Characterization of NOM in WTP

Your proj.-ID/ our proj.-ID:	**/ teolli_1/A217**		
	jani.vuorinen@teollisuudenvesi.fi/maija.vidquist@teollisuudenvesi.fi		
Project Partner/ contact:	**Jani Vuorinen / Maija Vidquist**		
# and type of samples:	**7 (6?) (water)**		
Measuring conditions:	**column: 711 / 015**	**flows: 1.0 / 0.3 / Ø**	**buffer: STD**

Sampling date:	**2009-Oct-28+11/02**	**STD** ☐	**MC** ☐
Incoming date:	**2009-Oct-30+11/03**	**report:**	**Y** ☒ **N** ☐
Measuring date:	**2009-Oct-30+11/04**	**data processing:**	**Dr. S. Huber**
Date of Report:	**2009-Nov-04**	**report:**	**Dr. S. Huber**

***Disclaimer*: We guarantee the correctness of analytical data according to the actual state or standard of science and technology. All interpretations are based on the assumption that samples are representative for a situation under investigation. We do not take responsibility for any action that is taken on the basis of our reports, irrespective of whether such action has been recommended by us or not. Reports are treated confidentially and are exclusive property of customer. Anonymized data may be used for scientific purposes if no additional agreements are made.**

Technical note: *LC-OCD stands for "Liquid Chromatography – Organic Carbon Detection". Separation is based on size-exclusion chromatography (SEC) followed by multidetection with organic carbon (OCD), UV-absorbance at 254 nm (UVD) and organic bound nitrogen (OND). All concentration values refer to mass of organic bound carbon (OC). As a „rule-of-thumb" compound mass is about twice (for acids threefold) the value of OC. Chromatograms are processed on the basis of area integration using the program ChromCALC. In many samples the acid fraction contains low-molecular mass humic acids which are subtracted by ChromRES on the basis of SAC/OC ratio for HS. Thus, despite the visible presence of an acid peak there may no LMW acids be present.*

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INORGANIC COLLOIDS *(respond only in UV-Chromatograms): Negatively charged* ***inorganic*** *polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al, S or Si are detected by UV light-scattering (Raleigh-effect).*

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With LC-OCD all water-soluble synthetic organic compounds can be quantified and identified (after comparison with model compound) down to the low ppb-range. However, chromatographic resolution in SEC is moderate (about 15000 theoretical plates/metre). Typical examples for SOM are flocculant polymers, antiscalants, org. additives like amines, resin leaching products like polysulfonic acids (PSS) or trimethyl amine (TMA).

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SUVA (SAC/DOC): *Additional parameter derived from the ratio of DOC and SAC.*

Results

Project: teolli_1	DOC	HOC	CDOC	Approx. Molecular Weights in g/mol: >>20.000				~1000 (see separate HS-Diagram)						300-500	<350	<350		
	Dissolved	Hydrophob.	Hydrophil.	BIO-polymers	DON (Norg)	N/C	% Proteins in BIOpol.*	Humic Subst. (HS)	DON (Norg)	N/C	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Position in HS diagram	Building Blocks	LMW Neutrals	LMW Acids	Inorg. Colloid. SAC	SUVA (SAC/DOC)
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	µg/µg	% BIOpol.	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	--	ppb-C	ppb-C	ppb-C	(m^{-1})	L/(mg*m)
	% DOC	% DOC	% DOC	% DOC	--	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC	--	--
B.Raakavesi	**21751**	**356**	**21395**	**1300**	**129**	**0,10**	**30**	**13051**	**315**	**0,02**	**4,32**	**713**	**A**	**3511**	**3280**	**254**	**5,84**	**3,53**
Raw Water	100%	1,6%	98,4%	6,0%	--	--	--	60,0%	--	--	--	--	--	16,1%	15,1%	1,2%	--	--
Kempon	**4868**	**304**	**4564**	**130**	**11**	**0,08**	**25**	**1225**	**27**	**0,02**	**2,76**	**613**	**B**	**1489**	**1639**	**81**	**0,00**	**1,54**
Clarified Water	100%	6,2%	93,8%	2,7%	--	--	--	25,2%	--	--	--	--	--	30,6%	33,7%	1,7%	--	--
VKE 28/10/09	**4708**	**225**	**4484**	**150**	**14**	**0,09**	**28**	**1153**	**27**	**0,02**	**3,06**	**609**	**C**	**1537**	**1523**	**121**	**0,00**	**1,65**
before Scavenger	100%	4,8%	95,2%	3,2%	--	--	--	24,5%	--	--	--	--	--	32,6%	32,3%	2,6%	--	--
VKE 02/11/09	**4327**	**191**	**4136**	**320**	**15**	**0,05**	**14**	**1180**	**26**	**0,02**	**2,72**	**619**	**D**	**1488**	**1080**	**68**	**0,01**	**1,85**
before Scavenger	100%	4,4%	95,6%	7,4%	--	--	--	27,3%	--	--	--	--	--	34,4%	25,0%	1,6%	--	--
VKE 02/11/09	**3379**	**137**	**3243**	**260**	**13**	**0,05**	**15**	**847**	**18**	**0,02**	**1,62**	**606**	**E**	**1261**	**875**	**n.q.**	**0,02**	**1,67**
after Scavenger	100%	4,0%	96,0%	7,7%	--	--	--	25,1%	--	--	--	--	--	37,3%	25,9%	--	--	--
Sarja 2, A2	**763**	**43**	**720**	**60**	**3**	**0,05**	**16**	**n.q.**	**n.q.**	**--**	**--**	**--**	**--**	**24**	**635**	**1**	**0,02**	**0,22**
after WBA+SBA	100%	5,6%	94,4%	7,9%	--	--	--	--	--	--	--	--	--	3,1%	83,2%	0,2%	--	--
MB	**635**	**50**	**585**	**73**	**5**	**0,06**	**19**	**n.q.**	**n.q.**	**--**	**--**	**--**	**--**	**9**	**502**	**2**	**0,03**	**0,28**
after Polisher	100%	7,9%	92,1%	11,4%	--	--	--	--	--	--	--	--	--	1,4%	79,0%	0,3%	--	--

LMW = low-molecular weight

DON = Dissolved organic nitrogen

n.q. = not quantifiable (< 1ppb; signal-to-noise ratio)

n.m. = not measured

"Biopolymers" = Polysaccharides, Proteins, Aminosugars

"Building Blocks" = mostly breakdown products of humics

"Neutrals" include mono-oligosaccharides, alcohols, aldehydes, ketones and amino sugars

