Natural organic matter from catchment to drinking water: a case study of Pori waterworks, Finland

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ABSTRACT

In this study Natural organic matter (NOM) characteristics and variations of catchment samples (brooks and collector lakes) from Western Finland, and drinking water produced from the same catchment were examined. Seasonal and spatial NOM variations were followed by means of DOC and HPLC-SEC with UV and fluorescence detection. NOM decreased from drains to lakes by 35 to 75% and from drains to drinking water by 73 to 94%. Drains had a higher NOM content in summer and a lower NOM content in winter and spring. Lakes showed inverse patterns and had a higher NOM content in winter and spring and a lower NOM content in summer. HPLC-SEC separated 8 molecular weight fractions. In drains the HMW fractions represented up to 80% of the NOM, in lake waters HMW fractions accounted for 50 to 70% of the NOM. In drinking water IMW fractions dominated. Increased NOM in raw water during winter was associated with increased IMW fractions and the appearance of HMW fractions in drinking water, DOC increasing from 1.4 mg C/L in summer to 5.8 mg C/L in winter. SPH-Tryptophan correlated with the dissolved organic nitrogen and DOC of the samples. The drain affected by agriculture generally presented higher SPH-Tryptophan values than the unaffected drain.

Key words | catchment, drinking water, fluorescence, HPLC-SEC, NOM

INTRODUCTION

The concentrations of organic matter in the brooks and lakes of water catchment areas in Finland are generally high and show relatively low seasonal variations, although most of the organic matter in boreal catchments is transported during snow melt in spring and rain events in autumn (Laudon et al. 2004; Matsson et al. 2005). Organic matter in surface waters in Finland originates mainly from natural sources. Natural Organic Matter (NOM) is generated through microbial processes within the water body or in the surrounding area from plant or algal material. Compositionally NOM is a complex mixture of refractory and biodegradable compounds such as, high molecular weight (HMW) humic and fulvic substances and smaller molecules of proteins, amino-acids, carbohydrates (Leenheer & Croué 2003).

In recent decades, a significant increase in the NOM content of surface waters and a change in NOM properties has been observed in Nordic and Central Europe. This has been associated with changes in catchment area management and changes in anthropogenic impacts on waters (Worral & Burt 2005). The removal of NOM is a priority in a water treatment plant, the efficiency of NOM removal depends on its characteristics and composition (Sharp et al. 2006), and these vary spatially and temporally (Hongve 1999; Scott et al. 2001; Andersen & Gjessing 2002). Therefore understanding these variations within a particular catchment that serves as a raw water source for drinking water production is crucial for proper water management.

There are several methods for aquatic NOM analysis, High Performance Liquid Size Exclusion Chromatography (HPLC-SEC) coupled with in-line UV detection is a powerful system that gives quantitative and qualitative information on the Molecular Weight Distribution of
NOM. In the SEC column the components of NOM are separated based on their size. Higher molecular weight compounds penetrate to a lesser extent the pores of the column and are eluted earlier than smaller molecules (Vartiainen et al. 1987; Pelekani et al. 1999). Fluorescence spectroscopy has been found to be a useful tool in the non-destructive organic matter analysis of water samples. NOM has two distinct classes of fluorophores; humid-like and protein-like (respectively, tyrosine-like and tryptophan-like) fluorophores (Leenheer & Croué 2003). Wastewaters’ organic matter shows intensive protein-like fluorescence, tryptophan being the most fluorescent amino-acid in the sewage samples (Baker 2002). Protein-like fluorescence measurements have been successfully applied for the detection of wastewater impact on river waters (Baker 2001) and HPLC-SEC with additional fluorescence detection has been proven to be a useful system for the identification of protein-like components of NOM from groundwater, surface water and wastewater effluent samples as a function of molecular weight (Her et al. 2003).

