NOM Characterization and Removal by Water Treatment Processes for Drinking water and Ultra Pure Process Water

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ABSTRACT
Kvarnagården water treatment plant (WTP), located in Varberg, Sweden and operated by VIVAB, supplies drinking water to both the municipality of Varberg and the nuclear power plant Ringhals. The owner of the nuclear power plant has raised concerns of increasing NOM content in the drinking water for more than 5 years. This paper describes the NOM characterization by using Liquid Chromatography – Organic Carbon Detection (LC-OCD), from the water source, over drinking water treatment and production of ultrapure process water. Biopolymers, humic substances, building blocks, low molecular-weight acids, low molecular-weight neutrals and hydrophobic organic carbon have been quantified for these waters. Rapid sand filtration and disinfection do not affect the composition of NOM, nor does ultrafiltration (UF). Humic acids seem to foul ion exchangers and RO membranes in the power plant’s demineralization facility. Pilot-scale UF with pre-coagulation effectively removed the humic fractions of NOM. If applied in full-scale at Kvarnagården WTP, this treatment combination could improve the performance of the demineralisation plant at Ringhals power plant and prolong the operational time of the ion exchangers.

KEYWORDS:
Ion exchanger, membrane, ultra filtration, permeate, coagulation, humic substances, SEC, HS-diagram, biopolymers

INTRODUCTION

Ringhals: desalination of municipal drinking water
During the establishment of the nuclear power plant Ringhals near the City of Varberg in the early 1970's, an agreement between utility company Vattenfall and the municipality of Varberg was signed for the supply of municipal drinking water. This agreement governs the conditions of water supply (quantity and quality) and the financing of co-owned infrastructure (water treatment plant and distribution network). Of the approximately 5 million m³ of drinking water produced annually at the main water plant Kvarnagården in Varberg, more than 1 million m³ are delivered to Ringhals. Main applications are flush water to the switchgear and storage of firefighting water. About one third of this amount of water is used for internal process water (e.g. reactor cooling and production of steam). Ringhals nuclear power plant is dependent on pure feed water to the facility to meet current requirements for corrosion and safety. Due to the high turnover of water in this process, can already low concentrations of corrosive substances cause serious operational problems. Humic Substances (HS) are normally relatively harmless, but at high temperatures HS can decompose and release the humus-bound corrosive substances such as chlorides and sulfates. In order to meet the requirements for ultra-pure water, Ringhals has its own treatment plant for desalination of incoming raw water from the municipal Water Treatment Plant (WTP) in Varberg. The desalination plant comprises ion exchangers consisting cation, anion and mixed polishing resin beds followed by a membrane filtration plant for Reverse Osmosis (RO). The quality of feed water to the internal processes must correspond to a conductivity of <0,1 µS/cm and a low content of organic pollutants at <50 ppb Total Organic Carbon (TOC).
Operational problems with desalination
Since 2005, Ringhals has noticed a gradual deterioration of the internal water treatment in terms of increasing conductivity and TOC concentrations. As a result, the desalination plant could not operate at full capacity. Operational problems have been traced to rising levels of HS in the incoming raw water, i.e. drinking water from the municipal water plant. Humic fractions caused deposits on the ion-exchange resins, which reduced ion exchange and resulted in an increased concentration of organic matter in the treated water. During operation of the ion exchangers, the conductivity increased in the outlet of anion resin beds and mixed polishing resin beds within a short time, leading to deteriorating water quality and reduced plant capacity. Also, unexplained conductivity peaks where detected after the Mixed polishing resin Beds (MB). The subsequent RO plant showed a good reduction of conductivity and TOC, but was exposed to a higher foulant load compared to design criteria.

Trials with alternative pre-treatment processes
Over the years, a number of measures were taken to improve the availability and degree of purification of the existing treatment plant. More frequent changes of ion exchange resins and higher circulation of raw water basins as well as pilot trials for increasing the capacity of the RO plant have proved to be only temporary solutions, while the operational problems of the ion exchangers are still remaining. Thus, an improvement of the feed water to the ion exchangers is a longer-term solution. Pilot experiments were performed at the end of 2009 to reduce the levels of organic matter in the feed to the desalination plant. Tests with advanced oxidation technology (AOT) based on UV photocatalysis on titanium dioxide indicated a positive effect on resin regeneration intervals (data not shown in this paper). Membrane filtration (UF) gave the best results in term of longer intervals for regeneration and less wear on the ion-exchange resins, as well as lower consumption of regeneration chemicals. An upgrade of the existing pre-treatment for RO at Ringhals with another membrane step would require large investments. Therefore, Ringhals and VIVAB cooperate in investigation options to upgrade the treatment process at Kvarnagården WTP.

