

NOM DIAGNOSTICS FOR THE ASSESSMENTS OF SOURCE WATER TREATABILITY AND TREATMENT PERFORMANCE AT WATER SUPPLY SYSTEMS IN NORWAY

NOM-analys för att bedöma ytvattens behandlingsbarhet och beredningsegenskaper från vattenverk i Norge

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Abstract

This paper presents data on water quality and NOM characteristics from analyses of raw and treated water samples from some 30 water supply systems in Norway. Three different water treatment technologies were applied: (1) Enhanced Coagulation (EC); (2) Ozonation-Biofiltration (OBF); or (3) Nano-filtration (NF). The water samples were analysed using simple NOM characterisation methods and user-relevant parameters like TOC, DOC, colour, UV-absorbance, SUVA, hydrophobic and hydrophilic NOM fractions and BDOC. The data, collected over a 10-year period (2004–2014), provide valuable information on NOM characteristics and treatability by various methods. In addition, the data provide information on the interactions between treatment and distribution, i.e. treatment-specific effects on biostability (BDOC) and metal residuals that may contribute to the formation of biofilms and deposits that may adsorb NOM and microorganisms. Correlations between selected NOM-related quality parameters are presented, and the results show significant treatment technology-specific differences in NOM removal characteristics. The data also form a reference basis for future assessments of possible climate-change driven changes in NOM concentrations, NOM composition and NOM characteristics.

Key words – Drinking Water; NOM Characteristics; NOM Removal; NOM fractions, BDOC

Sammanfattning

I artikeln redovisas vattenkvalitetsparametrar och NOM-egenskaper från analyser av råvatten och dricksvatten från ungefär 30 vattenverk i Norge. Tre olika beredningsmetoder för reduktion av organiskt material har undersökts: (1) Förstärkt koagulation; (2) Ozon-Biofiltrering (OBF); respektive (3) Nanofiltrering (NF). Vattenproverna analyserades med hjälp av standardmetoder för karaktärisering av NOM avseende användarrelevanta parametrar som TOC, DOC, färg, UV-absorbans, SUVA, hydrofob och hydrofilt innehåll av NOM-fraktioner och BDOC. Mätvärdena, vilka samlats in under en tioårsperiod (2004–2014), ger värdefull information om NOM-egenskaper och behandlingsbarhet med olika metoder. Mätvärdena berättar också om samspelet mellan beredning och distribution, dvs behandlingsspecifika effekter om hur biostabilitet (BDOC) och metallrester medverkar till att biofilmer och avlagringar som kan adsorbiera NOM och mikroorganismer kan bildas. Korrelationer för valda NOM-relaterade kvalitetsparametrar redovisas och resultaten visar signifikanta skillnader i vilken NOM som avskiljs med olika beredningsmetoder. Uppgifterna utgör även en grund för att bedöma effekter på NOM-halter, NOM-sammansättning och NOM-egenskaper orsakade av klimatförändringar framöver.

Introduction

Natural organic matter (NOM) affects water treatability, water treatment performance and water distribution in a number of ways. Thus there are numerous reasons why

NOM should be removed from drinking water (Eikebrokk et al., 2007). Knowledge of NOM nature and properties is however important in order to be able to select the best treatment technology, to optimize water treatment performance, and to control regrowth, bio-

film formation and depositions in the distribution system. The large number of more or less advanced diagnostic tools available (Matilainen et al., 2011) can all contribute to a better understanding of NOM treatability, NOM nature and NOM properties. Some methods are however more end-user-relevant and more applicable in practice than others.