"Acids" = Summaric value for monoprotic organic acids < 350 Da

***:under the presumption that all org. N in the BIOpolymer fraction is bound to proteinic matter**

Sample	Raw Water	Clarified Water	Before Scavenger (28/10 + 02/11)	After Scavenger (02/11)	After WBA+SBA	After MB
DOC	**21751 ppb**	**4868 ppb**	**4708/4327 ppb**	**3379 ppb**	**763 ppb**	**635 ppb**
Humics (HS) quantitative	13 ppm or 60% of NOM	1225 ppb, reduction by 94 %			Fully removed	
Humics (HS) qualitative	Pedogenic FA	Between aquagenic and pedogenic area				
Building Blocks (BB)		Reduction by about 50 %			Almost fully removed	
Biopolymers (BP)	1300 ppb or 6 %. Absolutely very high, relatively moderate	Reduction by 90 %	On 02/11 BP are much higher		60 ppb only	73 ppb – perhaps due to normal fluctuations.
Neutrals (NEU)		Reduction by about 50 %			635 ppb!	503 ppb!
LMW Acids	Traces	Reduction by about 70 %	Traces	Traces	Fuly removed	Fully removed
Other Compounds	Fraction NEU: Unusual Compound x1 perhaps not visible due to high matrix. Unusual Compound X2 clearly visible (see Fig 1)	X1 and X2 now dominate NEU fraction.	28/11: Identical to Clarified Water. 02/11: Compound X1 is only about 50 %, compound X2 is missing. We assume temporal fluctuation.	X1 is not found anymore, reason unknown: slightly ionic or fluctuation or degradation?	X1 is present and dominates fraction NEU. This is understandable because this sample was taken on 28/10. Thus X1 breaks through fully. X2 is removed, presumably it is anionic. X1 makes up about 500 ppb.	X1 breaks fully through.
Comments	A very “difficult“ water for demineralisation. Nitrate and ammonium present in traces only (ppb range).	Clarification works excellent. Reduction rates are remarkable.	Except for X1 and X2 and BP identical to Clarified water.	Scavenger additionally removes some BP and some humics. This is no drastic improvement in water quality. However, X1 is removed!	Poor quality due to X1! Otherwise this would be an excellent make-up water!	MB has only little impact on NOM because WBA+SBA work excellent . X1 is assumed non-ionic and cannot be removed.

(Void boxes = no peculiarities)

Discussion

Excellent performance of all units. Product water “should” be very good basically. Such values without membranes with such a difficult raw water is outstanding.

However, there is a compound “X1” which rises DOC to around 600 ppb. The compound is low in molecular weight, non-ionic, saturated and hydrophilic. It could be an alcohol, an aldehyde, a ketone or a monosaccharide. This compound X1 most likely originates either from the raw water source or from chemicals added in flocculation process.

Also compound X2 most likely originates from the Raw Water but is presumably anionic as it is removed in WBA+SBA.

It is difficult to understand why X1 and X2 differ in concentration within 5 days of sampling. Therefore the other option would be a contamination during sampling. If this is the case then everything is “perfect” . Should you experience problems with the water in terms of TOC or steam conductivity then we have to come back the “Raw Water contamination issue”.

Then the next step would be to localise the source of the contaminant(s).

