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Abstract

Two methods have been tested for the determination of trace metals associated with colloid species in surface waters, using test water from Eckarfjärden (PFM000070) in Forsmark; 1) fractionation (ultra filtration) using special membrane filters with cut-offs of 1 kD and 5 kD and 2) filtration using a system of standard membrane filters with varying pore sizes connected in series. Both methods were somewhat modified compared to previous methods for colloid determination in groundwater within the site investigations at Forsmark and Laxemar (PLU).

The results show that, in general, the largest amounts of metals associated with a colloid phase were recovered in the fraction between 1kD and 5 kD which indicates that the metal ions are associated with low molecular weight organic acids. Similar amounts were recovered on the filters in the filtration experiment. A minor part of the colloidal phase metals was recovered in the fraction larger than 5 kD i.e. metal ions associated with larger organic acids or colloidal size clay minerals.

The metals present preferably as colloids in the fractionation experiment were: iron, thorium, cerium, uranium, neodymium, titanium, zirconium and yttrium. The filtering experiment showed larger parts of titanium and aluminum in the colloid phase than the fractionation experiment while the iron and cerium portions were equal and the uranium, yttrium and neodymium portions were lower. The results from the fractionation test showed that the dissolved parts were large for barium, manganese, strontium and rubidium. In the filtration test, uranium, yttrium and rubidium, were also present mainly as dissolved ions. The detection limit for filter analysis of thorium was high, and the part of thorium present as colloids was determined to <50%.

Issues and methodological problems:

- Severe contamination caused interpretation difficulties for several metal ions, especially chromium, nickel and zinc.
- Both methods are time consuming and difficult to use as regular routine procedures.
- The results from the two methods show some discrepancies but also give complementary information. This makes it difficult, at the present stage, to recommend one of the methods over the other for continuing colloid studies.

Possible improvements:

- Measures to take in order to reduce contamination problems; general cleaning and inventory of metal details in the laboratory and exchange of material when possible, exchange of tube fittings in the experiment setup for the filtering method and introduction of a clean bench facility for the experimental work.
- The filtering method may be speeded up if the pump system is changed. Simultaneous filtering of more than one sample at a time using several simpler experiment setups would be possible.
- At the present stage, it is not possible to recommend one of the methods as the best one for continuing work since both have advantages and disadvantages. Both methods are too advanced and difficult to be carried out regularly as a standard procedure.

Sammanfattning

Två olika metoder har testats för bestämning av spårmetaller bundna till kolloider i ytvatten, med hjälp av provvatten från Eckarfjärden (PFM000070), belägen i Forsmarksområdet; 1) fraktionering (ultrafiltrering) med speciella membranfilter med cut-off på 1kD respektive 5 kD och 2) filtrering med ett system av standardfilter (membranfilter av polykarbonat) med olika porstorlekar kopplade i serie. Båda metoderna är något modifierade jämfört med tidigare användning för kolloidbestämningar i grundvatten inom platsundersökningarna i Forsmark och Laxemar (PLU).

Resultaten visar, generellt, att största mängderna av de analyserade metallerna i kolloidal fas återfinns i fraktionen mellan 1 kD och 5 kD vilket indikerar att metalljonerna är bundna till lågmolekylära organiska syror. För de flesta av elementen var metallinnehållet som observerades på filtren av samma storleksordning i filtreringsexperimentet. En mindre andel av metallerna i kolloidal fas återfanns i fraktionen större än 5 kD d.v.s. metalljoner bundna till något större organiska syror och kolloidala lermineral.

De metaller som företrädesvis förekom som kolloider vid fraktioneringen var järn, torium, cerium, uran, neodym, titan, zirkonium och yttrium. Filtreringen påvisade större andelar av titan och aluminium i kolloidal form än fraktioneringen medan järn och cerium visade samma andelar och uran, yttrium samt neodym visade lägre andelar. Vid fraktioneringen var andelen lösta joner stor för barium, mangan, strontium och rubidium. Vid filtreringen förekom även uran, yttrium och rubidium huvudsakligen som lösta joner. Detektionsgränsen för filteranalysen av torium var hög, och andelen torium bundet till kolloider var <50%.

Frågeställningar och metodproblem:

- Omfattande kontaminering orsakade tolkningsproblem för många av metalljonerna, i särskilt hög grad gäller detta krom, nickel och zink.
- Båda metoderna är tidskrävande och svåra att tillämpa i återkommande rutinmässiga undersökningsaktiviteter .
- Resultaten från de två metoderna visar skillnader och ger kompletterande information vilket gör det svårt i nuvarande läge att rekommendera en av metoderna för fortsatta kolloidstudier.

Möjliga förbättringar:

- Åtgärder för att reducera kontamineringsproblemen; allmän rengöring och inventering av metallförekomst i laboratoriet samt utbyte av material där det är möjligt. Byte av slangkopplingar i experimentuppsättningen för filtrering. Introduktion av renluftsbänk för experimentarbetet.
- Filtreringsmetoden skulle kunna snabbas upp om man byter pumpsystem. Samtidig filtrering av mer än ett prov med hjälp av flera experimentuppsättningar med enkla filterhållarpaket är också en möjlighet.
- För närvarande är det inte möjligt att rekommendera en av metoderna som den bästa för det fortsatta arbetet eftersom båda har sina fördelar och nackdelar. Båda metoderna innebär dessutom ett alltför avancerat och komplicerat laboratoriearbete för att kunna utföras regelbundet som ett standardförfarande.

Contents

1 Introduction

The site investigations at Forsmark /1/ for a future repository were, on the whole, finished in June 2007 and a less intensive long-term monitoring phase commenced. The monitoring programme /2/ encompasses several geoscientific and ecological disciplines and includes sampling and chemical analyses of deep and shallow groundwaters, surface waters and precipitation. The first programme extended until 2009 and was reviewed and adjusted 2010 after the choice of Forsmark as the site for the repository see AP PF 400-09-012. This document reports the data/results gained by a pilot study for the determination of trace metals associated with colloid species in surface waters. This pilot study was a complementary activity to the regular hydrochemical monitoring of surface waters. The work was carried out in accordance with activity plan AP PF 400-10-003. In Table 1-1 controlling documents for performing this activity are listed. Both activity plan and method descriptions are SKB's internal controlling documents.

Table 1-1. Controlling documents for performance of the activity.

Activity plan	**Number**	**Version**
Pilotförsök: Metodval för bestämning av mängden spårmetaller bundna till kolloider i ytvatten	AP PF 400-10-003	1.0
Method descriptions	**Number**	**Version**
Mätsystembeskrivning för fraktionering av humus- och fulvosyror	SKB MD 431.043	1.0
Mätsystembeskrivning för kolloidfiltreringssystem	SKB MD 431.045	In progress

The regularly collected samples within the hydrochemical monitoring programme for surface waters and near-surface groundwaters are filtered through 0.40 µm polycarbonate membrane filters and metal ions associated with colloids passing through the filter will erroneously be included in the water phase. This problem was identified quite recently in connection with calculations of K_D-values for the partitioning of various constituents between dissolved phase and solid phase. As K_D-values are among the most important factors when modeling transport of radionuclides, the lack of data is unsatisfactory. Therefore, in order to address the problems with the determinations of K_D-values, it was necessary to investigate possible methods for the analysis of colloid matter in surface waters.

The sampling activity in this reported study is stored in the primary data base (Sicada) but the obtained analytical data are only available from this report. The sampling activity is traceable by the activity plan number.