In this paper, results from 10 years of NOM characterization activities at SINTEF are presented, based on the use of simple tools like rapid NOM fractionation (Chow et al., 2004) and rapid BDOC measurements (Eikebrokk et al., 2007) for the assessment of water treatment performance, identification of best available treatment technologies, and for optimization efforts. The use of the rapid NOM fractionation activity in Norway was initiated in 2002 as an collaboration between SINTEF and the Australian Water Quality Centre (AWQC), and AWQC analyzed water samples from a number of Australian and Norwegian utilities using the same methods (Fabris et al., 2007). Since then, SINTEF have applied the rapid fractionation method at a large number of utilities, and linked NOM fractionation and BDOC measurements to provide information on biodegradability as well. This is an important issue for the chlorine-free distribution systems used in Norway, where UV is the dominating disinfection technology. Thus, the data provided by this survey can be used to investigate how different water treatment technologies affect NOM removal and NOM fraction removal efficiencies, as well as the biological degradability of the remaining NOM (BDOC). Furthermore, the information can be applied for studying possible effects of different treatments on NOM properties, for diagnosing source water treatability by different methods, for optimization of treatment performance, and for better linking of treatment and water distribution performances. In addition, the data can be used to investigate possible relationships between water quality/NOM-related parameters.

Methods

Water sampling and water treatment

The survey is based on analyses of water samples collected at different seasons from some 30 utilities in Norway during the years 2004–2014. Water sampling included untreated raw water, effluent water from different treatment steps, sampling prior to and after UV-disinfection, as well as sampling from the distribution system. The treatment technologies applied by the involved utilities were: (i) Enhanced coagulation (EC), (ii) Ozone-biofiltration (OBF), or (iii) Nano filtration (NF) followed by UV-disinfection (40 mJ/cm²). Due to the pre-

vailing pristine drinking water sources (mainly lakes) and the good source water quality, the described treatment technologies are normally applied as single-stand processes in combination with corrosion control and disinfection, thus allowing a direct comparison of water quality and treatment performance between the technologies. Some utilities also applied low dose chlorination, however without rendering any free chlorine residuals in the distribution system.

Water quality analyses

The applied water quality analyses included conventional parameters and simple NOM diagnostic tools like rapid NOM fractionation and biodegradability (BDOC) measurements.

Conventional parameters

Water samples were sent to SINTEF and analyzed with respect to conventional parameters like pH, turbidity, colour, UV-absorbance, TOC, DOC and metals. Colour and UV-absorbance were analysed by a spectrophotometer (Hitachi U-3000) in accordance with the Norwegian Standard Methods (NS 4787 and NS 9462, respectively). Metals were analyzed by a Thermo Electronics HR-ICP-MS-Element 2; Milestone Ultraclave. TOC was analyzed by a Teledyne Tekmar TOC Fusion analyser.

Rapid NOM fractionation

In addition to the conventional water quality analyses described above, four fractions of NOM (DOC) were identified according to the rapid NOM fractionation method described by Chow et al. (2004). By measuring DOC concentrations (Teledyne Tekmar TOC Torch analyser) in pre-filtered (0.45 µm) samples before and after contact with the NOM fractionation resins DAX-8, XAD-4 and IRA-958, the organic carbon concentrations of four fractions of NOM were determined: (i) Very hydrophobic acid (VHA), (ii) Slightly hydrophobic acid (SHA), (iii) Charged hydrophilic matter (CHA), and (iv) Neutral hydrophilic matter (NEU), based on subtractions of the DOC concentrations of subsequent resin effluents (Figure 1).

VHA and SHA are predominantly composed of high-molecular weight humic and fulvic acids, highly coloured, with low biodegradability. The hydrophilic substances (CHA, NEU) are typically biologically derived, more biodegradable and more low-molecular weight compounds such as polysaccharides and proteins. The NEU fraction is recalcitrant to removal by metal-based coagulation processes, and the NEU fraction concentration may in fact increase during coagulation treatment,



Figure 1. Rapid NOM-fractionation (left) and BDOC columns-in-series set-ups (Eikebrokk, 2014).

presumably due to the NOM-neutralizing effects of the cationic coagulant species. The removal of particular NOM fractions is dependent upon treatment conditions such as applied coagulant dose, pH, etc. and treatment conditions can be optimized based on the character of the organic matter present in the raw water. It is also known that ozonation processes are capable of transforming the hydrophobic NOM fractions (VHA, SHA) into more hydrophilic and more biodegradable fractions (CHA, NEU).