End of Report

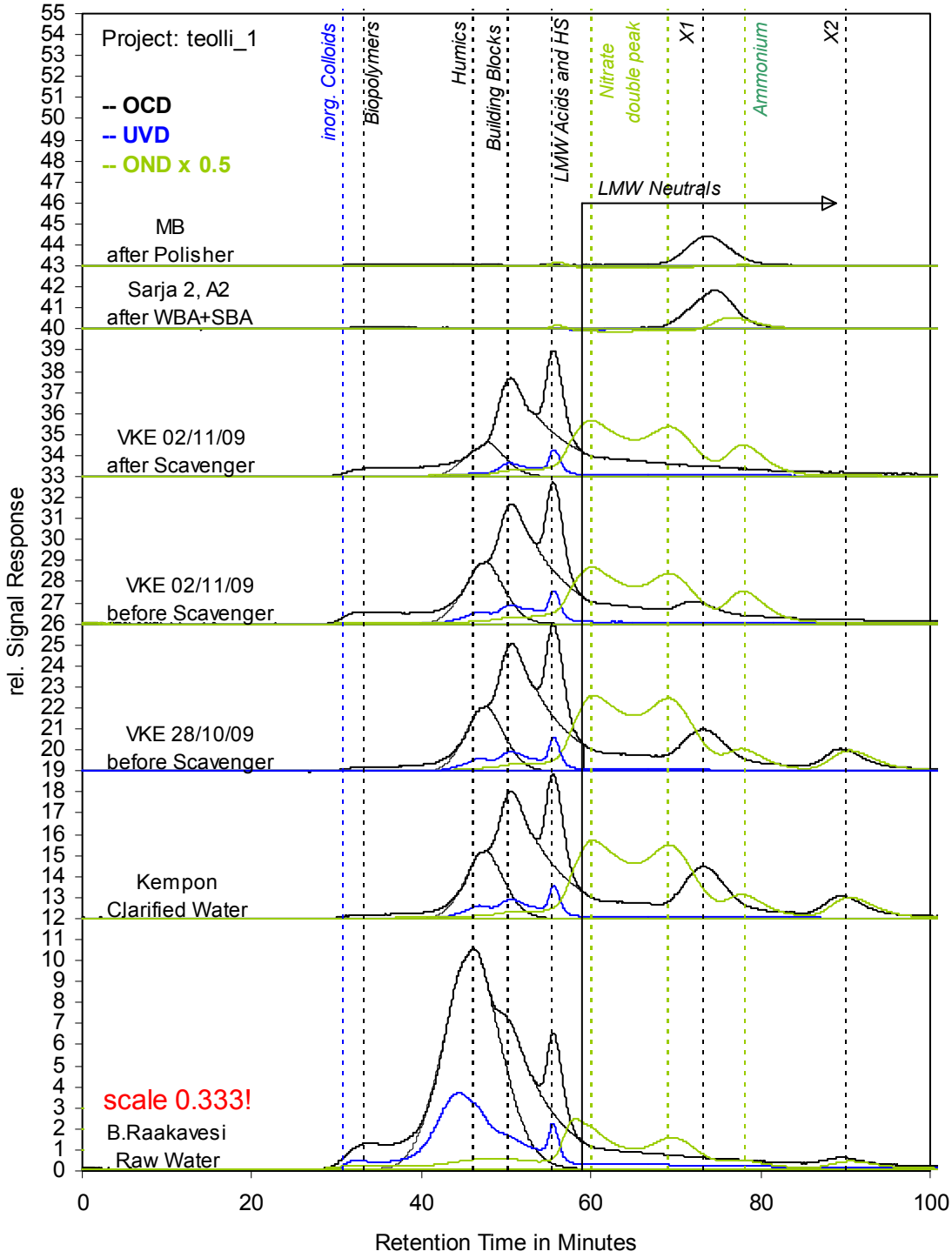

Fig. 1: LC-OCD chromatograms

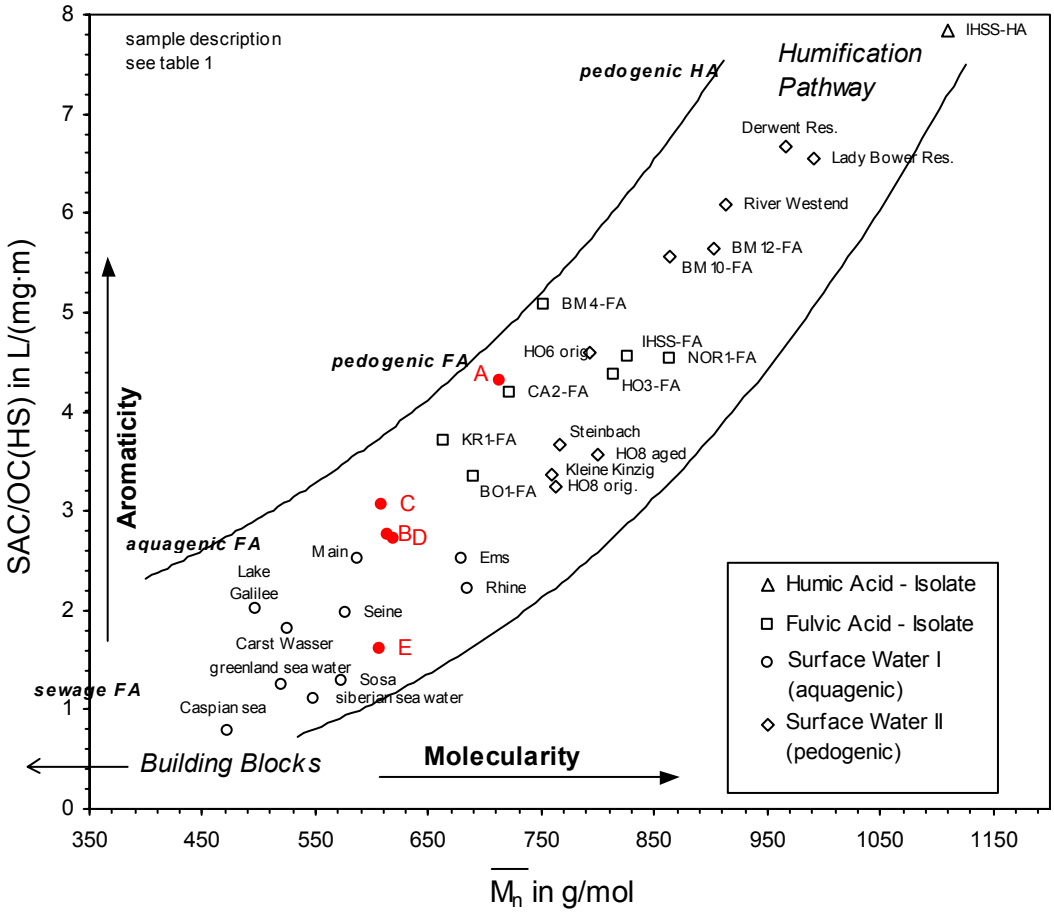

Fig. 2: Humic substances diagram

DOC characterisation of NOM in WTP (Nov. 2009)

Your proj.-ID/ our proj.-ID: / **Teolli_2 (A 2205)**
Project Partner/ contact: **J. Vuorinen, M. Vidqvist / jani.vuorinen@teollisuudenvesi.fi, maija.vidqvist@...**
 # and type of samples: **3 (water)**
Measuring conditions: **column: 50711 / 015 flows: 1.0 / 0.3 / Ø buffer: STD**

Sampling date:	**2009-Nov-23**	**STD** ☒	**MC** ☐
Incoming date:	**2009-Nov-27**	**report:**	**Y** ☒ **N** ☐
Measuring date:	**2009-Nov-27**	**data processing:**	**Dr. M. Abert**
Date of Report:	**2009-Nov-30**	**report:**	**Dr. M. Abert**

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Project: Teolli_2	DOC	HOC	CDOC	Approx. Molecular Weights in g/mol: >>20.000				~1000 (see separate HS-Diagram)						300-500	<350	<350		
	Dissolved	Hydrophob.	Hydrophil.	BIO-polymers	DON (Norg)	N/C	% Proteins in BIOpol.*	Humic Subst. (HS)	DON (Norg)	N/C	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Position in HS diagram	Building Blocks	LMW Neutrals	LMW Acids	Inorg. Colloid.	SUVA
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	µg/µg	% BIOpol.	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	--	ppb-C	ppb-C	ppb-C	SAC (m^{-1})	L/(mg*m)
	% DOC	% DOC	% DOC	% DOC	--	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC	--	--
1: Raaka vesi	9232	406	8825	175	29	0,17	50	6259	133	0,02	3,85	714	A	1352	989	51	n.q.	3,02
	100%	4,4%	95,6%	1,9%	--	--	--	67,8%	--	--	--	--	--	14,6%	10,7%	0,6%	--	--
2: Saostetto vesi	2963	271	2692	62	6	0,09	27	927	17	0,02	1,82	501	B	1016	687	n.q.	n.q.	1,73
	100%	9,2%	90,8%	2,1%	--	--	--	31,3%	--	--	--	--	--	34,3%	23,2%	--	--	--
3: Suolanpoisto sarsan	182	58	124	7	n.q.	--	--	n.q.	n.q.	--	--	--	--	8	107	1	n.q.	0,56
	100%	31,9%	68,1%	4,1%	--	--	--	--	--	--	--	--	--	4,3%	59,0%	0,7%	--	--

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***:under the presumption that all org. N in the BIOpolymer fraction is bound to proteinic matter**

Sample	1: Raaka vesi	2: Saostetto vesi	3: Suolanpoisto sarsan
DOC	9232 ppb	2963 ppb	182 ppb
Humics (HS) quantitative	6.3 ppm C or 68% of DOC	927 ppb C, decrease by 85 %	HS are quantitatively removed.
Humics (HS) qualitative	Character of pedogenic FA.	Aquagenic FA area. HS diagram (compare fig. 2) indicates that flocculation removes HS exhaustively. Flocculation parameters are optimised.	
Building Blocks (BB)	1.4 ppm C or 15 % of DOC. Typical value in relation to HS percentage for untreated surface water.	Decrease by about 25 %. BB are less affected by flocculation as expected.	Traces.
Biopolymers (BP)	175 ppb C or 2 % of DOC. Absolutely seen in lower to medium range. Relatively seen very low. Calculated protein content in BP fraction is 50 %.	Decrease by 65 %	Traces.
Neutrals (NEU)		Decrease by 31 %	LMW Neutrals represent 59 % of DOC. Two peaks with low carbon concentration are visible. Signals may be hidden by matrix in samples 1 and 2.
LMW Acids	Free LMW Acids are found in small amounts.	All LMW Acids can be assigned to (LMW) HS.	
Other Compounds			
Comments	Despite high content of HS a good water for demineralisation because BP are relatively low.	Flocculation works well. Rates of decrease for HS are quite remarkable.	Assuming BP concentration reflects a representative concentration a possible target value of 200 ppb C will be reached. If BP concentration varies strongly with season target value may be exceeded.

