MONITORING QUALITY OF WATER INTENDED FOR HUMAN CONSUMPTION IN ROMANIA; DETERMINATION OF NOM FRACTIONS AND BDOC

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Abstract

An investigation has been performed to monitor the raw and drinking water quality in the Romanian counties Calarasi and Braila in the south-east of Romania. As a part of this investigation, fractioning of the natural organic matter (NOM) and determination of the regrowth potential as biodegradable organic matter (BDOC) has been performed.

The plants treating raw water from the river Danube had a DOC in raw and treated water of 3.4–4.1 mg C/L and 2.0–2.7 mg C/L, respectively. The DOC content in the different NOM fractions VHA, SHA, CHA and NEU in the raw water was 1.2–1.9 mg C/L, 0.3–0.6 mg C/L, 0.2–0.7 mg C/L and 0.3–1.0 mg C/L, respectively. The raw water colour was approximately 10 mg Pt/L, and was reduced to \leq 3 mg Pt/L during treatment. The measurements of the NOM fractions and the BDOC during treatment showed that coagulation removes parts of the very hydrophobic NOM, minor parts of the other NOM and a great part of the BDOC, while the chlorination through oxidation increased the BDOC. The overall effect of the treatment on the BDOC, which means on the regrowth potential, was negligible.

The groundwater had BDOC levels of 0.0-0.3 mg C/L, which increased to 0.4-0.9 mg C/L in treated water, because of the rather high chlorine dosages applied.

Key words – Water supply, water quality, treatment, monitoring, NOM, fractioning, SUVA, BDOC, Romania, Danube

Sammendrag

Det er gjennomført en undersøkelse av kvaliteten på råvann og drikkevann i de to Rumenske fylkene Calarasi og Braila. Som en del av denne undersøkelsen er det gjennomført fraksjonering av naturlig organisk materiale (NOM) og måling av begroingspotensialet målt som biologisk nedbrytbart organisk karbon (BDOC).

Der kilden var Donau inneholdt råvannet 3,4–4,1 mg DOC/l og rentvannet 2,0–2,7 mg C/l. DOC-innholdet i de forskjellige NOM-fraksjonene VHA, SHA, CHA og NEU i råvannet var henholdsvis 1,2–1,9 mg C/l, 0,3–0,6 mg C/l, 0,2–0,7 mg C/l og 0,3–1,0 mg C/l. Råvannsfargen var ca 10 mg Pt/l, og ble redusert til \leq 3 mg Pt/l etter behandling. NOM-fraksjonering og analyse av BDOC viste at koaguleringen fjerner deler av det svært hydrofobe NOM, mindre deler av det øvrige NOM og en stor del av BDOC, mens kloreringen øker BDOC.

Grunnvannet hadde BDOC verdier på 0,0–0,3 mg C/l, og kloreringen økte BDOC-verdiene til 0,4–0,9 mg C/l i rentvannet.

1 Introduction

An investigation has been performed to monitor the raw and drinking water quality in the Romanian counties Calarasi and Braila in the south-east of Romania. As a part of this investigation, fractioning of the natural organic matter (NOM) and determination of the regrowth potential as biodegradable organic matter (BDOC) has been performed. The NOM fractioning and the BDOC measurements are valuable tools in the assessment of

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NOM treatability by different methods, treatment performance and biostability (Eikebrokk et al, 2010).

The raw water for Chiscani, Braila, Movila Miresii, Ianca, Calarasi and Oltenita was taken from the river Danube, while the raw water for Budesti, Urziceni and Lehliu was ground water. With raw water from the Danube, the treatment consisted of coagulation, settling, filtration and chlorination, with minor design variability. The local chlorination practice aims to have 0.5 mg free Cl₂/L at the outlet of WTP (distribution network inlet) and 0.25 mg free Cl₂/L at the tap.

2 Objectives

The objectives of both the entire investigation and the fractioning of NOM and the BDOC measurements were to monitor the present drinking water quality in order to identify any non-compliance with the regulations, and further to identify raw water treatability characteristics and possible inadequate treatment steps causing this non-compliance.

3 Materials and Methods

3.1 Sampling

All the samples were taken as grab samples in the Romanian counties Calarasi and Braila. All samples were taken by INCD-ECOIND in the period January 18–21 and May 25–27 2010, and shipped to SINTEF in Trondheim. Calarasi, Braila and Chiscani were sampled in both of the periods, Gropeni only in May and the rest only in January. The organic content in raw water from the river Danube was slightly higher in January 2010 than in May 2010.