Thus the rapid fractionation technique can be applied as a tool for operators of treatment plants to control and monitor the treatment process in the most effective way for NOM removal. The rapid fractionation technique can also be used to identify situations where treatment is not effective for DOC removal, either due to lack of optimisation or problems with routine operation.

BDOC columns-in-series

The BDOC set-up used in this study was a modification of the column-based BDOC analysis used by others (Volk et al., 1997; Ribas et al., 1991; Lucena et al., 1990) and consisted of multiple bioreactors in series (Figure 1). Water samples from the investigated water facilities were sent to SINTEF's laboratory in 4-liter fluorinated high-density polyethylene bottles (Nalgene), and pre-filtered through a 0.45 μm membrane filter. Sodium bicarbonate (Na_2CO_3) was used for controlling pH at 7–7.5. If a sample could not be analysed immediately, it was frozen. Each of the glass columns ($H = 29$ cm, $\varnothing = 2.5$ cm, Chromaflex, USA) was filled with 200 g of glass carrier beads ($\varnothing = 6$ mm, surface area

$= 3.76$ cm^2/g). The water samples were continuously pumped upwards through the columns by a peristaltic pump (REGLO Analog tubing pump ISM 828, Ismatec, Switzerland). The empty bed volume of each column was 147 mL, while the real volume after subtracting the volume of the glass beads was about 70 mL. When columns were not in use for BDOC testing, biological activity was maintained by recirculation of ozonated water from a 5 L sample beaker through the columns and then back to the beaker. The water was changed at intervals of a few days. In this mode, the columns were operated with two in series (three parallel lines) to maintain a high biological activity. The columns were operated at room temperature and were covered with black plastic to prevent algal growth.

Feeding of the test water into the columns was started in the afternoon and the pumping through the columns continued overnight before DOC sampling was carried out, thus providing about 17 hrs of acclimation time before sampling. This is in line with the adaptation requirements found within the EU project TECHNEAU (Eikebrokk et al., 2007). After acclimation, water sampling was started from the last column. As soon as enough sample volume was collected (one hour), the flow was redirected from the previous (i.e. second-last) column into a new sample beaker. This procedure continued until effluent samples from all six columns were collected. In addition, inlet (raw) and outlet samples were analysed. The sample beaker was weighed before and after sampling to verify a correct flow rate. The collected (i.e. seven) samples were filtered through 0.45 μm membrane filters before dissolved organic carbon

Table 1. Raw water quality characteristics (31 surface water sources).

All Raw Waters	pH	Color mg Pt/L	UV-Abs 1/m	Turb NTU	TOC mg/L	DOC mg/L	BDOC mg/L	Al µg/L	Fe µg/L	P µg/L
Avg	6.7	29	17.5	0.43	4.2	4.1	0.10	73	61	3.0
StDev	0.5	24	11.9	0.38	2.7	2.5	0.16	31	76	1.7
Min	5.6	4	4.0	0.13	1.2	1.1	0.00	24	5	1.4
Max	7.5	144	78.4	2.06	17.0	17.5	1.29	149	357	10.0
N	33	65	87	35	70	93	73	36	35	25

All Raw Waters	Distribution of NOM Fractions (% of DOC)				BDOC % of DOC	SUVA L/mg m
	VHA	SHA	CHA	NEU		
Avg	67	15	6	12	2.6	4.3
StDev	6	3	3	5	2.3	0.7
Min	48	5	0	3	0.0	2.3
Max	81	24	12	27	11.9	6.3
N	93	93	93	93	73	87

