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Application of cross-flow ultrafiltration for the determination of colloidal abundances in suboxic ferrous-rich ground waters [☆]

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Abstract

A suboxic groundwater from a sandy coastal aquifer was sampled using a new air free, large volume sampling method. Subsequent processing for size fractionation was completed with a modified cross-flow ultrafiltration (CFF) system equipped with a 1 kDa CFF membrane. By purging the CFF system with nitrogen, no oxygen was able to reach the sample. With this optimization, the sample was processed with higher than 90% recovery in terms of both iron and phosphate. Only about 4% of iron and 20% of phosphate in the filtered (0.2 μm) groundwater sample was found to be in colloidal form in the groundwater. In contrast, if no care was taken to maintain the suboxic environment of the original sample, iron was rapidly and completely oxidized and subsequently adsorbed to the CFF membrane. Other elements, such as phosphorus, were also lost to the CFF membrane to a substantial degree, and the mechanism is most likely coprecipitation with iron oxides. This study thus strongly supports the importance of maintaining ambient redox conditions during sampling and fractionation, especially for the determinations of colloid abundances in groundwater.
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1. Introduction

Groundwater colloids have received increased attention due to their potential role in facilitating the transport of particle reactive elements and/or contaminants (McCarthy and Zachara, 1989; Puls, 1990; Kretzschmar et al., 1999; Sen and Khilar, 2006). This topic is of great importance to issues such as underground waste storage and drinking water safety. Groundwater colloids can migrate through the porous media, yet still have a very high inherent binding capacity for many particle reactive elements and organic molecules (Ryan and Elimelech, 1996). For example, it has been shown that trace elements are often bound to organic colloids in groundwater (Killey et al., 1984; Mills et al., 1991; Dunnivant et al., 1992; Oden et al., 1993). Even more attention has been given to colloid-facilitated transport of radionuclides. It has been hypothesized that colloid-facilitated transport is an important pathway for the transport of plutonium at the Nevada Test Site

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(Buddemeier and Hunt, 1988; Kersting et al., 1999). Understanding and quantifying the extent of colloid associations is thus a key to evaluating contaminant transport in groundwater.

A complicating factor in subsurface sampling is the fact that groundwater is a redox confined environment. Many groundwater aquifers are partly or completely depleted of dissolved oxygen (DO) as a result of degradation of organic matter. When DO levels become low, iron oxide-reducing bacteria are favored and the aquifer becomes richer in reduced forms of iron. Ferrous iron in such groundwater is easily oxidized to iron (III) and rapidly hydrolyzed to form amorphous iron oxides when oxygen becomes available (Dzombak et al., 1990; Davison et al., 1992; Ledin et al., 1994; Emmengger et al., 1998). Groundwater samples are thus easily affected by exposure to ambient air during sampling and analysis. As such, groundwater sampling requires extreme caution in both initial groundwater sampling and subsequent colloid separation procedures, in order to maintain in situ redox conditions and hence chemical speciation. This is important for redox-sensitive elements other than Fe and also for particle reactive species that may be sorbed onto Fe oxides.

In addition to careful redox control, the importance of ground water sampling protocols, such as flow rate, pump type and purging time have been studied, as there are concerns with artifacts related to artificially creating or mobilizing colloids during sampling (Puls, 1990; Backhus et al., 1993; McCarthy and Degueldre, 1993). In general, the optimum sampling protocol uses a positive displacement pump, such as a bladder pump, using a low flow sampling rate (~ hundreds of mL/min) mimicking the natural groundwater flow. It is recommended that prior to sampling, one purges the well at low flow rates (micro-purging) until stable values for turbidity, dissolved oxygen, pH, conductivity and temperature are obtained (Puls, 1990).

