

# NOM-removal by the SIX®-process

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## Abstract

Some waters can have elevated concentrations of dissolved organic carbon (DOC), especially sources like surface waters that are under the influence of secondary effluent, recreation, heavy population, farming and industry. In a number of locations in North-West Europe, for example the United Kingdom and Scandinavia, DOC levels are increasing over time most likely due to climate change effects and changes in land use. For these types of water, ion exchange (IX) is of interest as a pre-treatment because the removal of colour and DOC by IX will increase the efficiency of all downstream processes including; coagulation, membrane filtration, advanced oxidation processes (AOP) and granular activated carbon filtration (GAC). It will also lead to improved water quality (i.e. less by-product formation) and most likely improvements in biostability within the distribution network. Surface waters also contain suspended and colloidal matter making it nearly impossible to use standard state-of-the-art, fixed bed IX columns. This is because these beds will foul quickly (i.e., head loss build-up) with the suspended matter. When this happens, the IX bed starts to function as a filtration bed rather than as an adsorption media. The newly developed suspended ion exchange process SIX® (suspended ion exchange, PWN Technologies, Netherlands) presents an advanced solution for a world-wide challenge: how to remove natural organic matter (NOM/DOC) as a first step in surface water treatment to improve the efficiency of downstream processes and water quality. Besides the possibility to treat water that contains suspended matter another advantage is that the process has advanced to an economically and technically feasible process, requiring low contact times and small resin inventories and with a large tolerance for flow fluctuations. Depending on the water source, adding a relatively low concentration of coagulant after IX removes even greater quantities of DOC, especially in the fraction of the high molecular weight organic carbon (whilst the IX primarily removed the humic and fulvic organic fractions). The most important advancement is that almost any commercially available resin can be used, creating the desired flexibility in resin suppliers for water supply companies. This paper describes the process and its advantages and disadvantages compared to conventional technologies. NOM-characterisation with size exclusion chromatography, liquid chromatography – organic carbon detection (SEC/LC-OCD) before and after this process showed the outstanding performance of the process, especially on water types which contain high colour/DOC-concentrations and low total dissolved solids, which are typical of the majority of the surface waters in the North-West of Europe.

## Keywords

NOM-removal, DOC-removal, ion exchange, SIX, LC-OCD

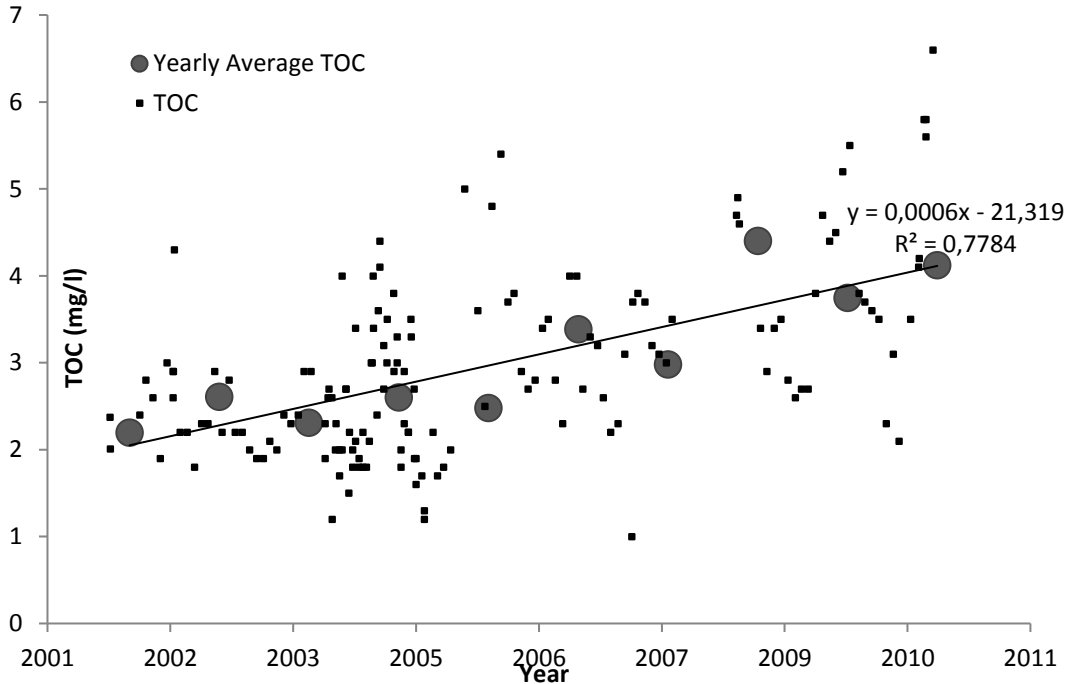
## BACKGROUND

Natural organic matter (NOM) (also described as dissolved organic carbon (DOC) or dissolved organic matter (DOM)) describes a complex mixture of organic compounds, such as humic and hydrophilic acids present in natural water sources. Operationally, DOC is defined as comprising any organic compound passing through a 0.45 mm filter. The total amount of organic carbon prior to filtration is defined as the total organic carbon (TOC) concentration. The number of organic compounds present in surface water is effectively limitless, and it is thus impossible to provide a general chemical description of DOC. DOC might be harmless in itself but it can cause problems in the water treatment by reducing the efficiency of processes, i.e energy consumption for UV-processes (Martijn *et al.* 2010) or regeneration frequencies of carbon filters (Köhler *et al.* 2016) and by reacting with disinfectants (Metcalf *et al.* 2015) such as chlorine to form disinfection by-products (DBP's). The effect of DOC on water treatment processes and methods for DOC characterisation have been well described in the literature (see

almost whole reference list at the end of this paper). Previous research has shown that high DOC-concentrations negatively impact all water treatment processes. DOC-related challenges vary widely temporally and spatially but where DOC concentrations are elevated, or the organic compounds are difficult to treat, the outcomes are similar; Reduced efficacy of downstream treatment processes and issues with water quality such as elevated DBP concentrations and reduced biostability. Therefore, processes which can increase the removal of DOC provide potential benefits for water utilities to meet water quality and efficiency challenges. Four source waters in northwestern Europe experience elevated DOC concentrations, and the following descriptions showcase their specific challenges.

**South West Water, the United Kingdom**

South West Water (SWW) is a water utility in south-west England, providing water and sewerage services in Devon, Cornwall, and small sections of Dorset and Somerset. SWW owns and operates 29 water treatment works (WTWs) to serve approximately 1.6 million residents. The majority of water (~95%) is supplied from surface waters (rivers and reservoirs), with groundwaters only making up around 5% of the supplies. SWW continues to meet and/or exceed drinking water quality regulatory requirements, but strives to continue to improve the quality of water provided to their customers. As such, SWW is interested in new treatment technologies which can provide better water quality. One of the future challenges is related to significant increases in the concentration of DOC in UK surface waters during the last few decades (Matilainen *et al.* 2010; Ritson *et al.* 2014), linked to reduced acid deposition, elevated temperature, changes in land use, altered precipitation patterns and increased frequency of extreme weather events associated with climate change. A study by Evans *et al.* (2004) showed that the average DOC concentration of 22 UK surface waters increased by 91% over a 15 year period. SWW have observed similar increases to those documented by Evans *et al.* (2004), with the concentration of NOM in many of the surface waters they utilise significantly increasing over recent times.