3.2 Fractionation of NOM

A rapid fractionation technique was presented by Chow (2004) and further described in Eikebrokk and Juhna (2010).

The fractioning is a 3-step lab procedure, with subsequent pH-adjustment and filtration through the following filter materials:

- DAX-8: Acidify the 500 ml filtered sample to pH 2 with HCl and pass it through the DAX-8 column at a rate of 3ml/min (i.e. 0.2 bed volumes/min). Discard the first two bed volumes (30ml) and collect the remaining effluent (470ml). Collect a sub sample of 100ml for DOC analysis.
- XAD-4: The remaining effluent (370ml) should be passed through XAD-4 column at a rate of 3 ml/min. Discard the first two bed volumes (30ml) and collect the remaining effluent (340ml).Then collect a sub sample of 100ml for DOC analysis.
- IRA-958: Adjust the remaining effluent (240ml) to pH 8 with NaOH and pump it through the IRA-958 column at a rate of 3 ml/min. Discard the two first bed volumes (30ml) and collect the remaining effluent (210ml) for DOC analysis.

The DOC samples are analyzed using Teledyne Tekmar TOC Fusion analyzer.

All the results are given as mg DOC/L after the following calculations:



Figure 1. Apparatus for NOM fractioning.



Figure 2. Experimental set-up for BDOC column test.

VHA = very hydrophobic acids = RAW – (DAX-8 effluent) SHA = slightly hydrophobic acids = (DAX-8 effluent) – (XAD-4 effluent)

CHA = hydrophilic charged = (XAD-4 effluent) – (IRA-958 effluent)

NEU = hydrophilic neutral = IRA effluent

3.3 BDOC

The column in series BDOC test is thoroughly described in Eikebrokk and Juhna (2010). The set-up is based on six glass columns filled with 200 g of glass carrier beads ($\emptyset = 6$ mm, surface area = 3.76 cm²/g). Across the columns, the sample is continuously pumped upward. The empty bed volume of each column is 147 ml.

The columns were originally inoculated by recirculating a mixture of raw water from Trondheim water work and pilot-scale biofilter effluent through the columns. When columns are not used for the BDOC test, the biological activity is maintained by recirculating ozonated water from a pilot plant in VIVA from a 5 liter bottle. The columns are operated at room temperature.

During the BDOC test, the columns are operated as six in series. Figure 2 shows a simplified set-up of the columns. A valve configuration allows redirecting water flow after each column into a sampling port. The water flow is adjusted to 1.63 ml/min, which results in EBCT of 1.5 hrs in each column.

The tested water samples were sent to SINTEF in 4-liter fluorinated high-density polyethylene bottles (Nalgene) and filtered through 0.45 µm membrane filter. If a sample could not immediately be analyzed, it was frozen. Thio sulphate was added to chlorinated samples in order to remove residual chlorine before the BDOC test. Feeding the test water into the columns was started in the afternoon and it was pumped through the columns overnight before the DOC sampling was carried out. This gave about 17 hrs acclimation time for the columns. This was around four times the actual retention time in the columns. After acclimation, the DOC sampling was started from the last column. When enough water was collected, the flow was redirected from the previous column into a new sample beaker. This was done until effluent from each column had been collected. Each column was sampled for one hour. The DOC samples were filtered through 0.45 μ m membrane filter before the organic carbon analysis. The values were then compared to the DOC of the original sample. The difference between the feed and the effluent from the last column (EBCT of 9 hrs) gave the BDOC, while intermediate samples (EBCTs with 1.5 hrs intervals) gave indication of the biodegradation kinetics of the sample. Figure 3 shows as an example of one set of samples analyzed from Braila treatment plant.



Figure 3. BDOC Results from Braila water treatment plant. The samples RW are raw water and the samples marked PW are treated water.

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4 Results and Discussion

4.1 Analysis of raw and finally treated water

The results from the rapid NOM fractioning and the BDOC analysis are shown in Table 1.

The plants treating raw water from Danube – Braila, Calarasi, Oltenita, Movila Miresii, Ianca and Chiscani had a DOC in raw and treated water of 3.4–4.1 mg C/L and 2.0–2.7 mg C/L, respectively. The DOC content in the different NOM fractions VHA, SHA, CHA and NEU in the raw water was in 1.2–1.9 mg C/L, 0.3–0.6 mg C/L, 0.2–0.7 mg C/L and 0.3–1.0 mg C/L, respec-

tively. All NOM fractions were reduced during the treatment, even though the highest reductions were seen in the very hydrophobic fraction.