Cross-flow ultrafiltration (CFF) is a common method for size fractionation in surface waters which has also been applied to groundwater. For example, CFF has been used to size fractionate groundwater actinides (Kersting et al., 1999; Dai et al., 2002) and trace elements (Jensen et al., 1999; Sañudo-Wilhelmy et al., 2002). The main advantage of CFF is its use as a preparative fractionation method that allows for processing of large volumes of sample (10–100's L). Large volumes and high concentration factors enrich the "retentate" fraction with colloids such that sufficient materials are isolated to ensure that analyte concentrations were above the limits of detection. Consequently, colloid abundances can be determined for elements found at even the lowest concentration levels ($<10^6$ atoms/L, e.g. Pu in groundwater) provided that the CFF blanks are low (Dai et al., 2002, 2005).

It should be noted however, that many operational factors, such as transmembrane pressure, flow rate, CFF membrane characteristics, concentration factor, etc. can impact the separation of colloids using CFF (Buesseler et al., 1996, 2003). Therefore, over the last decade, CFF protocols have been studied and optimized for the size fractionation of colloids in both natural marine (Buesseler et al., 1996; Gustafsson et al., 1996; Wen et al., 1996; Dai et al., 1998, 2001; Guo et al., 2000; Larsson et al., 2002) and fresh waters (Hoffmann et al., 1981; Buffle et al., 1992; Pham and Garnier, 1998). These studies have led to protocols designed to better calibrate membrane cutoffs, improve sample mass-balances and quantify blank controls.

It is also well known that the size distribution of colloids in natural waters can easily change due to aging, changes in pH, ionic strength, redox conditions, light or surface exposure (Chen and Buffle, 1996a,b). The processes that can potentially alter the size distributions of the colloids include coagulation, adsorption to surfaces, hydrolysis and precipitation. In addition to these processes, associated trace constituents are also affected by sorption processes, solution complexation and redox precipitations.

One recent example of where a different scientific conclusion was obtained as a result of using refined groundwater CFF sampling, is the case of colloid facilitated transport of plutonium. Dai et al. (2002) applied low flow rate well sampling and on site CFF with redox control and found no significant association of plutonium with colloids in groundwater at DOE Savannah River Site F-area. This is in contrast to an earlier study at this site with no redox control, where investigators found a significant Pu colloid association (Kaplan et al., 1994). What is clear from this work is that careful attention needs to be paid to groundwater sampling and CFF methods if one seeks to understand transport of colloid associated elements in groundwater (Buesseler et al., 2003).

Despite the potential impact of redox conditions on earlier research results, direct evidence for the oxidation of iron (II) upon exposure to air during groundwater sampling and CFF processing has not been reported for any natural groundwater settings. Moreover, there have not been any recommendations that clearly illustrate the precautions that investigators should take during both groundwater sampling and subsequent CFF processing to avoid redox related artifacts. The objective of this study was to evaluate the importance of maintaining

Table 1
Chemistry of the studied groundwater

Temperature	Conductivity	Salinity	Dissolved oxygen		pH	Iron$_{filterpassing}$
°C	mS/cm		% sat	mg/L		$\mu mol\ L^{-1}$
14.6	0.23	0.14	<3	0.24	6.7	60

ambient redox conditions in assessing the distribution of colloids and associated elements in groundwater using CFF. In order to maximize the effect, an iron-rich aquifer with reducing conditions were selected for the study.

In this manuscript, phosphate is used as an example of a contaminant whose groundwater speciation is potentially impacted by ambient redox conditions since its transport can be enhanced by association with iron-rich colloids (Crosby et al., 1981; Zhang et al., 2003; Wolthoorn et al., 2004; Ren and Packman, 2005). Phosphate transport in soil and groundwater is often a major concern in discharge to the oceans (Smith et al., 1991; Moore, 1999).