**Figure 1** Increasing TOC of a south west UK upland reservoir over 10 years (2001-2010).

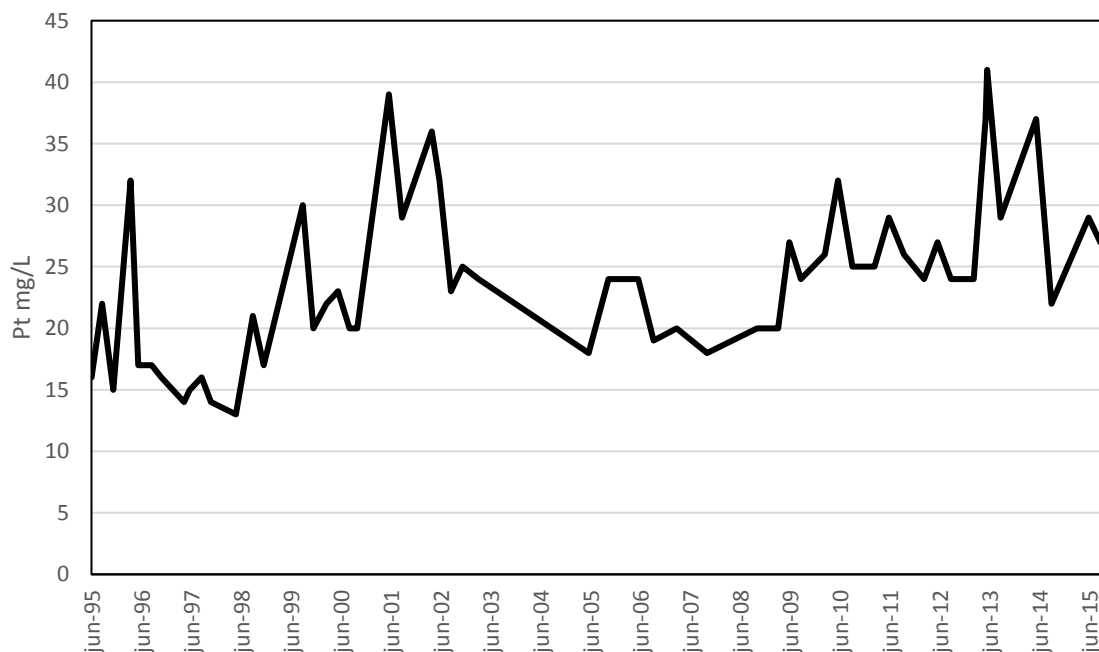
As an example, Figure 1 shows significant seasonal variation and a near doubling of the average total organic carbon (TOC) concentration during a ten year period (2001-2010) within one of the upland reservoirs that is treated by SWW. SWW has a long term strategic goal to build a new water treatment works (WTW) to replace the existing Crownhill WTW (Plymouth, UK). During the periodic review in 2014 (PR14), SWW reviewed and restated drinking water treatment goals for new WTWs to include:

- Provision of an absolute barrier to *Cryptosporidium*.
- Enhancement of water quality, particularly DOC removal and DBP reduction and effective removal of pesticides where present.
- Use of efficient design to realise improved operability (compact footprint, automation, reliability and robustness of processes).
- Sustainability (chemicals, energy, waste, life expectancy).
- Application of innovative, forward looking technology where applicable.

The two primary goals for the selection of treatment processes for the new WTW were driven the desire to provide an absolute barrier to *Cryptosporidium* and reduce DOC and DBP formation. These goals were in part related to the company's reliance on surface waters (95% surface water abstraction), the increasing challenge from raw water organic compounds and elevated *Cryptosporidium* risk related to the agricultural environment.

### Norrvatten, Sweden

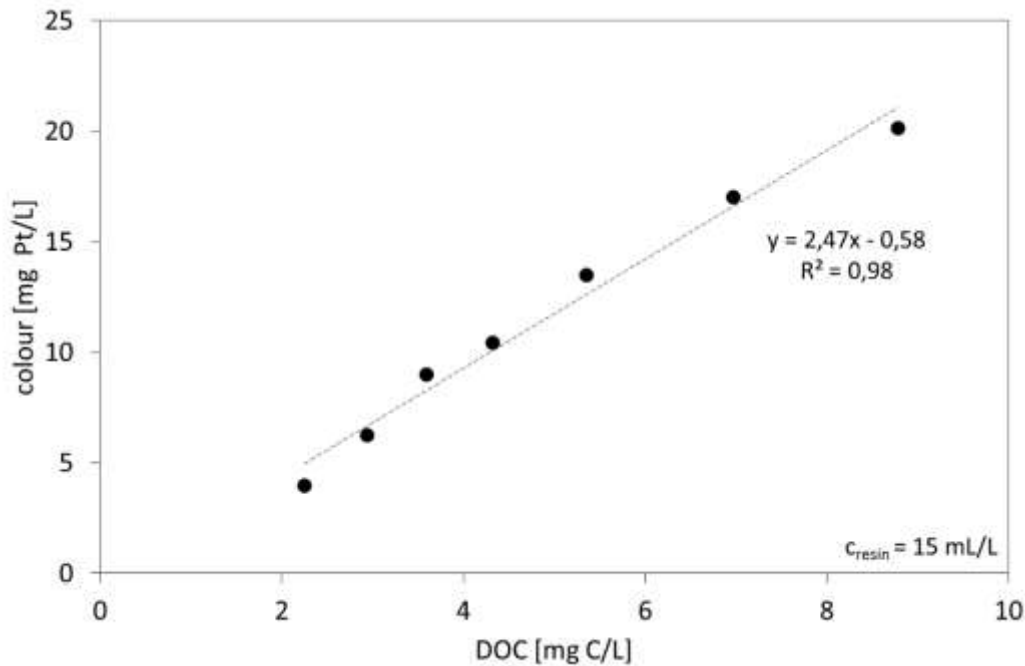
Water treatment plant (WTP) Görvålverket of Norrvatten (125MLD) produces potable water from surface water which is under the influence of secondary effluent, recreation, population, farm land and industry. The water source for WTP Görvålverket is Lake Mälaren, which has 1100 km<sup>2</sup> of surface area, and is one of the largest fresh water lakes in Europe and serves as the source for drinking water for almost two million people. Besides Norrvatten, Stockholm Water also uses this source for their potable water production. The current treatment process for WTP Görvålverket consists of a deep intake, micro-sieves, coagulation, sedimentation, sand filtration, carbon filtration, UV-disinfection followed by monochloramine and pH control with lime.



**Figure 2** Color in Pt mg/L at 0,5m depth in Lake Mälaren (Sweden) over the last 10 years

The biggest challenge that this current treatment process is facing is the increasing levels of DOC in the raw water which is not sufficiently removed by the coagulation process. Figure 2 shows the increasing trend in the concentration of colour in the Lake at 0,5 m depth (Lake Mälaren, Sweden) over the last 10 years. .

There is no historical data of the DOC concentration at the intake but recent experiments show that a good linear relationship exists between color and DOC (Figure 3). This indicates that for the last 6 years the DOC concentration is most likely on average around 10 mg/L or higher.



**Figure 3** Color as a function of residual DOC for Lake Malaren water during SIX<sup>®</sup> treatment with Lewatit S5128 (15 mL/L) (data derived from bench scale tests at 6-1-15)

The increased level of DOC at this site results in blinding and fouling of the GAC (Köhler *et al* 2016), which was developed as a treatment need when the micro contaminants started to increase during the late 1970s. The most likely cause of this increase in DOC concentration is related to climate change effects as well as changes in land use. Higher levels of DOC likely lead to inefficiencies with the existing treatment processes (i.e., coagulation, GAC and UV-disinfection) and are already responsible for reduced biostability in the network.

Norrvatten is currently investigating DOC removal with direct nanofiltration in collaboration with 4 other interested utilities in Sweden. The advantage of direct nanofiltration compared to coagulation, sedimentation and sand filtration according to Köhler *et al* (2016) is its compactness, high retention of DOC and absolute barrier against colloids (independent of capacity and raw water quality) and the retention of a few micro-contaminants. Possible disadvantages are related to controlling membrane fouling to enable acceptable permeability, recovery, membrane integrity, membrane lifetime, and life cycle costs. NOM is effectively removed by nanofiltration, but NOM also has high fouling properties for this membrane process. At the moment Norrvatten is seriously considering nanofiltration as a feasible supplement after the existing coagulation process, or if possible as an alternative for the coagulation, sedimentation and sand filtration however, they want to compare this option with another feasible alternative.

### **Scottish Water, the United Kingdom**

Scottish Water (SW) provides drinking water to 2.46 million households and 150,000 business customers in Scotland. Every day it supplies 1.34 billion litres of drinking water and takes away 847 million litres of waste water from customers for treatment prior to returning it to the environment. SW has 137 Water Treatment works, over 80% of which serve small rural communities across the Scottish Highland and Islands. Drinking water in Scotland comes from a number of sources including, upland reservoirs, rivers, springs and bore holes. All sources are treated to ensure that comply with the regulatory standards. The extent and type of treatment required depends on the nature of the supply, its quality and any potential risks to quality that are present. All water in Scotland supplied by SW is disinfected, normally by chlorine disinfection.