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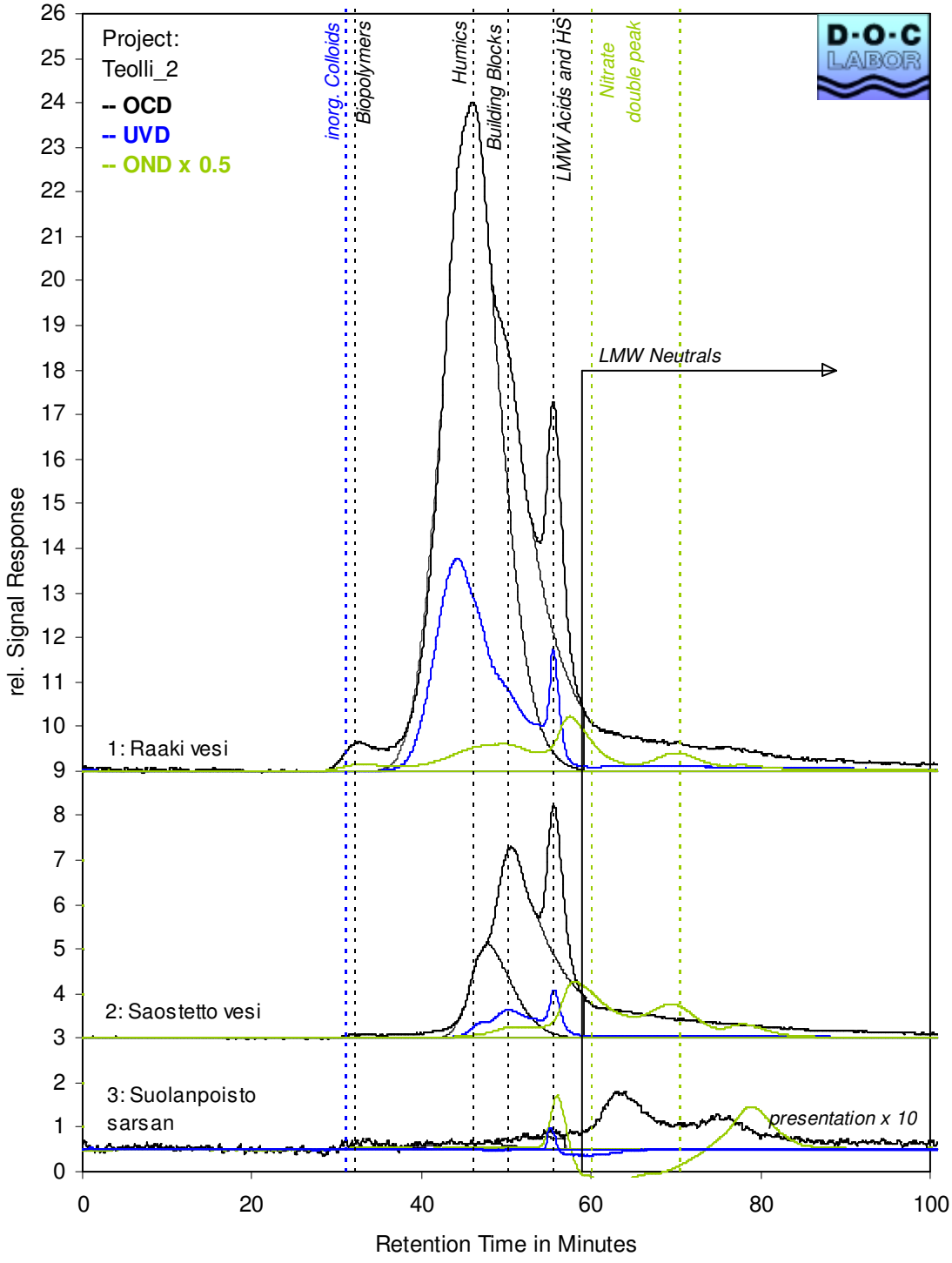
End of Report



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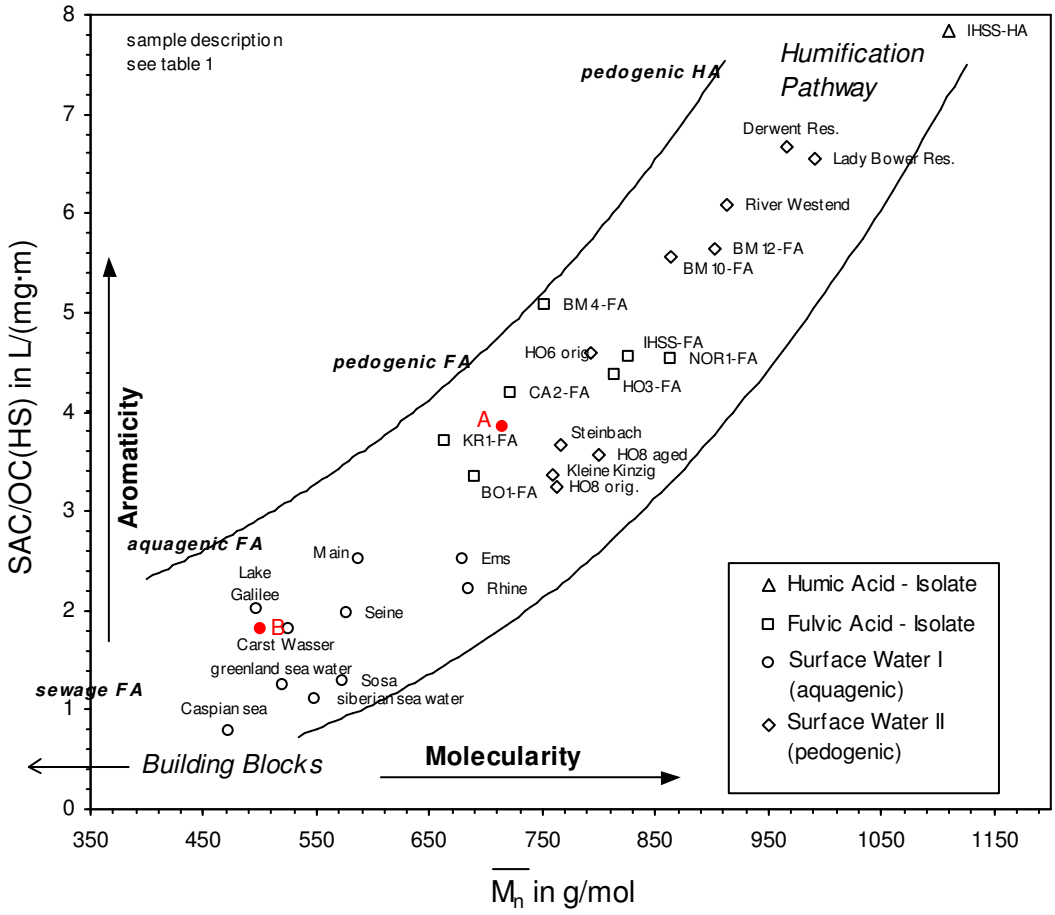

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Your proj.-ID/ our proj.-ID: / Teolli_3 (A 2208)
Project Partner/ contact: J. Vuorinen, M. Vidqvist / jani.vuorinen@teollisuudenvesi.fi, maija.vidqvist@...
 # and type of samples: 3 (water)
Measuring conditions: column: 50711 / 015 flows: 1.0 / 0.3 / Ø buffer: STD

Sampling date: 2009-Dec-01 STD ☒ MC ☐
Incoming date: 2009-Dec-02 report: Y ☒ N ☐
Measuring date: 2009-Dec-02-03 data processing: Dr. S. Huber
Date of Report: 2009-Dec-04 report: Dr. S. Huber