RESEARCH OBJECTIVES

Cooperation between Ringhals with VIVAB: pilot trials for improved water quality
The raw water to Kvarnagården WTP consists of 80% surface water and 20% groundwater. The surface water source is an oligotrophic lake surrounded by mixed woodland. The lake has an average depth of around 19.3 m (max. depth: 57.0 m) with a water volume of approx. 61.1 million m³, and a theoretical turnover equivalent to 7.4 years. The long retention time has contributed to low humic content consisting mainly of colorless fulvic acids. In line with the ongoing browning of lakes and rivers in large parts of Scandinavia, a rising trend in color and COD has been observed also in the surface water abstracted by Kvarnagården WTP.
The water arriving at the water works is less colored than the surface water, due to the addition of groundwater. No significant reduction of humic substances is achieved with the current treatment process at Kvarnagården WTP, because the drinking water guidelines were complied with using filtration and disinfection only. Due to long-term trends in the raw water quality, as well as new demands on the microbiological barriers, a pilot scheme was initiated that includes ultrafiltration in combination with coagulation for enhanced NOM removal. The effects on NOM concentrations and composition were investigated by far-reaching NOM characterization from source to tap. As a co-owner of the municipal water plant, Ringhals has been involved in various pilot studies of the effects on their desalination.

**Kvarnagården WTP: Existing treatment process**

Kvarnagården WTP, located in Varberg, is the largest municipal water treatment plant for the municipality of Varberg. The facility is owned mainly by VIVAB, a municipal company. VIVAB is responsible for operation and maintenance of the municipal water supply, waste
water treatment and waste disposal management. The raw water (80% surface water and 20% groundwater) is transported in a 20 km long pipeline from the water source to plant. The difference in elevation between the surface water source and the water plant is about 70 m, which allows energy recovery by a water turbine. The produced electric energy, in average 65 kW, corresponds to one third of the energy required for plant operation. The treatment process includes:
- pH adjustment with lime and carbon dioxide
- Rapid sand filtration
- Disinfection (Chloramines followed by UV irradiation)

Kvarnagården WTP produces drinking water for approximately 45,000 people. The average production is 14,000 m³ per day, and max. 25,000 m³ per day.

**Process scheme: Kvarnagården Water Treatment Plant**

**Desalination at Ringhals**
Two identical ion exchange plants for each reactor block, with subsequent polishing by reverse osmosis produce ultrapure feed water for plant operation.

**Process scheme: Desalination**
The resins are operated according with upstream flow, reversed during regeneration by sulfuric acid (cation exchanger) or sodium hydroxide (anion exchanger). The outlet from the ion exchanger is treated in an RO plant for further reducing of conductivity and TOC contents. To meet current regulations for corrosion and security, TOC concentrations may not exceed 50 ppb in the permeate from reverse osmosis.

**METHODOLOGY**

A chronological summary of trials and research activities at Ringhals and Kvarnagården WTP is shown below:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Description of trial</th>
<th>Period</th>
<th>Activities</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Ringhals: Trials– optimization of internal water treatment</td>
<td>2009 - 2010</td>
<td>Ringhals: various pilot trials for improved desalination</td>
<td>AOT and membrane processes</td>
</tr>
<tr>
<td>1</td>
<td>NOM-characterizaton: A Winter</td>
<td>8-10 February 2009</td>
<td>Water source – WTP - Ringhals</td>
<td>Reference Sampling: municipal drinking water treatment and desalination process at Ringhals</td>
</tr>
<tr>
<td>2</td>
<td>Kvarnagården WTP: UF-pilot trial</td>
<td>June 2010</td>
<td>Commissioning of UF-pilot trial</td>
<td>UF-pilot plant: Micro-filter and UF membrane module</td>
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<tr>
<td>3</td>
<td>NOM-characterizaton: B Autumn UF without coagulation</td>
<td>16 November 2010</td>
<td>Surface water – UF-pilot –water treatment (nuclear power plant)</td>
<td>Ultrafiltration with pretreatment (micro-filter)</td>
</tr>
<tr>
<td>4</td>
<td>Ringhals/Kvarnagården WTP Ion exchange: pilot trials</td>
<td>Nov.-Dec. 2010 A: 3-5 November B: 1-3 December C: 8-10 December D: 15-17 December</td>
<td>Ion exchange pilot trial Existing desalination at Ringhals, UF with pretreatment at Kvarnagården</td>
<td>A: Existing process (Ringhals) B: Permeate from UF-pilot C: Permeate from UF-pilot D: Existing process (Ringhals)</td>
</tr>
<tr>
<td>5</td>
<td>Kvarnagården WTP: UF-pilot with coagulation prior micro-filter</td>
<td>March 2011</td>
<td>Coagulation and UF Precipitation prior pretreatment</td>
<td>Various trials with precipitation prior micro-filter</td>
</tr>
<tr>
<td>6</td>
<td>Kvarnagården WTP: UF-pilot with direct coagulation</td>
<td>April 2011</td>
<td>Coagulation and UF: Direct precipitation on the membrane (no pretreatment)</td>
<td>Various experiments with direct precipitation prior membrane module</td>
</tr>
<tr>
<td>7</td>
<td>NOM-characterizaton: C Spring UF with coagulation</td>
<td>18 April 2011</td>
<td>Surface water – UF-pilot –water treatment (nuclear power plant)</td>
<td>Ultra-filtration with pretreatment and with coagulation</td>
</tr>
<tr>
<td>8</td>
<td>Ringhals/Kvarnagården WTP Ion exchange: pilot trials</td>
<td>April-May 2011 A: 11-14 April B: 2-5 May</td>
<td>Ion exchange: pilot trial ○ UF without pretreatment/with coagulation</td>
<td>A: Permeate from UF-pilot with coagulation B: Permeate from UF-pilot with coagulation</td>
</tr>
<tr>
<td>9</td>
<td>NOM-characterizaton: D Ion exchange: pilot trials</td>
<td>3 May 2011</td>
<td>Ion exchange: pilot trial Permeate from UF with coagulation</td>
<td>Sampling from cation exchanger, CAT, SBA, WBA and MB</td>
</tr>
</tbody>
</table>