It is not uncommon for raw waters in Scotland to have relatively high concentrations of DOC, anything between 5 to 15mg/l would not be considered unusual and traditional coagulation and filtration techniques have proved an efficient treatment process for such water sources. However, where chlorine is used to disinfect potable water, NOM is recognised as the most important source of disinfection by product precursors. The characteristics of NOM are therefore of great importance. The efficient removal of DBPs precursors is essential to minimise subsequent formation of DBPs after disinfection. Different NOM fractions can also significantly influence the NOM removal efficiency of coagulation processes with hydrophilic, low molecular weight organics typically being recalcitrant to the process. The chemical and physical properties of NOM therefore play important roles throughout the water treatment process such as, coagulation, filtration and disinfection, both in terms of NOM removal efficiency and achieving DBP compliance at customer taps. Therefore, NOM fractionation techniques e.g. resin adsorption processes etc, are being used by SW to assess the NOM removal efficiency of treatment processes, the impacts of seasonal variations and the resulting DBP formation potential.

NOM fraction analysis has provided SW with new insights in the ability of traditional coagulation processes to remove the DBP precursors associated with certain NOM fractions. It became clear that, in some cases, there was a need to look at alternative processes to improve the NOM removal efficiency, especially the removal of low molecular weight humics, which can form DBPs during the disinfection process. Following further investigation with Cranfield University, Ion Exchange processes were identified as a treatment option that required further investigation and assessment at pilot plant scale was performed (Bond *et al.* 2011). A further challenge for Scottish water is that there are a large number of small WTW in remote rural areas, which are not always easily accessible. This means that treatment works need to be robust, reliable and efficient.

### **Water Supply Company PWN, the Netherlands**

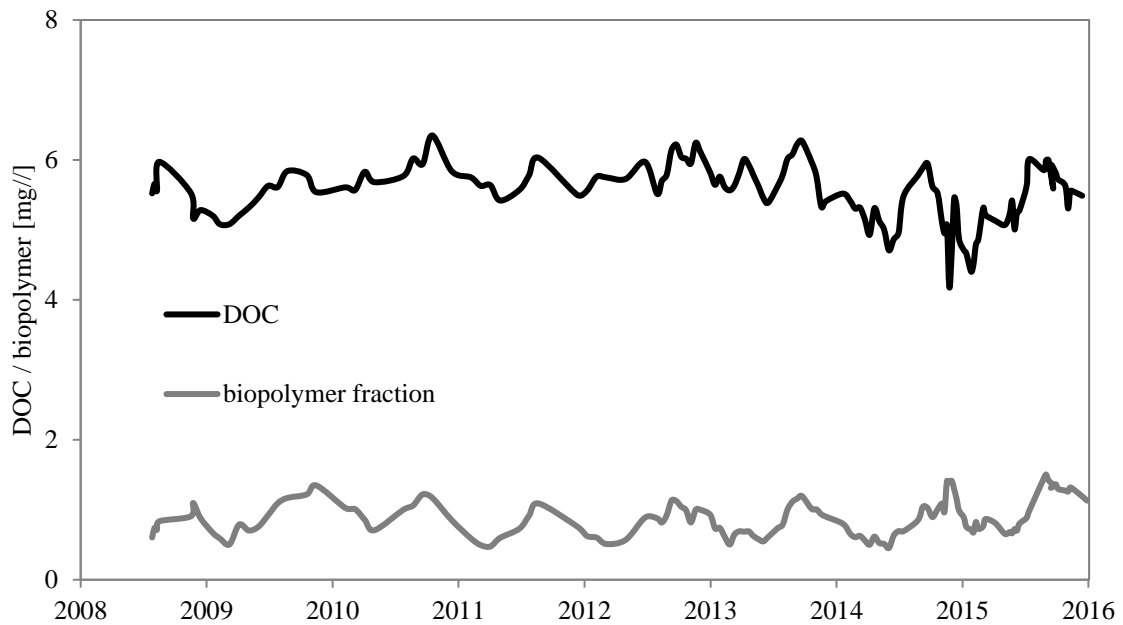
In 1920, when Water Supply Company North Holland PWN (PWN) was founded, the demand for drinking water was satisfied by ground water extraction. However, due to growing drinking water demand PWN was compelled to utilize surface water as an additional source. Therefore, in 1968 Water Treatment Plant Andijk (WTP Andijk) was constructed for the direct production of drinking water from the IJssel Lake (River Rhine). Originally the plant consisted of micro-straining, breakpoint chlorination, coagulation, sedimentation, rapid filtration and post disinfection with ClO<sub>2</sub>. In 1978 the plant was upgraded with pseudo moving bed GAC filtration. In the beginning of the 90's a minor improvement in water quality was made by softening in the raw water reservoir by dosing NaOH in the intake from the IJssel Lake to the reservoir,

followed by pH adjustment with CO<sub>2</sub> prior to the the micro-strainers. After almost 40 years of operation, WTP Andijk still complied with all Dutch drinking water standards. Nevertheless a second large upgrade was desired to install a universal barrier against pathogenic micro-organisms such as protozoa and organic micro pollutants such as pesticides (Kruithof *et al.* 2000). This retrofit included the world's first large scale application of advanced oxidation with UV/H<sub>2</sub>O<sub>2</sub> which became operational in 2004 (Kruithof *et al.* 2005). This advanced oxidation process is placed between the existing pre-treatment and the GAC filtration process. The GAC treatment provides removal of residual H<sub>2</sub>O<sub>2</sub> and easily assimilable organic carbon (AOC). Since the advanced oxidation with UV/H<sub>2</sub>O<sub>2</sub> requires a higher UV dose (compared to standard UV disinfection), superior disinfection is provided and breakpoint chlorination can be abandoned (Kruithof *et al.* 2000 and 2005). In a third phase the existing pre-treatment which still dates from 1968 was renewed. The desire to retrofit the pre-treatment was based on a few challenges:

- increase the UV-transmission (UVT) to improve the efficiency of the AOP;
- increase the removal of DOC to improve the efficiency of the AOP and to lower the formation of AOC;
- remove nitrate to improve the efficiency of the AOP and to lower the formation of nitrite;
- provide an absolute barrier to suspended and colloidal matter independent of the feed water quality;
- increase the overall capacity from 3000 to 5000 m<sup>3</sup>/h.

The requirement to remove all suspended matter quickly led to the idea of using micro- or ultrafiltration (MF/UF). A former PWN study (Galjaard *et al.* 2005) indicated that the direct treatment of IJssel Lake water with MF/UF was only possible after the removal of the low molecular weight (LMW) DOC fractions with an anion resin (at that time Magnetic Ion EXchange (MIEX<sup>®</sup>, Ixom Watercare, Australia previous Orica), which resulted in a high gross flux rate with almost no fouling. The use of anion exchange also increased UVT considerably and removed a large amount of nitrate and DOC.

The pre-treatment of ion exchange followed by MF/UF looked promising to fulfil the needs for the downstream-treatment and resulted in the first full scale SIX plant which has been in operation since 2014 (120 MLD, Andijk III WTW). At the moment research is still being conducted to see how the predicted increase in certain DOC fractions affects the process and what measures are possible to deal with any further increases in raw water DOC. Figure 4 shows the DOC concentrations at the WTW intake which reveals a recent increase in the high molecular weight organic fraction (biopolymers).



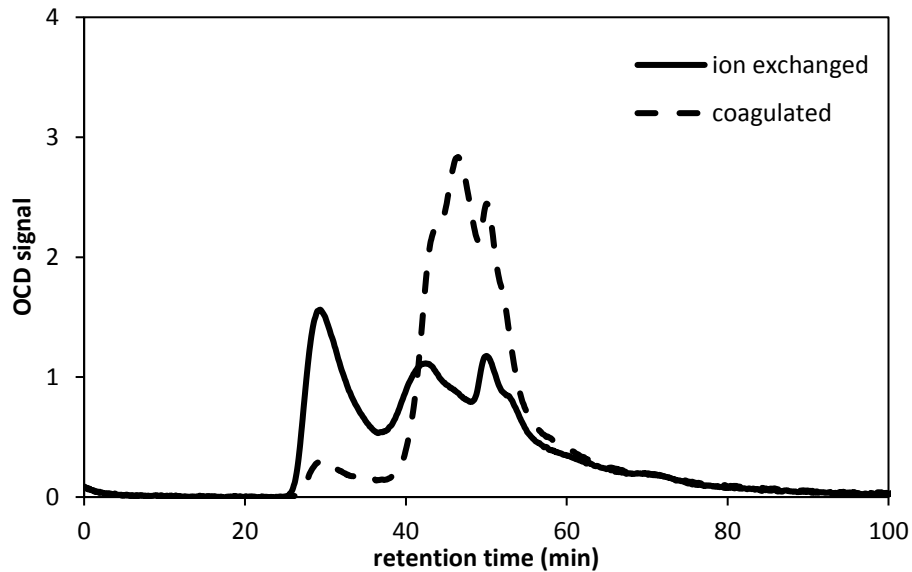
**Figure 4** DOC level ( $\mu\text{g/L}$ ) in the IJssel Lake (the Netherlands) over the last 8 years

## INTRODUCTION

### Ion exchange (IX)

Coagulation has been the most commonly applied process for NOM removal (within conventional water treatment processes). However, anion exchange processes have been identified as an efficient alternative or supplementary process to other NOM removal processes, such as coagulation, activated carbon filtration etc. (Bolto *et al.* 2004; Bond *et al.* 2011; Watson *et al.* 2015).