The objective of this study was: to determine NOM characteristics and follow NOM variations within a catchment, in drinking water produced from that catchment, and seasonally by the means of conventional indicators and HPLC-SEC with UV and fluorescence detection. For the study a typical catchment from South Western Finland was selected; the catchment of the lakes Tuuruja¨rvi and Joutsija¨rvi. Tuuruja¨rvi is a small lake, which is connected to a bigger lake called Joutsija¨rvi. For the past four decades the quality of Tuuruja¨rvi has deteriorated considerably due to changes in catchment management (forest cutting) and has shown a significant increase in brown colouration, which suggests an increase of NOM.

**MATERIALS AND METHODS**

**Site description**

The catchment area of Joutsijärvi and Tuurujärvi in South Western Finland is 117 m², which consists of 3.4% agricultural field, 56% forest and 30% mire (Figure 1). Tururujärvi serves as raw water source for the Pori Waterworks, which supplies the municipality of Pori with drinking water for around 75.000 inhabitants. The majority of the area’s agricultural activities (croplands, animal farms) are concentrated around Jylhäoja. In the Ahmausoja sub-catchment forests and drained mire-areas are mainly found. The forests consist of coniferous trees mixed with deciduous stands. The drainage area of Jylhäoja and Ahmausoja makes up 84% of the total catchment. The surface of Joutsijärvi-lake is 840 hectares and Tuurujärvi-lake is 139 hectares. In both of the lakes the brown colouration has significantly increased over the last decades.

The water treatment process at Pori Waterworks consists of coagulation with polyaluminium-chloride, flotation, sand filtration followed by artificial groundwater recharge through basin infiltration with 2 to 3 weeks residence time. Then the drinking water is treated with sodium-hypochlorite and lime.

**Sampling and analyses**

Our period of study was 2.5 years. Samples were collected from two drains, Jylhäoja and Ahmausoja, from the lakes Joutsijärvi and Tuurujärvi and from the drinking water distribution network. Drain waters were sampled at about 20 cm depth from the surface. Lake water samples were taken from the upper layer of the lake from a depth of 50 to 100 cm. Six sets of samples were collected from December 2006 to May 2008.

The DOC of the samples was determined with a TOC-analyzer SHIMADZU TOC-5000 after the filtration of the samples through a 0.45 μm filter (Whatman). For the HPLC-SEC measurements the samples were first filtered through a 0.45 μm filter (Whatman) and then fractionated with a Hewlett-Packard HPLC 1100 system with a TSKgel G3000SW 7.5 mm × 30 cm column and a diode array UV detector and a fluorescence detector. The UV detection wavelength was set to 254 nm. Sodium acetate of 0.01 M was used as an eluent at a flow-rate of 1 ml/min, the injection volume was 30 μl. This method has been widely used for the characterization of NOM in Finland (Vuorio et al. 1998; Nissinen et al. 2001; Matilainen et al. 2002). In addition, the fluorescence detector was set to detect tryptophan-like fluorescence at excitation/emission wavelengths of 270 nm/355 nm, which is based on previous
studies (Baker 2002; Her et al. 2003), in order to detect the possible effects of wastewater discharge in the drains.

In addition to the DOC and HPLC-SEC data we used the COD-Mn of the catchment samples determined for the years 2000 to 2007, respectively the Total-N and NO23-N values of the studied samples. The Total Organic-N of the samples was calculated as the difference between Total-N and NO23-N.

RESULTS AND DISCUSSION

DOC results

The seasonal variation plot of the KMnO4-number measured over a 6 year period from 2001 to 2006 is presented in Figure 2. This plot shows that the lowest organic content in the drains occurs during winter frost but then increases during the spring snow melt and summer period and reaches a peak in late autumn.

The average, median, maximum and minimum DOC values of water samples are presented in Table 1. The median DOC values of the lake waters examined in this study were 13.2 mg/L for Joutsijärvi-lake and 8.8 mg/L for Tuurujärvi-lake (raw water), which are commonly found in lakes in Finland (Kortelainen et al. 1989; Nissinen et al. 2001). The median DOC values for the Jylhäojaj-drain (19.5 mg/L) and the Ahmausoja-drain (21.3 mg/l) are also quite similar to those found previously in brooks in Finland (20 mg/l—Mattson et al. 2003).