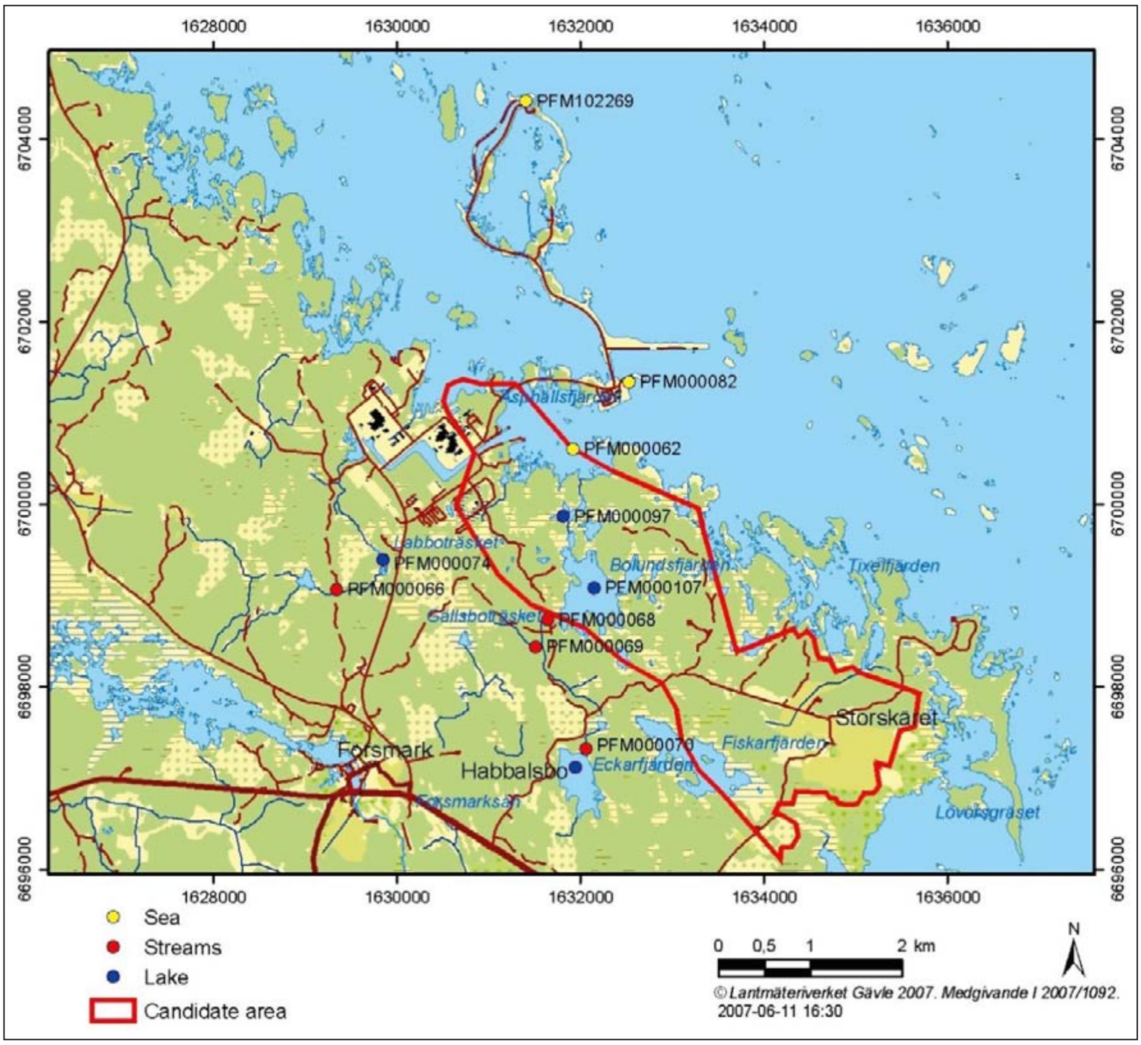

Figure 1-1. *Sampling locations within the surface water monitoring programme. The location PFM000070 (Eckarfjärden) was selected as sample water source for the pilot test.*

2 Objective and scope

Two methods for the determination of colloids in surface waters were tested. The methods have been used earlier for groundwaters within the site investigations in Forsmark and Laxemar. The tests were performed in order to investigate if the methods are suitable for surface waters and if any of the methods could be used on a regular basis in the monitoring programme. The two methods are:

1. Ultra filtration/fractionation using special filters (modified SKB MD 431.043). Sample water was pumped through filters with cut-offs of 1 kD and 5 kD. The different fractions were analyzed for DOC, major components and trace metals. The method yielded DOC and metal ion contents in the fractions <1kD, >1 kD but <5 kD and >5 kD.
2. Filtration through membrane filters connected in series (modified SKB MD 431.045). The sample water was lead by suction/pressure through a ”filter unit” (filters with different and decreasing pore sizes connected in a series) into a container collecting the water. The filters were analysed for major components and trace metals. The filtered water in the collecting container was analysed for major components, trace metals and DOC.

3 Equipment

3.1 Equipment for colloid fractionation using 1 kD and 5 kD membrane filters (Method 1)

The equipment consists of membrane filters with a defined cut-off (pore size), a membrane pump, flexible tubing and vessels. Generally, each of two water sample portions are filtered through filters of different size (1,000 D and 5,000 D, D=Dalton, 1D=1 g/mol). The equipment and performance are described in SKB MD 431.043 (*Mätsystembeskrivning för fraktionering av humus- och fulvosyror*, SKB internal controlling document). Figure 3-1 shows the equipment setup and Figure 3-2 describes schematically the function of a membrane.

3.2 Equipment for colloid filtration through filters connected in series (Method 2)

The equipment for colloid filtration of groundwater samples collected *in situ* was modified/simplified and used at atmospheric pressure and without protecting gas (argon) for the filtration of the surface water sample. The water was pumped directly via a membrane pump through the filter unit and finally collected in a vessel connected to the outlet. The number of connected filters was modified between the two different runs; in run number 1, five filters (2.0, 2.0, 0.4, 0.2 and 0.05 µm) were used and in run number 2, the number of filters was reduced from five to three (0.4, 0.4 and 0.05 µm). This was done to facilitate the passage of sample water through the connected filters. The filtration equipment for groundwater is described in SKB MD 431.045 (*Mätsystembeskrivning för kolloidfiltreringssystem, handhavandedel*, SKB internal controlling document to be published). Figure 3-3 shows the equipment set-up for surface water filtration.

Figure 3-1. *Equipment for fractionation of humic and fulvic acids.*

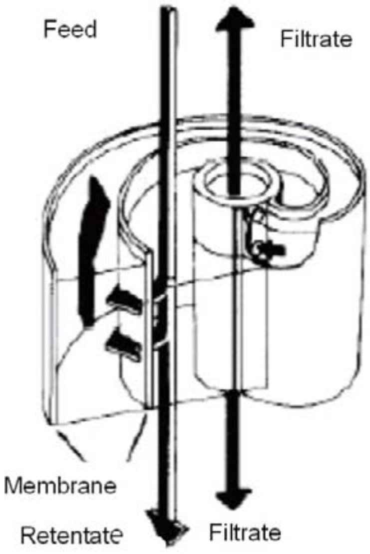

Figure 3-2. *Outline of membrane filter showing water flow directions.*

Figure 3-3. *Equipment for filtering surface water through the filter unit (to the right in the picture). Test run number 2 with three membrane filters.*

4 Performance

4.1 General

Sample water (20 L) from Eckarfjärden (PF000070) was collected on April 12, 2010. The test filtrations (including filter washing) were performed between April 13 and April 21, 2010, at the mobile laboratory facility at Forsmark (L3). After the field work, the water samples and the filter samples were sent to laboratories for analyses, and evaluation of the results was performed during May to August 2010. Analytical results from untreated and filtered sample water are presented in Appendix 1-1.

Planned tests according to the activity plan (AP PF 400-10-003) were:

Method 1 (SKB MD 431.043, SKB internal document)

- Pre-filtering with a chosen pore filter size.
- Ultra filtration of pre-filtered water samples using 1 kD and 5 kD membrane filters.
- Repeated ultra filtration, change of pore size of the pre-filter and/or change of sample volume.

Method 2 (SKB MD 431.045, SKB internal document)

- Test of methods for pumping sample water through the filter unit including adaption of tube fittings between the different parts in the sample water line.
- Filtering of water through the filter unit containing membrane filter with decreasing pore sizes. The first two filters are connected in parallel. If possible, one litre of sample water should be filtered.
- Repeated filtering of sample water through the filter package. Change of pre-filter and/or membrane filter pore size or change of sample volume.

4.2 Preparations

4.2.1 Colloid fractionation (Method 1)

Prior to filtering of sample water, the new membrane filters (1 kD and 5kD) were washed with 0.1 M phosphoric acid solution, then with 0.1 M sodium hydroxide solution and finally with deionised water. Samples of the rinsing water (blanks) from each membrane filter were sent for analysis. The analytical results from the analyses of blanks are presented in Appendix 1-2.

4.2.2 Colloid filtration (Method 2)

All parts made of PEEK were washed with 1 M nitric acid solution. Prior to filtering of sample water, deionised water was pumped through the filter unit and sample blanks were collected from the outgoing water. Blank samples from the incoming and outgoing water, as well as the three filters in the filter unit were sent for analyses. The analytical results for the blank samples are presented in Appendix 1-2.

Table 4-1. Analytical programme.

Analyses	Filter sample	Water sample		
			Preparation/ Conservation	Sample volume (mL)
TOC/DOC, tot-P, tot-N	No	Yes	Freezing	25 + 100
Na, Ca, K, Mg, S, Sr, Si, Li, Sr, Fe, Mn, Al, As, B, Ba, Cd, Cu, Cr, Co, Hg, Ni, Zn, Pb, V, Mo, Nb, Se, U, Th, Sc, Rb, Y, Zr, In, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ti, Ra, Ag, Sn, I*	Yes	Yes	1% HNO_3 (Suprapure)	100

*Within the actual test performance, analysis of some elements (I, In, Se and ^{226}Ra) were excluded due to analytical problems; see Nonconformities.

4.3 Execution of field work

4.3.1 Colloid fractionation (Method 1)

Organic acids were separated in fractions with respect to molecular weight using an ultra-filtration technique. Sample water was first filtered through a 2.0 µm filter and then two different portions were filtered through membrane filters with cut-off sizes of 1kD and 5 kD, respectively. The initial water volume, prior to filtration, was approximately 4 litres. The final retentate and permeate volumes following the filtration runs were approximately 1 and 3 litres, respectively, which gave an enrichment factor of three in the retentate. Water samples were collected from the retentate and permeate as well as from the untreated groundwater. Each sample was analysed for dissolved organic carbon (DOC), major constituents and trace metals (analysed by ICP-AES/ICP-SFMS).

4.3.2 Colloid filtration (Method 2)

Two different filtration experiments were performed. Run number 1: 70.5 mL sample water pre-filtered using a 2.0 µm filter was filtered through five connected filters (2.0, 2.0, 0.4, 0.2 and 0.05 µm). Run number 2: 187.5 mL sample water, pre-filtered using first a 2.0 µm and then a 0.4 µm filter, was filtered through three connected filters (0.4, 0.4 and 0.05 µm).