Ion exchange (IX) is considered to be both an adsorption process and a sorption process (Wachinski, 2006). The term ion exchange describes the unit process of IX, which is widely used in water treatment to remove unwanted contaminants. The most common application of IX is softening, but there are many kinds of resin, and anion IX resins can be used for the removal of anions such as nitrate, DOC, and arsenate. IX has been introduced by the World Health Organisation (WHO) as a nitrate removal technology and approved as the Best Available Technology (BAT) for nitrate removal by United States Environmental Protection Agency (US EPA). Cation ion-exchange refers to the removal of cations, such as calcium and magnesium. Wachinski and others argue that the role of IX in water treatment is changing. This is because of the proposed brine discharge legislation in California, Montana, and Texas and also because of advanced membrane technologies, AOP and the need for many utilities to lower DBP formation potential. Anion IX offers a very good opportunity for enhanced removal of organic matter for source waters that contain medium to high concentrations of NOM because the majority of compounds which make up NOM are negatively charged.



**Figure 5**, SEC-OCD chromatogram of ion exchanged and in-line coagulated IJssel Lake water

The size exclusion chromatography-liquid chromatography-organic carbon detection (SEC-LC-OCD) method is a powerful analytical tool to characterize organic matter and to observe relative differences in DOC. The SEC broadly groups the organics into five fractions: biopolymers (MW $\gg$ 20,000 Da), humics (MW $\sim$ 1,000 Da), building blocks (MW 300-500 Da), LMW acids and LMW neutrals (MW < 350 Da) (in the order of retention time). Two detectors, organic carbon detector (OCD) and ultraviolet detector (UVD) detect the organics. The OCD spectrum is used to determine the total mass of organic carbon, whereas the UVD spectrum detects only the UV adsorbing species (i.e., double bond carbon), the so-called chromophoric DOM. Figure 5 shows an example of an OCD signal where the same surface water is treated with enhanced coagulation and anion IX. It is clear that enhanced coagulation removes a part of the biopolymer fraction (around 30 minutes retention time) and a small portion of humics (around 40 minutes retention time). The IX removed most of the humics with the highest molar absorption coefficients and LMW fractions (around 40 and 50 minutes retention time) but it has almost no impact on biopolymer removal. As a result, the UVT 254nm for enhanced coagulation was 82 percent while anion IX achieved a treated water UVT of 94 percent.

### **Ion exchange and related challenges**

Currently available technologies to treat surface waters containing suspended and colloidal matter with ion exchange are based on fluidized bed reactors or on totally-mixed reactors with very high concentrations of resin (>400 mL/L), like in the MIEX<sup>®</sup> process (an acronym for Magnetic Ion Exchange, manufactured and commercialized by Orica) or in suspended plug flow reactors like in the SIX<sup>®</sup>-process of PWN Technologies. The SIX<sup>®</sup> process evolved out of the disadvantages of the fluidised bed and MIEX<sup>®</sup>-processes. The MIEX<sup>®</sup> process has several different process configurations, but the main two are: the classical dual-stage MIEX<sup>®</sup> process and the high-rate MIEX<sup>®</sup> process. In the classical dual-stage MIEX<sup>®</sup> process, one or two totally mixed contactors in series are fed with raw water and resin leading to an average resin concentration of 20 to 40 mL/L of resin in the contactors. Approximately 5 to 10% of the settled resin is pumped to a regeneration station, regenerated and re-loaded to the remainder of 90 to 95% resin.



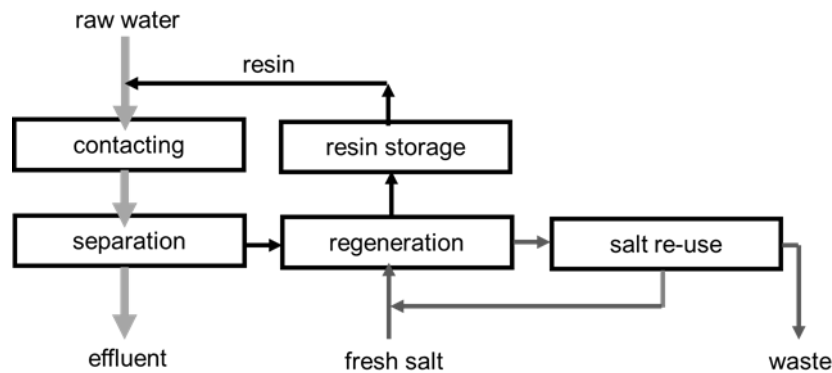
In the case of the high-rate MIEX® process, the resin concentration in the contactors is 200 to 500 mL/L. The resin stays in the contactor and the water flows through. Only a very small amount (~ 0.1%) of the resin is pumped to regeneration vessel while, at the same time, regenerated resin is pumped into the contactors. From the available literature on the high-rate MIEX® process (Verdict *et al* 2011) it is not exactly clear how much resin is pumped to the regeneration system over the course of time, as the 0.1% of the total resin is being regenerated without a direct correlation to time or capacity. Based on the information reported by end users and customers, one concludes that the effective resin concentration in the process is between 1 to 2.5 mL/L. This theoretically yields a number of BVs (bed volumes) treated of 400 - 1000 before regeneration and a resin residence time 1000 times higher than the hydraulic residence time, which is not known. This may explain why the process has been called high-rate. The hydraulic residence time and contact time of the water may be short (although not confirmed in the literature) compared to the dual-stage process, but the resin inventory and residence time until regeneration are much larger (Verdict *et al.* 2011).

The fluidised bed and the MIEX®-process treat a high number of bed volumes (i.e., > 1000 volumes of water per volume of resin) until the resin is regenerated (Slunski *et al*, 1999). Under some water quality conditions, this approach could present quite a few disadvantages which would make the technology less economically attractive. For example, the anion exchange MIEX® process used to remove dissolved organic carbon from raw surface waters is sometimes not efficient due to nutrients such as nitrates and phosphates in the water, which adsorb to the resin during the long retention times (designed to minimize the number of regenerations) and, along with the existing carbon and porous characteristic of the resin beads, create an ideal environment for bacterial growth. The biofilm formed on the resin “blinds” the active sites of the resin resulting in serious operational and performance challenges. In addition, the loss of adsorption capacity (Wachinski, 2006) requires higher resin concentration or longer contact time (Cornelissen *et al.* 2009; Verdict *et al.* 2011;), factors which increase the operational costs and/or lower the plant capacity. Another real problem is that eventually the biofilm releases organic matter or adenosine triphosphate (ATP), both known as detrimental to downstream water treatment processes, particularly to membranes (Cornelissen *et al.*, 2010).

To overcome the ‘resin blinding’, fixed bed reactor systems are flushed regularly with high pH solution to destroy the biofilm as much as possible. In the case of MIEX® processes, which use hydrophobic resins, it is not possible to use high pH solutions to control the biofilm formation since the resin is not resistant to alkaline agents, and eventually the resin will be degraded, thus shortening the lifetime of this relatively expensive resin.