2. Materials and methods

2.1. Sample collection

In January and February of 2001, sampling of a reduced, anoxic, ferrous-rich groundwater aquifer was conducted. The sample well is situated at the head of Waquoit Bay, Cape Cod, MA, USA, about a hundred meters above the saltwater intrusion zone. The well is 11.6 m deep, and the well casing is made of PVC, 4'' diameter with a 1.2 m long stainless steel screen. Prior to sample collection, the well was purged at a low flow rate (0.5 L/min) for a total volume of 100 L using a

bladder pump (Dai et al., 2005). DO and the other parameters in Table 1 were monitored using an YSI-650/600R multi-parameter probe in a flow-cell until constant readings, before sampling started. The measurements of the multi-parameter probe after purging are shown in Table 1. Samples were filtered with an in-line 0.22 μm Millipore cellulose cartridge, and the outlet from the cartridge were plumbed directly to the sample barrel inlet.

A special sampling barrel was developed for the sample collection, transportation and subsequent CFF processing to eliminate exposure to oxygen. The barrel is a modified "bag-in-a-bottle" from Berghof (Coral Springs, FL, USA) consisting of a Teflon (PTFE) bag in a Polyethylene over pack barrel (Fig. 1). The lid was modified to have an inlet port with a closing valve and Teflon tubing inside leading to the bottom of the bag, inside the barrel. Prior to sampling, the acid-cleaned bag was purged with nitrogen gas and evacuated three times to remove any oxygen inside and then sealed. To begin collection, a sample line was connected to the barrel inlet and simultaneously the inlet valve was opened. The sample size in the collapsed bag was monitored gravimetrically during collection. When full, the valve was closed and the sample line disconnected simultaneously. CFF began immediately after the sample was transported back to the laboratory facilities. The elapsed time from collection to CFF processing was approximately 30 min.
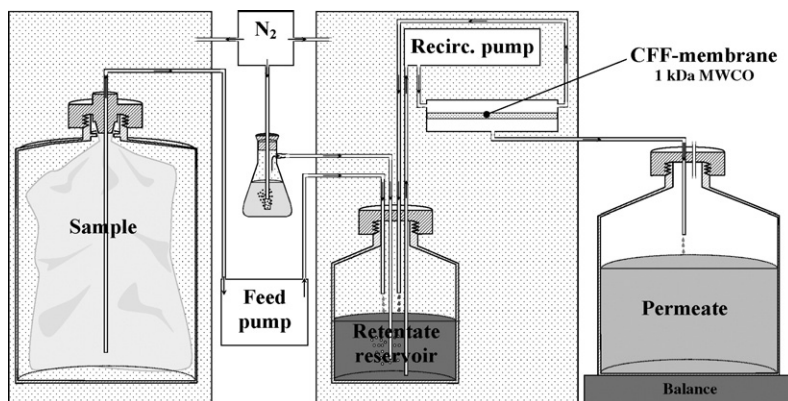

Fig. 1. The cross-flow ultrafiltration system in a nitrogen purged tent including feed and recirculating pumps, membrane and the retentate reservoir. The sampling barrel is in a separate purged tent.

Table 2
Procedure for the CFF method

1	Assembly
2	Reservoir filled with 4 L of Q-water N2-purged
	Process to 3 L to rinse system
	Empty
3	Fill with 4 L of sample for preconditioning
	Process 3 L to precondition membrane
	Empty
4	Fill with 4 L of sample for flushing
	Flush out 3 L
5	Fill up to 1.5 L with sample
6	CFF processing starts
	Feed pump maintains reservoir at 1.5 L
7	Subsampling permeate and retentate (reservoir)
8	CFF processing ends
	Recirculate reservoir for 15 min
	Reservoir liquid collected
9	Sampling of integrated permeate and retentate
10	Cleaning of the system

2.2. Cross-flow ultrafiltration

The colloidal fraction is operationally defined here as being material that passes through a 0.22 μm prefilter and is retained by a CFF membrane with a nominal molecular weight cutoff of 1000 Dalton (1 kDa). The material that is retained by the ultrafilter is concentrated in the retentate reservoir, while the material smaller than the ultrafilter cutoff passes through to the permeate. As the fractionation progresses the retentate reservoir becomes more concentrated. The concentration factor (cf) is described by:

$$cf = \frac{(\text{permeate volume} + \text{retentate volume})}{\text{retentate volume}} \quad (1)$$

