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Project name: Characterization of soil solution and stream water DOC and its association to metals with SEC-DAD-ICP-MS

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Aim of visit
The motives for this cooperation project between LIFE, University of Copenhagen and Mid Sweden University was to deepen the understanding of the association of metals to DOC in soil solution and stream water, and the influence of DOC on the mobility of metals in aquatic system and in the interface between terrestrial and aquatic systems. Earlier work performed by the applicant at Mid Sweden University, has produced some remarkable results with much more extensive association of cations to DOC than has been reported earlier. To further investigate these findings, complementary advanced analytical techniques and expertises are available at LIFE.

In earlier work by the applicant, size fractionation of soil solution and stream water has been accomplished by use of ultrafiltration (UF with a 1 kDa cut-off membrane), and the samples have subsequently been analysed by inductively coupled plasma mass spectrometry (ICP-MS) and a total organic carbon analyzer to measure the inorganic and organic contents in the two fractions. In the current project, size exclusion chromatography (SEC) should be used to separate the components of the samples, thereby achieving a continuous fractionation over the mass range rather than the static one obtained by ultrafiltration. On-line detection with serially coupled UV spectroscopy (DAD) and ICP-MS will be used to monitor the effluent from the SEC system (Persson et al. 2006; Persson et al. 2009). From the SEC-DAD signals and calibration with reference compounds, semi-quantitative information on the size distribution of the dissolved humic substances in the waters will be obtained (Laborda et al. 2009). The results for the SEC-ICP-MS analysis will add detailed quantitative information on the metal speciation (preferentially Ca, Mg, Fe and Al, but also trace elements in the water samples) in the full size distribution range of metal-DOC. For comparative purposes, the same soil solution and stream water samples (all from the well studied research site at Bispgården, Sweden) will in parallel also be analyzed with the UF method described above.

The goal of the project is that the data obtained from the SEC-ICP-MS analyses will *i*) characterize the full range size distribution of metal-DOC complexes in the soil solution and stream water, *ii*) give a more complete picture over the speciation of common metal cations associated to organic ligands in soil solution and stream water, *iii*) verify the earlier UF results and identify potential differences between the two methods, *iv*) characterize the association of additional metals, e.g. heavy metals to organic compounds in the waters, and *v*) identify the presence of any inorganic colloidal phases in the stream water.
The purpose was also to obtain competences with a new technique, SEC-DAD-ICP-MS, for analysis of the association of Fe, Al, Ca and Mg to dissolved organic carbon (DOC) in soil solution and stream water samples.

Method
Samples were collected in two streams in Bispgården at four different occasions in the autumn of 2010. Pre treatment and fractionation through ultra filtration and analysis of dissolved organic carbon (DOC), inorganic anions, carboxylic acid content and content of low molecular mass organic acids (LMMOAs) was performed at Mid Sweden University in Sundsvall, Sweden. The rest of the samples were stored frozen until transport to the host institution at the Faculty of Life Science, University of Copenhagen.

In Copenhagen, method development for SEC-DAD-ICP-MS was undertaken, with the major quest being search for usable mass standards, that not required oxygen mode for the ICP (since oxygen mode interfere with the detection of Ca etc). A first screening of the samples was also performed.

Results
The fraction of high molecular mass (HMM) DOC was found to be as high or even higher in the streams as previously reported (Norström et al. 2010), and around 50% of the carboxylic acid content appeared to be of HMM origin, which would imply a higher site density for the low molecular mass (LMM) DOC in accordance with the findings of Reemtsma & These (2003) and Shin et al. (1999). By ion chromatography, it was registered that around 20 % of the F and 70% of SO_4 anions disappears when the sample is subjected to ultra filtration with a 1 kDa cut-off, which would indicate a possible electrostatic interaction with HMM counter ions not passing through the filter.