(DOC) analysis (Teledyne Tekmar TOC Fusion analyzer). All values were then compared to the DOC of the inlet (raw) water sample, and the difference in DOC between the inlet sample and the effluent sample from the actual column constitutes the biodegraded DOC according to the EBCT after that specific column. The difference in DOC between the inlet sample and the effluent sample from the last column (i.e. EBCT of 9 hrs) gives the final BDOC, while the results from the intermediate samples (i.e. EBCTs with 1.5 hrs intervals) indicate the biodegradation kinetics of the sample. In order to provide information on kinetics at lower EBCTs, i.e. close to the normal design values of 20–30 minutes, the volume of the first column was reduced to about one third in some of the experiments (as shown in Figure 1).

During the BDOC test, the columns were operated with six in series. A three-way valve configuration allowed effluent water sampling from each column. The water sample flow was adjusted to 1.63 mL/min, i.e. an EBCT of close to 1.5 hrs in each column. This flow was chosen for practical reasons and from experience with the actual DOC degradation rates of the tested NOM water samples. With this approach, the resulting EBCTs (i.e. 9 hours in total) were considered reasonable.

Parallel testing of water samples in the conventional batch BDOC measurement (28 days) and the bioreactor-based method used here (9 hrs) showed good agreement. In ozonated water samples the measured BDOC levels were 0.46 and 0.42 mg/L, and in ozonated and biofiltered water samples the BDOC concentrations were 0.28 and 0.25 mg/L for the batch method and the six bioreactor-in-series method, respectively. In a separate set of experiments, additional nutrients (N, P, Ca,

K; 1 mg/L each) were added to the water samples prior to the BDOC analysis. Only minor influence on DOC degradability was detected (< 0.1 mg BDOC/L), indicating that organic carbon was the limiting substrate.

Results and discussion

Source water quality

Analytic data for all source (raw) water samples are summarized in Table 1, including routine parameter values, NOM-fraction distributions and BDOC data. It appears from the data that the hydrophobic NOM-fractions dominate, that the raw waters are biologically stable, and that the raw waters along with the NOM also contain significant amounts of metals (Al, Fe) and phosphorous. The high SUVA-values indicate good treatability by coagulation. As illustrated in Figure 2, TOC and DOC correlate well, showing that the particulate fraction of NOM is negligible. Furthermore, Figure 2 shows that the correlation between UV-abs and DOC is better than the correlation between color and DOC, and that UV-abs and color correlates well for the tested raw waters tested.

Enhanced coagulation (EC) treatment performance

Table 2 summarizes the data from 10 utilities applying EC treatment, i.e. elevated coagulant doses and strict control of coagulation-pH, on raw waters containing 4.8 ± 2.3 mg DOC/L (average \pm stdev). The data show that enhanced coagulation processes provide good treat-