The abundance of a chemical element in the colloidal fraction is calculated as

$$[Me]_{coll} = \frac{[Me]_{ret} - [Me]_{perm}}{cf} \quad (2)$$

which is valid at any point during the fractionation and also on the integrated fractions at the end of a fractionation. The ability of the membrane to retain

a component is defined as the retention coefficient (RC):

$$RC = 1 - \frac{[Me]_{perm}}{[Me]_{ret}} \quad (3)$$

The mass balance is evaluated by comparing the sum of the colloidal component (Eq. (2)) and the permeate component with the total filter passing component:

$$Loss\% = \frac{[Me]_{tot<0.2\mu m} - ([Me]_{coll} + [Me]_{perm})}{[Me]_{tot<0.2\mu m}} \times 100 \quad (4)$$

The CFF system consists of a 4 L reservoir bottle, re-circulating pump (Flowjet), 1 kDa regenerated cellulose ultrafiltration membrane (0.5 m^2 surface area, Millipore Pellican 2) with cassette holder (Millipore Pellicon) and the sample barrel with a feed pump (Fig. 1). The entire system was surrounded by a nitrogen purged tent to minimize redox change during the sample processing. CFF was operated with a cross-flow to permeate flow-rate ratio of 15 to achieve high recovery (Larsson et al., 2002). The cross membrane pressure drop was approximately 0.4 bar, and the permeate flow rate was approximately 120 mL/min for all experiments.

The CFF procedure is summarized in Table 2. After the membrane was mounted in the holder, the reservoir was filled with Q-water, which was de-aerated by N$_2$ purging and the system was enclosed in the N$_2$ purged tent. After the remaining NaOH storage solution (pH=10) was rinsed from the membrane with the N$_2$ purged Q-water, the reservoir was drained and filled with 4 L of sample for preconditioning the membrane. The preconditioning step was included in order to have any active sites on the membrane be coated with components of the particular sample that has affinity for it. Then after the preconditioning, the membrane is less susceptible to adsorb components of the sample (Dai et al., 1998). Preconditioning was performed by running the recirculating pump until reservoir level was reduced

Table 3
Calibration of ultrafiltration performance

	Conc. factor	Retention coefficient	Retentate conc. [a]	Permeate conc. [b]	Loss
10 kDa Dextran (C_0=86.5 nM [c])		99.5%	2.85 μM	15.5 nM	−8.9%
3 kDa Dextran (C_0=40.2 nM)		99.6%	690 nM	2.78 nM	−3.8%
Vitamin B12 (1.35 kDa) (C_0=1.85 μM)	16.9	98.8%	15.8 μM	0.187 μM	39.9%

[a] Retained by 1 kDa membrane.
[b] Passed through 1 kDa membrane (truly dissolved).
[c] Initial concentration.

to 1 L and the permeate discarded, upon which a new acid-cleaned reservoir was used, and the tent and bottle were purged again with nitrogen gas. The reservoir was then fed with 4 L of sample for a flushing step where both retentate and permeate valves were directed to the waste and reservoir flushed until 1 L remained. The reservoir was filled again to 1.5 L and CFF processing started.

Sample was fed into the reservoir bottle by the feed pump at the same rate as the membrane permeate flow. Separate variable transformers regulated each of the pumps. Subsamples (10 mL) was taken from both the permeate and the retentate lines during the course of the processing for total iron and phosphate analysis. The processing was stopped when a cf of at least 15 was reached. At that time the permeate outlet was closed and the retentate recirculated for 15 min before the retentate was collected into the retentate reservoir. Any remaining liquid was emptied out and weighed for mass balance calculations. The total permeate sample was also sampled. Between CFF sampling, the system was cleaned sequentially by Q-water, HCl and NaOH (Dai et al., 1998, 2002). The membrane was placed in a pH 10 solution during storage.