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					(Norg)				(Norg)		(SUVA-HS)	$\overline{(Mn)}$	HS diagram				SAC	(SAC/DOC)
Project: Teolli_2	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	µg/µg	% BIOpol.	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	--	ppb-C	ppb-C	ppb-C	(m^{-1})	L/(mg*m)
	% DOC	% DOC	% DOC	% DOC	--	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC	--	--
Before HUMUS	3813	94	3719	138	14	0,10	30	1164	27	0,02	2,73	624	A	1623	794	n.q.	n.q.	2,02
RAUMA	100%	2,5%	97,5%	3,6%	--	--	--	30,5%	--	--	--	--	--	42,6%	20,8%	--	--	--
After HUMUS	4018	147	3870	149	14	0,10	29	1169	30	0,03	2,71	625	B	1662	881	9	0,00	2,00
RAUMA	100%	3,7%	96,3%	3,7%	--	--	--	29,1%	--	--	--	--	--	41,4%	21,9%	0,2%	--	--
After Anion	447	62	384	72	3	0,04	13	n.q.	n.q.	--	--	--	--	34	277	1	-0,01	0,34
RAUMA	100%	14,0%	86,0%	16,1%	--	--	--	--	--	--	--	--	--	7,5%	62,1%	0,2%	--	--

LMW = low-molecular weight

DON = Dissolved organic nitrogen

n.q. = not quantifiable (< 1ppb; signal-to-noise ratio)

n.m. = not measured

"Biopolymers" = Polysaccharides, Proteins, Aminosugars

"Building Blocks" = mostly breakdown products of humics

"Neutrals" include mono-oligosaccharides, alcohols, aldehydes, ketones and amino sugars

"Acids" = Summaric value for monoprotic organic acids < 350 Da

***:under the presumption that all org. N in the BIOpolymer fraction is bound to proteinic matter**

Sample	Before HUMUS, Rauma	After HUMUS, Rauma	After Anion, Rauma
DOC	3813 ppb	4018 ppb	447 ppb
Humics (HS) quantitative	1164 ppb C or 31% of DOC	No difference	HS are quantitatively removed.
Humics (HS) qualitative	Character of aquagenic FA.	No difference	
Building Blocks (BB)	1632 ppb C or 43 %	No difference	Traces
Biopolymers (BP)	136 ppb C or 3.6 %	No difference	Break through IEx by about 50 %. This is not unusual
Neutrals (NEU)	794 ppb C or 21 %	No difference	277 ppb (or 62 %) are due to NOM, hereof mainly to urea! (see below)
LMW Acids	None	traces	Not significant
Other Compounds			Urea, see below
Comments	A Raw Water after intensive flocculation.	We do not know what HUMUS means but it has no impact.. DOC is slightly higher due to an increase in HOC (hydrophobic matter).	This is one of the rare cases where urea dominates DOC in a demin water. We assume that about 150 ppb of DOC are due to urea. A precise quantification is possible upon request. Urea cannot be removed by IEx. We do not know the origin of the raw water but assume a strong agricultural input. Without urea the demin water should be close to or below 200 ppb C.

(Void boxes = no peculiarities)

