

## **DETERIORATION OF DRINKING WATER SOURCES THROUGH LEACHING OF ORGANIC MATTER - DEVELOPMENT OF A METHOD TO IDENTIFY THE SOURCE OF LEACHING**

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### **ABSTRACT**

Infiltration of the natural and anthropogenic organic matter into groundwater and increase in NOM content of the surface waters are global problems. The increased organic matter in waters causes aesthetic problems and sometimes indicates faecal contamination. The aim of this study was to identify the source of pollution by HPLC-SEC. We analyzed: municipal wastewater treatment plant secondary effluent, small-scale wastewater purification systems effluent, surface waters (lake waters and drains) and groundwater samples from Western Finland by HPLC-SEC- (High Performance Liquid Size Exclusion Chromatography) coupled with in-line UV and fluorescence detector. In addition we determined DOC (Dissolved Organic Carbon) of the samples and nitrate concentration of the groundwater samples. The results revealed typical surface-water and wastewater-type DOM in wells, suggesting that HPLC-SEC-UV method can be used for identification of leaching.

**Keywords:** well water, wastewater, DOM, leaching, HPLC-SEC

### **1.INTRODUCTION**

DOM (Dissolved Organic Matter) of water samples contains recalcitrant natural organic matter NOM (higher molecular weight humic and fulvic substances) and low molecular weight proteins, organic acids, carbohydrates and other possible anthropogenic compounds. Increased organic matter in drinking water causes aesthetic problems (increased colour) and reacts with chlorine forming potentially carcinogenic disinfection by-products. (Leenher et al., 2003)

For the past 15 years a significant increase in the NOM (Natural Organic Matter) content of surface waters and change of NOM properties has been observed in Nordic and Central Europe, that has been associated with climate change, forest and land management (Eikebrokk et al., 2004; Korth. A. et al., 2004). Higher amount of NOM in raw water will increase considerably the costs of the public water treatment plants and may cause deterioration of drinking water quality. Compared to surface waters DOM, groundwater/well waters DOM got less attention. Our studies so far revealed that faecal contamination and high organic and nitrate content are common among wells from rural agricultural and sparsely populated area in Finland (Szabo et al., 2006).

The sources of DOM /NOM in drinking water can be natural (soil, water) or anthropogenic (wastewater, industrial emissions). As numerous previous studies revealed, water sample's NOM composition and structure depends on the source. Nowadays there is an increasing interest in using NOM as indicator of leaching. (Frimmel et al., 1999; Nissinen et al.,2001; Leenher et al.,2003)

HPLC-SEC (High Performance Liquid Size Exclusion Chromatography) coupled with in-line UV and fluorescence detection is a powerful tool in analysis of the DOM. This system provides quantitative and qualitative information on MW (molecular weight) components of DOM of different types of raw- water samples without any laborious pre-treatment. In the SEC column the molecules are separated according to their size, the lower molecular size compounds penetrate better the pores of the gel and are eluted later than the higher molecular size compounds. However, during size exclusion other electrostatic and hydrophobic

interactions can occur between column gel and solute molecules, and they will then interfere with the determination (Wu et al., 2003).

## 2. OBJECTIVES

The scope of our study was to characterize by HPLC-SEC the DOM from different type of waters (surface waters from lakes and streams, on-site and municipal wastewater effluents and well waters) in order to identify the source of leaching and pollution.

## 2. MATERIALS AND METHODS

We sampled the effluents from on-site septic systems, from Tampere municipal wastewater treatment plant, from lake and small river waters from the lake catchments and from wells of sparsely populated areas and farms of Finland. The on-site septic systems were generally 2 or 3 compartment septic systems. The samples were taken from the end point of the purification, where the effluent enters the environment (in most of the cases from the last septic tank outlet tube). All the water samples were fractionated by a Hewlett-Packard HPLC 1100 system with a TSK gel G3000SW column and detected by two detectors: a diode array UV detector and a fluorescence detector. UV detection wavelength of 254nm was selected based on previous studies on detection of humic-type substances (Nissinen et al., 2001, Matilainen et al. 2002). For detection of protein-type fractions tryptophan-like fluorescence (270nm/355nm) and tyrosine-like fluorescence (270nm/310nm) were selected upon scanning of wastewater samples. Our results agree with the results of previous studies (Baker, 2002; Ahmad et al., 1995). All wastewater, surface waters and well water samples were analysed for DOC-(Dissolved Organic Carbon). Well water samples were also analysed for nitrate.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Fluorescence detection