Each filtration resulted in three filter samples (0.4, 0.2 and 0.05 µm and 0.4, 0.4 and 0.05 µm pore sizes for run no. 1 and run no. 2, respectively) and two water samples (water in and water out). All samples from the two filtration runs were sent for ICP-AES/ICP-SFMS analyses (major constituents and trace metals).

4.4 Data handling/post processing

4.4.1 Colloid fractionation (Method 1)

The concentrations of organic and inorganic constituents in the retentate and permeate were re-calculated to obtain the carbon and metal concentrations in each fraction, i.e. with molecular weights lower or higher than the cut-off size of the filter. The mass balance equations used for the re-calculation are given in SKB MD 431.043, (*Mätsystembeskrivning för fraktionering av humus- och fulvosyror*, SKB internal controlling system). Evaluation of the four concentration values obtained from the fractionation experiments results in concentration values for three fractions i.e. smaller than 1kD, 1 kD to 5 kD and larger than 5 kD. From this pilot test, the total fractions larger than 1kD and less than 5 kD are also reported. The concentrations of the organic carbon and the trace metals in each fractionation are reported in Appendix 1-3.

4.4.2 Colloid filtration (Method 2)

The concentration of the colloid portion retained on each filter (from the filtration followed by detection with ICP-AES/ICP-SFMS) is calculated with the assumption that the water volume coming out into the collecting container is equal to the volume going into the system. This is not quite true since up to ten millilitres will be left in cavities in the filter holder unit, in the tubing and in valves. A small volume of about 0.01 to 0.06 mL is left in each filter after the filtration and its content of the different elements is included in the analysis. The measurement uncertainty of each colloid concentration is calculated from the "sum" of the measurement uncertainties of the filter analyses and estimated volume error (volume passing through the filters) according to the equation below:

$$U = \sqrt{\left(\frac{1}{V^2} \cdot (\Delta m)^2 + \frac{m^2}{V^4}(\Delta V)^2\right)}$$

where U = measurement uncertainty [µg/L]
V = water volume through the system [L]
ΔV = estimated volume error, 0.010 L
m = amount on filter [µg]
Δm = measurement uncertainty of the filter analysis, 20% [µg]

The calculated results from the colloid filtration through the connected filters are reported in Appendix 1-4.

4.5 Nonconformities

- Not all of the elements planned to be analysed according to the Activity Plan (AP PF 400-10-003) were analysed. Iodine was not possible to analyse at the commissioned laboratory. Indium and selenium were excluded due to analytical costs and 226Ra was excluded due to lack of approved analytical method.
- The concentrations in sample water of Ag, Li, B, Sc, Cs and Tl were below the detection limit. The amounts of many of the analysed elements (Ca, K, Na, S, Si, Ag, Cd, Cu, Hg, Li, Mo, Pb, Sn, As, Sb, Eu, Tb, Tm and Lu) were below the detection limit on all of the connected membrane filters in the filtration experiments. The amounts on the filters of some of the elements (Mn, Nb, Hf, Pr, Sm, Gd, Dy, Ho, Er and Yb), were very low and could only be detected for filtration run no.2 when the filtered sample volume was larger. Therefore, neither of these elements was included in the method comparison. The element La was present in the sample water, but excluded in the calculations due to time constraints.
- High amounts of chromium, nickel and zinc were found on the connected blank filters in the filter package. These elements also showed higher concentrations in the outgoing water then in the ingoing water and these elements consequently could not be included in the comparison. Cobalt also showed higher concentration in the outgoing water than in the incoming water but cobalt was not found on the blank filters.
- The DOC results showed an unreasonably high concentration in the permeate from the 1 kD filtration, with higher values than for the original sample water. Therefore, an alternative DOC calculation was performed, using the maximum concentration i.e. the same concentration as in the raw water.

5 Results

Comments on the test results described in Section 4.1 are as follows:

Method 1

- Pre-filtering was performed with 2 µm filters, which worked without problems.
- The difference between using 1 kD and 5 kD membrane filters is mainly shown in the analytical results, see below. The filtering speed when using the 1kD filter (the slowest filter) was c. 2 l/h.
- No repetition of the ultra filtration was considered necessary.

Method 2

- When sample water was pumped through the filter unit (2.0, 2.0, 0.4, 0.2 and 0.05µm filters; run number 1), the counter-pressure was large and the filtering was very time consuming. Therefore the setup was modified to include only three membrane filters (0.4 µm and 0.4 µm in parallel and 0.05 µm in series; run number 2) in order to reduce the counter-pressure.
- In run number 1, pre-filtering was performed through a 2.0 µm filter and in run number 2, the pre-filtering was performed first through a 2.0 µm filter and then through a 0.4 µm filter. The flow rates through the filter package in the tests were 20 mL/h and 160 mL/h, respectively.
- Because of the large counter-pressure, the filtered sample volume did not reach 1 L which was desired. The filtered volumes were 70.5 mL and 187.5 mL in run number 1 and 2, respectively.

The reported activities are stored in the primary data base Sicada but without data. The activities are traceable in Sicada by the Activity Plan (AP PF 400-10-003) but the obtained data are only available from this report.

5.1 Fractionation (Method 1)

5.1.1 Trace metals

The samples from fractionation experiments were analysed using ICP-AES/ICP-SFMS. The analytical results for the trace elements are re-calculated in Appendix 1 to give the sizes of the five fractions < 1 kD, <5 kD, > 1 kD, >5 kD and 1 kD<x<5 kD, and also the amounts adsorbed on the 1 kD and 5 kD filters. The elements considered important as colloid species were Fe (iron), Al (aluminium), Ba (barium), Co (cobolt), Mn (manganese), Sr (strontium), Ti (titanium), V (vanadium), U (uranium), Th (thorium), Rb (rubidium), Y (yttrium), Zr (zirconium), Ce (cerium) and Nd (neodymium).

Barium, strontium and rubidium as well as manganese existed mainly as dissolved species (or associated with very small organic acids) with a molecular weight less than 1 kD (g/mol). Such species are too small to be referred to as colloids.

Several of the elements (Fe, Al, Ti, Ce, U, Th, Y and Nd) existed mainly in the fraction > 1 kD but were neither found in the fractions < 5 kD nor >5 kD, probably due to adsorption on the 5 kD filter caused by electrostatic forces, which are not related to size. Cobalt and vanadium were quite evenly distributed between the fractions <5 kD. Zirconium was present mainly in the fraction larger than 1 kD but smaller than 5 kD.

Table 5-1 shows the mass balances in % from the membrane filter tests i.e. (m_{raw} (Me) – m_{ret} (Me) – m_{perm} (Me)/ m_{raw} (Me)) × 100. The blank samples, i.e. de-ionised water collected after passing through the washed filters, showed significant concentrations of barium and zinc (Appendix 1-2).

Table 5-1. Mass balances ((m_{raw}(Me) – m_{ret}(Me) – m_{perm}(Me) /m_{raw}(Me)) × 100) in the 1 kD and 5 kD membrane filter tests. A value close to zero signifies an appropriate mass balance.

Element	Mass balance 1 kD/%	Mass balance 5 kD/%
Fe	16	73
Co	–4.0	36
Ti	31	76
Al	8.3	63
Mn	–17	6.2
V	13	32
Ba	–3.5	4.5
Sr	5.2	15
Ce	14	65
U	24	72
Th	13	64
Zr	6.9	60
Rb	3.4	17
Y	11	56
Nd	15	63

5.1.2 Organic constituents

The results for organic acids from the fractionation experiments are presented in Table 5-2. Important to mention in this context is the large difference in colour between the permeate and the retentate after fractionation of sample water using the 1 kD membrane filter. The permeate was colourless while the retentate had a brown colour. Fractionation with the 5 kD filter resulted in a much smaller colour difference. The dissolved organic acids in sample water, with a total content of 25 mg/L, were present mainly (2/3) as a fraction smaller than 1 kD, i.e. very low molecular weight organic acids. Approximately ¼ of the carbon belonged to the fraction > 1 kD but < 5 kD, which contributes to the brown colour, and the fraction >5 kD is rather small. As explained in Section 4.5, the DOC analysis of the permeate showed an unreasonably high value. Therefore, an alternative calculation based on the maximum DOC content, representing the sample water is presented in Table 5-2.

The mass balance, i.e. ((m_{raw}(DOC) – m_{ret} (DOC) – m_{perm}(DOC) / m_{raw}(DOC)) × 100) for DOC in the 1 kD and 5 kD membrane filter fractionations, were –66% and 22%, respectively.

Table 5-2. Summary of fractionation results for organic acids (alternative calculation, see text).

Fraction	DOC/mg/L
< 1 kD	16.4 ± 3
> 1 kD but < 5 kD	6.9 ± 3
> 5 kD	1.6 ± 0.7
Adsorption 1 kD	–
Adsorption 5 kD	5.5 ± 3.4

5.2 Filtration (Method 2)

The results from filter analyses and water analyses (input and output) for inorganic constituents in run number 2 are presented in Figures 5-1 to 5-18.

The bars in the diagrams represent amounts (µg) of the analysed elements entering the filter unit, accumulated on each filter and present in the collecting container.

The concentrations in the blank samples (rinsing water) show significant concentrations of barium, cobalt, chromium, manganese, nickel, titanium, vanadium and zinc, see Appendix A1.2. The blank filters, however, contained insignificant amounts of barium, manganese, titanium and vanadium and the concentrations in sample water were much higher. Also for cobalt, the content on the filters were insignificant but the outgoing sample water contained more cobalt than the incoming water. The contents of chromium, nickel and zinc were, however, relatively similar on the blank filters as on the sample filters and the results could not be used for method comparison.