End of Report

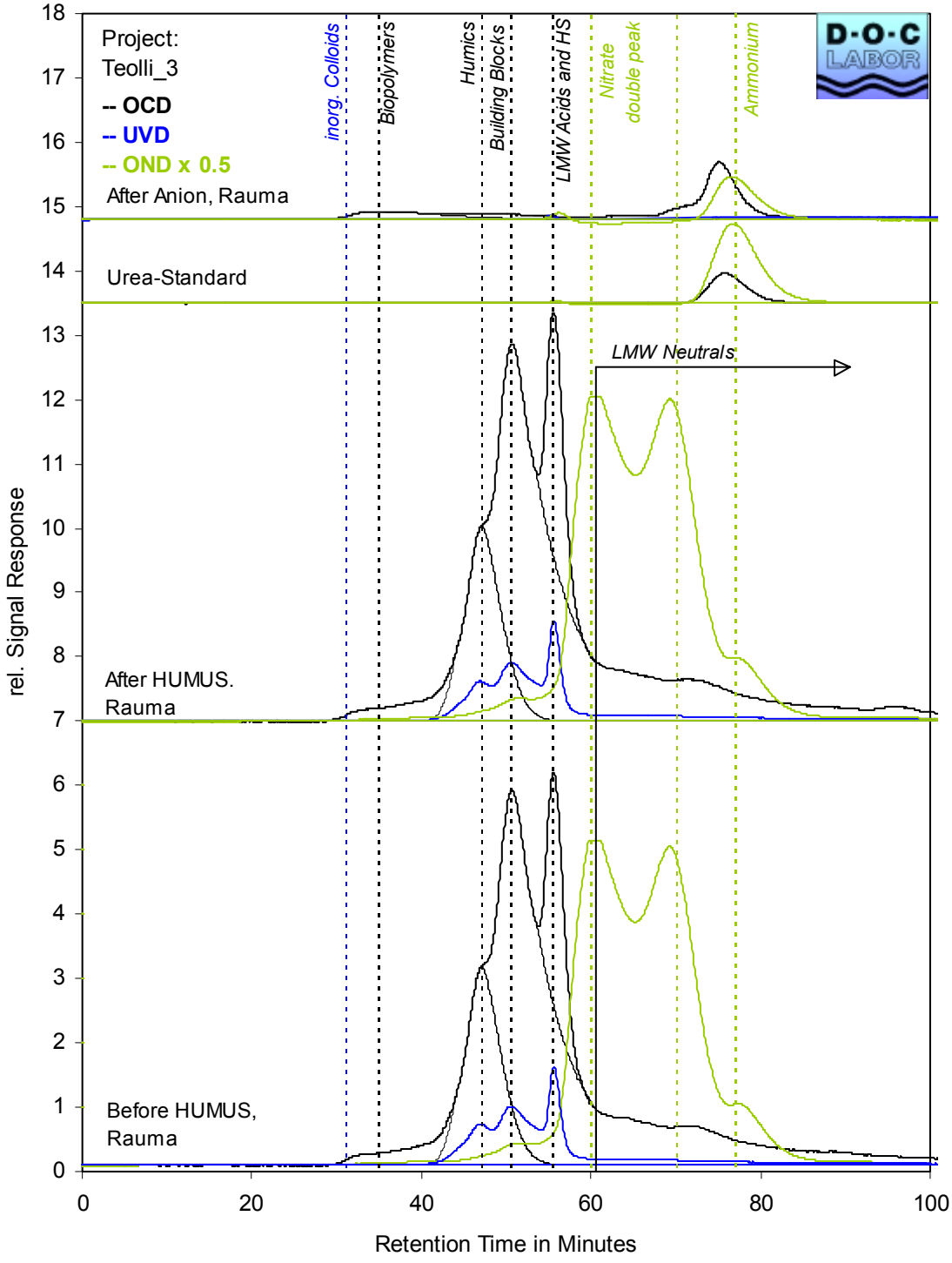

Fig. 1: LC-OCD chromatograms

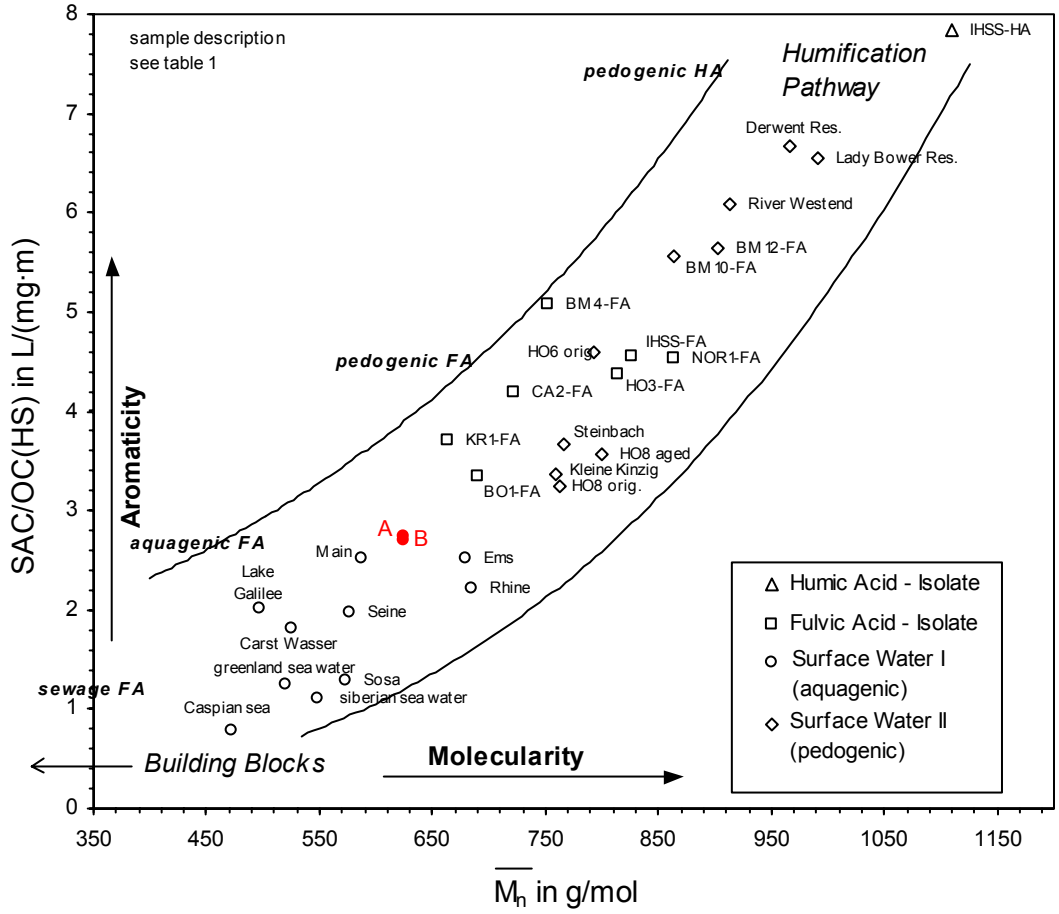

Fig. 2:

Humic substances diagram

Report on the UV-treatment of TOC containing water

Customer:	**Teollisuuden Vesi - Industrial Water**
Project:	**elimination of TOC in water**
Carried out by:	Dr. Sörensen, Hr. Zegenhagen
Date:	14-21/12/09
Date of report:	21/12/09
Sampling date:	by client
Samples:	**1) Chemically treated water, TOC app. 4 mg/l "before Humus"** **2) Ion exchange treated water, TOC app. 1 mg/l "after A2"**

Introduction

UV-irradiation in combination with hydrogen peroxide has been shown to oxidize organic and inorganic compounds in groundwater or industrial wastewater. Successful industrial use by a.c.k. Enviolet® UV-oxidation plants is shown for several years e.g. at BASF in Germany and a multitude of other companies all over the world.
The Enviolet® UV-oxidation process developed by a.c.k. constitutes the technical solution and secures the oxidation of organic compounds in almost every matrix.

Aim of treatment

The aim of treatment is the elimination of organic matter (TOC).

Analytical parameters and methods

TOC	total organic carbon (Teledyne Tekmar Phönix 8000)
H_2O_2	concentration of Hydrogenperoxide (titrimetric, a.c.k. method)
T	temperature

Photo 1: Laboratory scaled Enviolet® UV-plants (UV-reactors with different types of light sources)

Experimental setup

For the laboratory treatment an Enviolet® lab-scaled plant is used (Photo 1). Due to the same design this system guarantees a treatment und conditions equal to that of a full-scale plant.
The main advantages of the Enviolet® reactor design are:

- A high turbulence in the UV-reactor guarantees a very good material transfer and even in very strongly UV absorbing and turbid media an optimal process treatment.
- The abrasive rotational flow avoids deposits on the UV-module (unit of quartz glass tubes and UV-lamp).
- Due to the high quality of the material chosen even very acidic and concentrated solutions like copper or nickel electrolytes can be treated at high temperatures.

The system contains: Batch tank with integrated process equipment, dosing stations for chemicals required, static mixer, media pump, Enviolet® - UV – reactor, continuous measurement for important parameters, piping, heat exchanger.

Experimental procedure

The tank is filled with a defined amount of water. After adjustment of process conditions (H_2O_2-concentration etceteras) the water is pumped circular via the UV-reactor and the UV-lamp is switched on. The treatment is a batch process; that means the energy input is rising with treatment time.

Irradiation source: Enviolet® low-pressure lamp
Power: 30 W

Lab Treatment

Main process: treatment by irradiating the water in presence of H_2O_2 (process - controlled H_2O_2 dosing)

During the main process samples for analytical purposes were drawn.

Results

In the diagram the “dimensionless treatment time” is used as a universal parameter for lay-out. This is an operating parameter determined by all lab investigation and related to our central data base. As soon as all necessary information for the commercial plant are known, like charge volume, amount of water per day and power of the plant, the dimensionless treatment time can be transformed into treatment hours of the related commercial unit.

The plant was cleaned very thoroughly and extensive before the treatments. Nevertheless bleeding of TOC could not be avoided completely.
Tests carried out beforehand have shown, that during the treatments approx. 0,05 mg/L TOC could go into solution. In relation to the initial TOC values this is tolerable.