The small scale wastewater effluent samples had intensive tyrosine-and tryptophan-like fluorescence. The secondary effluent of municipal wastewater treatment plant had some tryptophan-like fluorescence. Therefore there is small degree of purification of the on-site wastewater effluents compared to the municipal wastewater treatment plant's secondary effluent. No significant tyrosine- and tryptophan-like fluorescence was found in the surface and groundwater samples. This shows that protein-like components of DOM are decomposed before reaching the groundwater.

### 3.2. Detection at UV 254nm

At UV 254 nm detection 11 fractions were eluted: HMW (high molecular weight) humic fractions I, II, III and IV ; IMW (intermediate molecular weight) humic fractions V and VI and LMW (low molecular weight) non-humic fractions: VII, VIII; IX and X. (Fig. 1, 2, 3, 4)

First fraction (fraction 0) and LMW fractions IX and X were present only in the on-site wastewater effluents and all present protein-like fluorescence also. Based on a previous study (Wu et al., 2003) fraction 0 is probably an association of smaller molecules that present electrostatic repulsion with the column material.

Fractions IX and X are likely hydrophobic protein-type compounds that contain aromatic amino-acid moieties.

All of the wastewater effluents present high amount of IMW fraction VI , WTP and SSc Mixed effluents present also high amount of LMW fraction VII and IMW fraction V (Fig. 2). It has been shown in a

previous study (Szabo et al., 2007) that fraction VII partly represents the nitrate concentration of the sample (nitrate absorbs, too, at the detection wavelength). So this fraction represents the degree of nitrification of the protein-type compounds. From the chromatograms it is obvious, that wastewater effluents with higher DOC have higher number and higher amount of LMW and IMW fractions.

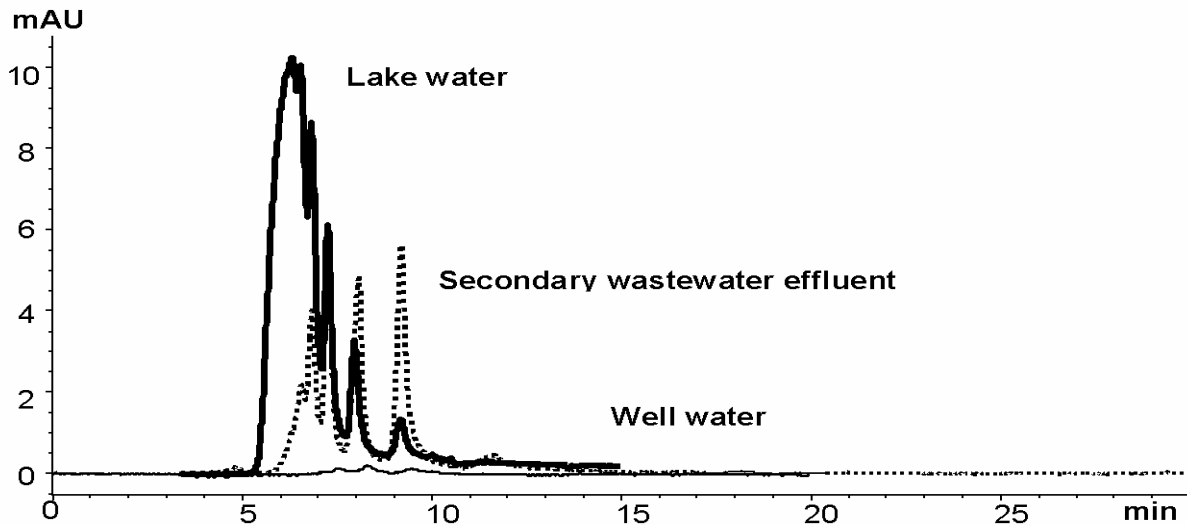


Figure 1. Typical chromatograms of surface water, secondary wastewater effluent and low DOM well water