The concentrations of DOC, total phosphorous and total nitrogen were analyzed in the incoming and outgoing water from the filter package. The difference in DOC concentration between the incoming and outgoing water was very small and within the analytical error. The nitrogen concentration increased after the filtration and this was most likely due to contamination from remaining nitric acid in the filters after the washing. The decrease from incoming to outgoing total phosphorous, however, was 4.2 µg/L.

The degree of contamination for the different element ions is indicated in Figure 5-19. The bars represent the sums of the different ions caught on the filters and passing through the filters. A recovery higher than 100% indicates contamination although possible analytical errors may also need to be considered.

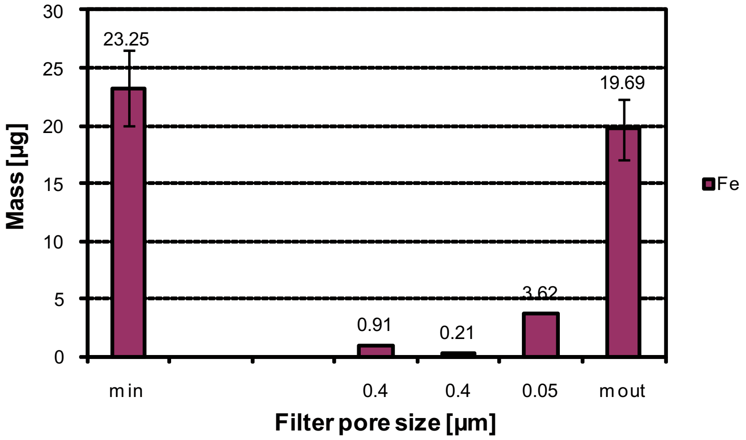

Figure 5-1. Amount of iron entering the filter system (m in), in the filters and in the collecting container (m out).

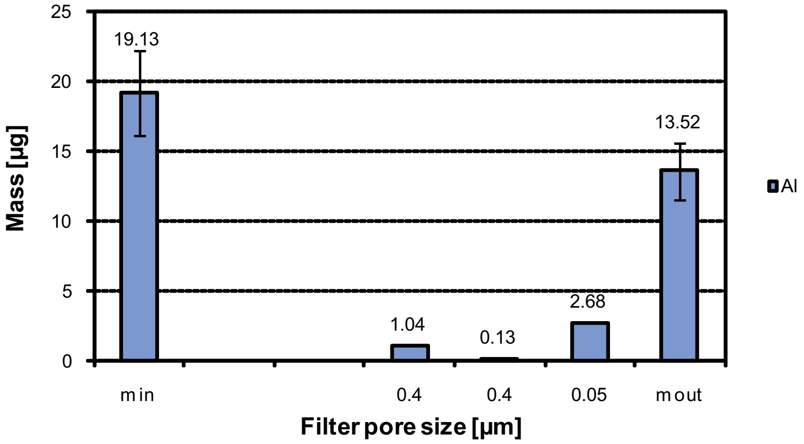

Figure 5-2. Amount of aluminium entering the filter system (m in), in the filters and in the collecting container (m out).

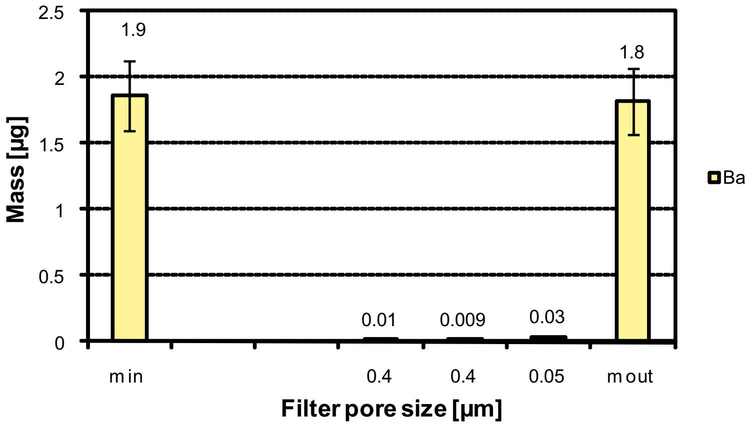

Figure 5-3. Amount of barium entering the filter system (m in), in the filters and in the collecting container (m out).

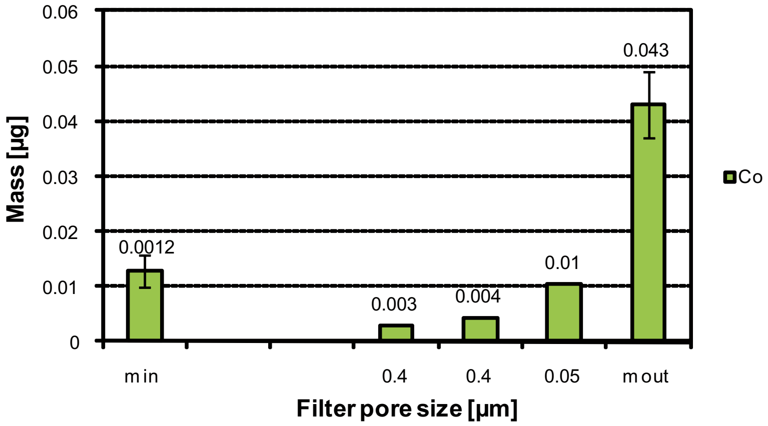

Figure 5-4. Amount of cobalt entering the filter system (m in), in the filters and in the collecting container (m out).

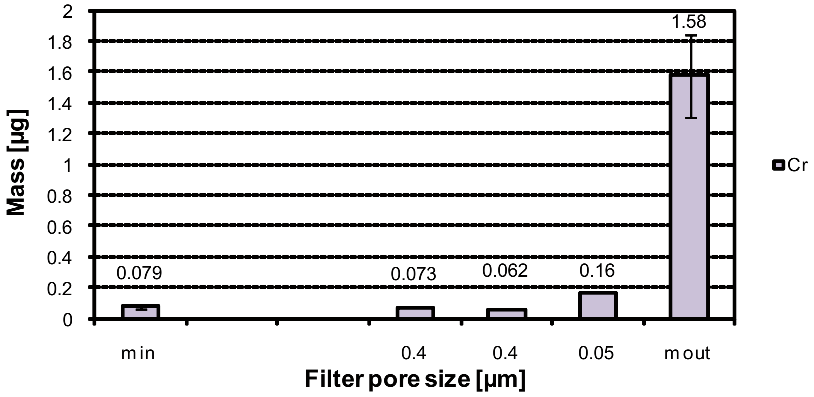

Figure 5-5. Amount of chromium entering the filter system (m in), in the filters and in the collecting container (m out).

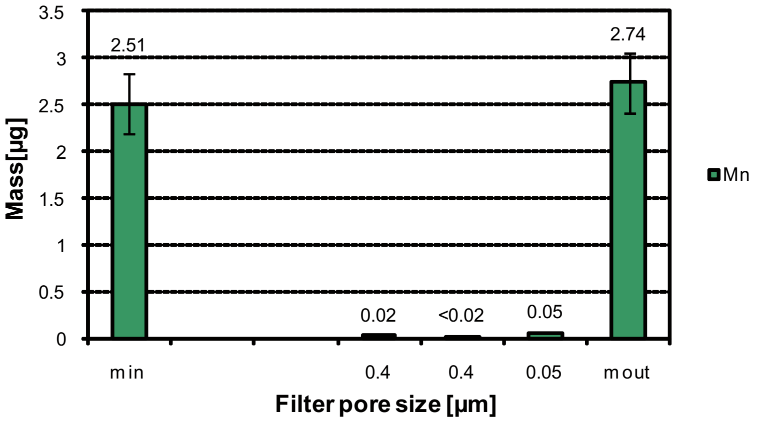

Figure 5-6. Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out).

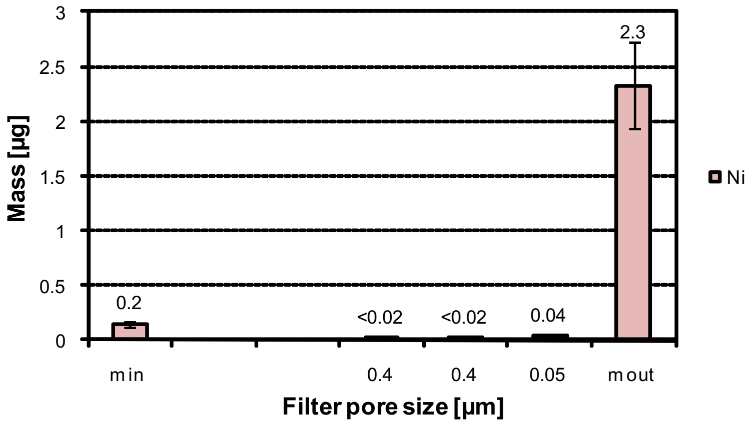

Figure 5-7. Amount of nickel entering the filter system (m in), in the filters and in the collecting container (m out).