A PWN study (Galjaard *et al.* 2005) showed that the direct treatment of IJssel Lake water with MF/UF was only possible after the removal of the low molecular weight (LMW) DOC fractions with an anion resin. Consequently, PWNT pursued further research studies which resulted in the development of a new ion exchange process, namely the suspended ion exchange process (Galjaard *et al.* 2009). Unlike other ion exchange processes treating waters with high content of suspended matter, the ‘single pass’ or ‘suspended’ ion exchange process (SIX®) developed by PWNT achieves full control on the adsorption process minimising ‘blinding’ the resin or producing biomass. The process uses almost any commercially available resin, and all resins experimented to-date can be treated with alkaline solutions for biofilm control, if necessary. In the SIX® process, the resin is dosed from a dosing tank into the raw water at a low concentration of 4 to 20 mL resin/L, depending on the raw water quality, desired treated water quality and resin type. This mixture then flows through plug flow contactors. In these contactors, the resin has the same residence time as the treated water, because the resin travels together with the water through these contactors. This is different than MIEX®, in which the resin is retained

in the contactors. The number, shape, and design of the contactors play an important role in the adsorption kinetics. The aim of design is to approach the ideal contactor conditions of a plug-flow reactor characterized by shorter residence time of the resin, and therefore shorter contact time. After the contact time in the contactors, the resin is separated from the treated water using a customized lamella settler. The resin collects in the hopper, and is then immediately regenerated and returned to the dosing tank (figure 6).



**Figure 6** Schematic diagram of the SIX® process developed and implemented by PWN Technologies

Knowing the exact residence time of the resin makes it possible to regenerate all of the resin equally, leading to an equally low number of regenerations. The relatively short contact time (e.g.,  $10 \text{ min} < t < 30 \text{ min}$ ) of the treated water with the resin before the regeneration procedure overcomes the problematic issues of bacteria growth, resin blinding and ensures that the resin operates continuously at stable adsorption kinetics.

Another advantage of this process is that because the resin is not fully loaded prior to starting the regeneration, the regeneration (which is an equilibrium process) requires less salt and lower contact times for the regeneration procedure. The regeneration of the resin (time and volume) and the discharge of the brine are the primary factors which drive the costs for these ion exchange processes.

## PROBLEM DESCRIPTION

South West Water, Norrvatten (in close co-operation with Stockholm Vatten), Scottish Water and PWN are investigating new approaches to lower the amount of DOC at the beginning of the treatment works to such an extent that:

- low pressure membranes as a barrier for suspended matter and colloids can be used without severe fouling problems (CIP frequency  $> 3$  months);
- blinding or fouling of carbon filtration at the end of the treatment process is minimized such that it leads to economically acceptable backwash frequencies and regeneration frequencies (BW  $> 1/\text{month}$  and regeneration  $> 2$  years);
- efficiency of UV-process or advanced oxidation processes are increased;
- DBPFP in final product are reduced (THM's  $< 25 \mu\text{g/L}$ );
- biostability within the network is increased (AOC  $< 25 \mu\text{g/L}$ ).

For these reasons all parties are interested in the feasibility of the SIX® process and the use of an in-line coagulant dose after the SIX®-process to increase the removal of DOC further. The following objectives are listed to achieve an initial assessment of feasibility:

- Analysis of raw feed water quality (for the SIX® process);
- Establish a correlation between UV254 and DOC concentration;

- Determine absolute removal rate of DOC with IEX;
- Establish a model for the removal rate to generate initial design parameters for the SIX® process (i.e. the resin concentration and contact time);
- Determine the desorption rate to define initial design parameters for the regeneration of the resin;
- Determine water quality after the SIX® process and after the CeraMac® process with and without in-line coagulation

## **MATERIAL AND METHODS**

Raw water samples were taken from the different sites and brought to the PWNT research facility at Andijk, Netherlands. These samples were subjected to a series of laboratory and bench scale experiments. Furthermore, samples were periodically taken from the current treatment processes for each individual treatment step in order to verify how the NOM composition is being affected by these treatment processes. On the occasions where pilot studies have already started further insight could be achieved on the economic feasibility.

### **Anion exchange resin**

Lewatit® S5128 (Lanxess Engineering Chemistry, Germany) was selected for the experimental research. This resin is a food grade, gellular, strongly basic anion exchange resin (type 1) based on an acryldivinylbenzene copolymer, with a homogenous size distribution and especially suitable for NOM removal from surface waters. The resin is from a so called chloride form, i.e.: the counter anion that is being exchanged with other anions such as sulphate or nitrate is the (weakly) absorbable chloride anion. This acrylic gel resin has been chosen above available macroporous resins because of its characteristics which result in relative ease of regeneration. The adsorption kinetics are potentially slower in comparison to macroporous resin but the resin needs less contact time and a lower salt concentration for regeneration (to exchange all adsorbed anions for chloride). In practice this means that the resin concentration in the contactors are likely to be higher, but the overall inventory is reduced including the volume that needs to be regenerated, leading to a smaller regeneration facility requirement.

### **NOM determination and chemical analysis**

NOM composition was determined at the certified laboratory “Het Waterlaboratorium (HWL)” (Haarlem, Noord-Holland) according to the LC-OCD procedure, described by Huber *et al.* (2011). NOM, bicarbonate, DOC and colour were measured at HWL.

### **NOM adsorption kinetics**

Raw water samples were used for both one series of jar tests and a bench scale test. With the jar tests DOC removal kinetics were investigated for several (pre-rinsed) virgin resin concentrations. See table 1 and 2 for more details. DOC was measured in house using a spectrophotometer (Hach DR 6000) and Hach-Lange (LCK 321) cuvette test tubes. For more accurate DOC analysis the samples were sent to the HWL. In addition, UV-Transmittance at 254 nm was measured in house, using a Hach-Lange DR 6000 spectrophotometer. Normally UV measurements correlate well with DOC, giving the opportunity to estimate DOC levels from UVT<sub>254</sub> values.

**Table 1** jar test protocol for batch adsorption tests for different resin concentrations

jar	resin conc. (g/L)	sampling intervals (min)	details
1	5	0,2,6,10,14,20,30,24 h	initial volume = 1,5 L; mech. stirring at 200 rpm
2	10	0,2,6,10,14,20,30,24 h	initial volume = 1,5 L; mech. stirring at 200 rpm
3	15	0,2,6,10,14,20,30,24 h	initial volume = 1,5 L; mech. stirring at 200 rpm
4	20	0,2,6,10,14,20,30,24 h	initial volume = 1,5 L; mech. stirring at 200 rpm
5	25	0,2,6,10,14,20,30,24 h	initial volume = 1,5 L; mech. stirring at 200 rpm
6	30	0,2,6,10,14,20,30,24 h	initial volume = 1,5 L; mech. stirring at 200 rpm

**Table 2** bench scale protocol for batch adsorption kinetic studies for a selected resin concentration

ves sel	resin conc. (g/L)	sampling intervals (min)	details
1	15, <sup>1)</sup> , 20 <sup>2)</sup> , 30 <sup>3)</sup> mL/L	0,2,6,10,14,20,30	initial water volume = 60 L; stirring with blade impeller at rotation speed, suitable for equal resin distribution over water volume. t = 0 min and 30 min samples were sent to the lab (HWL) for NOM analysis

<sup>1)</sup>: Malaren; <sup>2)</sup>: Invercarnie, North Hoy; <sup>3)</sup>: Burncrooks

Immediately after the bench scale adsorption experiment, the loaded resin was collected by decanting the supernatant. The loaded resin was subjected to a series of desorption jar tests. About 20 L of the supernatant was collected and used for another jar test experiment aimed at further removal of residual NOM by coagulation with Poly Aluminum Chloride (PACl). Table 3 describes an example experimental procedure that was used.

