

# **Comparison of methods for isolation of natural organic matter (NOM) from loose deposits of drinking water distribution systems**

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## **Abstract**

Drinking water distribution systems are overloaded with loose deposits. Natural organic matter adsorbed on these sediments affect many chemical and microbiological processes, decreasing water microbiological stability. To estimate this effect it is necessary to know the amount of organic matter adsorbed on loose deposits. The special procedure for isolation of organic matter is needed for this purpose. Aim of this work was to compare commonly used methods for extraction and analyses of organic matter in loose deposits from drinking water distribution networks. For this extraction procedures (alkali extraction methods, sonication) were tested on 11 loose deposits samples. No correlations were found between extraction methods during this study. The natural organic matter extraction method using hot NaOH in combination with non-purgable organic carbon determination method is more accurate than other methods tested in this study for measure organic matter in loose deposits.

## **Catchwords**

Loose deposits, Natural organic matter, extraction

## **Introduction**

Drinking water distribution systems contain large amounts of loose deposits. Natural organic matter (NOM) attached at the interface between the water and the loose deposits plays significant role in many microbiological and physical processes and may affect water quality at the consumers' tap. Although the effect of dissolved organic matter

entering from the treatment plant and leaching from the plastic pipes well studied (Van der Kooij, 2003), the role of organic matter incorporated in the deposits has not been addressed sufficiently. These knowledge are especially important nowadays when the potential threat from deliberate terrorist attack is increasing whereas the loose deposits may serve as the temporary sink of the contaminants which are introduced in the networks.

There are two general approaches usually used: extraction of organic matter with the following determination of carbon and direct analyses of weight loss after combustion of the sample. Organic matter has a strong affinity to iron oxides (Gu et al., 1994) and thus an aggressive procedure of extraction is usually needed. The aim of this study was to compare efficacy for determination of organic matter concentration in loose deposits from water distribution networks with conventionally used methods. Three methods which include extraction (strong base at different temperatures and sonication) with the following analyses of carbon and one combustion method was tested with loose deposits which were sampled from five networks in Latvia.

## **Materials and methods**

### **Distribution system and sampling**

Loose deposits samples were collected from several different drinking water distribution systems both from pipes and water reservoirs (WR). The samples of loose deposits were collected during a planned campaign of unidirectional flushing of distribution networks or from the bottom of WR in small towns of Latvia during the annual cleaning. All samples were collected in glass bottles or sterile plastic containers. After that the samples of loose deposits were delivered to the laboratory where they were concentrated on 0.45 µm pore-size cellulose filters, rinsed with 100 ml of sterile ultra pure water (Elga PureLab Ultra, Veolia Water Ltd., UK) and then dried at 57°C for 24 h before being analyzed.

### **Organic matter isolation methods**

A. NOM isolation technique for freshwater sediments (Akkanen et al., 2005) was applied. Samples of loose deposits (0.5 g) were gently shaken with 1 ml of 0.5 M sodium hydroxide (NaOH) solution after which the mixture was heated for 30 min at 80°C. The suspension was centrifuged for 10 min at 6000g (g - gravitational acceleration). NOM extract was transferred into clean vial. The procedure was repeated. The first and the second NOM extracts were mixed (1:1).

B. A modified method developed by Thurman and Malcolm (1981) for the extraction of aquatic humic substances adsorbed on XAD-8 resin. 0.5 g of dried loose deposits sample was shaken with 1 ml of 0.1 M NaOH solution for 30 min at room temperature. NOM extract was transferred into clean vial.

C. The protocol was used by authors (Mermillod-Blondin et al., 2001) for detaching biofilms from sandy sediments. A sonication method using a narrow tip ultrasonic generator (Model: CPX130PB, 130W; Cole - Parmer USA) was used at: power = 40 W, for 180 s.

### **Volatile suspended solids determination method**

Method of evaluation of volatile suspended solids (VSS) is described in Standard Methods for the Examination of Water and Wastewater (2540). Briefly loose deposits samples were dried at 105°C and weighted. The samples were then combusted at 550°C for 6h and weighted again. The mass difference after the combustion was attributed to volatile solids expressed as %.