**Pilot Plants**

In cooperation between Ringhals and VIVAB two different pilot plants were used for common trials on improving water treatment.

**Pilot Plant for Ion exchange**

The test facility was designed to simulate full-scale process as far as possible. The pilot plant consisted of four ion exchange columns, using same ion-exchange resins as the full-scale plant.
Table: Plant characteristics

<table>
<thead>
<tr>
<th>Process design</th>
<th>Desalination (full-scale)</th>
<th>Pilot plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (l/h)</td>
<td>59 000</td>
<td>26-30</td>
</tr>
<tr>
<td>Resin bed volume per time unit (l)</td>
<td>14</td>
<td>13-15</td>
</tr>
</tbody>
</table>

Process scheme for the pilot plant: ion exchanger

![Image: Pilot plant for desalination]

The conductivity of the filtrate from anion and mixed bed resins was monitored online.

Image: Pilot plant for desalination

Pilot plant for ultrafiltration

The test facility consisted of three process steps:
- In-line coagulation (optional)
- Pre-filtration
- UF

The pilot plant was fully automated and equipped with various sensors for on-line measurement of pressure, temperature, flow, turbidity. Collection of data, process monitoring and remote control were achieved by connecting to the SCADA system of water works. Feed water for the test facility was taken directly from the incoming raw water pipe, in order to obtain representative experimental results in terms of composition and pressure of the raw
water. Coagulants could be added flow proportional to the raw water with subsequent static mixing.

Image: Dosing pump, static mixer

Dosing pump for addition of coagulants

Static mixer for optimum reaction time

Pre-filtration was done with a pressurized fiber-filter, 3FM ® (Flexible Fiber Filter Module), with a cut-off of 5-10 microns. The fiber-filter was backwashed with raw water and pressurized air after predefined intervals. It was possible to bypass the pretreatment for specific test runs.

Image: Pretreatment, valves for process settings

Pretreatment: fiber-filter

Flexible polyamide fibers

Inlet valves in front of the UF-pilot

The filtrate from the fiber-filter or non-pretreated raw water passed first through a cartridge filter (150 microns), and finally a pressurized ultrafilter. Both the pretreatment and the UF pilot plant had a maximum capacity of 6 m³/h, corresponding to approximately 1 % of incoming average daily flow to the full-scale plant. The UF pilot plant was equipped with a Koch HF 10-48-35-PMPW membrane module, containing 20,000 fibers with a diameter of 0.9 mm. The membrane material is polysulfone with a nominal Molecular Weight Cut-off (MWCO) of 100,000 Daltons, corresponding to a pore size of 0.05 microns. The membrane area of the pilot module was 52.4 m² and the maximum allowable flux 115 l/m²*h. The maximum allowable Trans Membrane Pressure (TMP) was 2.4 bar.

The pilot plant offered three operating modes for ultrafiltration:
I. Dead-end filtration
II. Cross-flow with flow proportional retentate outlet
III. Cross-flow with periodic retentate outlet
In operation mode II and III, raw water was recirculated in the membrane module to increase the flow rate over the membrane surface. Backwashing was carried out automatically at
preselected intervals, with or without chemicals. Citric acid, sodium hypochlorite or sodium hydroxide were used for Chemically Enhanced Backwash (CEB) and for membrane Cleaning in Place (CIP). A typical frequency for CEBs was 60 min with alternating acidic backwash (pH ~ 3) and alkaline backwash (pH ~ 12). CIPs were performed only at critical events of increasing TMP (transmembrane pressure), or between specific test runs to reset the start conditions for membrane.

