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1. Purpose of the visit

The aim of the visit was to test a novel extraction technique for the extraction of organic compounds from aqueous matrices without the use of solvents. The method is based on sorptive extraction with magnetic stirring rods coated with polydimethylsiloxane. These stir bars, so-called Twisters™ (Gerstel GmbH, Müllheim a/d Ruhr, Germany) have proven to be a sensitive technique that also is non-destructive, reliable, robust and generally fast. For our visit to a remote region in the Russian-Arctic, where export of samples is a factor that still limits the quantity of scientific results, these stir bars were a great opportunity.

2. Description of work carried out during visit

We collected river and stream water from a range of locations (Table 1), varying from mud streams flowing directly from eroding Pleistocene mud cliffs (Duvanni Yar), and floodplain tributaries draining recently deposited material (Filipovka, Ambolika, Pantaleikha), to the immense Kolyma River with its large drainage basin underlain by continuous permafrost. All water samples were kept cool between sampling and extraction, and were filtered through 0.70 um (GF/F) or 0.45 um (PES) filters to remove particles. After filtration, the samples were stored and extracted in pre-combusted glass vials capped with Teflon-coated septa. To improve extraction efficiency, we added 5% methanol to the filtrates. Solvent extraction from the samples was performed at room temperature, for 90 minutes while stirring at 1000 rpm. Afterwards, the stir bars were rinsed with milliQ water, dried and stored cool in their original vials.

Table 1

Location	**Date**	**Extracted volume (mL)**	**DOC (mg/L)**
Duvanni Yar stream	2011-07-22	22	150
Kolyma * under-ice	2011-05-29	40	2.26
Kolyma * spring flood	2011-06-04	40	13.6
Kolyma * summer	2011-07-07	20	4.49
Kolyma at mouth	2011-07-08	20	5.84
Filipovka	2011-07-17	35	12.3
Ambolika	2011-07-18	39	12.3
Pantaleikha	2011-07-18	40	13.2

3. Description of main results obtained

The stir bars were analyzed by Dr. Matthew Makou at the Fye Lab Mass Spectrometry facility of the Woods Hole Oceanographic Institution (US). In this laboratory they have a thermal desorption unit connected to the GC/MS that makes direct desorption of the entire extract possible. There are a few initial observations we can make based on the results from these analyses:

Sample volume and extraction time

Available literature (Kawaguchi et al., 2006; David & Sandra, 2007) report sample volumes ranging from 5 to 100 mL, and extraction times between 30 and 240 minutes, depending on the application. To make sure we obtained sufficiently large extracts, we chose sampling volumes between 22-40 mL and extracted for 90 minutes. Judging from the chromatograms (Figs 1 and 2) this was more than enough, and most likely smaller sampling volumes would have sufficed (~10 mL). A longer extraction time (i.e. overnight) would make sure all compounds are extracted, resulting in a more complete extraction and a cleaner signal.

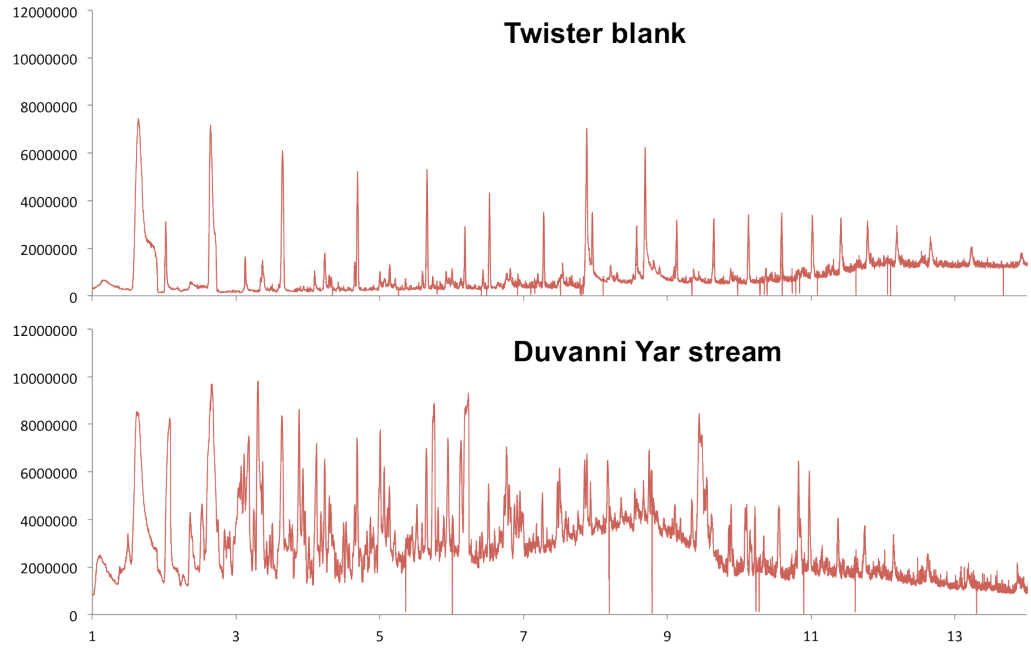
Addition of methanol

Judging from these chromatograms (Figs 1 and 2), there are a lot of compounds that the stir bars extract from the dissolved phase, and also many polar compounds. The thermal desorption unit allows direct desorption of the entire extract, but also has the disadvantage of introducing these polar compounds directly onto the GC/MS. Normally, one would derivatize the samples before analyses. Peak shapes are therefore not optimal and make direct interpretation of the chromatograms difficult. The current samples have been extracted after addition of 5% methanol (v/v). For future extractions, one could add more methanol to lower the tendency of polar compounds to be adsorbed onto the stir bar phase.