The work carried out in Copenhagen consisted to a large part of method development. The new size exclusion column took quite some time to reach stability and several different mass standards were tried out before satisfactory results were achieved. After several tries it was decided to use the DAD-signals of sulphonated poly styrenes for mass calibration. Furthermore, Vitamin B12 was identified as a suitable internal standard and thus added to all samples. Vitamin B12 is a rather stable organometallic molecule containing Co, an element which is present in very low or undetectable amounts in the stream water. This makes it possible to detect by both DAD and ICP-MS and hence its signals can also be utilized for correction in time between the two different detectors in use.

Screening of the stream water samples showed good repeatability (*Figure 1*) and provided initial information about the size distributions for some of the elements. For instance it was found that Mg and Ca are not recovered in the same size fraction, although it remains to be decided exactly what the different size distributions are. At this point, most of both Ca and Mg seem to be distributed to the LMM fraction, which would contradict the earlier results received from the ultrafiltration. When comparing Mg in a filtered and an ultra filtrated sample (*Figure 1*), the Mg-peak was much smaller in the ultra filtrated sample but still registered at the same retention time. This implies that Mg in both samples is of similar size, which in turn indicates that Mg might be prevented from passing the filter by forming new associations to HMM organic matter during the ultra filtration process. For both Fe and Al, the distribution in the mass range was broader compared to Mg, which showed a pretty sharp peak. For Fe, two separate peaks were detected implying that this element is distributed between at least two different size fractions in the stream water.