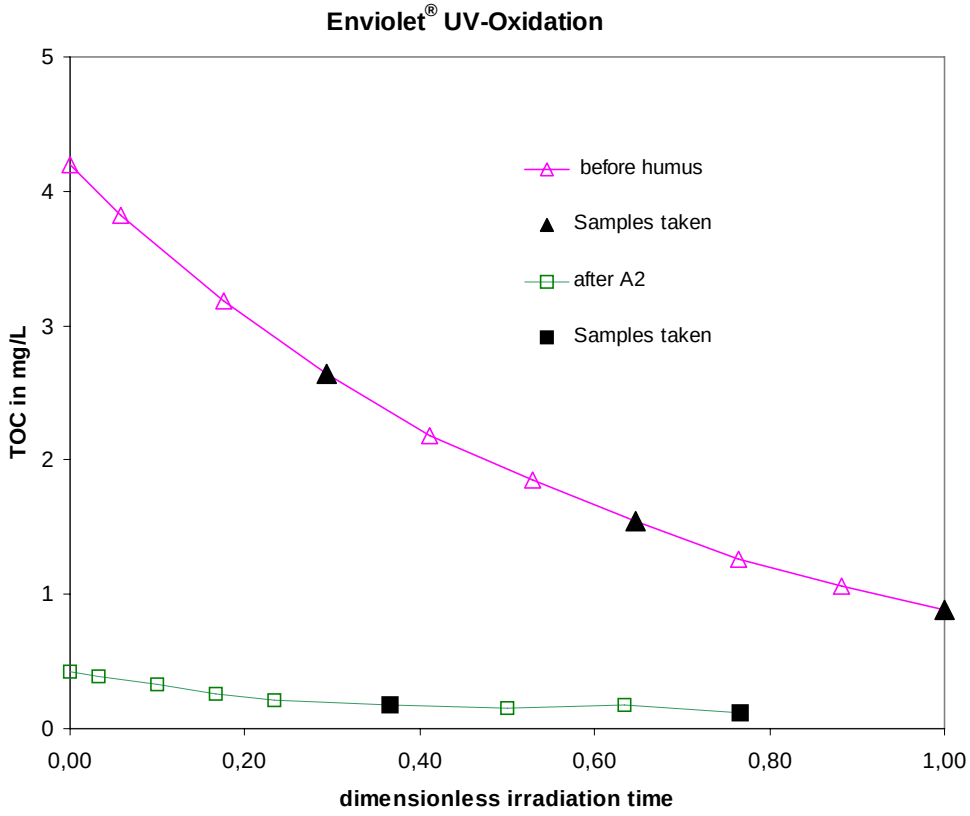

Diagram 1: Degradation of TOC during both UV-treatments. Samples sent to DOC-Huber Lab are marked.

Enviolet® UV- irradiation leads to continuous degradation of TOC in both samples. The degradation curves are shown in diagram 1 and the values are given in table 1. During the treatment samples were taken and sent to DOC Huber laboratory. These are displayed in the diagram and listed in table 1 and 2.

Table 1: Samples and results / **"before humus"**

	TOC in mg/L	remarks
Original Sample	4,25	
Sample 1 ("BH P3")	2,64	
Sample 2 ("BH P6")	1,54	
Sample 3 ("BH P9")	0,88	

Table 2: Samples and results / **"after A2"**

	TOC in mg/L	remarks
Original Sample	0,42	
Sample 1 ("A2 P5")	0,18	
Sample 2 ("A2 P8")	0,12	

Table 3: flow rates

	m³/h	remarks
Before Humus	Not known	
After A2	Not known	

Summary and Prospects

The laboratory investigations were successful, since the UV-Oxidation leads to the degradation of TOC. The investigations of DOC Huber Laboratory will show how the oxidation process changed the structure of the remaining TOC. It has to be decided by the customer which samples he likes to have analysed by DOC Huber Laboratory.

The samples were already transferred to DOC Laboratory on 22.12.2009. Dr. Huber (DOC-Laboratory) is expecting the instruction from Tellisuuden which sample have to be investigated.
We recommend using the red marked samples in Table 4a and 4b as minimum.

Table 4a: Samples and results / **"before humus"**

	TOC in mg/L	remarks
Original Sample	4,25	
Sample 1 ("BH P3")	2,64	
Sample 2 ("BH P6")	**1,54**	
Sample 3 ("BH P9")	0,88	

Table 4b: Samples and results / **"after A2"**

	TOC in mg/L	remarks
Original Sample	0,42	
Sample 1 ("A2 P5")	**0,18**	
Sample 2 ("A2 P8")	0,12	

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Commerzbank Karlsruhe
Konto-Nr. 2 222 560
BLZ: 660 400 18

DOC characterisation of NOM in WTP (Dec. 2009 – 2nd)

Your proj.-ID/ our proj.-ID: / Teolli_3b (A 2208b)
Project Partner/ contact: J. Vuorinen, M. Vidqvist / jani.vuorinen@teollisuudenvesi.fi, maija.vidqvist@...
 # and type of samples: 3 (water)
Measuring conditions: column: 50711 / 015 flows: 1.0 / 0.3 / Ø buffer: STD

Sampling date:	2009-Dec-21	**STD** ☒	**MC** ☐
Incoming date:	2009-Dec-21	**report:**	**Y** ☒ **N** ☐
Measuring date:	2009-Dec-21-22	**data processing:**	**Dipl.-Ing. A. Balz**
Date of Report:	2009-Dec-23	**report:**	**Dr. S. Huber**

Technical note: *LC-OCD stands for "Liquid Chromatography – Organic Carbon Detection". Separation is based on size-exclusion chromatography (SEC) followed by multidetection with organic carbon (OCD), UV-absorbance at 254 nm (UVD) and organic bound nitrogen (OND). All concentration values refer to mass of organic bound carbon (OC). As a „rule-of-thumb" compound mass is about twice (for acids threefold) the value of OC. Chromatograms are processed on the basis of area integration using the program ChromCALC. In many samples the acid fraction contains low-molecular mass humic acids which are subtracted by ChromRES on the basis of SAC/OC ratio for HS. Thus, despite the visible presence of an acid peak there may no LMW acids be present.*

SUMMARIC PARAMETERS:

DOC (Dissolved OC): *Determined in the column bypass after in-line 0.45 µm filtration.*

HOC (Hydrophobic OC): *Difference DOC minus CDOC, thus all OC retained on the column is defined as „hydrophobic". This could be natural hydrocarbons or sparingly soluble "humins" of the humic substances family.*

INORGANIC COLLOIDS *(respond only in UV-Chromatograms): Negatively charged* ***inorganic*** *polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al, S or Si are detected by UV light-scattering (Raleigh-effect).*

CDOC (Chromatographic DOC): *This is the OC value obtained by area integration of the total chromatogram. Chromatographic subfractions of CDOC are:*

ROM = Refractory Organic Matter:

A: Humics (HS): *In LC-OCD measurements there is a tight definition for HS based on retention time, peak shape and SAC. Calibration on the basis of „Suwannee River" Standard IHSS-FA and IHSS-HA. In addition, statistical data are given, like number-averaged molecular mass (Mn) and aromaticity (SAC/OC).*

B: Building Blocks (BB): *The HS-fraction is accompanied by shoulders, shape, concentration and UV-activity varies. This are sub-units of HS with molecular weights of 300-450 g/mol. Building Blocks are considered to be natural breakdown products of humics. They cannot be removed in flocculation processes.*

BOM = Biogenic Organic Matter:

C: Biopolymers (BP): *This fraction is very high in molecular weight (100.000 - 2 Mio. g/mol), hydrophilic, not UV-absorbing. BP are typically polysaccharides but may also contain proteinic matter (this is quantified on basis of OND). BP exist only in surface waters.*

D: LMW Organic Acids (OA): *In this fraction all aliphatic, low-molecular weight (LMW) organic acids co-elute due to an ion chromatographic effect. A small amount of HS may fall into this fraction and is subtracted on the basis of SAC/OC ratios.*

E: LMW Neutrals (NEU): *Low-molecular weight (LMW weakly or uncharged hydrophilic or slightly hydrophobic ("amphiphilic") compounds appear in this fraction. This includes alcohols, aldehydes, ketones and amino acids. The hydrophobic character increases with retention time, e. g. pentanol appears at 120 min, octanol at 240 min. NEU may be in part refractory.*

SOM = Synthetic Organic Matter

With LC-OCD all water-soluble synthetic organic compounds can be quantified and identified (after comparison with model compound) down to the low ppb-range. However, chromatographic resolution in SEC is moderate (about 15000 theoretical plates/metre). Typical examples for SOM are flocculant polymers, antiscalants, org. additives like amines, resin leaching products like polysulfonic acids (PSS) or trimethyl amine (TMA).