However, when comparing the DOC values of the two drains studied, Ahmausoja proved to have a consistently higher DOC than Jylhäojaj. According to previous studies, this may be due to the fact that Ahmausoja has more extended mire and forest areas, which contribute greatly to the increase of the DOC export in the boreal catchments (Laudon et al. 2004; Mattson et al. 2005). DOC concentration decreased from the drains to the lakes, as shown by the fact that 18 to 59% of DOC was eliminated by drainage into Joutsijärvi and 35 to 75% of the DOC was eliminated by drainage into Tuurujärvi (raw water). This is in agreement with the results of previous studies showing that lakes in general act as sinks for DOC upon sedimentation and microbial degradation (Rantakaari et al. 2004; Mattson et al. 2005). From drains to the drinking water DOC concentration

Figure 1 | The catchment area of Joutsijärvi/Tuurujärvi in South Western Finland.
in both the catchment and water treatment plant was reduced by 73 to 94% (Figure 3a and b).

With respect to seasonal variation, the DOC of the water samples from the catchment varied significantly across the period of investigation and correspondingly varied in the drinking water. In drains the highest DOC concentrations were found in the August 2007 samples (25 mg/L in Ahmausoja and 20.4 mg/L in Jylhäoja) and the lowest DOC values were measured in April 2007 (15.6 in Ahmausoja and 12.6 in Jylhäoja). These results are in agreement with some previous results which show that soil microbial activity in summer and early autumn is intensified and wet episodes during summer and autumn rainfalls leach freshly produced organic matter from coniferous and deciduous litter (Hongve 1999; Scott et al. 2001).

The lakes show a lag in the DOC and KMnO4-number with respect to drains as they generally have their lowest organic content in late summer and autumn. At that time concentrations increase and reach a maximum in late winter (February) (Figures 2 and 3). Similar trends for boreal lake water organic content were observed elsewhere (Matilainen et al. 2002; Andersen & Gjessing 2002). Lakes are large water bodies with a high residence time compared to rivers and drains which attenuates organic inputs through various mechanisms such as dilution, sedimentation and transformation (Rantakaari et al. 2004; Mattson et al. 2005). Andersen & Gjessing (2002) found that transformation through biodegradation in the hypolimnion and photodegradation in the upper layer epilimnion are the main removal mechanism for NOM in a boreal lake and that these processes are at their most intense in summer and early autumn and therefore the lowest DOC content of the lakes generally occurs during this period. Accordingly, decreased bio- and photodegradation during dark and cold winter periods in boreal climates, which follows the autumn mixing of the lake, might be the cause of the increased DOC concentration in the lakes during winter.

The DOC in the drinking water was one magnitude lower than in the drain waters. The seasonal variation of drinking water DOC follows the raw water DOC variation (Figure 3), with the higher organic content of raw water causing a higher DOC in the drinking water. From drinking water samples the highest DOC values were seen in the winter and spring samples from 2008 (5.8 mg/L and 4.8 mg/L), while the

Table 1 | DOC values measured in catchment and drinking water

<table>
<thead>
<tr>
<th>Ahmausoja-drain</th>
<th>Jylhäoja-drain</th>
<th>Joutsijärvi-lake</th>
<th>Raw water</th>
<th>Drinking water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>21.32</td>
<td>19.5</td>
<td>13.2</td>
<td>8.78</td>
</tr>
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<td>Average</td>
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<td>18.61</td>
<td>13.5</td>
<td>9.55</td>
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<td>Max</td>
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<td>17.36</td>
<td>13.9</td>
</tr>
<tr>
<td>Min</td>
<td>15.61</td>
<td>12.64</td>
<td>10.2</td>
<td>6.24</td>
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lowest DOC was measured in summer 2007 (1.4 mg/L). The summer 2007 measurement also had the highest percentage of DOC elimination at the catchment and water treatment plant (94%). During winter and spring the DOC elimination percentage was consistently lower (72% to 89%) (Figure 3). The results obtained during this research show that the water treatment plant cannot eliminate seasonal variations in DOC from the raw water source. The less effective purification performance during winter and spring can also be explained by the lower performance of some treatment units e.g. flotation and/or filtration during the cold season. Flotation has been found to be sensitive to low temperatures (Matilainen et al. 2005) and also biological activity during filtration in winter time has been found to be reduced (Matilainen et al. 2006).