Three CFF experiments with samples from the same well were conducted using increasing degrees of redox control, referred to as "no redox control", "partial redox control" and "full redox control". The experiment with no redox control in sampling and processing was actually performed last. In the partial redox control experiment, the nitrogen tent around the system was purged, and the CFF reservoir bottle was purged at intervals. In the full redox control experiment, the reservoir bottle was continuously purged throughout the CFF with a modified cap design with the sample barrel being put in a second smaller purge bag to exclude any introduction of air to the system. The nitrogen gas was directed through a wash bottle containing sample water to pre-equilibrate the nitrogen purging gas with the sample to minimize purging effects of changing partial pressure of carbon dioxide and pH.

2.3. Calibration of membrane cut-off

Prior to the application of the CFF, the membrane was calibrated against standards of known molecular weight. The results are shown in Table 3. The calibration was done using a prefiltered fresh water matrix from Goodwill Pond, Cape Cod, MA, USA. The calibration samples were spiked with fluoresceine tagged 3 kDa and 10 kDa Dextran standards, and with 1.3 kDa Vitamin B12 on separate occasions.

2.4. Total iron analysis

Subsamples for iron and phosphate were taken in preacidified bottles (pH ~ 1) to minimize oxidation of the ferrous iron. Total dissolved iron (II + III) was measured in subsamples after reduction using the ferrozine method (Stookey, 1970). In the reduction step, 15 mL samples were incubated at 60 °C for 1 h after addition of 0.2 mL 1 M hydroxylamin hydrochloride where all iron is transformed into Fe(II), which is determined by spectroscopy. The quantifications were done with standard curve using an atomic absorbance spectroscopy Fe standard.

2.5. Phosphate analysis

Phosphate was determined spectrophotometrically using a Lachat Quick-chem 8000 (Zellweger Analytics) automated flow injection ion analyzer. The Lachat method used is 31-115-01-1-H "Measurement of Orthophosphate by Flow Injection Analysis" which is based on a colorimetric flow injection analysis where phosphate reacts with ammonium molybdate and antimony potassium tartrate (pH<1) to form a blue complex. Quantifications were carried out using standard calibration curve.

3. Results and discussion

3.1. CFF membrane performance

Presented in Table 3 are the membrane characteristics for the different molecular weight standards represented by RC, retentate and permeate concentrations as well as loss percentages. RCs for both 10 kDa and 3 kDa Dextrans are >99% indicating, in terms of retention, good integrity of the CFF membrane used in this study. The mass balance for Dextran was quite good (loss terms −9% and −4%) indicating neither significant contamination nor losses of these standard molecules to or from the membranes. However, there was a 40% loss of Vitamin B12 during the fractionation, which is attributed to sorption to the membrane that was visibly colored by Vitamin B12 after the experiment. The inherent humic fluorescence of the pond water matrix was used for mass balance cross check of natural dissolved organic matter. The humic fluorescence showed a very small loss rate (3% and 2%).

3.2. Groundwater ultrafiltration

In the "no redox control" experiment, the CFF results for iron are shown in Fig. 2A. The loss of iron was rapid

and the longer the processing continues, the more iron was lost. The fact that there is an increase in the loss term, up to 100% after a cf of 10, is interpreted as iron being precipitated on the membrane during the CFF processing while the samples were exposed to air and oxidized. Both precipitation and scavenging can take place with the precipitate formed being an efficient co-precipitation agent for additional iron. A mechanism of autocatalysis of Fe(II) oxidation onto Fe(III) colloids have been observed (Tamura et al., 1976; Pullin and Cabaniss, 2003) and should be taken into account when interpreting these data. It is worth noting that the membrane became so rust colored that it had to be discarded after the no redox control experiment was completed.

The loss of phosphate reached 100% even faster than Fe (Fig. 2B). The reason that phosphate is reaching a 100% loss at a lower cf (quicker) than iron is that the fresh precipitates being formed on the membrane are efficient in scavenging phosphate and there is higher total concentrations of iron than phosphate.