Image: UF-pilot plant, dosing pumps for CEB

Raw Water Quality
Monitoring of raw water quality has been as follows:
1. Continuous monitoring of surface water in the inlet chamber at the lake
2. Weekly sampling of surface water and mixed raw water (surface and ground water)
3. Far-reaching NOM characterization from water source to tap by extensive measurement campaigns at different seasons and test runs

Continuous monitoring of surface water quality:
In September 2010, a measuring station was installed in the intake chamber to the surface water source for continuous monitoring of the raw water quality. Data from submersible probes were recorded every minute for the following parameters:
- UV absorption at 254 nm
- Turbidity
- Oxygen
- Temperature
The measuring station was connected to the SCADA system of the water plant, which enables monitoring of current values by graphical interface and process flow schematic. The online measurements have been stored in a database for evaluation of seasonal variations in surface water quality.

Image: InSitu probes in the inlet chamber for surface water

Submersible probes
UVAS-probe for UV254 measurement
Maintenance with sc1000 Display module
**Weekly water analysis:**
Weekly analyses of raw water and of various samples from pilot trials have been conducted with respect to the following parameters:
- Color
- Turbidity
- COD, TOC, DOC, UV absorbance (254 nm)
- SUVA (UV absorbance/DOC) as calculated index value
- Fe and Mn

**Advanced characterization of NOM by liquid chromatography:**
On three occasions, sampling for NOM characterization was conducted from water source to tap, and beyond. Sampling dates were chosen based on seasonal characteristics, and the test runs of the UF pilot plant. On one occasion, NOM analysis was performed of various water samples from the pilot plant for desalination. NOM characterization of the water samples was carried out by a specialized laboratory, DOC-Labor Dr. Huber in Karlsruhe, Germany. For analysis of NOM, DOC-LABOR used LC-OCD (Liquid chromatography – Organic Carbon Detection). Size-Exclusion Chromatography combined with three detectors is applied to subdivide the pool of organic matter in the water samples into six major sub-fractions which can be assigned to specific classes of compounds:
- Biopolymers
- Humic Substances
- Building Blocks
- Low Molecular-weight Acids
- Low Molecular-weight neutrals

The nitrogen contents of the Biopolymers and the fractions of the Humic Substances (HS) are estimated. By using a specific HS-diagram which illustrates the aromaticity of HS against its nominal molecular weight, the HS may be further characterized. The HS-diagram gives information about the origin of the water sample, replacing the operational distinction between humic and fulvic acids by a continuum. According to DOC-LABOR, the LC-OCD-OND is a robust method with sufficient sensitivity to measure low NOM-waters directly, such as demineralized waters and RO permeates.

**Tests with ion exchangers (Ringhals and Kvarnagården)**

**Approach**
Pilot tests with ion exchangers were conducted with several feed waters:
- Municipal drinking water after storage at Ringhals
- Permeate from ultrafiltration with pre-filtration
- Drinking water from the municipal drinking water plant (before distribution)
- Permeate from ultrafiltration in combination with pre-coagulation

Each test was repeated twice, but only the results from the second run are reported. During the first run the equipment of the pilot plan was controlled in terms of reliable flow regulation.

**Regeneration of resins**
The cation resin was replaced after each trial. The mix polishing bed was not reconditioned between the runs, due to low load with high salinity. The anion resin was regenerated by sodium hydroxide (3.5% solution, 80°C) after each run. Finally, the resin was washed with RO permeate until the conductivity was below 0.5 μS/cm in the outlet of the anion column.
Conductivity

During the test runs conductivity was recorded with on-line sensors in the outlet from the SBA and the MB columns. The data were automatically collected and aggregated every ten minutes by an internal logger. Incoming water was measured with a portable conductivity meter.

Test program

<table>
<thead>
<tr>
<th>Test run</th>
<th>Location</th>
<th>Feed water</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>Ringhals</td>
<td>Incoming drinking water</td>
<td>New ion-exchange resins</td>
</tr>
<tr>
<td>Test 2</td>
<td>WTP</td>
<td>Permeate from UF-pilot plant without coagulation</td>
<td>Replacing of CAT resin, Regeneration of anion resin</td>
</tr>
<tr>
<td>Test 3</td>
<td>WTP</td>
<td>Outlet – drinking water</td>
<td>Replacing of CAT resin, Regeneration of anion resin</td>
</tr>
<tr>
<td>Test 4</td>
<td>Ringhals</td>
<td>Incoming drinking water</td>
<td>Comparison of new and used anion resins</td>
</tr>
<tr>
<td>Test 5a/5b</td>
<td>WTP</td>
<td>Permeate from UF-pilot plant with coagulation</td>
<td>New ion-exchange resins, Comparison with test run 2</td>
</tr>
</tbody>
</table>

UF-pilot trial (Kvarnagården WTP)

Approach

Pilot tests were carried out with different operating modes and in combination with coagulation:

- Operating Mode 3 (cross-flow with periodic retentate outlet), without coagulation
- Operating Mode 3, pretreatment by fiber filter, without coagulation
- Operating Mode 3 and direct precipitation without pretreatment

Process scheme: UF-pilot plant (SCADA Graphical Interface)
Coagulation

A Poly Aluminium Chloride (PAC) product\(^1\) was chosen as coagulant, based on results of initial laboratory tests. The feed rate of coagulants during the pilot trials was 1g Al per cubic meter of raw water. The coagulant was dosed in-line, with a residence time in the pipe larger than 1 minute. Rapid mixing of the coagulant was achieved with a static blender. There was no pH-adjustment required in conjunction with coagulant dosing. The correct addition of coagulants was monitored by on-line pH measurement.