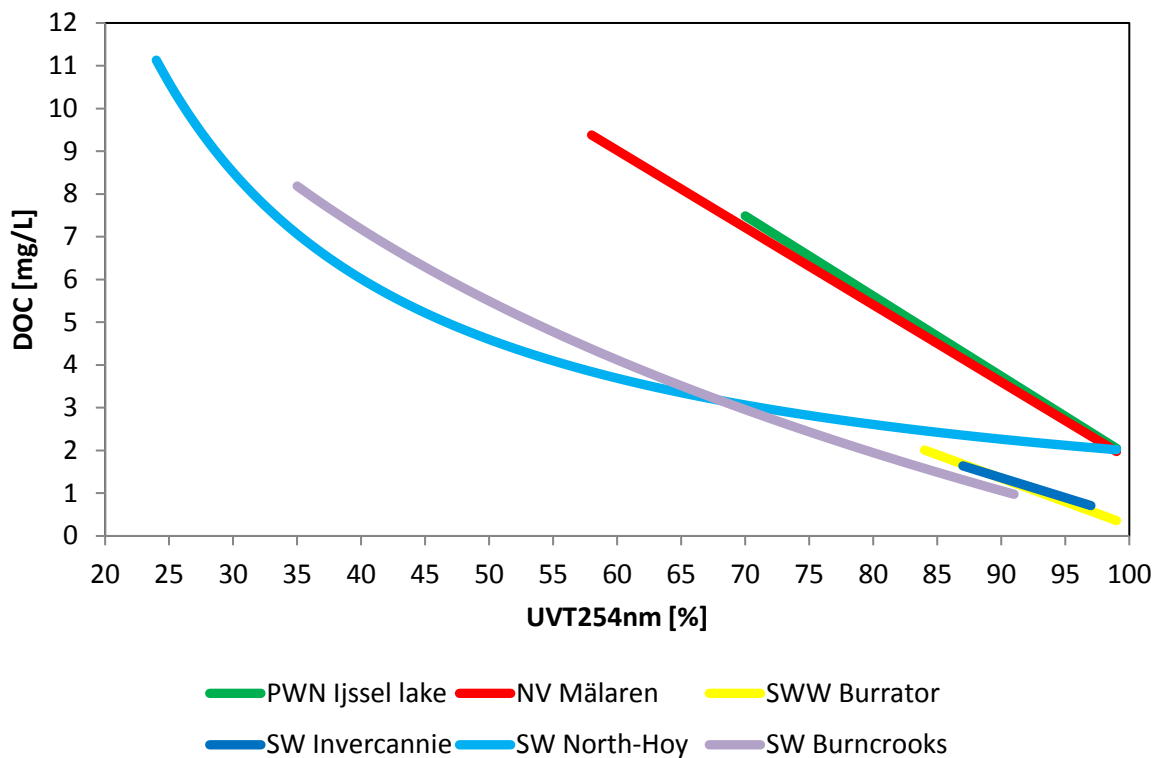
**Table 3** jar test protocol for the simulation residual NOM removal by in line coagulation with Poly Aluminum Chloride (Sachtoclar; 5,35% Al; density 1,21 g/mL)

jar	coagulant dosage		mixing		0,2% HCl dosage	details
	as PACl (ppm)	as Al <sup>3+</sup> (ppm)	rapid (s/rpm)	slow (min/rpm)	mL	
1	15	0,8	10/400	20/40	0,5	SIX treated water volume = 1,2 L; PACl (Sachtoclar) and HCl were dosed during rapid mixing; HCl was dosed to reach a target pH around 6,4; samples taken at 2,5 min contact time for NOM analysis

## RESULTS AND DISCUSSION

### UV Transmission and DOC Correlations

Figure 7 shows the relationship (trendlines with R2 values above 99%) between the UVT at 254nm and the DOC concentrations measured during and after SIX® treatment mimicked at lab and bench scale. UVT<sub>254</sub> was first measured after the samples were filtered over a 0,45 µm filter. The main reason to make this relation is to use UVT<sub>254</sub> as a guide parameter for DOC during the anion adsorption process for a given resin concentration and contact time. It also provides valuable information about the DOC characteristics, in particular the UV absorbing compounds of the DOC during IEX. This extra information should be regarded as complementary to the LC-OCD analysis with the UV-detector in combination with the organic carbon detector.

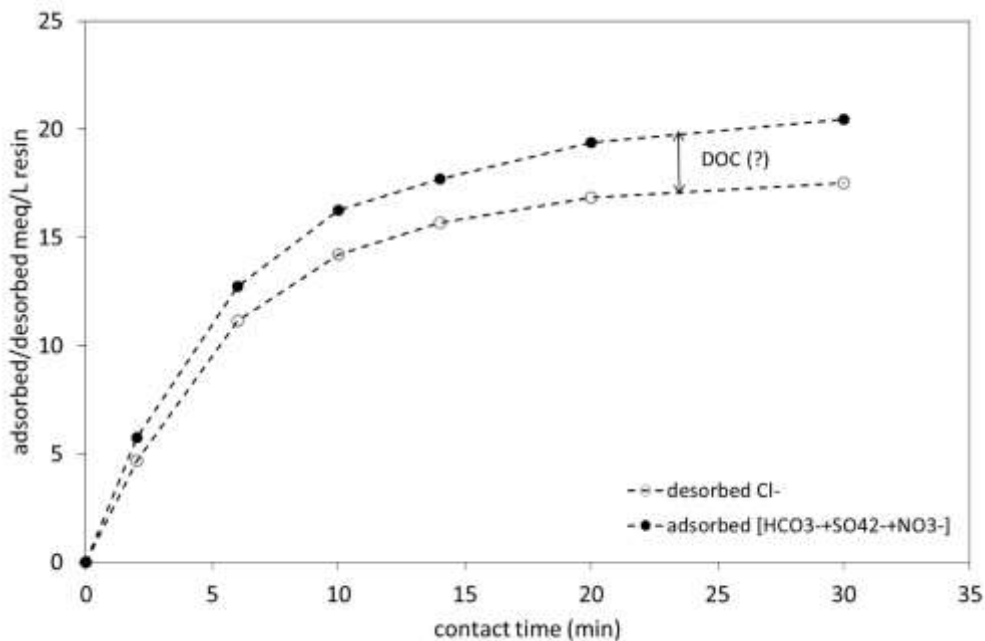


**Figure 7** DOC vs UVT<sub>254</sub>nm trend lines for the tested raw waters (measured with 1 cm cuvette)

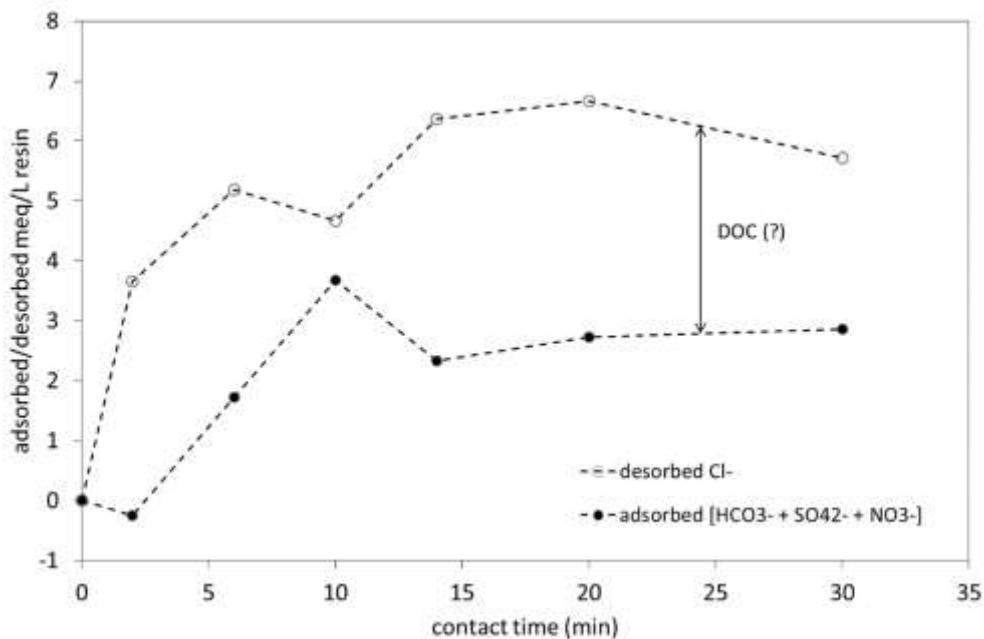
As can be seen from the figure, this relationship for the IJssel Lake, Lake Mälaren, Burrator reservoir and Lake Invercannie seems to be more linear compared to Burncrooks and North-Hoy raw water. However, this linear relationship is also present at Burncrooks and North-Hoy for UVT values higher than about 60%. The remarkable differences between the various water qualities with regard to UVT<sub>254</sub> and DOC content are rather dependent on the NOM matrix of the various waters and the extent to which it changes during anion exchange. Both Mälaren and IJssel Lake raw waters have a much higher UV transmission for a given DOC content, which means that the UV-absorbing fractions of the DOC have a lower specific UV absorbance (SUVA) than the other raw waters. Further, it is notable that Invercannie, IJssel Lake and Mälaren raw waters have a relatively high residual DOC content at 100% transmission, which, in turn, means that a significant part of the DOC does not absorb UV light at 254 nm at all. For IJssel Lake water the latter can be explained by the presence of a high molecular weight biopolymer fraction, especially in the residual DOC fraction after SIX treatment. For the IJssel Lake it was determined that the biopolymer fraction does not absorb UV light at 254 nm (Koreman, 2016).