In the partial redox control experiment a significant decrease in the loss rates of iron was observed, compared to the no redox control condition (Fig. 2C). The loss of iron slowly increases with cf, but was below 20% even at cf=15. The quick decrease in colloidal iron can be interpreted as fast oxidation of reduced iron due to the oxygen initially presents, after which the oxidation process became limited due to the limited oxygen supply. The colloidal iron was about 8% constantly after cf=5.

The loss rate for phosphate during the partial redox control experiment was again higher than for iron, and increased from ∼ 20% to 50% during the processing (Fig. 2D). The fraction of phosphate determined to be colloidal was higher than iron and was constant at ∼ 20% after cf=5. The permeate concentration decreased with increasing cf corresponding to increasing losses. This suggests loss of the permeate to the membrane since any breakthrough of either low or high molecular weight colloids would have resulted in an increase in permeate
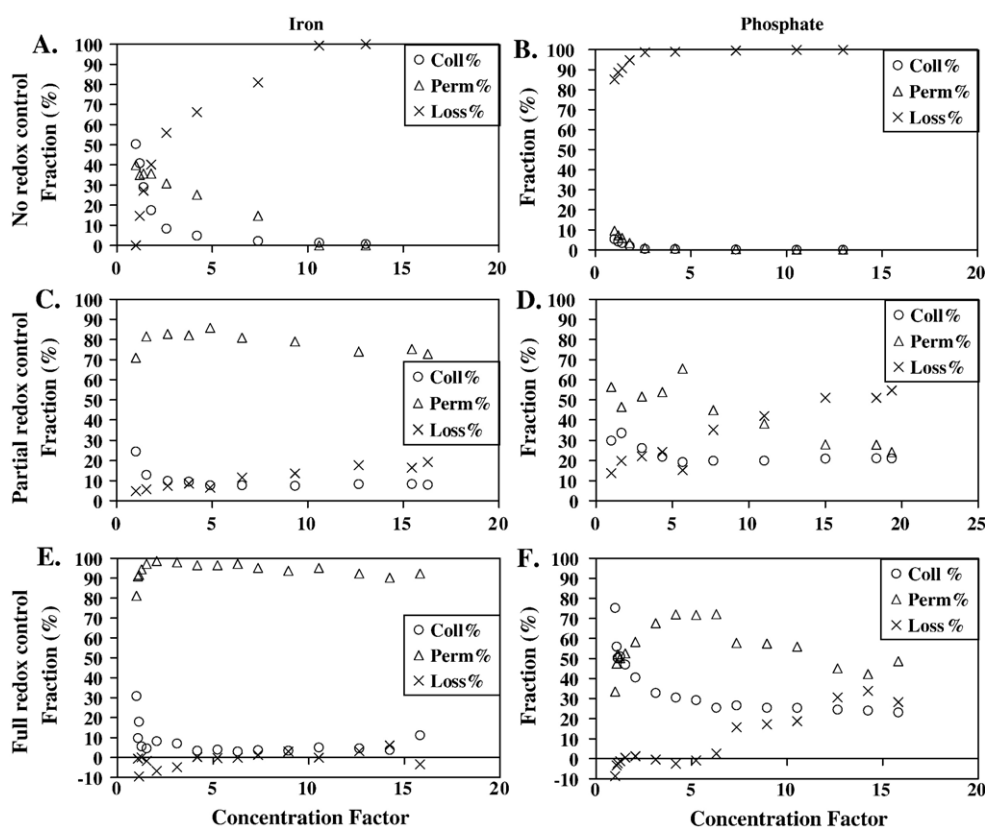

Fig. 2. The cross-flow ultrafiltration results shown as percentage colloidal, permeate (<1 kDa) and loss for; A) iron from the no redox control experiment (C_0=50.4 μM), B) the no redox control phosphate results (C_0=3.33 μM), C) the iron results for the partial redox control experiment (C_0=49.0 μM), D) the partial redox control phosphate results (C_0=4.22 μM), E) the iron data of the full redox control experiment (C_0=56.7 μM) and F) the full redox control experiment phosphate results (C_0=3.36 μM).

concentration (Dai et al., 1998). Since the colloidal fraction was relatively constant and the loss rate was increasing, this suggests that precipitates were formed on the membrane rather than a production of iron oxide colloids during the processing. It is possible that the oxidized iron colloids are very reactive and rapidly adsorbing on surfaces or on already formed precipitates (autocatalysis).