Blanks

A stir bar extracted in milli-Q water (i.e. blank) does not give a very clean signal. Several compounds, originating from the polydimethylsiloxane phase are visible (Figure 1). When one analyzes the obtained data from samples, this has to be taken into account.

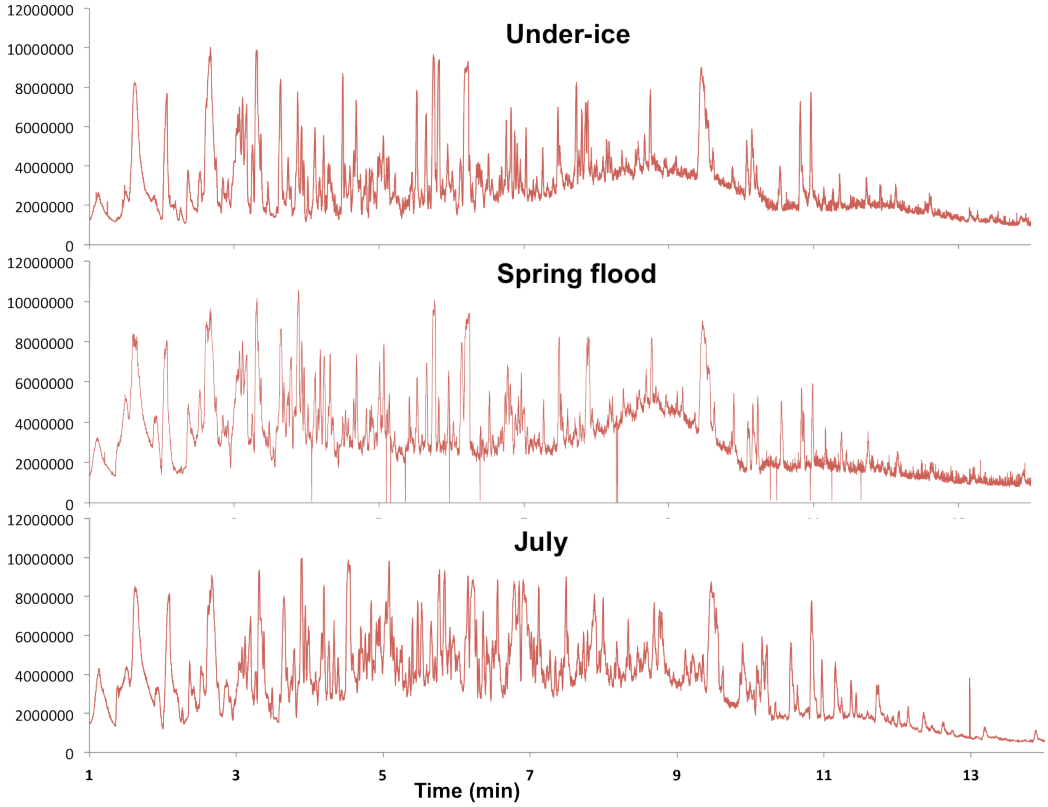
Figure 1



River samples

Figure 2 shows three examples from river water extracts of the Kolyma River during three periods when the river characteristics are distinctly different (i) pre-spring flood (river still ice-covered; 29 May), (ii) spring flood (snow and ice melt causes an extreme peak in run-off; 4 June), and (iii) summer (lower flow and release of organic matter from deeper soil layers that are now thawing; 7 July). While the TIC (total-ion current) chromatograms look similar, differences can be observed when targeting individual compounds by using MS detection in selective ions. We detect several polycyclic aromatic hydrocarbons (PAHs; e.g. methylnaphtalenes, fluoroanthene), sterols (e.g. cholesterol, ß-sitosterol), n-alkanes, and other compounds such as squalene and hopanes.

Figure 2: Kolyma River water extracts



4. Future collaborations with host institution

We have an active ongoing collaboration with Sergei and Nikita Zimov from the Northeast Science Station in Cherskiy. The Polaris Project led by Robert Holmes from the Woods Hole Research Center (US), that also organized our stay this year, is funded until 2014. Currently we are making arrangements to go back in July 2012.

5. Projected publications/articles

After a more detailed analyses of the GC/MS results (identify more compounds), we are planning to submit an abstract to the European Geosciences Union conference in April 2012 and hopefully in a later stage (potentially more field data are required) a research article.

References

Kawaguchi, M., Ito, R., Saito, K., Nakazawa, H. *Journal of Pharmaceutical and Biomedical Analysis 40*, 500-508 (2006)

David, F., Sandra, P., *Journal of Chromatography A* 1152, 54-69 (2007).