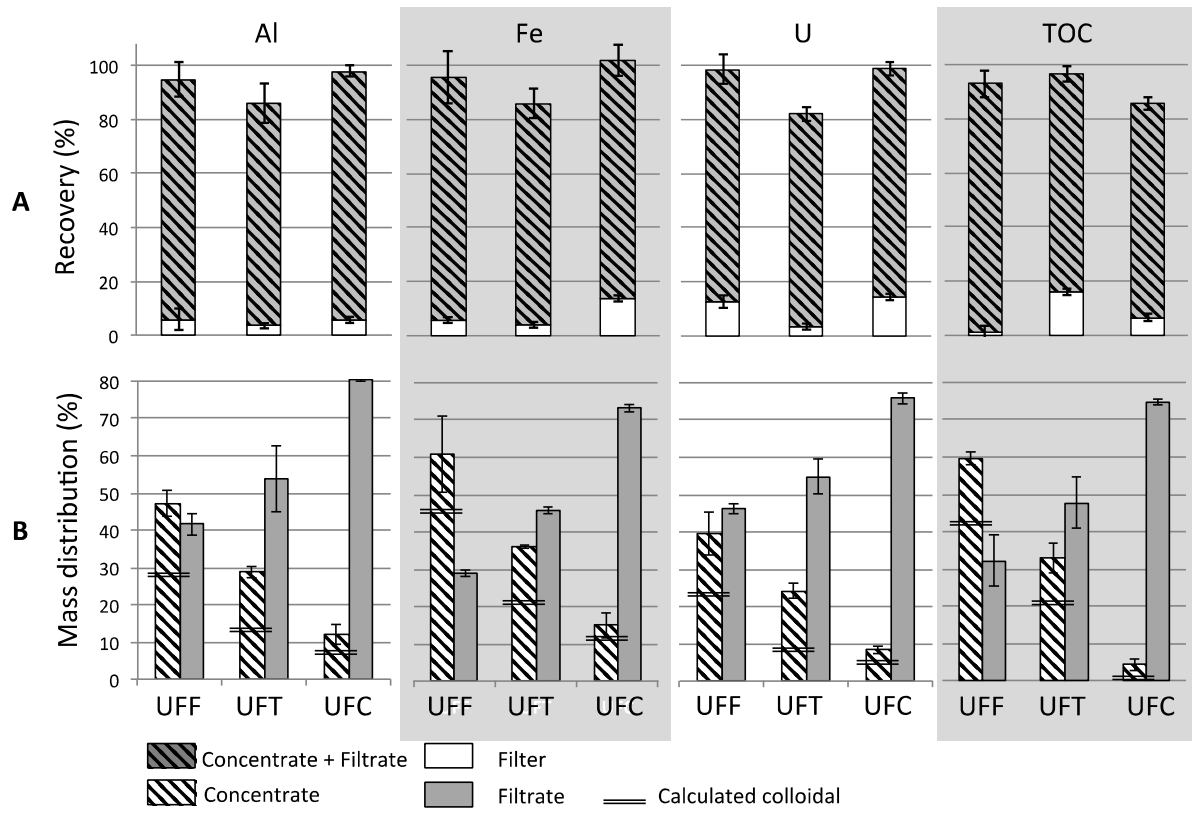


Figure 3



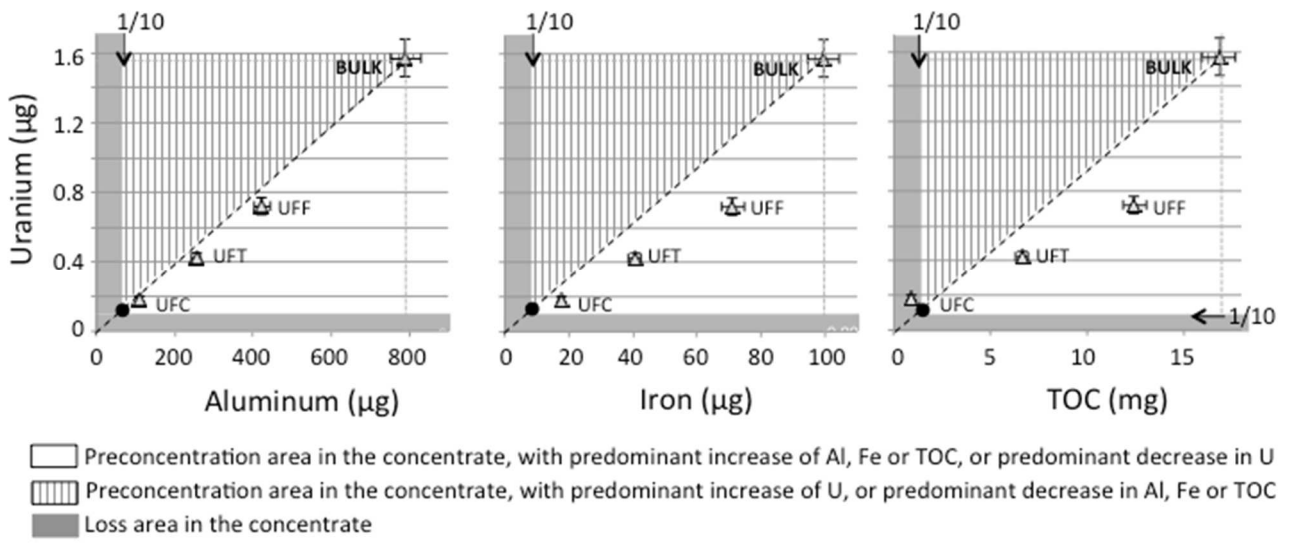


Figure 4

Table 1

<b>UF method</b>	<b>Filtration Time</b>	<b>Filtration rate</b>	<b>Maximum Volumes</b>	<b>Additional operations</b>	<b>Suitable for anoxic water</b>	<b>Suitable for field analyses</b>
Dead-End	$\geq 6$ hours	0.42mL/min	Up to 250 mL	Rinsing of the filter	Yes	No
Tangential	$\leq 30$ minutes	5mL/min	Up to several liters	Filter cartridge cleaning	Yes	Yes
Centrifugal	$\leq 15$ minutes	6mL/min	100 mL maximum	Rinsing of the filter	Yes	Yes