### **Non-purgable organic carbon (NPOC) determination**

The concentration of the organic carbon was determined as NPOC, because the samples contained higher concentration of the inorganic carbon compared to the organic carbon (European Standard EN 1484:1997, 1997). NPOC was determined of filtered and acidified sample using Shimadzu TOC 93 5000A total organic carbon analyzer (Shimadzu Corporation, Kyoto, Japan). Samples were sparged with CO<sub>2</sub> free oxygen for 6 min prior to analyses. The blank and control solution were analyzed with each series of NPOC sample in order to verify the accuracy of the results obtained by the method. All NPOC samples were tested in duplicate and the mean value calculated (CV<sub>≤</sub>2%).

### **Determination of total and organic carbon**

Total organic carbon (TOC) and dissolved organic carbon (DOC) measurements were performed with a TOC-5000A Analyzer and auto sampler ASI-5000 (Shimadzu Corporation, Kyoto, Japan) based on high temperature and acidification of sample and by the difference of the total carbon and inorganic carbon measurement, according to the European Standard EN 1484:1997, 1997. For determination of DOC samples were filtered through the 0.45 µm pore size membrane filters (Millipore Corporation, USA), which were carefully rinsed, first with sterile ultra pure water and then with the water

sample. Each sample was tested in duplicate and the mean values were calculated ( $CV \leq 2\%$ ). The blank and control solutions were analyzed with each series of sample in order to verify the accuracy of the results obtained by the method. The detection limit was 560  $\mu\text{g/l}$ .

### **Statistical analysis**

To compare all methods of NOM isolation and NOM quantity determination statistically significant assays of the differences (procedure for computing one way ANOVA) were developed, with paired samples when possible (Fower et al., 1998)

### **Results and discussion**

Eleven loose deposits samples were obtained from five drinking water distribution systems and water reservoirs of Latvia and analysed for concentration of organic matter with three NOM extraction methods followed with analyses of carbon and direct determination method with combustion.

Firstly, we compared methods for determination of concentration of organic matter in loose deposits (TOC, NPOC). Concentrations of organic matter determined as organic carbon (OC) were in range from  $0.7 \pm 0.3$  to  $279 \pm 68$  mg per gram of sample. As the concentrations of inorganic carbon were high (70 - 80 % from the total carbon concentration in each sample) the conditions for determination of organic carbon using TOC can not be satisfied. Therefore TOC analysis can not give correct results and NPOC method must be used for determination of organic carbon. The highest concentrations of OC in samples were obtained by VSS method which was then excluded (as a significant error) by ANOVA analysis. It should be mentioned that VSS analysis may overestimate the organic matter fraction in loose deposits due to volatilization of metal oxides and hydroxides (Gauthier, 1999).

Secondly, we compared NOM extraction methods. To exclude significant error Z-test was applied. Z-test for NOM isolation methods B and C showed that the difference between TOC and NPOC results is not statistically significant: 0.02 and 0.2 respectively, which means that these methods of extraction probably are not suitable for loose deposits. Z-test and t-test for NOM isolation method A showed that difference between NPOC and TOC results is statistically significant: 22.5 and 38.8 respectively. This proves that the

conditions for using TOC method are not reached; otherwise NPOC and TOC should have shown the similar results. Removing of the inorganic component during sample acidification and sparging, disturbing effect was reduced, and thus NPOC method potentially can give the most accurate results (repeatability=17 %).

It can be concluded that concentrations of OC (measured both by TOC and NPOC) obtained after isolation of NOM with methods B and C are understated. Method A for isolation of OC from loose deposits in combination with NPOC analysis gave the most accurate results (Figure 1).