All plants have treatment processes that include coagulation, sedimentation, filtration and chlorination. Coagulation followed by sedimentation and filtration are expected to remove parts of the NOM, in particular the very hydrophobic fraction, through adsorption to metal hydroxides and through sweep-floc coagulation. The chlorination implies residuals after 30 min contact time of 0.5 mg Cl_2/L , which requires high doses that may partly change the NOM composition through oxidation.

Table 1. Summarized results from OM fractioning and BDOC measurement (RW=raw water, PW=treated water). See Chapter 3.1 for information on sampling time and method. At plants with two samplings, the sampling in January is marked 1st and the sampling in May is marked 2nd. RW=raw water and PW=prodused water (plant outlet).

Sampling point	Colour	UV-abs 254 nm (1/cm)	DOC (mg C/L)						SUVA
	(mg Pt/L)		Total	VHA	SHA	CHA	NEU	BDOC	m ⁻¹ L/ mg C
Chiscani RW, 1 st	9	0.078	3.63	1.89	0.49	0.55	0.71	0.34	2.1
Chiscani PW, 1st	2	0.038	2.18	0.96	0.50	0.39	0.33	0.40	1.7
Chiscani RW, 2 nd	9	0.078	2.88	1.41	0.56	0.37	0.54	0.43	3.2
Chiscani PW, 2 nd	1	0.036	2.10	1.10	0.38	0.21	0.41	0.19	1.7
Braila RW, 1 st	8	0.070	3.35	1.60	0.51	0.66	0.58	1.14	2.1
Braila PW, 1 st	2	0.012	1.96	0.92	0.31	0.31	0.42	0.40	0.6
Braila RW, 2 nd	8	0.065	2.39	1.19	0.54	0.28	0.38	0.19	2.9
Braila PW, 2 nd	2	0.041	2.04	1.01	0.49	0.12	0.43	0.28	2.0
Movila M RW	9	0.064	3.91	1.71	0.56	0.66	0.98	1.92	1.6
Movila M PW	3	0.052	2.67	1.22	0.40	0.50	0.55	0.69	1.9
Ianca RW	8	0.074	4.03	1.92	0.56	0.65	0.90	1.30	1.8
Ianca PW	2	0.040	2.51	1.16	0.37	0.36	0.62	0.85	1.6
Calarasi RW, 1 st	9	0.068	3.73	1.68	0.55	0.89	0.86	1.90	1.8
Calarasi PW, 1 st	2	0.037	2.74	1.01	0.29	0.74	0.70	1.22	1.3
Calarasi RW, 2 nd	8	0.065	2.28	1.30	0.44	0.23	0.31	0.21	2.9
Calarasi PW, 2 nd	1	0.037	1.80	0.93	0.39	0.17	0.30	0.15	2.1
Calarasi RW	10	0.079	2.79	1.82	0.33	0.22	0.42	0.23	2.8
Calarasi Prechlorination	0	0.035	2.22	1.00	0.66	0.21	0.35	0.41	1.6
Calarasi Settling	4	0.047	1.98	1.02	0.39	0.19	0.37	0.11	2.4
Calarasi Coagulation	5	0.050	2.02	1.11	0.41	0.15	0.35	0.00	2.5
Calarasi Filtration	3	0.046	1.94	0.97	0.45	0.17	0.34	0.11	2.4
Calarasi Chlorination basin	1	0.029	2.07	1.05	0.38	0.24	0.39	0.39	1.4
Calarasi PW	1	0.037	1.97	1.06	0.37	0.22	0.31	0.23	1.9
Oltenita RW	11	0.07	4.11	1.72	0.61	0.74	1.05	1.11	1.7
Oltenita PW	1	0.013	2.73	1.07	0.38	0.48	0.80	1.04	0.5
Budesti RW	<1	0.022	1.08	0.49	0.28	0.06	0.25	0.23	2.2
Budesti PW	1	0.024	1.80	0.49	0.43	0.20	0.68	0.65	1.3
Urziceni RW	5	0.07	3.15	1.90	0.60	0.27	0.37	0.03	2.3
Urziceni PW	5	0.062	3.12	1.83	0.51	0.20	0.59	0.45	2.0
Lehliu RW	17^{1}	0.13^{1}	2.71	1.99	0.38	0.10	0.23	0.32	4.8
Lehliu RW	22^{1}	0.17^{1}	3.32	2.37	0.32	0.22	0.42	0.01	5.1
Lehliu PW	7	0.09	3.67	2.10	0.38	0.40	0.77	0.86	2.5
Gropeni RW – Braila WTP	8	0.062	2.36	1.21	0.42	0.26	0.46	0.30	2.6
Gropeni PW – Braila WTP	3	0.038	1.98	1.01	0.42	0.19	0.35	0.18	1.91

¹ The colour and UV absorbance may have been caused by sulphur compounds. There was a considerable precipitation in the samples (sulphur).