### MSD distribution of DOC in wastewater effluent samples (UV, 254nm)

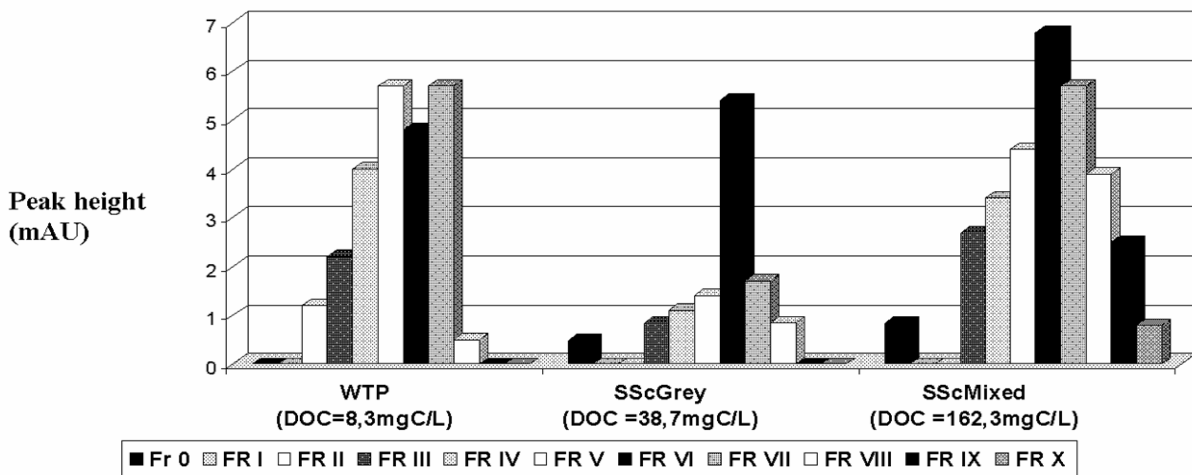


Figure 2. *WTP*: secondary effluent of municipal wastewater treatment plant; *SScGrey*: on-site greywater effluent; *SScMixed*: on-site mixed wastewater effluent; *mAU*-milliAmperUnits, *DOC*-dissolved organic carbon

Unlike wastewater effluents, the surface water samples present other type, HMW-profile chromatograms (Fig. 3). Surface water samples with increased DOC have considerable higher amount of HMW fractions I, II and III and also higher IMW fractions IV and V, than those with lower DOC. HMW and IMW fractions contain humic- and fulvic -type compounds that leach from the soil. Our observations so far suggest that in lake-catchment areas the streams and ditches contain higher amount of DOC and consequently higher amount of HMW fractions, than the collector lake. IMW fraction V and LMW fraction VI were relatively constant for all surface water samples analysed.

**MSD distribution of DOM from streams and lake waters (UV 254)**

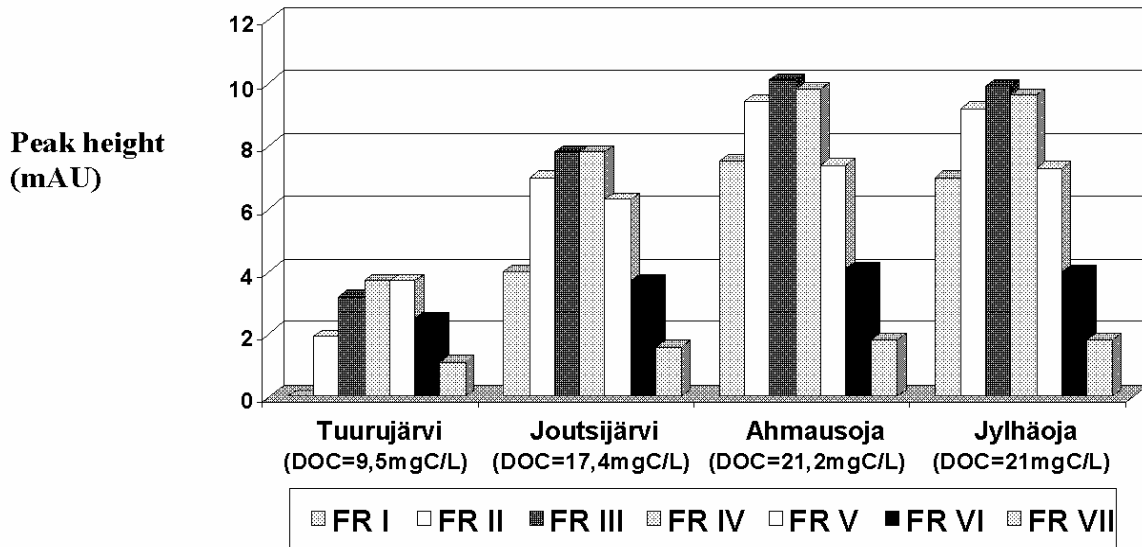


Figure 3. *Ahmausoja, Jylhäoja*: collecting streams from forest and agricultural zones of the same catchments area; *Joutsijärvi*:-the collector lake; *Tuurujärvi*: lake in contact with Joutsijärvi, used as raw water source for Pori municipal drinking water treatment plant