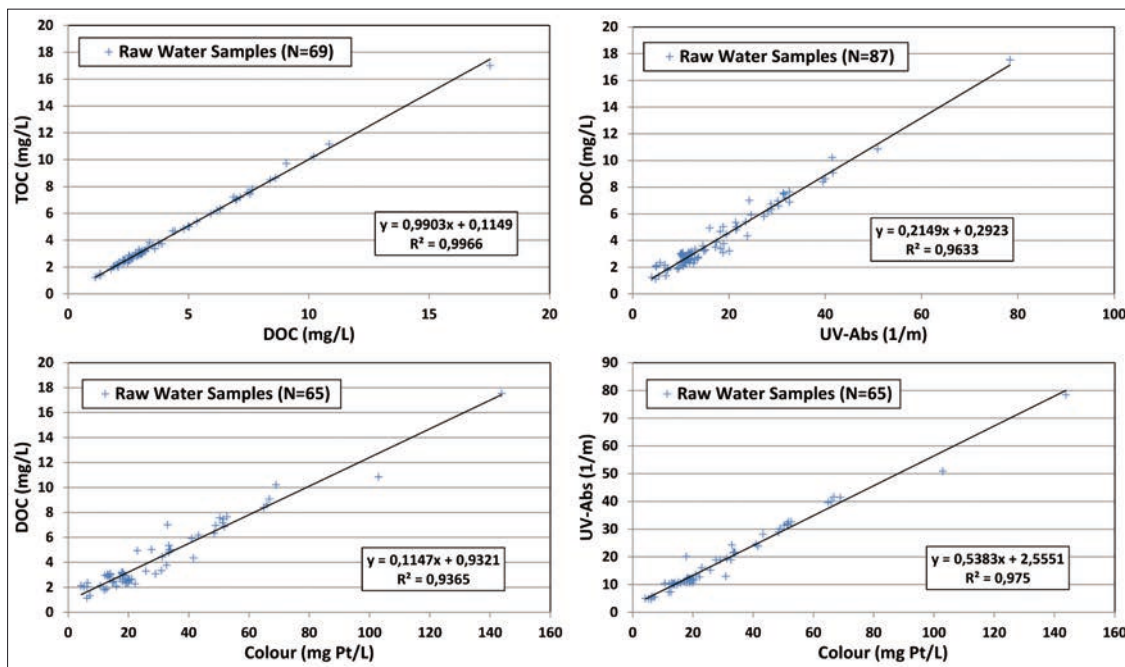


Figure 2. Raw water characteristics and correlations: (i) DOC to TOC, (ii) UV-Abs to DOC; (iii) Colour to DOC, and (iv) Colour to UV-Abs.

ed water quality and effective removal of colour, UV-abs, turbidity, Al, Fe, TOC, DOC, BDOC and NOM fractions. The exception is NEU, for which coagulation on average removes 7% only. This is not critical, since the CHA and NEU concentrations are low in the raw waters, on average 0.2 and 0.5 mg/L, respectively (see Table 1). This situation can however change

in the future as a result of climate change, thus influencing on enhanced coagulation process capabilities and competitiveness relative to alternative treatments. The low levels of BDOC, Al, Fe and P remaining after enhanced coagulation treatment indicate that the potential for regrowth and formation of deposits in the distribution system is rather limited.

Table 2. Characteristics of EC-treated waters (10 utilities).

EC Treated	pH	Color mg Pt/L	UV-Abs 1/m	Turb NTU	TOC mg/L	DOC mg/L	BDOC mg/L	Al µg/L	Fe µg/L	P µg/L
Avg	7.8	4	3.8	0.10	1.8	1.9	0.06	22	5	1.8
StDev	0.7	1	1.8	0.04	0.9	0.9	0.04	8	4	0.4
Min	6.4	2	0.9	0.05	0.5	0.4	0.00	13	2	1.4
Max	8.3	7	6.3	0.15	3.2	3.2	0.12	35	11	2.4
N	6	25	36	8	32	40	17	7	6	4

EC Treatment	NOM Fraction Removal Efficiencies (%)				DOC	BDOC	Color	UV-Abs
	VHA	SHA	CHA	NEU				
Avg	75	54	54	7	65	32	91	83
StDev	10	20	64	30	8	77	4	6
Min	51	4	-217	-95	47	-234	83	64
Max	100	100	100	54	77	100	96	93
N	52	52	52	52	52	24	37	48

Table 3. Characteristics of OBF-treated waters (12 utilities).

OBF Treated	pH	Color mg Pt/L	UV-Abs 1/m	Turb NTU	TOC mg/L	DOC mg/L	BDOC mg/L	Al µg/L	Fe µg/L	P µg/L
Avg	7.2	7	5.9	0.27	2.7	2.6	0.39	57	23	3.0
StDev	0.6	3	2.9	0.12	1.4	1.3	0.26	22	11	1.5
Min	6.2	3	2.1	0.16	1.0	1.0	0.14	20	11	1.1
Max	8.0	14	11.5	0.52	5.2	5.3	0.99	100	41	4.7
N	9	17	20	11	18	20	20	10	10	7