Figure 4. The correlation between BDOC and hydrophilic DOC in samplers taken from raw water and produced water at several Romanian waterworks in January and May 2010.

The plants treating groundwater – Budesti, Urziceni and Lehliu, had a DOC in raw water of 1.1–3.2 mg C/L and in treated water of 1.8–3.7 mg C/L. The increase in DOC during treatment that was seen in Budesti and Lehliu could have been accidental, and then an indication of variations in DOC, or the chlorination had oxidized and hydrolyzed some particulate organic carbon.

The plants treating raw water from Danube – Braila, Calarasi, Oltenita, Movila Miresii, Ianca and Chiscani, had BDOC values in January in raw and treated water of 0.3-1.9 mg C/L and 0.4-1.2 mg C/L, respectively. In all raw and treated waters the values were so high that massive biofilm formation would be expected in the absence of the rather high concentrations of the biocide chlorine. The highest values for raw water were found in Movila and Calarasi. The highest BDOC-values for treated water were found in Calarasi and Oltenita, the two plants closest to possible discharges from Buchuresti. In May the BDOC was considerably lower in the raw waters in Braila and Calarasi than in January, and lower in all treated waters analysed at both times, showing that the variations in BDOC were dependent on weather conditions and season. The BDOC in raw and treated water at Gropeni, using the Danube as raw water, was in the same range as Chiscani, Calarasi and Braila, as may be expected.

The plants treating groundwater, Budesti, Urziceni and Lehliu, had BDOC levels in raw and treated water of 0.0–0.3 mg C/L and 0.4–0.9 mg C/L, respectively. The increase in BDOC during treatment is likely to be explained by the oxidation of organic matter during chlorination.

The correlation between BDOC and the sum of the hydrophilic fractions of DOC (CHA+NEU) is shown

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for both raw waters and treated waters in Figure 4. Previous research has shown that the biodegradable part of DOC in NOM in Norwegian waters is mainly small molecules (molecular weight < 1000) (Hem and Efraimsen, 2001). For a number of Norwegian waters treated by coagulation or ozonation and biofiltration a good correlation ($\mathbb{R}^2 > 0.8$) between BDOC and the hydrophilic fractions of the DOC was demonstrated (Eikebrokk, 2009) (Figure 5). The results in Figure 4 indicate that also for Romanian water supply the main part of biodegradable DOC is related with a good correlation to the hydrophilic fractions that may be expected to contain the smaller molecules. However, the BDOC levels in both raw and treated water in Romania are generally higher than in the Norwegian waters.

All results are summarized in Table 1. This includes BDOC, NOM fractioning, DOC, colour and UV ab-



Figure 5. Correlation between hydrophilic NOM fractions (CHA, NEU) and BDOC concentrations found at 10 Norwegian water works with enhanced coagulation (incl. four in the city of Bergen) or ozonation-biofiltration treatment (Eikebrokk et al., 2010).

sorbance. In addition is the specific UV-absorbance (SUVA) calculated as follows:

 $SUVA=UV_{abs}/DOC$ UV_{abs} in 1/m DOC in mg C/L

Van Benschoten and Edzwald (1990) defined the suitability for coagulation for DOC removal based on SUVA. If the SUVA is 4-5, DOC will mainly originate from humic and fulvic acids and by coagulation processes one would expect high DOC removal. With SUVA < 3, DOC will mainly originate from non-humic substances, DOC will have little influence on necessary coagulant dosage and the expected DOC removal will be limited. The surface water used in this study had a SUVA ≤ 2.1 and the DOC would then be defined to originate from non-humic substances. In spite of the fact that the hydrophobic parts of the NOM did not originate from humic substances coagulation, settling and filtration removed approximately 30 % of the NOM. Experiences with coagulation for removal of humic substances from natural waters may then not be relevant. For the groundwater sources, Lehliu had a colour and UV absorbance that could have been caused by sulphur compounds. The sulphate content was typically 30 mg/L and the sulphide content typically 4 mg/L. The two other groundwater plants had a SUVA \leq 2.2. The SUVA values were reduced during treatment for all plants, by coagulation and oxidation for surface water and by oxidation for groundwater sources.