In the full redox control experiment, the loss of iron through the CFF process was only $0 \pm 5\%$ (Fig. 2E). The colloidal fraction of iron calculated from the integrated permeate and the retentate from the end of the experiment was 5%. Note that there was an initial increase in permeate concentration until cf=1.5, which represents 1 L processed from a total volume of 28 L. The reason could be related to the initial secondary conditioning of the membrane after the first conditioning and flush. This small initial increase is negligible for the integrated permeate.

The full redox control experiment revealed colloidal iron to be 5% of total iron. The same CFF analysis of phosphate found the colloidal fraction to be equal to 25% of the total (Fig. 2F). Phosphate also showed higher losses of 21% compared to iron, which was in agreement with the other experiments relative to iron. The ratio of $HPO_{4colloidal}/Fe_{colloidal}$ was approximately 0.25.

In Fig. 3 the permeate iron concentration from the experiment with full redox control is plotted against from the experiment with no redox control. Full redox control permeate concentrations are quite stable and are just below the total iron concentrations of 57 µM. A slight decrease was observed as the fractionation progressed. Samples for the no redox control experiment were stored overnight without redox controls. In this experiment, the total iron concentration had only been reduced from 57

to 50 µM (data not shown), however the first permeate subsamples had an iron concentration around 20 µM. This suggests the sample without redox control had to a large extent formed colloids or microparticulates in solution. Permeate concentrations continued to decrease rapidly throughout the CFF processing. After a cf=10 was achieved, permeate subsamples had no detectable iron left. The decrease in permeate iron concentrations along with observed discoloration of the membrane was interpreted as iron precipitate forming on the membrane during the initial sample processing became more efficient in precipitating further iron.

4. Conclusions

This size fractionation study of suboxic groundwater found colloidal fractions of 5% iron and 20% phosphate provided full redox controls were followed. Without these precautions, colloidal fractions would otherwise be erroneously estimated as was evident from results found in the no redox control experiment. Results from the partial redox controlled experiment showed a slight overestimation of the colloidal fractions of iron and phosphate. It can be concluded from this study that great care must be taken to maintain the ambient redox conditions for a groundwater sample during collection, transport and fractionation, in order to accurately determine the colloidal size distribution. Moreover, the oxidation and hydrolysis of iron (II) are not only affecting the size distribution of iron itself, but influenced other elements such as phosphorus shown here, due to its high affinity of iron oxides to adsorb/scavenge other elements. This study indicates the need for similar redox precautions to be applied during sampling and CFF procedures, to avoid artifacts that erroneously affect results and subsequent conclusions regarding colloidal-facilitated transport in groundwater. An incorporation of on-line measurement of dissolved oxygen or redox potential (without contaminating the sample reservoir) would be a good improvement to be able to validate that no additional oxygen is being introduced in the process.
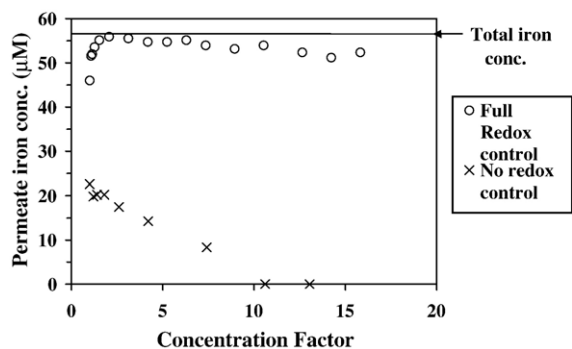
Fig. 3. The permeate subsample iron concentration is plotted as a function of concentration factor for the experiment with full redox control and the experiment with no redox control.

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