OBF Treatment	NOM Fraction Removal (%)							
	VHA	SHA	CHA	NEU	DOC	BDOC	Color	UV-Abs
Avg	54	-28	-250	-14	21	-454	65	59
StDev	9	42	366	35	7	555	8	5
Min	39	-177	-1657	-98	9	-1980	42	50
Max	74	20	5	35	38	-59	78	69
N	19	19	18	19	19	18	16	19

Ozone-Biofiltration (OBF) treatment performance

Table 3 summarizes the data from 12 utilities applying OBF treatment, i.e. ozonation prior to biological filtration on raw waters with 3.5 ± 1.7 mg DOC/L. Although complying well with the water quality regulations, OBF processes removes far less TOC and DOC compared to EC treatment. Colour, UV-abs, turbidity, Al, Fe and P concentration levels are also higher after OBF treatment. The BDOC concentration is significantly increased from the raw water levels, due to the ozone-induced transformation of the hydrophobic VHA fraction into the more biodegradable CHA fraction. Thus when ap-

plying OBF as a stand-alone treatment process, care should be taken in order to control regrowth and the formation of deposits/biofilm in the distribution networks.

Nano filtration (NF) treatment performance

Table 4 summarizes the data from 3 utilities applying NF treatment for raw waters containing 10.3 ± 7.5 mg DOC/L. The data show that the NF processes provide good and stable treated water quality and effective removal of colour, UV-abs, turbidity, Al, Fe, TOC, DOC, BDOC and NOM fractions, in spite of the fact that NF

Table 4. Characteristics of NF-treated waters (3 utilities).

NF Treated	pH	Color mg Pt/L	UV-Abs 1/m	Turb NTU	TOC mg/L	DOC mg/L	BDOC mg/L	SUVA L/mg m
Avg	6.6	6	7.4	0.18	2.6	2.2	0.06	3.3
StDev	0.7	5	5.1	-	2.2	1.6	0.08	0.7
Min	6.0	1	1.6	0.18	0.6	0.5	0.01	2.8
Max	7.3	11	10.6	0.18	4.9	3.7	0.12	4.1
N	3	3	3	1	3	3	2	3

NF Treatment	NOM Fraction Removal (%)							
	VHA	SHA	CHA	NEU	DOC	BDOC	Color	UV-Abs
Avg	85	62	85	24	78	80	91	84
StDev	5	9	12	8	1	16	2	4
Min	81	52	76	17	77	68	89	80
Max	90	69	98	33	79	91	93	87
N	3	3	3	3	3	2	3	3

processes are applied on raw waters with by far the highest NOM concentration levels. The NF processes seem capable of removing also the NEU fraction more effectively than EC, with 24 % removal efficiency on average. It should be noted however, that the data covers only 3 NF utilities.

Conclusions

The NOM diagnostics applied in this study reveal significant differences in performance among the investigated treatment technologies. NF appears as the most effective technology in terms of DOC and NOM fraction removal efficiency, followed by EC and OBF. However, due to the significantly higher NOM concentrations in the raw waters at the utilities applying NF, the residual colour, UV-abs, and DOC concentrations are higher from these utilities compared to the utilities applying EC treatment.

Treated waters from EC and NF appear as biologically stable, with very low residual BDOC. OBF treated waters on the other hand show relatively high BDOC residuals. This is a result of the significant ozone-induced transformation of hydrophobic NOM fractions (VHA) into more biodegradable fractions (CHA) with downstream biofilters rendering the BDOC levels significantly above the raw water levels, thus imposing increased risks for regrowth and biofilm formation in the distribution system. The results also indicate a need for revisions of the biofilter design criteria when used in OBF-applications, in order to obtain more efficient BDOC removal in the biofiltration process. The results also reveal treatment-specific differences in residual metal concentrations, thus indicating differences also in the formation potential of NOM-absorbing metal hydroxide deposits within the distribution network.

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