### Chloride exchange

During sorption, chloride ions are exchanged not only with NOM molecules, but also with sulfate, nitrate, and bicarbonate, which are the most dominant anion constituents for many natural waters. The selectivity of anion exchange resins for different anions is typically as follows:  $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^- > \text{OH}^-$  (Wachinski, 2006). In addition, for IJssel Lake water it was figured out that the order of desorption rate during regeneration holds:  $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{DOC}$  (Im, 2015). This order cannot be directly derived from the selectivity order, since we have also to take into account the total amount of the various anions that are being adsorbed onto the resin, which is not only dependent on adsorption rate but also on initial concentration. For the IJssel Lake this implies that the total chloride exchanged during SIX adsorption/desorption is mainly determined by  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  and to a much lesser extent by the target “anions” DOC and  $\text{NO}_3^-$ . This can be explained by the higher initial concentrations for  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  and highest removal efficiency for  $\text{SO}_4^{2-}$  (sulfate for more than 95%). In the Scottish Water locations the situation differs. During bench scale adsorption experiments, chloride increase was determined and converted to desorbed meq Cl-/L resin and compared with total amount of adsorbed  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  meq/L resin, while for these anions molar anion equivalencies are assumed to be 2, 1 and 1 respectively. Since these are by far the most dominant anions within the water matrix, the gap between both curves in figure 8 is likely to be (mainly) related to DOC adsorption (see figure 8 a and 8b).



**Figure 8 a.** Chloride desorption versus anion adsorption during bench scale adsorption test expressed as meq/L for Invercannie raw water (30-6-2015)



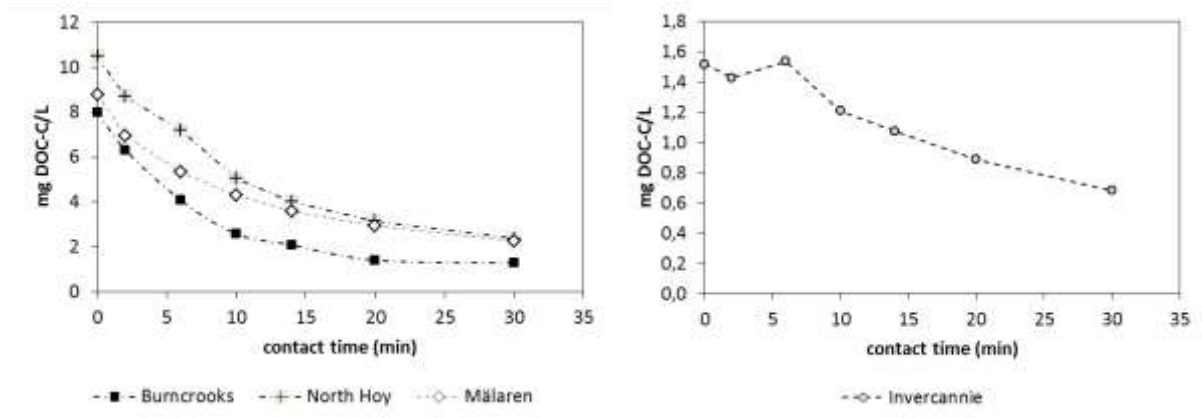
**Figure 8 b.** Chloride desorption versus anion adsorption during bench scale adsorption test expressed as meq/ L for Burncrooks (23-6-2015)

It can be seen in figure 8b that especially for Burncrooks, the chloride efficiency i.e. the amount of chloride that is involved in the DOC sorption process, is very high because of the low total anion and high DOC content. Moreover, the total amount of meq/L for SW raw waters involved in anion sorption with Lanxess Lewatit S 5128 resin is 10 - 20 fold lower compared with IJssel Lake water (150 - 200 meq/L resin). An intermediate position must be assigned to Lake Mälaren raw water, where 80 meq/L resin are exchanged during SIX<sup>®</sup> treatment and regeneration. The lower the amount, the lower is the total chloride consumption and, as a consequence, the salt (NaCl) demand during regeneration.

Optimization of the regeneration process at PWNT research facility (Andijk) has resulted, among other things, in a drastic reduction of the total salt consumption due to controlled blinding (0,2-0,3 kg NaCl/m<sup>3</sup> SIX effluent) (Koreman, 2016). Based on this finding and because of the much lower anion content compared to Andijk, it is to be expected that for the investigated SW locations this amount will be lower than 0,02 kg NaCl/m<sup>3</sup> and lower than 0,1 kg NaCl/m<sup>3</sup> for Lake Mälaren.

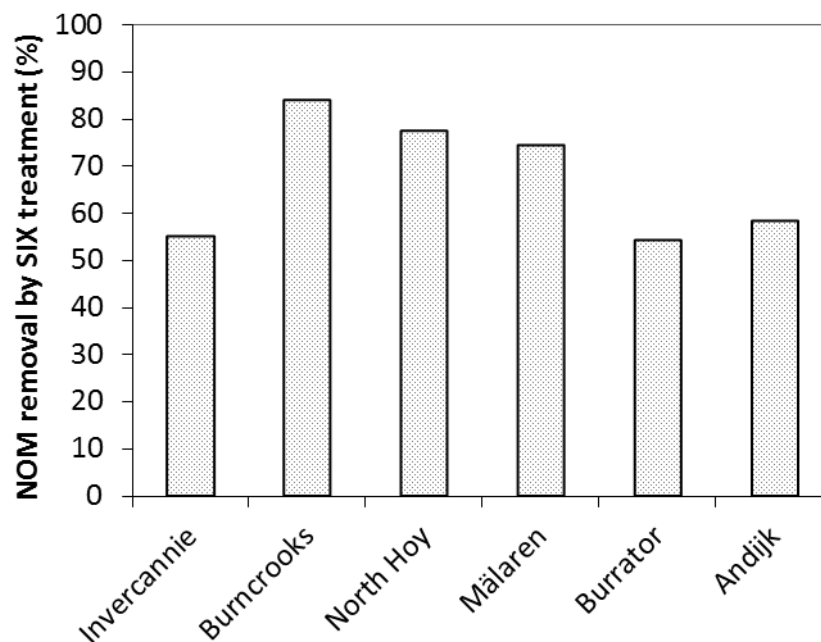
### **NOM adsorption**

Figure 9 shows the NOM removal as a function of contact time during SIX<sup>®</sup> treatment. The graphs clearly demonstrate that, except for Burncrooks, the adsorption is still in a non-equilibrium state. But after 30 minutes contact time the vast majority of the adsorbable NOM seems to have been removed. Hence the adsorption can be regarded as being in a near equilibrium state, as is also the case with Lake IJssel SIX<sup>®</sup> treated water (Koreman, 2016).



**Figure 9.** DOC removal during SIX treatment with Lanxess Lewatit S 5128: bench scale results for SIX<sup>®</sup> treated water samples from the Scottish Water production locations Invercannie, (20 mL/L), Burncrooks (30 mL/L), North-Hoy (20 mL/L) and Lake Mälaren (Stockholm/Norvatten, 15 mL/L) (resin concentrations in parentheses)

Besides Invercannie, over-all DOC removal for the Scottish Water locations is at least 75% and even 85% for Burncrooks as (Figure 10). DOC removal for Invercannie and Burrator reservoir it is somewhat lower, most likely due to the much lower initial DOC concentrations (i.e. < 2,0 mg C/L), since the adsorption rate is proportional with the DOC load, i.e.  $[DOC(t) - DOC_{equilibrium}]$ . Against this background, Andijk (45 – 58 % removal) might be considered as an intermediate situation ( $4,5 \text{ mg/L} < DOC_{initial} < 5,5 \text{ mg/L}$ ).