**HPLC-SEC-UV254 measurements**

By HPLC-SEC eight molecular size fractions were separated (Figures 4 and 5). Fraction 0 is an association of smaller molecules and it was present in all of the drain samples and, during winter and spring it was found in lake waters too. Fractions I, II, III and IV are considered to be “High Molecular Weight“ HMW fractions; fractions V and VI are the “Intermediate Molecular Weight” IMW fractions and fraction VII is the “Low Molecular Weight” LMW fraction (Vuorio et al. 1998; Nissinen et al. 2001). For the quantitative characterization of a particular fraction the height of the fraction’s peak (Peak height-PH) was used. For the quantitative characterization of the total NOM the sum of the fractions’ peak heights (Sum of Peak Heights, SPH-254) was used.

The SPH-254 of the samples correlates with the DOC (Pearson correlation coefficient 0.981) and demonstrates similar patterns to DOC both seasonally and within the catchment.

In drain waters HMW fractions account for 70 to 80% of the total NOM given as SPH-254. In the Ahmausoja-drain water the absolute peak of the HMW and IMW fractions was greater than those of the Jylhäoja-drain, which shows that the larger mire and forest areas around Ahmausoja compared to Jylhäoja contributed to the increased NOM content in Ahmausoja mainly by increasing the amount of HMW and IMW compounds. The lake water samples compared to the drains contain lower relative amounts of HMW (50 to 70%). (Figure 5)

Lake waters have lower HMW and higher IMW peaks in the August 2007 samples and furthermore FR0 and FR I
are absent. It has been shown that during the spring-summer stratification of the lakes in the upper epilimnion layer the HMW, especially allochtonous compounds, are degraded into lower molecular weight compounds through photodegradation (Osburn et al. 2001; Andersen & Gjessing 2002). This explains the low amount of HMW and the increased amount of LMW fractions in the summer lake samples of this study. The winter and spring samples have higher HMW peaks and FR 0 and FR I are present in the chromatograms. One explanation for this observation is that during summer and autumn HMW compounds are produced in the hypolimnion through bacterial activity (Osburn et al. 2001) and then these HMW compounds enter the upper parts of the lakes during autumn mixing.

In the drinking water the IMW fractions dominate (60 to 70%). The HPLC-SEC-254 measurements obtained from the drinking water samples show that the water treatment chain eliminates most of the HMW fractions, which is in agreement with a series of previous results (Vuorio et al. 1998; Nissinen et al. 2001; Matilainen et al. 2002). However, there were residual HMW fractions II, III and IV and relatively high IMW fractions V and VI found in the drinking water when the raw water contained an increased amount of NOM. The marked seasonal changes in the raw waters’ NOM composition which were observed in this study by changes in molecular weight distributions (Figure 5), were previously associated with changes in the hydrophobic-hydrophylic character that affected the treatment process (Sharp et al. 2006). Since the relative elimination of the fractions from raw water across the research period were roughly the same it can be concluded that seasonal variations in raw water quality can be seen in the drinking water through the variations of the IMW fractions and the appearance of HMW fractions II, III, IV, respectively.

With regard to drains, drinking water samples showed a 95 to 100% elimination of the HMW fractions, an 63 to 90% of elimination of the IMW fractions and a 45 to 76% elimination of the LMW fraction. The April 2007 and February 2008 samples had a lower relative elimination and...
Figure 5 | Seasonal HPLC-SEC Molecular Weight Fractions of water samples from catchment and drinking water.
the August 2007 sample had the highest relative elimination for all of the fractions.