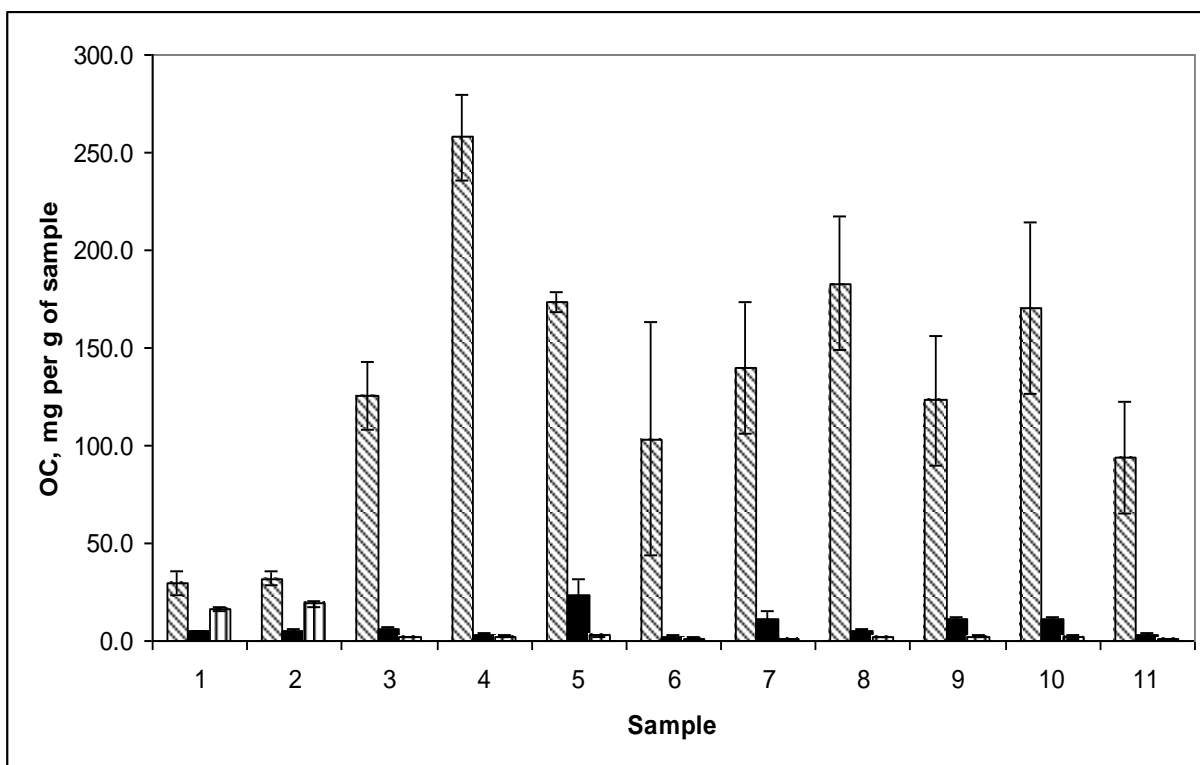


Figure 1. Organic carbon concentrations (measured as NPOC) obtained by different extraction methods from loose deposits samples

It should be mentioned that there is a great variations in results obtained with different NOM extraction methods (NPOC analysis was used for all the samples to determine OC concentrations). For extraction methods A and B the same reagent (NaOH) was used and differences were only in concentration of reagent and temperature), but results for A method for all of the samples were 82-98 % higher. Obviously with hot and more concentrated NaOH more (even 98% more) NOM can be extracted from loose deposits in

comparison with room temperature NaOH. Also no correlations were found between extraction methods during this study.

Other studies (Stevenson, 1982) showed that using strong bases (like NaOH) it is possible to extract maximum 80% of humic substances from soil. To extract other types of organic matter other reagents (acids) should be used. On the other hand Chow et al. (2004) used 1 M NaOH (for DAX-8 and XAD-4 resins) and 10 M NaOH (for IRA-958 resin) to extract organic matter from resins. As a result very hydrophobic organic matter (VHA), slightly hydrophobic organic matter (SHA), charged hydrophilic substances (CHA) and neutrals (NEU) were the components of organic matter mixture, thus providing the full spectra of organic matter.

## Conclusions

1. The most accurate results for determination of organic carbon in loose deposits showed NPOC determination method.
2. VSS method is not suitable for evaluation of OC in the loose deposits, because it may overestimate results even for 3 times.
3. The natural organic matter extraction method using hot NaOH (developed by Akkanen et al. (2005) for sandy sediments) in combination with NPOC determination method is more accurate than other methods tested in this study for measure organic matter in loose deposits.

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