Process scheme: Pretreatment and coagulation (SCADA Graphical Interface)

RESULTS

Evaluation of ultrafiltration with coagulation (general NOM parameters):

Consisting of rapid filtration and disinfection, the existing water treatment process at Kvarnagårdens WTP had no noteworthy impact on bulk parameters of NOM.

Figure: Comparison of inlet and outlet, WTP

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\(^1\) PlusPac 1465 (Al-content: 7.3%, basicity: 64%)
Pre-coagulation prior to UF (pilot plant) had a considerable clear effect on color in the permeate. Weekly samples indicated a significant reduction in NOM. The SUVA-index was calculated by dividing the UV-absorbance at 254 nm with DOC concentration. A higher value means a higher content of aromatic compounds and vice versa. SUVA less than 3 indicates mostly hydrophilic materials with low molecular weight (can cause problems for precipitation processes). SUVA greater than 4: indicates the content of hydrophobic and aromatic NOM fractions with high molecular weight (more suitable for removal by precipitation processes). In this case, the calculated index value is between 3 and 4. Pre-coagulation predominantly removed humic substances, which resulted in a low SUVA in the pilot trials with pre-coagulation.

### Table: Composition of raw water and UF-permeate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Surface water inlet</th>
<th>Prior micro-filter</th>
<th>After micro-filter</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour (mg Pt/l)</td>
<td></td>
<td>16</td>
<td>8</td>
<td>11</td>
<td>8</td>
</tr>
<tr>
<td>Turbidity (PU)</td>
<td></td>
<td>0.20</td>
<td>0.20</td>
<td>0.30</td>
<td>&lt;0.10</td>
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<tr>
<td>COD (mg/l)</td>
<td></td>
<td>3.1</td>
<td>2.1</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>DOC (mg/l)</td>
<td></td>
<td>3.6</td>
<td>2.4</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>UV254 S cm cuvette</td>
<td></td>
<td>0.511</td>
<td>0.467</td>
<td>0.402</td>
<td>0.367</td>
</tr>
<tr>
<td>UV254 mg/l</td>
<td></td>
<td>10.22</td>
<td>8.14</td>
<td>8.04</td>
<td>7.34</td>
</tr>
<tr>
<td>SUVA* (mg l^-1 m^4)</td>
<td></td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Fe (mg/l)</td>
<td></td>
<td>0.036</td>
<td>0.047</td>
<td>0.033</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Mn (mg/l)</td>
<td></td>
<td>&lt;0.01</td>
<td>0.001</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al (mg/l)</td>
<td></td>
<td>0.08</td>
<td>0.20</td>
<td>0.044</td>
<td>0.044</td>
</tr>
</tbody>
</table>

* DOC = 2.0 corresponding to <2.0 mg/l (below detection limit)

NOM characterization of raw water and membrane permeates

**NOM characterization "A":**

In February 2009 a sampling program was conducted including samples from the water source, water treatment plant and water treatment as well as membrane experiments at Ringhals (see Appendix A)
Raw waters (drinking water plant and Ringhals)

The incoming raw water to the drinking water plant (Kvarnagården WTP) and the incoming drinking water to Ringhals are very similar in composition. Humics are pedogenic fulvic acids but at the “higher end” in the HS-Diagram (see Appendix B). This means that humics also contain humic acids to some content (perhaps 30%). This is important because humic acids may precipitate in the ion exchange plant’s cation filter.

Treatment at water works and supply to Ringhals

The sand filter at Kvarnagården WTP selectively removes biopolymers, possibly an indication of biological activity. There is almost no difference between Ringhals and after sand filtration at WTP.

The disinfection step at Kvarnagården WTP has very little impact on NOM. Generally, chlorination may lead to a bleaching of humics and sometimes formation of organic acids. Some bleaching was observed (aromaticity: 5.12 before disinfection [B], 4.95 after disinfection [C]). Acids are slightly higher (13 ppb instead of 10 ppb). Altogether, there is no significant NOM removal in treatment process at Kvarnagården WTP. Also, the reservoir for storage of drinking water at Ringhals has no impact on NOM.