**Typical MSD of DOM in well samples (UV 254nm)**

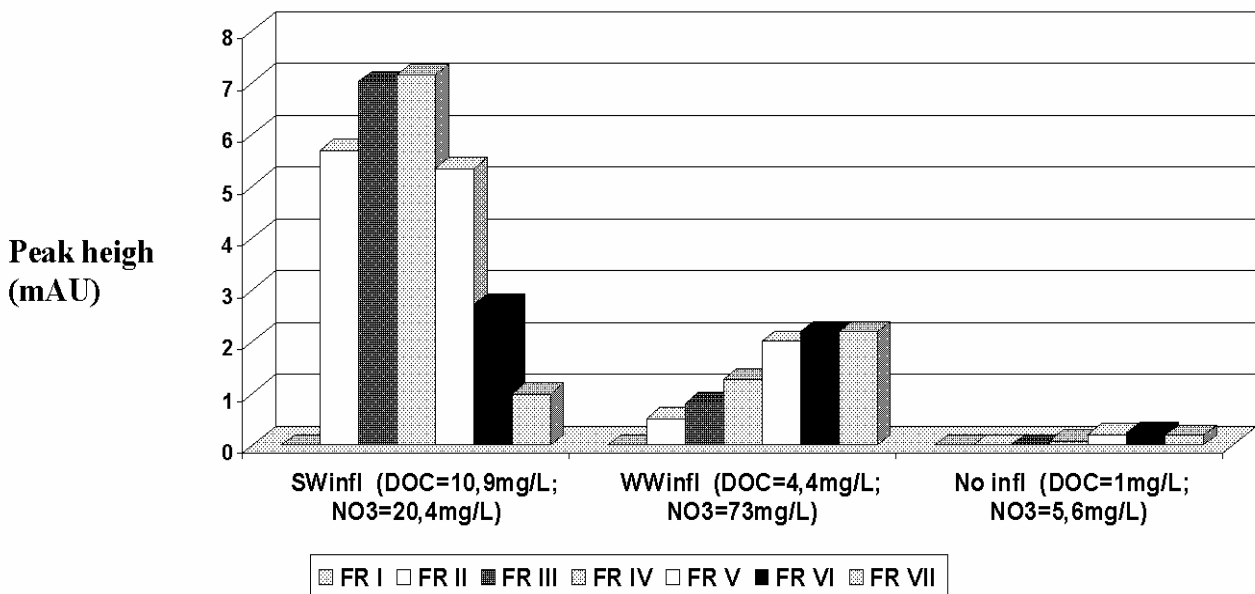


Figure 4. *Swinfl*-wells influenced by surface water leaching; *Wwinfl*-wells influenced by wastewater leaching; *No infl*-wells not influenced by leaching

In the well water samples UV detection at 254nm revealed typical surface-water and wastewater-type DOM (Figure 4.). Good quality well waters with low DOC (< 2 mg/L) and low nitrate(< 10 mg/L) concentrations had MSD fractions in low amount(Fig 1, 4). Well water samples presenting DOC values over 5 mg/L presented typical surface water-type chromatograms with high percent of HMW fractions. Wells with increased DOC (>2mg/L) and high nitrate concentration present chromatograms that resemble with the profile of WTP secondary effluent chromatogram, with more abundant LMW fraction VII.

#### 4.CONCLUSIONS

HPLC-SEC with UV detection at 254nm gives us a clear picture about the presence/absence and nature of leaching in the drinking water sources. Abundant HMW fractions in both surface- and groundwater samples indicate leaching of organic matter from the soil or infiltration of surface water into the well. Increased LMW fraction indicates increased nitrate amount in the samples, which often originates from wastewater effluents.

#### ACKNOWLEDGEMENTS

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