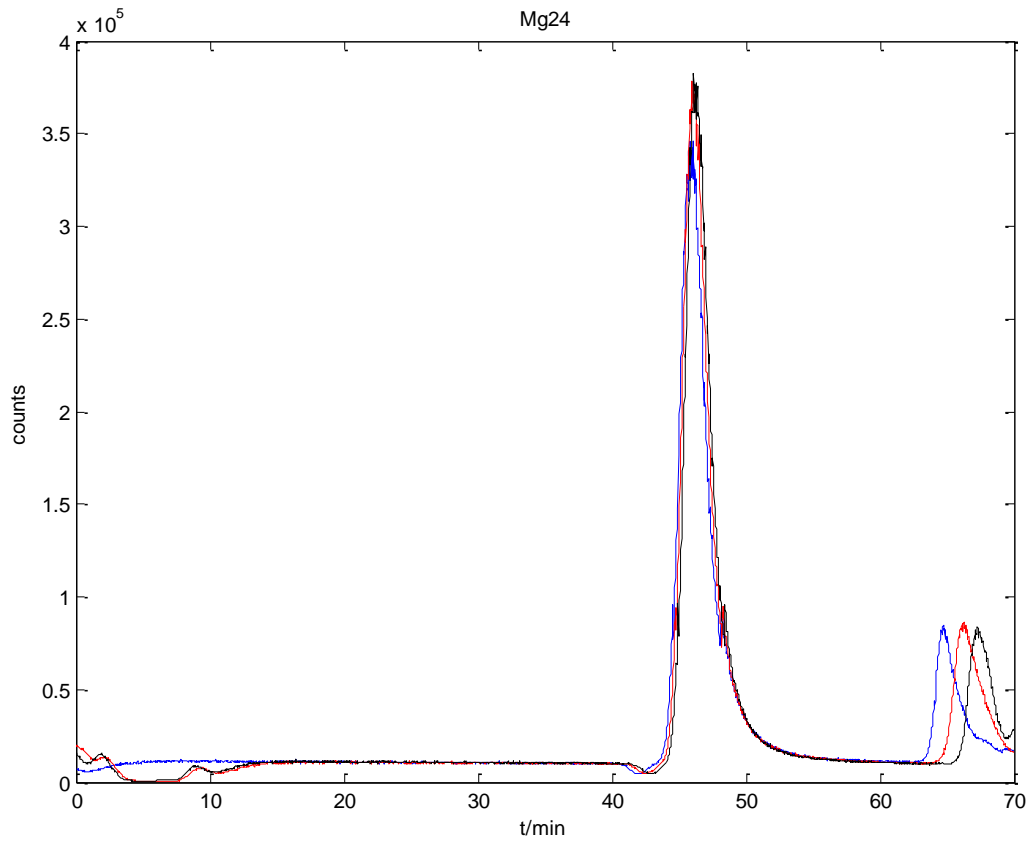
Figure 1. Tree replicates of a stream water sample from Fanbergsbäcken analysed by LC-ICP-MS. The peaks >60 min are EDTA peaks from cleaning.
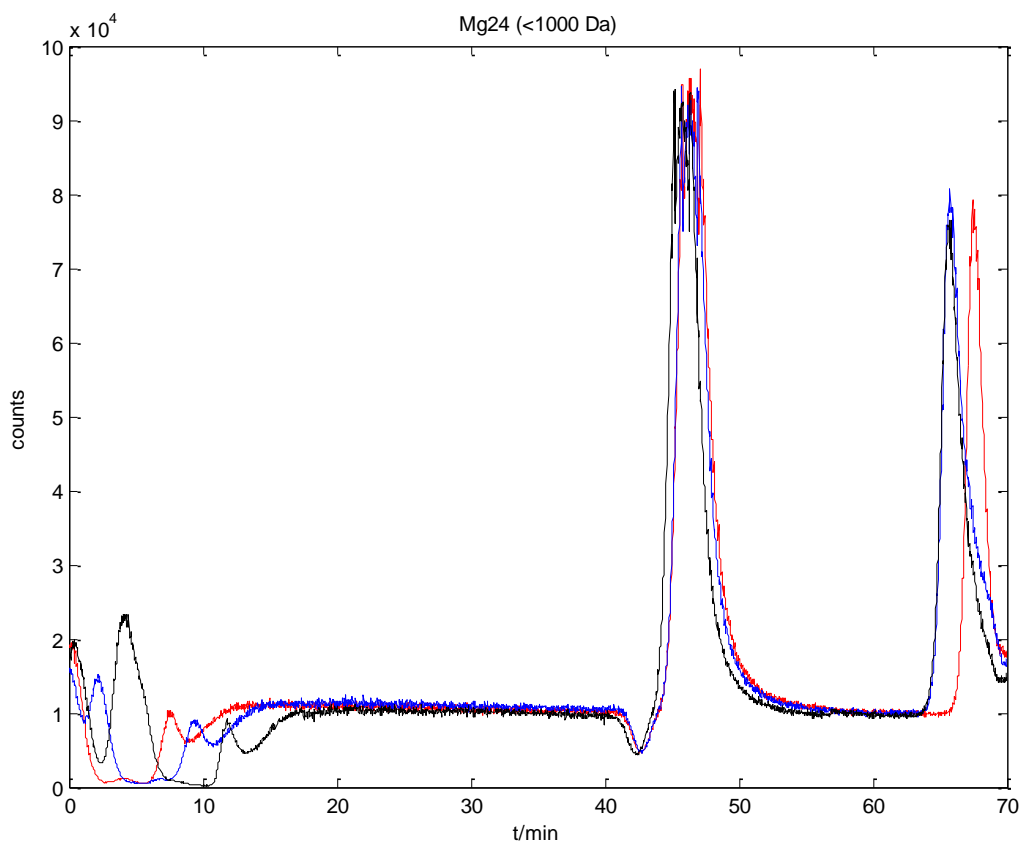
Figure 1b. Tree replicates of an ultra filtrated stream water sample from Fanbergsbäcken analysed by LC-ICP-MS. The peaks <10min and >60 min are EDTA peaks from cleaning.

Future plans

The work with method development is almost finished, however finding a working mass standard in the 1000 Da-range would be useful. The preliminary screening performed on stream water samples has given valuable insights regarding the questions addressed within the project, although further data analysis is needed.

To further evaluate this, stream water will be sampled during 2012 and analysed at both institutions (according to above). Hopefully, we will then also be able to receive water at conditions mimicking the summer storm event in 2003 when exceptionally high association of cations to HMM DOC was registered (Norström et al. 2010). Such a sampling could unfortunately not be made in 2011 since the summer was very wet and thus did not have the desirable traits that are a dry period followed by a storm flow.

Altogether, this should result in at least one publication, shedding additional light over the association of cations to DOC, and also set the ground for further cooperation between the research groups.

References

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