Demineralization (full-scale filters at Ringhals)

Cation Filter (CAT):

Ideally the Cation Filter should have no impact on NOM, because there are no organic cations in NOM. Reduction of NOM after cation filter is a matter of concern. As mentioned above the feed water contains humic acids which are not stable at low pH and may precipitate. This fact is observed in these samples: Humics are reduced by about 250 ppb compared with inlet water to Ringhals. The position of humics shifts to the lower left in HS diagram which shows that humic acids precipitated and are trapped in the cation filter.

Weak Bed Anion-Filter (WBA):

The results indicate the presence of humic-like material which is characterized by higher molecular weight. This findings do not fit in the HS-diagram. According to the results the humic-like material breaks even through Strong Bed Anion filter (SBA) and Mixed Polishing Bed (MB). A possible explanation for this phenomenon could be the humic acid material which precipitated in the cation filter (100 - 300 ppb). As this material is not truly dissolved after cation filter it is not removed in the anion filters.

Operational conditions: High Conductivity – Low Conductivity:

High conductivity was found after SBA where “humic acids” where highest: 226 ppb instead of 113 ppb for low conductivity. Increase in conductivity is probably caused by these “humic acids”.

As conductivity depends on the state of re-dissolution the variation of conductivity is time-depended. Moreover, as “humic acids” are higher in SBA than in WBA there is an “over-concentration” reflecting episodic or intermittent increases and decreases of conductivity. This impact is quite normal for not-dissolved matter.

RO-performance:

The full scale RO removes “humic acids” and biopolymers. The “humic acids” in the RO-feed are so high in molecular weight that they cannot be depicted in the HS-Diagram. According to DOC-Labor, this suggests that humic acids aggregated to larger units due to high concentration. Even the Pilot scale RO removes all humics and biopolymers. The membrane extract also is humic acid material of extremely high molecular weight. Thus humic acids are responsible for blocking of the membrane. The permeate is of high quality (DOC 18 ppb).
NOM characterization "B" and "C":
In November 2010 and April 2011 extensive sampling programs were conducted with focus on seasonal variations and permeate quality from ultrafiltration in combination with coagulation (see Appendix C and D).
According to DOC Labor, the comparison of data for the two different sampling dates shows in general a similar situation.

A. An oligotrophic surface water low in biopolymers and low in nitrate (not quantified).
B. An excellent ground water free of biopolymers, no nitrate but traces of ammonium (not quantified).
C. Mixed raw water of A+B, the dominant part is apparently A (about 80%).
D. Identical to C. Changes in “HOC” are due fluctuations in the amount of nanoparticles.
E. Identical to C. Changes in “HOC” are due fluctuations in the amount of nanoparticles.
F. Identical to C. Changes in “HOC” are due fluctuations in the amount of nanoparticles.
G. Identical to C, but biopolymers decreased with 16 -14 ppb in comparison to F. Most biopolymers are <100 kD (=MWCO).
H. Almost identical to C: Slight reduction in LMW-neutrals may reflect microbial activity in the sand filter.
I. Impact is low: Nanoparticles “HCO” are partly destroyed which leads to slight increases in some fraction, also some LMW-acids are produced. No bleaching of humics is observed.
J. Identical to I.
K. Similar to J. Increase in “HOC” suggests aggregation of dissolved matter to nanoparticles, a common phenomenon.
L. Biopolymers break fully through, which is normal. The presence of humics is unusual.

The outlet after MB shows humic-like matter which suggests a fouling issue with humics. The present humics in the water reservoir at Ringhals are in the area of pedogenic FA type. This shows that some of this humic-like material is of humic acid type which is not stable at low pH. In the cation filter it will precipitate and will impair the performance of the cation filter. In addition, humic acid “flakes” will break through the entire de-min train and will slowly re-dissolve to create a fouling problem for all anion filters. This could explain the presence of humics in the water after MB. These humics are of very high molecular weight and reflect humic acids. However, observed humic acids are too low in aromaticity which is unusual. There is an alternative that it is not humic acid matter but polystyrenesulfonate (PSS) material from cation resin(s). Additional analysis would be necessary to get more specific results.

Ion exchanger pilot tests
The pilot plant was found to be very sensitive to flow variations, which resulted in large variations of conductivity. For example, a low flow rate over the ion exchanger resulted in a long residence time in the resins and low conductivity in the outlet of each column. An excessively low flow however may disturb ion exchange. Both ion-exchange resins became progressively darker during the test period. The time for restoring the conductivity to 0.5 µS was increasing after each flushing of the weak anion resin with sodium hydroxide.

<table>
<thead>
<tr>
<th>Test</th>
<th>Temp. (°C)</th>
<th>Cond, (µS/cm)</th>
<th>CondSBA (µS/cm)</th>
<th>CondMB (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>175</td>
<td>~ 0.08</td>
<td>~ 0.07</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>129</td>
<td>0.15-0.20</td>
<td>0.20-0.25</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>188</td>
<td>0.10-0.15</td>
<td>0.15-0.20</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>~ 0.10</td>
<td>~ 0.15</td>
</tr>
<tr>
<td>5a</td>
<td>7</td>
<td>128</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>5b</td>
<td>7</td>
<td>128</td>
<td>0.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>
During Test 1 and 2, the conductivity was lower after the MB compared with the SBA. In test 2, conductivity increased at the start of the operation cycle and stabilized afterwards (Appendix E). This sequence illustrates exactly the same operational problem as noted in the full-scale plant for desalination at Ringhals.