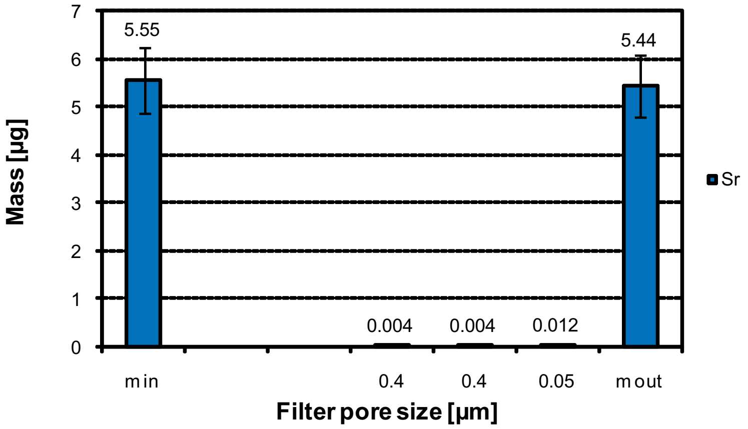

Figure 5-8. Amount of strontium entering the filter system (m in), in the filters and in the collecting container (m out).

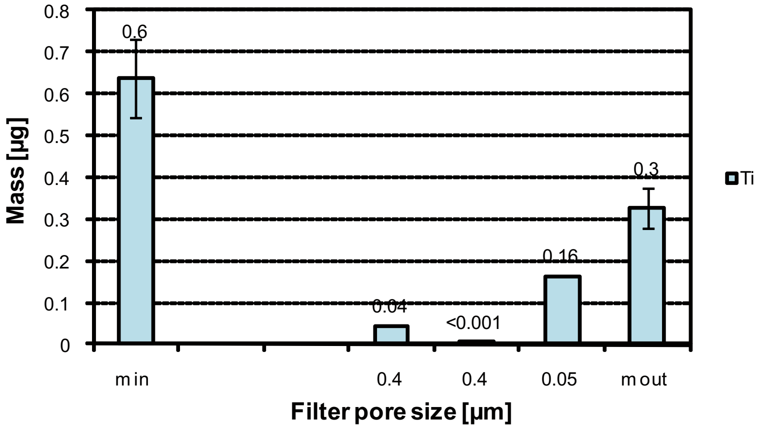

Figure 5-9. *Amount of titanium entering the filter system (m in), in the filters and in the collecting container (m out).*

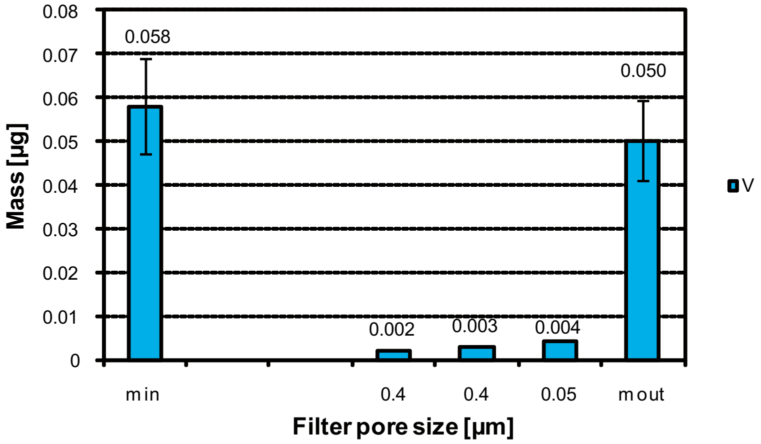

Figure 5-10. *Amount of vanadium entering the filter system (m in), in the filters and in the collecting container (m out).*

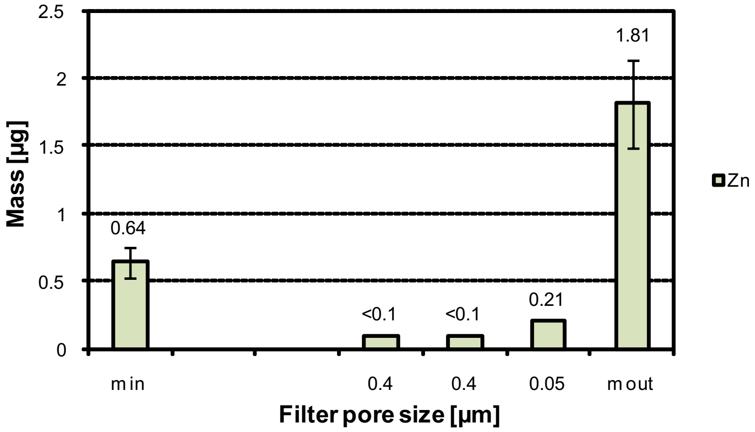

Figure 5-11. *Amount of zink entering the filter system (m in), in the filters and in the collecting container (m out).*

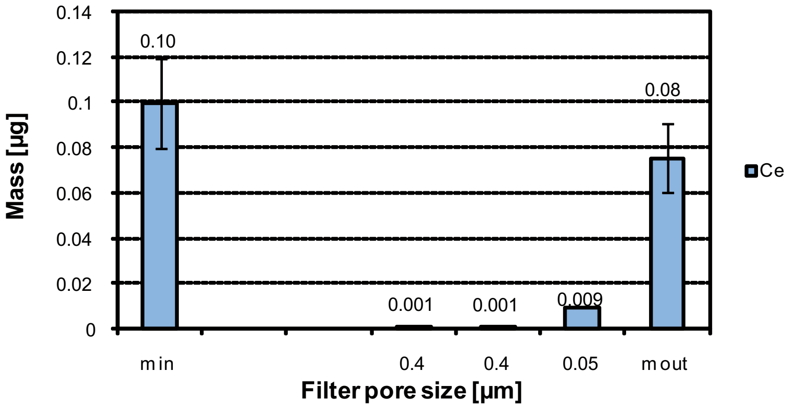

Figure 5-12. *Amount of cerium entering the filter system (m in), in the filters and in the collecting container (m out).*

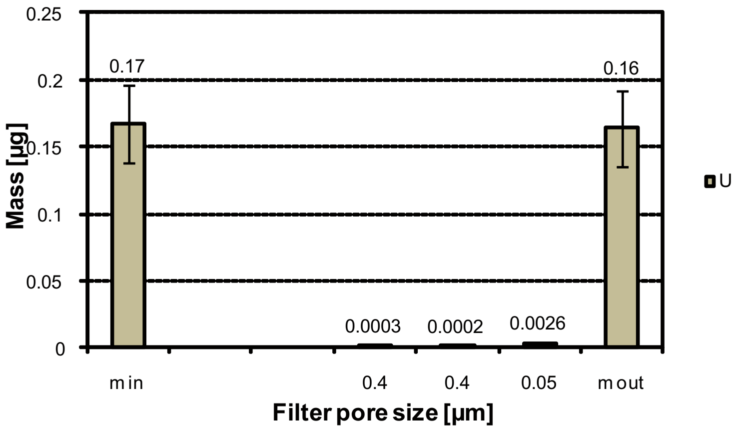

Figure 5-13. *Amount of uranium entering the filter system (m in), in the filters and in the collecting container (m out).*

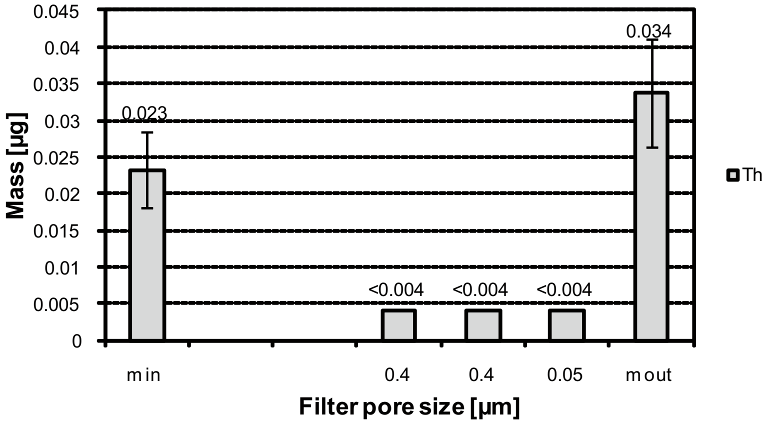

Figure 5-14. *Amount of thorium entering the filter system (m in), in the filters and in the collecting container (m out).*

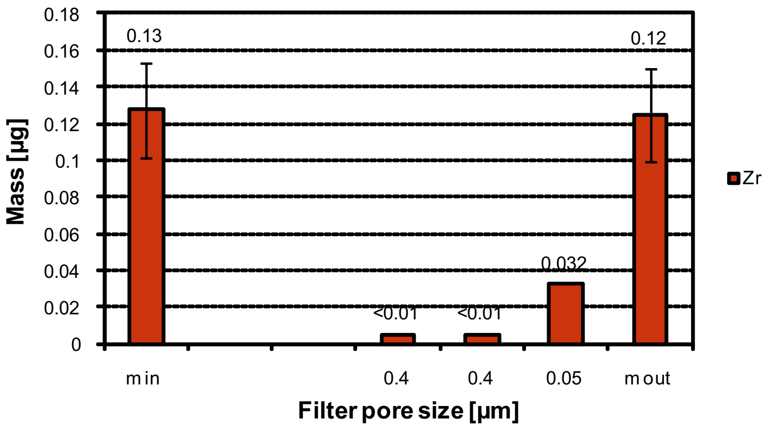

Figure 5-15. *Amount of zirconium entering the filter system (m in), in the filters and in the collecting container (m out).*