**HPLC-SEC-fluorescence measurements**

With tryptophan-like fluorescence detection (ex/em = 270/355) only fractions III, IV, V, VI and VII were detected (Figure 6). The fluorescence signals were relative weak and therefore only the sum of the fluorescence-peak heights SPH-Tryptophan was used for further sample characterization.

SPH-Tryptophan correlates rather strongly with the dissolved organic-N content of the samples (Pearson correlation coefficient 0.759) and weakly with NO\textsubscript{2,3}-N concentrations (Pearson correlation coefficient 0.171). SPH-Tryptophan also correlates strongly with the DOC and SPH-254 (respectively, the Pearson correlation coefficients 0.721 and 0.757). Strong positive correlation between DOC and total organic nitrogen in catchments from Finland has also been found in previous research (Mattson et al. 2003). Accordingly, SPH-tryptophan demonstrated similar patterns to DOC and SPH-254 spatially and temporally (Figure 6).

In contrast to the DOC and SPH-254, the Jylhääjoa-drain showed 5 to 30% higher tryptophan-like fluorescence than the Ahmausoja-drain, except for the August 2007 and February 2008 values when the fluorescence of Ahmausoja was only slightly higher (Figure 6). Theoretically, this could be explained by the ongoing agricultural activities (crop-lands and pig farm) in the Jylhääjoa-sub-catchment. Previous
studies have shown that organic nitrogen export within a catchment increases with an increase in the proportion of agricultural land (Rantakaari et al. 2004; Mattson et al. 2005). Additionally, it has also been found that pig slurry has a very intense tryptophan-like fluorescence that should be observable when diluted in rivers (Baker 2002). Hence, it is possible that the increased fluorescence of Jylhäoja compared to that of Ahmausoja reflects the anthropogenic activities around Jylhäoja.

CONCLUSIONS

The amount of NOM was high in the drains and went up to 25 mg C/L then decreased within the catchment to a median value of 9 mg C/L in raw water and reached a minimum value of 1.4 mg C/L in the drinking water produced from it. Correspondingly, 35 to 75% of DOC was eliminated from the drains to the terminal lake (raw water) and 75 to 94% of DOC was eliminated from the drains to the drinking water. The NOM demonstrated seasonal trends whereby the drains had a higher NOM content in summer and a lower NOM content in winter and spring. The two lakes showed inverse patterns and had a higher NOM content in winter and spring and a lower NOM content in summer.

The HPLC-SEC gave detailed information on NOM characteristics in terms of molecular weight composition and separated 8 peaks from the samples. In the drains HMW fractions accounted for up to 80% of the NOM, while in lake waters HMW fractions were about 50 to 60% of the NOM. In drinking water IMW fractions predominated. There was seasonality in the molecular weight distribution of the water samples from the catchment. In the lake waters the IMW fractions were more abundant in summer than in winter and spring, while HMW fractions were higher in winter and spring than in summer. Within the catchment the HMW fractions were eliminated to a greater extent than the other fractions.

The water treatment plant eliminated almost completely the HMW fractions and to a lesser extent the IMW and LMW fractions. There was a seasonal variation in the molecular weight distribution of the drinking water samples; increased NOM in raw water was associated with increased IMW fractions and the appearance of HMW fractions in drinking water. In terms of DOC, this was two to four times higher in the winter and spring samples than in the summer sample. The seasonal increase of NOM in raw water could not be entirely removed by the drinking water treatment system due to the simultaneous effect of low temperatures.

The HPLC-SEC-tryptophan-like fluorescence measurements were interpreted by means of the Sum of the Peak Height-Tryptophan (SPH-Tryptophan). The SPH-Tryptophan followed the same patterns as the DOC and SPH-254. The drain affected by agriculture generally showed higher SPH-Tryptophan values than the non-impacted drain suggesting that traces of wastewater can be detected by HPLC-SEC-fluorescence detection.

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REFERENCES