During Test 3, the ion exchanger was operated with drinking water from the WTP (before distribution), in order to compare the quality of the incoming drinking water at Ringhals (Test 1). Heavy flux variations during the test run resulted in a decrease of conductivity at the end of the trial period. Despite the variations in flow it reveals a trend of higher conductivity after MB compared with the SBA.

Test 4 corresponded to test 1, with the exception that the exchange resin had not been changed. The trend data for conductivity corresponded to process conditions and operational problems of the full-scale desalination facility.

In Test 5, the UF was applied with coagulation for improved NOM removal. In both trials the conductivity after MB was very low and stable throughout the operation cycle. Even the outlet of the anion exchanger showed a stabilization of conductivity, until the resin was depleted. There was no evidence of impaired function of the ion exchange resins.

**DOC characterization of Demineralization Pilot Plant (DeminPP)**

After the promising test results from the test run 5a, an extended DOC characterization of ion exchange process was conducted during the trial 5b (NOM characterization "D").

**Sampling points:**
- Incoming water to DeminPP (feed water: permeate from UF-pilot with pre-coagulation)
- Weak Base Anion outlet, WBA, (ion exchange pilot)
- Strong Base Anion outlet, SBA (ion exchange pilot)
- Mixed Polishing outlet, MB (ion exchange pilot)

**Incoming Water to DeminPP**

Regarding the position of humics in the HS-diagram (Sample label A in Figure 1, Appendix G), the pre-treatment of raw water by UF with pre-coagulation indicates an efficient removal of NOM. Also biopolymers have been removed to a greater extent compared to previous similar samples with ultra-filtration only (2010.11.16). Based on the NOM composition, the permeate seems to be very suitable as feed water for subsequent desalination process (see Appendix F).

**Weak Base Anion Outlet (WBA)**

Humics and building blocks are quantitatively removed, biopolymers are also reduced. As expected, the WBA is not capable to remove low-molecular weight organic acids (LMW-acids).

**Strong Base Anion Outlet**

According to expectations, there has been a significant removal of LMW-acids. The low content of DOC (60 ppb) is remarkable for a surface water prior to RO.

**Mixed Polishing Outlet (MB):**

No further improvement of water quality after the MB has been noticed, due to the excellent inlet (SBA outlet).
CONCLUSIONS

- Analyses of raw water for the past ten years indicate a slow browning of surface water.
- NOM characterization indicated oligotrophic surface water with low concentrations of biopolymers. No seasonal variations in NOM composition were found.
- The presence of NOM fractions in municipal drinking water caused organic fouling of ion exchange resins, which reduced the capacity of the existing full-scale desalination at the Ringhals power plant.
- NOM characterizations indicate a pH-related precipitation of humic substances on the cation ion-exchange resins. These humic fractions are eluting in an uncontrolled manner, leading to increased conductivity in the ultrapure water.
- Pretreatment of raw water with ultrafiltration (100,000 Dalton) had no positive effect on desalination.
- Ultrafiltration combined with coagulation resulted in a significant NOM-removal, resulting in significantly decreased fouling of the ion exchange resins.

RECOMMENDATIONS AND NEXT STEPS

The choice of future treatment processes for upgrade of Kvarnagården WTP is depending on the following factors:

- Increasing humus content in the surface water source, and fouling problems in the production of ultrapure water at Ringhals power plant.
- More stringent requirements for microbial risk assessment and microbial monitoring of drinking water.

On the basis of pilot plant trials, it should be considered to complement the existing treatment process at Kvarnagården WTP by ultrafiltration with pre-coagulation. Existing sand filters can be used for pre-treatment. Coagulation may be applied on demand (seasonal - or weather dependent), but the results indicate that the stable operation of ion exchange resins may require coagulation all year round.