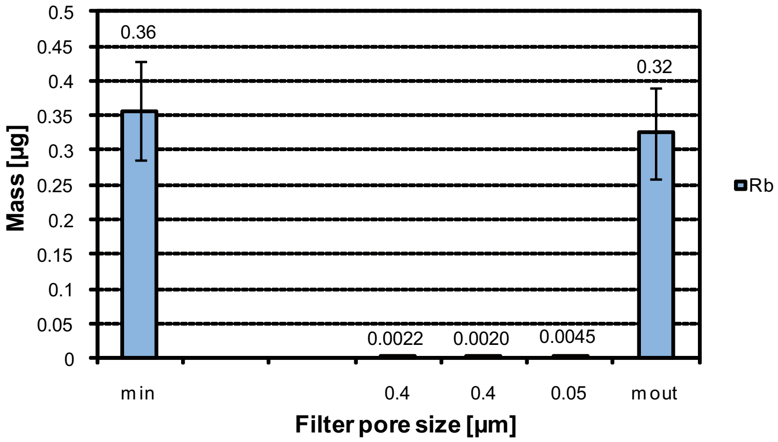

Figure 5-16. *Amount of rubidium entering the filter system (m in), in the filters and in the collecting container (m out).*

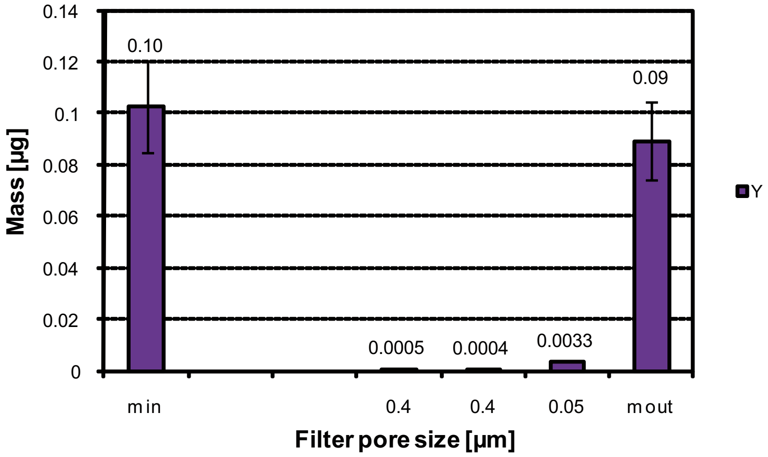

Figure 5-17. *Amount of yttrium entering the filter system (m in), in the filters and in the collecting container (m out).*

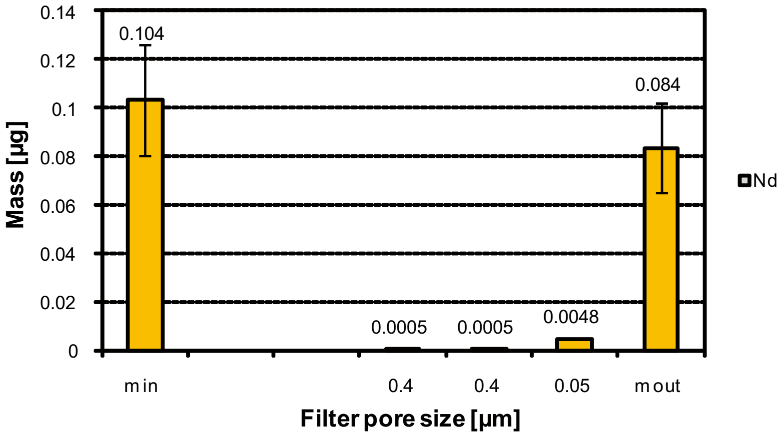

Figure 5-18. *Amount of neodymium entering the filter system (m in), in the filters and in the collecting container (m out).*

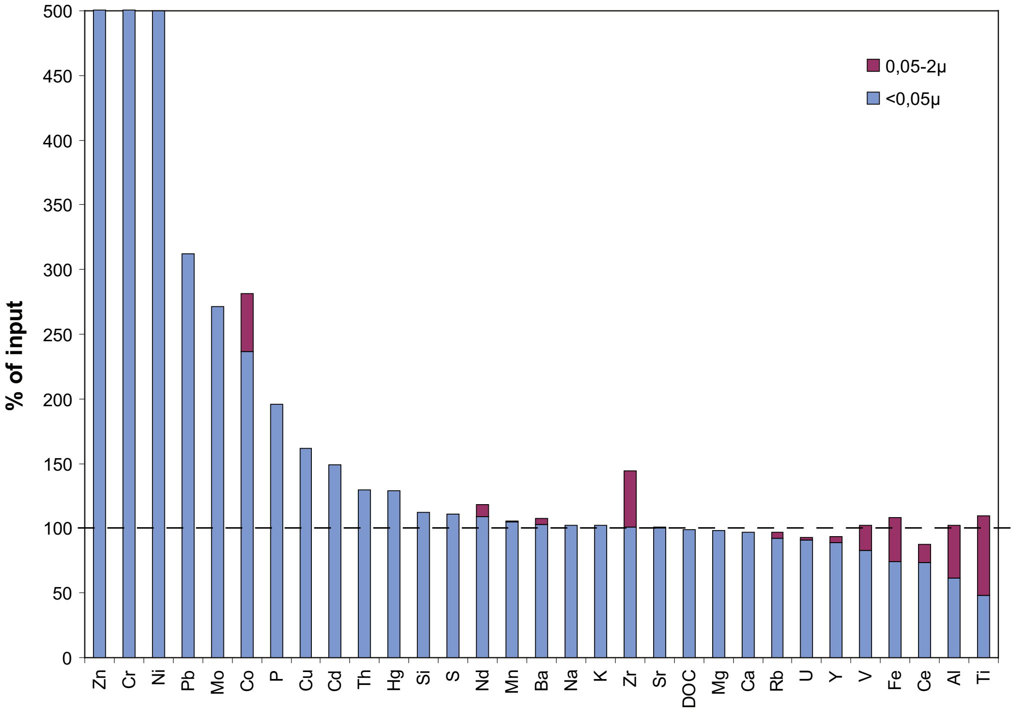

Figure 5-19. *Recovery of different ion species, Method 2. The bars represent the sum of the different ions caught on the filters (red) and measured in the filtered solution (light blue). Values exceeding 100% of the initial concentration indicate contamination from filters, equipment or other sources.*

5.3 Method comparison

From Method 1 and the experiment with the 1 kD membrane filter it was observed that most of the compared elements in the colloid phase were present in the fraction >1 kD, including metal ions associated with low molecular weight organic acids. From the experiment with the 5 kD filter the elements with significant presence in the fraction >5 kD were: iron 18%, thorium and cerium 16%, uranium and neodymium 15%, titanium, zirconium and yttrium, 14%, aluminum 13% and cobalt and vanadium 7%. For Method 2 (run number 2), the fraction 0.05<x<0.4 mm showed similar results as the fraction >5 kD. The elements with significant amounts on the 0.05 µm filters were: thorium <50%, titanium 30%, zirconium 25%, iron and aluminum 20%, vanadium 16%, cerium 11%, neodymium 6% and yttrium 4%. The largest differences between the two methods were obtained for uranium (only 2% with Method 2), yttrium and neodymium. As the results from the fraction >5 kD (Method 1) and the fraction 0.05<x<0.4 (Method 2) µm are similar, these methods are compared in Figures 5-20 to 5-22.

Barium, strontium and rubidium were present mainly as dissolved species (or associated with very small organic acids) with a molecular weight less than 1 kD (g/mol) according to Method 1. Such species are too small to be referred to as colloids. Method 2 gives the same result since these elements were not detected on the filters and consequently should be small enough to pass the 0.05 µm filter.

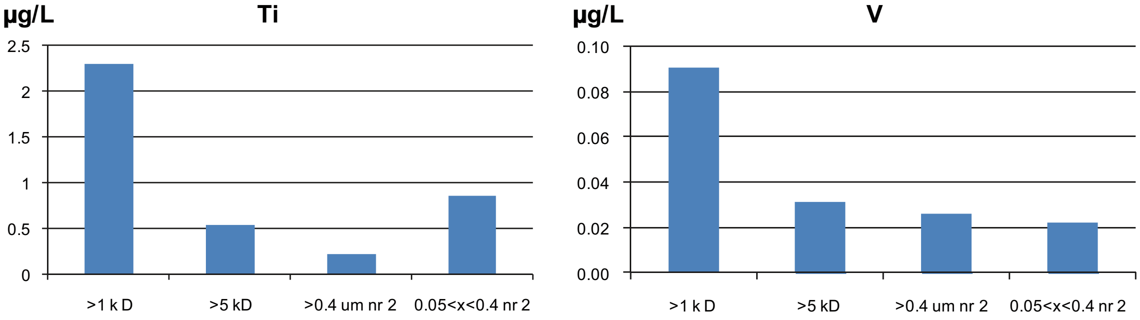

Figure 5-20. *Elements for which the amounts on the filters are larger than the >5 kD fraction.*