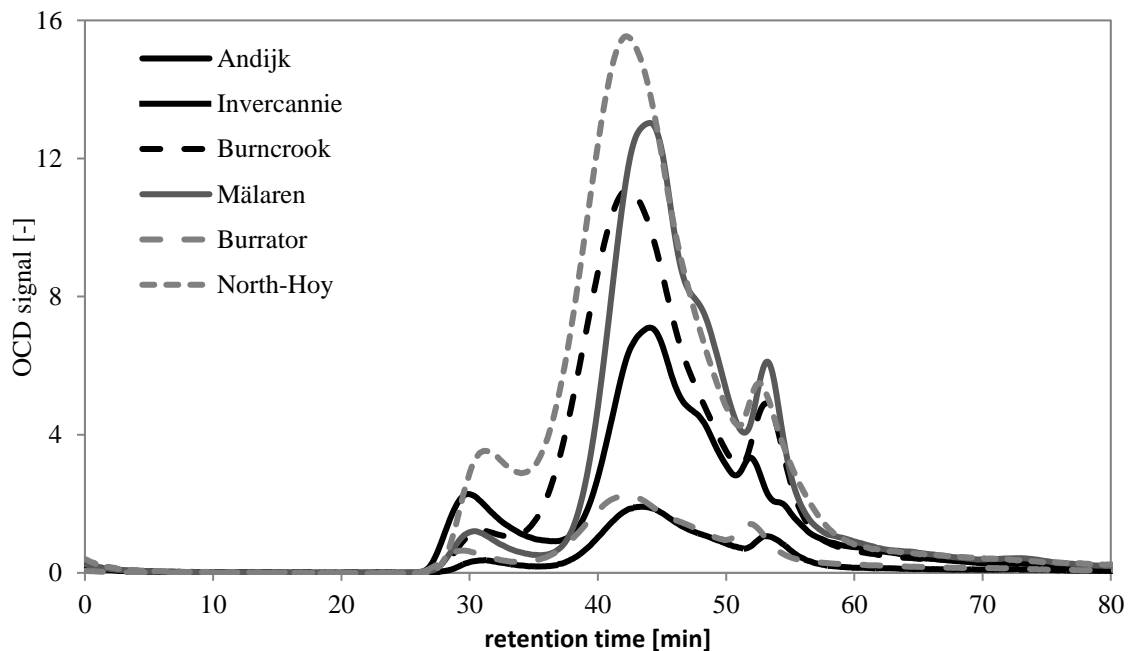


**Figure 10** DOC removal efficiencies for measured locations by SIX<sup>®</sup> treatment



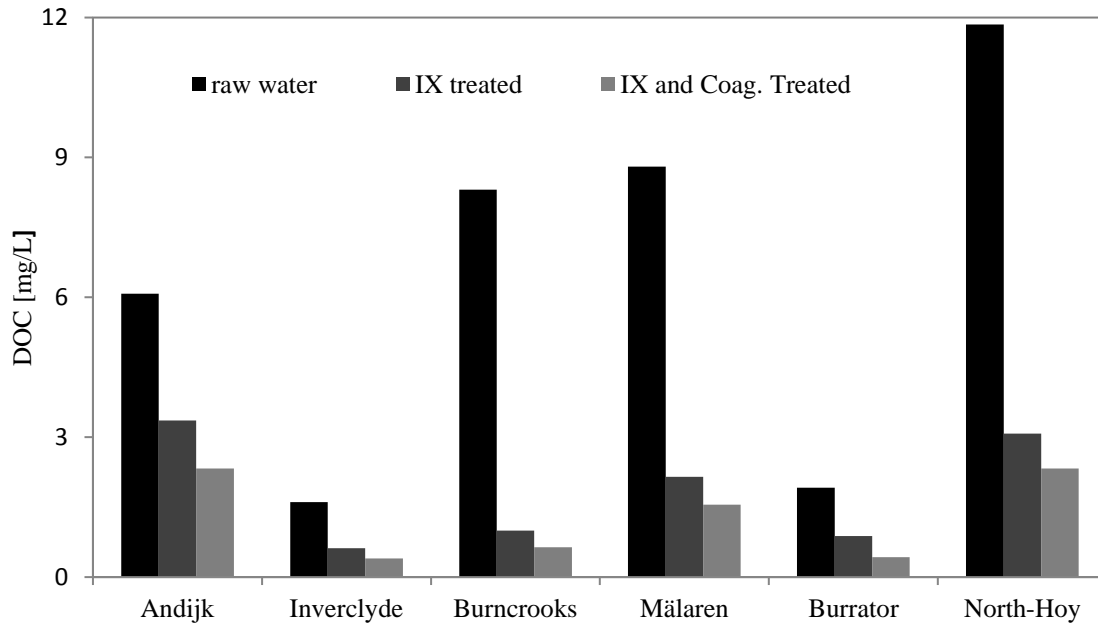
### SIX affected NOM fractions

Again, the OCD relative signal response at various retention times allows a more comprehensive interpretation of which NOM fractions are being affected during SIX<sup>®</sup> treatment. Figure 11 is illustrative for all investigated locations. From this figure and available literature (i.e. Bond et al. 2011) it can be denoted that anion exchange will be capable of very substantial NOM removal over a wide range of low molecular weight NOM (< 1 kDa apparent molecular weight). The removal of the high molecular weight fraction (>> 20 kDa) is however much lower.. According to the LC-OCD detection method this fraction is characterized as the ‘biopolymers’ fraction.



**Figure 11.** OCD signal spectrum for all raw waters

Figure 11 gives the relative differences between the different raw water sources, showing clearly similarities in the different NOM fractions and relative differences in quantities. Further, it will be obvious that post coagulation after SIX further reduces humics, but in particular this HMW biopolymer fraction. “In line” coagulation with Polyaluminum Chloride was mimicked with jar test experiments. As a result of applying inline coagulation on SIX treated water, DOC levels can be further reduced using low  $Al^{3+}$  doses of about 1 ppm to 0,4 – 2,3 mg C/L, depending on raw water quality (Figure 12).



**Figure 12.** DOC removal by SIX followed by in-line coagulation jar test results with virgin Lanxess S5128 resin

## CONCLUSIONS

The surface waters examined all have elevated concentrations of DOC. These DOC levels are increasing, most likely due to climate change effects. This increase differs and fluctuates depending on location but lays between 10-50% over the last 10 years. For these types of waters, ion exchange (IX) is of interest as a pre-treatment because the removal of colour and DOC by IX will increase the efficiency of all downstream processes, including coagulation, membrane filtration, AOP and GAC. In addition it will improve water quality (reduced by-product formation) and most likely improve biostability within the distribution network. These waters however contain significant amounts of suspended and colloidal matter which makes it nearly impossible to use standard state-of-the-art, fixed bed IX columns. This is because these beds will foul quickly (i.e., head loss build-up) with the suspended matter leading to frequent backwashing or damage to the resin and resin blinding.

Overall, the SIX-process functions very well and seems to be a potential solution for removal of DOC. The higher removal of DOC and other negatively charged ions theoretically impacts water quality and the efficiency of all the downstream processes. This has already been demonstrated in Andijk (Martijn, 2010) and Plymouth (Metcalf, 2015). The advantages of SIX compared to existing ion exchange processes and enhanced coagulation/sand filtration systems (ECSF) are:

- no (significant) resin ‘blinding’;
- capable of using almost any available commercial resin;
- low resin concentration and inventory;
- high effluent quality;
- costs comparable or lower to ECSF

From the results of the bench-scale SIX study performed on different raw waters the following can be concluded.:

- Depending on the regeneration regime, suspended ion exchange (SIX) results in substantial removal of NOM (55-85%) and colour (60-80%) for moderate resin concentrations (10-20 mL/L) and contact times (20 - 40 minutes);
- NOM reduction could be further improved relative to SIX pretreatment alone, by applying coagulation at low coagulant dosage (0,4 - 2,5 ppm as Al<sup>3+</sup>) and short contact time (2.5 minutes). This was especially important for the reduction of the residual biopolymer fraction after SIX treatment,
- The amount of salt necessary to regenerate the resin is relatively low compared to other IX methods. Most likely the highest salt concentration in the fresh brine solution will not exceed 20 g Cl/L (Andijk – because of its relative high anion content is excluded) meaning that after dilution (counter current regeneration over 5 brine vessels) and adsorption of chloride, the brine that needs to be discharged will have an estimated concentration of 1-5 g Cl/L.

The scenario of SIX, in combination with coagulation or not, followed by ceramic MF can therefore be a serious alternative for NOM reduction and suspended matter control next to NF polishing for all utilities. The advantages and disadvantages of this process compared to existing treatment processes included nanofiltration will be further studied within a pilot study at Scottish Water and Norrvatten in close co-operation with Stockholm Vatten starting in 2016, while it has already led to full-scale design at PWN and South West Water.

## ACKNOWLEDGEMENT

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