4.2 Analysis of samples taken from different parts of a treatment plant

In May 2010, samples were taken from different places along the process train in the Calarasi plant. These samples were analysed for NOM fractions and BDOC, and the results are shown in Figure 6 and 7.

The DOC content in the different NOM fractions VHA, SHA, CHA and NEU in the raw water was 1.8 mg C/L, 0.3 mg C/L, 0.2 mg C/L and 0.4 mg C/L, respectively. The overall removal efficiency for DOC in the plant was approximately 30 %. The very hydrophobic acids were considerably reduced through coagulation, most likely from adsorption to or entrapped in particles (flocs). The slightly hydrophobic acids showed some increase in the pre-chlorination on behalf of the very hydrophobic acids. In the rest of the plant, only minor changes in the hydrophobic acids were found. The amount of hydrophilic compounds (CHA+NEU) showed some increase through post-chlorination, but was almost unchanged through the rest of the plant. This is different from what is seen in Norwegian coagulation plants, where higher coagulant doses are used, and



Figure 6. Fractions of organic matter DOC in the Calarasi plant May 2010.

where considerable parts of both hydrophobic acids and charged hydrophilic compounds (CHA) are removed.

The BDOC was reduced through coagulation and settling. The BDOC increased then considerably in prechlorination due to the oxidation of organic matter. The BDOC was then reduced through filtration and finally increased again in the post-chlorination. The overall effect of the treatment on the BDOC, and thus the regrowth potential, was negligible.



Figure 7. BDOC in the Calarasi plant May 2010.

5 Conclusions

The plants treating raw water from the river Danube had a DOC in raw and treated water of 3.4–4.1 mg C/L and 2.0–2.7 mg C/L, respectively. The DOC content in the different NOM fractions VHA, SHA, CHA and NEU in the raw water was 1.2–1.9 mg C/L, 0.3–0.6 mg C/L, 0.2–0.7 mg C/L and 0.3–1.0 mg C/L, respectively. The raw water colour was approximately 10 mg Pt/L, and was reduced to less than 3 mg Pt/L during treatment. The measurements of the NOM fractions and the BDOC during treatment showed that coagulation removes parts of the very hydrophobic DOC and a great part of the BDOC, while the chlorination through oxidation increased the BDOC. The overall effect of the treatment on the BDOC, which means on the regrowth potential, was negligible.

The groundwater had BDOC levels of 0.0-0.3 mg C/L, which increased to 0.4-0.9 mg C/L in treated water, because of the rather high chlorine dosages applied.

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Abbravations

BDOC = biodegradable organic carbon

- DOC = dissolved organic carbon
- NOM = natural organic carbon
- EBCT = empty bed contact time
- VHA = very hydrophobic
- SHA = slightly hydrophobic acids
- CHA = hydrophilic charged
- NEU = hydrophilic neutral

References

Chow, C., Fabris, R., and Drikas, M. (2004). A rapid fractionation technique to characterise natural organic matter for the optimisation of water treatment processes. *Journal* of Water Supply: Research and Technology – AQUA, 53(2), 85–92.

Eikebrokk, B. (2009). Water treatment: Optimization for what? In van Hoven and Katzner (ed): TECHNEAU: Safe Drinking Water from Source to Tap – State of the art and perspectives. IWA Publishing, London, UK, ISBN: 1843392755; ISBN13:9781843392750, pp 265–280

- Eikebrokk, B. and Juhna, T. (2010). Optimization of water treatment: Enhanced Coagulation and Ozonation-Biofiltration. Summary report on performance assessment tools and optimization. TECHNEAU-Report D5.3.2B. www.techneau.org
- Eikebrokk, B., Thorvaldsen, G., Seim, A., Aasen, A. and Sekse, M. (2010). Optimization of water treatment: A first step towards safer and more sustainable water supply systems (In Norwegian). Proc. 7th Nordic Water Supply Conf. Copenhagen, Denmark, June 2010. ISBN: 87-90455-98-3, pp 134–145
- Fabris, R., Chow, C., Tran, T., Gray, S. and Drikas, M. (2008). Development of combined treatment processes for the removal of recalcitrant organic matter. Report No. 38, CRC for Water Quality and Treatment. ISBN 1876616636
- Hem, L.J. & Efraimsen, H. (2001). AOC in MW fractions of NOM. Water Research, 35:4:1106–1110.
- Van Benschoten, J. E. and Edswald, J. K. (1990). Chemical aspects of coagulation using aluminium salts: 2. Coagulation of fulvic acid using alum and polyaluminium chloride. Water Research: 24:1527–1535.