The proposed upgrade meets the following requirements:

- Multiple microbial safety barriers: precipitation (over existing sand filters, or directly on the UF membrane), separation (UF membranes) and inactivation (UV irradiation)
- Preparedness for future deterioration of raw water quality by enhanced NOM-removal
- Reducing the risk of regrowth in pipes
- Disinfection with chlorine can be reduced
- Improved “raw water quality” at Ringhals (positive effects on desalination processes)

For upgrading of WTP the following is proposed:

- Performance data of pilot trials to be used as the basis of enquiry/procurement and future life-cycle cost assessments.
- Procurement of full-scale UF plant facilities by retrofit of the existing plant.
- The purchasing process will proceed in two steps: (a) selection of appropriate contractors and (b) invitation of tenders for quote.
- The target date for completion of the retrofitted WTP is December 2014.
ACKNOWLEDGMENTS
As in any pilot demonstration project, many contribute to the success of the project and for these contributions we are very grateful. We would like to make special mention of the following:

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Anders Éden, SCADA-specialist, VIVAB
Jan-Olof Lundin, technician, VIVAB
Folke Lundquist, technician, VIVAB
Roland Hotz, commissioning engineer, Björks Rostfria AB
P-O Björk, CEO, Björks Rostfria AB

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APPENDIX

A Table: NOM Characterization, February 2009
B Humic Substances Diagram, February 2009
C Table: Comparison of LC-OCD-chromatograms, UF-pilot trials
D Table: Comparison of Humic Substances Diagrams, UF-pilot trials
E Figure: On-line Operational Output of Conductivity, Ion exchanger Pilot Trial
F Table: Characterization of ion exchange tests with permeate (Ultrafiltration with
coagulation)
G Humic Substances Diagram, Ion exchangers Pilot Trial
### A. Table: NOM Characterization, February 2009

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DOC</th>
<th>DOC</th>
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<tr>
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<td>1.4</td>
<td>0.6</td>
<td>1.4</td>
<td>0.6</td>
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**Sample description:** NOM Characterization, February 2009

3 samples from the municipal water treatment plant in Ytberg

B. Outfall of the sand filters

C. Final outlet from the treatment plant after disinfection treatment

D. Incubation from the municipal treatment plant 25 km away to check pipe influence

E. Outlet of reservoir No 1 supporting Demin plant No 1

F. Outlet of reservoir No 2 supporting Demin plant No 2

8 samples from the demin-plants production, showing the conductivity problem

O. Cation resin bed outlet (High Conductivity)

P. Weak anion bed outlet (High Conductivity)

R. Strong Anion bed outlet (High Conductivity)

T. Mixed polishing bed outlet (High Conductivity)

U. Cation resin bed outlet (Low Conductivity)

W. Weak anion bed outlet (Low Conductivity)

M. Strong Anion bed outlet (Low Conductivity)

N. Mixed polishing bed outlet (Low Conductivity)

4 samples from the RO treatment plants

Q. RO-Concentrate from the full-scale reverse osmosis system downstream the demin plant

R. RO-Concentrate from the pilot scale RO-system upstream the Demin Plant

S. RO-Fracwater from the pilot scale RO-system upstream the Demin Plant

T. One of the pilot plants RO-membrane was opened for investigation of minute cleaning agents and some of the brown jelly precipitate within the membranes were collected and frozen.

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B. Table: Humic Substances Diagram, February 2009

[Diagram of humic substances with various samples and pathways labeled.]

- Humification Pathway
- Molecularity
- Building Blocks
- M, in g/mol
- SAC/OC(HS) in L/(mg·m)

Sample descriptions from table 1:
- Humification Pathway
- Building Blocks
- M, in g/mol
- SAC/OC(HS) in L/(mg·m)
C. Table: Comparison of LC-OCD-chromatograms, UF-pilot trails

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<tr>
<th>Project</th>
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<td>91-100</td>
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UF-pilot trials in combination without coagulation  UF-pilot trials in combination with coagulation
D. Table: Comparison of Humic Substances Diagrams, UF-pilot trials

**UF-pilot trials without coagulation**

16.11.2010

**UF-pilot trials with coagulation**

18.04.2011
E. Figure: On-line Operational Output of Conductivity, Ion exchanger Pilot Trial

Test 1: Incoming drinking water at Ringhals (new ion exchange resin)

Test 2: Permeate from UF-pilot without coagulation

Test 3: Drinking water from WTP (outlet)

Test 4: Incoming drinking water at Ringhals (old ion exchange resin)

Test 5a: Permeate from UF-pilot combined with coagulation

Test 5b: Permeate from UF-pilot combined with coagulation
F. Characterization of ion exchange tests with permeate (Ultrafiltration with coagulation)

![Image of DOC LABORATORY results table]

<table>
<thead>
<tr>
<th>Project: Verti 27</th>
<th>DOC</th>
<th>MOC</th>
<th>CDOC</th>
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<tbody>
<tr>
<td>Ongoing Water Denise Plant</td>
<td>1985</td>
<td>127</td>
<td>1538</td>
</tr>
<tr>
<td>Weak Anion Outlet</td>
<td>100%</td>
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<td>92.4%</td>
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<tr>
<td>Strong Anion Outlet</td>
<td>100%</td>
<td>1.2%</td>
<td>98.8%</td>
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<tr>
<td>Mixed Polishing Outlet</td>
<td>100%</td>
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G. Humic Substances Diagram, Ion exchangers Pilot Trial

![Figure: LC-OCD chromatograms]

![Figure: Humic substances diagram]