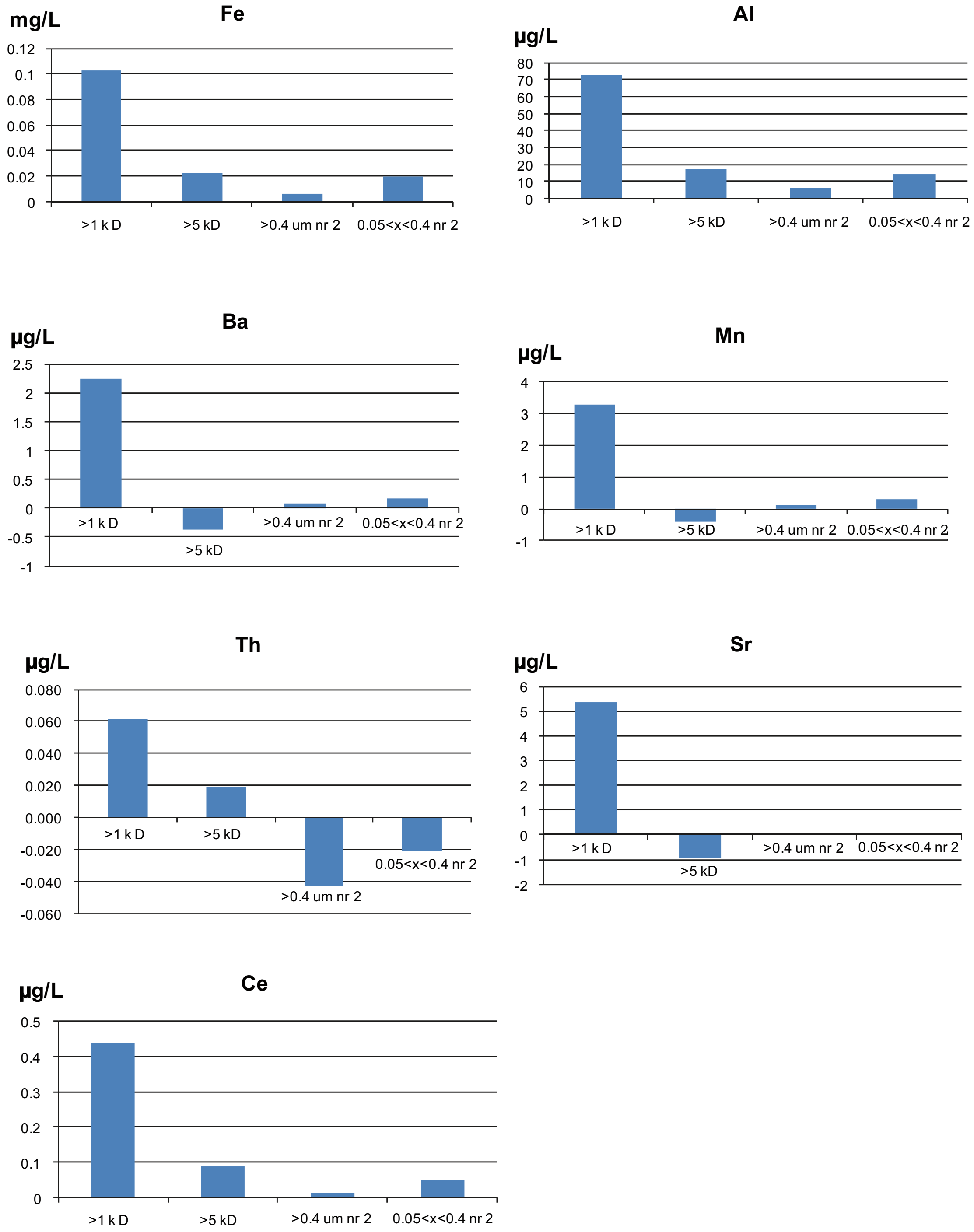

Figure 5-21. *Elements for which the amounts on the filters are similar to the >5 kD fraction. Bars with negative values show the detection limits.*

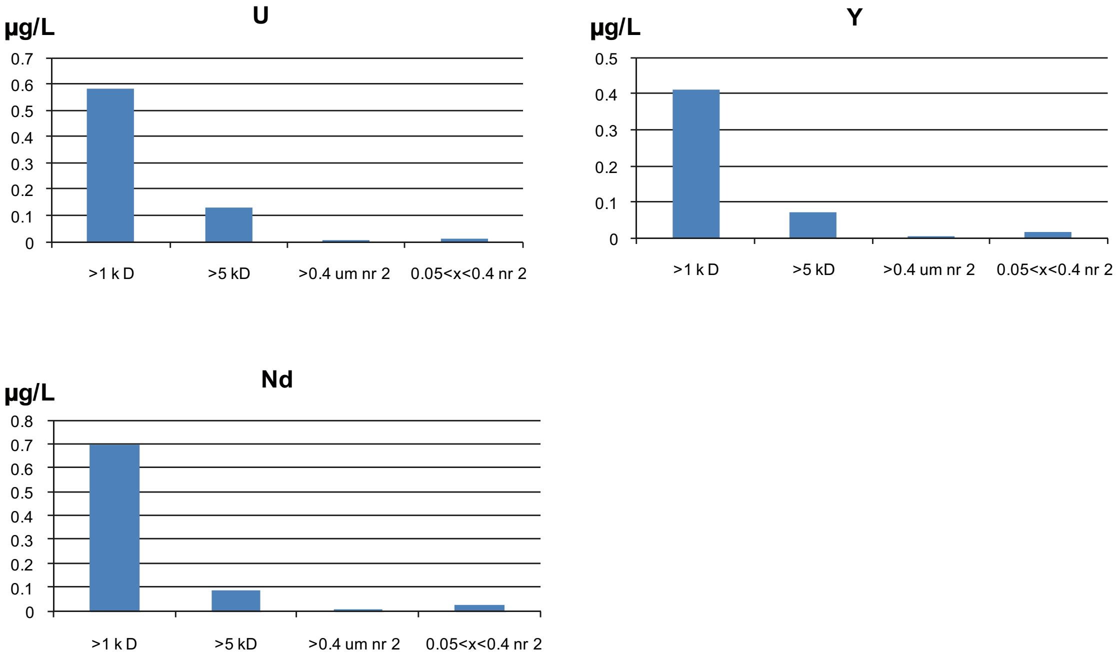

Figure 5-22. *Elements for which the amounts on the filters are smaller than the >5 kD fraction.*

6 Summary and discussions

The purpose of this study was to identify a method possible to use regularly in connection to sampling of surface waters within the monitoring program at the Forsmark site. A comparison between the two experimental methods is displayed in Table 6-1. The results show that at present it is not possible to single out one of the methods as the best one for continuing work since both have advantages and disadvantages. In addition, both methods are advanced and difficult, with respect to laboratory procedures, to be carried out regularly as a standard procedure within the current monitoring program.

Even though the methods are too extensive to carry out regularly, they contribute important information, complement each other and it could be useful to perform a restricted number of analyses of surface waters.

Table 6-1. Method comparison.

	Organic colloid fractionation using 1 kD and 5 kD membrane filters (Method 1)	**Colloid filtration through the membrane filter unit (Method 2)**
Analysis costs, per sample, 2010	1kD *or* 5 kD, trace metals and DOC: c. 12,000 SEK	Water samples and three membrane filters, trace metals: c. 24,000 SEK
Possibility of nitrogen and phosphorous analyses	Not relevant as the filters are washed with phosphorous and nitric acid before filtering	Unsuitable for phosphorous and nitrogen analyses, as the preparation of the filters are adjusted to metal analyses.
Similar results	Al, Fe, Mn, Ba, Sr, Rb, Ce, Zr and Th	Al, Fe, Mn, Ba, Sr, Rb, Ce, Zr and Th
	For the elements above, the amounts in the >5kD (Method 1) are equal to the amounts caught on the 0.05 µm filter (Method 2)	For the elements above, the amounts in the >5kD (Method 1) are equal to the amounts caught on the 0.05 µm filter (Method 2)
Different results	U, Y and Nd	Ti and V
	The amounts in the fraction with a size >5 kD (Method 1) are larger than the amounts on the filters with a size >0.05 µm (Metod 2) for U, Y and Nd.	The amounts on the filters with a size >0.05 µm (Method 2) are larger than the fraction with a size >5 kD (Method 1) for Ti and V.
Other issues	In general the fraction >1 kD is much larger than the fraction >5 kD (Method 1). Therefore, the most significant colloidal fraction seems to be the one 1 kD<x<5 kD.	If Method 2 is chosen, the pumping though the filter unit should be improved in order to speed up the experiments to allow filtering of several samples.

6.1 Contamination

- Contaminations from lead and zinc occurred for both methods. These elements are often present in the environment and precautions such as handling of samples in a clean-room must be taken. (However, lead was not present on the filters; Method 2)
- The tube fittings in the filter unit contain nickel and chromium and are not suitable for filtering of samples with very low metal contents. Therefore, another filter holder assembly than the one used in this study is recommended for future experiments.
- Copper, nickel, lead and chromium were not analysed in the colloid studies performed during the site investigations in Forsmark and Laxemar. Therefore, the contamination problems recognised here have not been addressed earlier.

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications.

/1/ **SKB 2001.** Platsundersökningar. Undersökningsmetoder och generellt genomförandeprogram. SKB R-01-10. Svensk Kärnbränslehantering AB.

/2/ **SKB, 2001.** Program för platsundersökning vid Forsmark. SKB R-01-42. Svensk Kärnbränslehantering AB.

/3/ **SKB, 2005.** Platsundersökning Forsmark. Program för fortsatta undersökningar av geosfär och biosfär. SKB R-04-75. Svensk Kärnbränslehantering AB.

/4/ **SKB 2007.** Forsmark site investigation. Programme for long-term observations of geosphere and biosphere after completed site investigations. SKB R-07-34. Svensk Kärnbränslehantering AB.

Appendix 1

A1.1 Sample water

Element/ substance	Unit	Raw water	Raw water, filtered 2 µm	Raw water, filtered 2 µm	Raw water, filtered 0.4 µm	Raw water, filtered 2 µm	Raw water, filtered 0.4 µm
			In, filtering #1 and 1 kD	In, 5 kD	In, filtering #2	Out, filtering #1	Out, filtering #2
Fe	mg/l	0,131	0,127	0,127	0,124	0,105	0,0902
Al	µg/l	109	106	128	102	72,1	62,3
Ba	µg/l	10	9,84	10,1	9,93	9,72	10,9
Co*	µg/l	0,0626	0,0659	0,0652	0,0687	0,23	0,0665
Cr*	µg/l	0,334	0,314	0,364	0,419	8,41	0,774
Mn	µg/l	12,7	12,2	11,8	13,4	14,6	12
Ni*	µg/l	0,588	0,68	0,805	0,804	12,4	3,39
Sr	µg/l	29,8	29,3	29,9	29,6	29	30,7
Ti	µg/l	3,68	3,29	3,66	3,4	1,74	1,81
V	µg/l	0,321	0,314	0,339	0,31	0,268	0,262
Zn**	µg/l	2,21	2,51	3,04	3,41	9,67	67
Ce	µg/l	0,547	0,524	0,546	0,532	0,402	0,403
U	µg/l	0,907	0,839	0,858	0,892	0,874	0,772
Th	µg/l	0,114	0,114	0,116	0,124	0,18	0,116
Zr	µg/l	0,621	0,597	0,618	0,679	0,665	0,592
Rb	µg/l	1,91	1,79	1,93	1,9	1,73	1,79
Y	µg/l	0,511	0,524	0,53	0,547	0,476	0,43
Nd	µg/l	0,409	0,917	0,561	0,552	0,446	0,445
DOC	mg/L	25,5	24,9	24,7	24,6	25	25,5

A1.2 Blank water

Element/ substance	Unit	Deionised water	Deionised water	Deionised water	Deionised water	Deionised water	Deionised water	Deionised water
		1 and 5 kD	Before filtering #1	After filtering #1	Before filtering #2	After filtering #2	1 kD, after filter washing	5 kD, after filter washing
Fe	mg/l	0,0005	0,0005	0,0044	<0.0004	0,0484	0,0235	0,021
Al	µg/l	22,4	1,76	6,31	10,5	11,1	13,7	32,6
Ba	µg/l	0,0524	0,0243	0,22	0,0275	0,738	0,263	0,455
Co	µg/l	<0.005	<0.005	0,0118	<0.005	0,218	<0.005	<0.005
Cr	µg/l	0,011	0,0236	0,498	<0.01	11,8	0,0769	0,0568
Mn	µg/l	<0.03	0,316	0,656	<0.03	12	0,0855	0,0916
Ni	µg/l	<0.05	0,453	1,3	<0.05	11,8	0,362	0,247
Sr	µg/l	0,299	0,0431	0,209	0,151	0,512	0,264	0,613
Ti	µg/l	0,0094	<0.001	0,0088	<0.001	0,09	0,0107	0,0545
V	µg/l	0,0074	0,0065	0,0102	<0.005	0,0549	0,0066	0,0243
Zn	µg/l	<0.2	1,31	50,2	<0.2	34	12,1	7,04
Ce	µg/l	0,0124	<0.005	0,0075	0,006	0,0291	0,007	0,0191
U	µg/l	<0.0005	0,0011	0,0021	0,0013	0,0154	0,0009	0,0016
Th	µg/l	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Zr	µg/l	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0,0963
Rb	µg/l	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Y	µg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Nd	µg/l	<0.005	0,0089	<0.005	<0.005	0,0065	<0.005	0,0074
DOC	mg/L	<0.25	–	–	–	–	3,9	2,1

A1.3 Filtered sample water

Element/ substance	Unit	<1 kD	>1 kD	1 kD<x<5 kD	<5 kD	>5 kD	Adsorbed, 1 kD	Adsorbed, 5 kD
		2 µm pre-filtered	2 µm pre-filtered	2 µm pre-filtered	2 µm pre-filtered	2 µm pre-filtered	2 µm pre-filtered	2 µm pre-filtered
Fe	mg/l	0.0032±0.0004	0.103±0.014	0.0082±0.016	0.011±0.002	0.023±0.014	<0.02	0.092±0.017
Al	µg/l	23.9±4.1	73.3±14.4	<7	29.9±5.1	17.0±4.1	<23	81±23
Ba	µg/l	8.0±1.0	2.24±0.88	<2	9.4±1.2	<0.4	<1.8	<1.8
Co	µg/l	0.022±0.005	0.047±0.014	0.016±0.010	0.037±0.009	0.0046±0.0035	<0.02	<0.02
Cr*	µg/l							
Mn	µg/l	11±1.4	3.3±1.3	7.6±1.9	10.9±1.3	<0.4	<2	<2
Ni*	µg/l	8.0±1.4	7.8±2.1	–6	2.0±0.4	<0.09	–15	–1,1
Sr	µg/l	22.4±2.8	5.4±2.3	<4	24.8±3.1	<1.0	<5	<5
Ti****	µg/l	0.019±0.004	2.26±0.45	0.341±0.072	0.360±0.072	0.53±0.12	1.0±0.8	2.77±0.75
V	µg/l	0.129±0.023	0.147±0.039	0.077±0.044	0.206±0.037	0.024±0.014	<0.07	0.11±0.07
Zn*	µg/l							
Ce****	µg/l	0.016±0.003	0.44±0.08	0.09±0.02	0.10±0.02	0.09±0.02	<0.1	0.4±0.1
U	µg/l	0.060±0.012	0.58±0.12	0.050±0.025	0.11±0.02	0.128±0.030	<0.2	0.62±0.018
Th	µg/l	<0.02	0.099±0.020	0.023±0.004	0.023±0.004	0.019±0.004	<0.03	0.074±0.021
Zr****	µg/l	0.0324±0.0065	0.52±0.11	0.129±0.032	0.161±0.032	0.0851±0.0043	<0.16	<0.13
Rb****	µg/l	1.54±0.31	<0.2	<0.4	1.56±0.31	<0.3	<0.5	0.139±0.021
Y****	µg/l	0.0129±0.0026	0.451±0.091	0.149±0.033	0,162	0.073±0.022	<0.1	0.295±0.022
Nd****	µg/l	0.0184±0.0032	0.76±0.14	0.0058±0.0025	0.121±0.024	0.0849±0.022	<0.2	0.36±0.12
DOC***	mg/L	39.5±4.3	<2.9	–22	17.6±1.9	1.62±0.70	–16±6	5.5±3.4
DOC, alternative	mg/L	16,4	8,5	6,9				

A1.4 Filtered sample water

Element/ substance	Unit	>0.4 um #1 (70.5 mL)	0.2<x<0.4 #1 (70.5 mL)	0.05<x>0.2 #1 (70.5 mL)	Sum #1 (70.5 mL)	>0.4 um #2 (187.5 mL)	0.05<x<0.4 #2 (187.5 mL)	Sum #2 (187.5 mL)
		2 µm pre-filtered	2 µm pre-filtered	2 µm pre-filtered	2 µm pre-filtered	0.4 µm pre-filtered	0.4 µm pre-filtered	0.4 µm pre-filtered
Fe	mg/l	0,0206	0,00979	0,00780	0,0382	0,006	0,0193	0,0253
Al	µg/l	22,1	13,0	3,80	39,0	6,21	14,3	20,5
Ba	µg/l	0,142	<0.1	0,142	0,284	0,0896	0,161	0,250
Co	µg/l	<0.04	<0.04	<0.04	<0.1	0,0235	0,0560	0,0795
Cr*	µg/l	0,851	2,84	1,70	5,39	0,720	0,859	1,58
Mn	µg/l	<0.3	<0.3	<0.3	<0.9	0,110	0,292	0,402
Ni*	µg/l	<0.3	0,407	0,566	0,973	<0.2	0,194	0,194
Sr	µg/l	0,0411	0,0652	0,118	0,224	0,0443	0,0640	0,108
Ti****	µg/l	1,08	0,652	0,199	1,93	0,220	0,853	1,07
V	µg/l	0,0355	0,0170	<0.01	0,0525	0,0261	0,0224	0,0485
Zn*	µg/l	3,45	<1	13,2	16,6	<1	1,10	1,10
Ce****	µg/l	0,0241	0,0199	0,0142	0,0582	0,0123	0,0480	0,0603
U	µg/l	0,00426	0,00284	0,00709	0,0142	0,00267	0,0139	0,0165
Th	µg/l	<0.001	<0.001	<0.001	<0.003	<0.04	<0.02	<0.04
Zr****	µg/l	0,0993	0,0823	<0.07	0,182	<0.05	0,172	0,172
Rb****	µg/l	0,0440	0,0298	0,00709	0,0809	0,0224	0,0240	0,0464
Y****	µg/l	0,00567	0,00567	0,00709	0,0184	0,00480	0,0176	0,0224
Nd****	µg/l	0,0128	0,00851	0,00851	0,0298	0,00533	0,0256	0,0309