Inorganic Colloids ***(only visible in UV-detection):*** *Inorganic colloidal or particulate matter eluting slightly before the biopolymer fraction becomes visible by Raleigh light scattering. This material could be iron oxid hydrates or colloidal sulfur.*

SUVA (SAC/DOC): *Additional parameter derived from the ratio of DOC and SAC.*

Results

Table 1

Project: Teolli_3b	DOC	HOC	CDOC	Approx. Molecular Weights in g/mol: >>20.000				~1000 (see separate HS-Diagram)						300-500	<350	<350		
	Dissolved	Hydrophob.	Hydrophil.	BIO-polymers	DON (Norg)	N/C	% Proteins in BIOpol.*	Humic Subst. (HS)	DON (Norg)	N/C	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Position in HS diagram	Building Blocks	LMW Neutrals	LMW Acids	Inorg. Colloid.	SUVA
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	µg/µg	% BIOpol.	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	--	ppb-C	ppb-C	ppb-C	SAC (m^{-1})	L/(mg*m)
	% DOC	% DOC	% DOC	% DOC	--	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC	--	--
Before HUMUS	**3813**	**94**	**3719**	**138**	**14**	**0,10**	**30**	**1164**	**27**	**0,02**	**2,73**	**624**	**A**	**1623**	**794**	**n.q.**	**n.q.**	**2,02**
01/12/09	100%	2,5%	97,5%	3,6%	--	--	--	30,5%	--	--	--	--	--	42,6%	20,8%	--	--	--
BH P3	**2403**	**52**	**2351**	**6**	**n.q.**	**--**	**--**	**1070**	**12**	**0,01**	**0,80**	**588**	**B**	**857**	**276**	**141**	**0,01**	**1,26**
21/12/09	100%	2,2%	97,8%	0,2%	--	--	--	44,5%	--	--	--	--	--	35,7%	11,5%	5,9%	--	--
BH P6	**1421**	**79**	**1342**	**2**	**n.q.**	**--**	**--**	**490**	**4**	**0,01**	**0,72**	**575**	**C**	**524**	**169**	**156**	**0,02**	**2,29**
21/12/09	100%	5,5%	94,5%	0,1%	--	--	--	34,5%	--	--	--	--	--	36,9%	11,9%	11,0%	--	--
BH P8	**846**	**57**	**789**	**3**	**n.q.**	**--**	**--**	**334**	**n.q.**	**--**	**0,49**	**576**	**D**	**292**	**139**	**21**	**0,05**	**1,40**
21/12/09	100%	6,7%	93,3%	0,4%	--	--	--	39,5%	--	--	--	--	--	34,5%	16,4%	2,4%	--	--
After Anion	**447**	**62**	**384**	**72**	**3**	**0,04**	**13**	**n.q.**	**n.q.**	**--**	**--**	**--**	**--**	**34**	**277**	**1**	**-0,01**	**0,34**
01/12/09	100%	14,0%	86,0%	16,1%	--	--	--	--	--	--	--	--	--	7,5%	62,1%	0,2%	--	--
A2 P5	**218**	**17**	**201**	**n.q.**	**n.q.**	**--**	**--**	**n.q.**	**n.q.**	**--**	**--**	**--**	**--**	**87**	**91**	**23**	**0,01**	**4,28**
21/12/09	100%	7,8%	92,2%	--	--	--	--	--	--	--	--	--	--	39,7%	41,7%	10,6%	--	--
A2 P8	**166**	**4**	**163**	**n.q.**	**n.q.**	**--**	**--**	**n.q.**	**n.q.**	**--**	**--**	**--**	**--**	**51**	**97**	**14**	**0,01**	**5,03**
21/12/09	100%	2,1%	97,9%	--	--	--	--	--	--	--	--	--	--	30,9%	58,1%	8,4%	--	--

LMW = low-molecular weight

DON = Dissolved organic nitrogen

n.q. = not quantifiable (< 1ppb; signal-to-noise ratio)

n.m. = not measured

"Biopolymers" = Polysaccharides, Proteins, Aminosugars

"Building Blocks" = mostly breakdown products of humics

"Neutrals" include mono-oligosaccharides, alcohols, aldehydes, ketones and amino sugars

"Acids" = Summaric value for monoprotic organic acids < 350 Da

***:under the presumption that all org. N in the BIOpolymer fraction is bound to proteinic matter**

Sample	BH P3	BH P6	BH P8	A2 P5	A2 P8
DOC	Decreases from 3813 ppb (Original) to 2403 ppb	1421 ppb	846 ppb	Decreases from 447 (Original) ppb to 218 ppb	166 ppb
Biopolymers (BP)	Almost fully removed	Fully destroyed	Fully destroyed	Fully destroyed	Fully destroyed
Humics (HS)	Strongly bleached, partly destroyed	Further destruction	Further destruction	Fully removed by Anion Exchange	Fully removed by Anion Exchange
Building Blocks (BB)	Partly destroyed	It is assumed that most of this material is oxalic acid	It is assumed that most of this material is oxalic acid	It is assumed that most of this material is oxalic acid	It is assumed that most of this material is oxalic acid
LMW Acids	New material (pres. formic acid and others) are produced by UV	New material (pres. formic acid and others) are produced by UV	New material (pres. formic acid and others) are produced by UV	New material (pres. formic acid and others) are produced by UV	New material (pres. formic acid and others) are produced by UV
Neutrals (NEU)	Partly destroyed	Further destruction	Further destruction	Comp. at 73 min. from Raw Water dominates this fraction.	Comp. at 73 min. is stable.
Other Compounds	Nitrate and Ammonium (both in traces) remain unaffected	Nitrate and Ammonium (both in traces) remain unaffected	Nitrate and Ammonium (both in traces) remain unaffected	Nitrate and Ammonium (both in traces) remain unaffected	Nitrate and Ammonium (both in traces) remain unaffected
Comments	Strong impact by UV on NOM. An new, inorganic UV-absorbing compound at 78 min. Is found. The compound is released in UV-process.	Strong impact by UV on NOM. An new, inorganic UV-absorbing compound at 78 min. Is found. The compound is released in UV-process.	Strong impact by UV on NOM. An new, inorganic UV-absorbing compound at 78 min. Is found. The compound is released in UV-process.	Strong impact by UV on NOM. An new, inorganic UV-absorbing compound at 78 min. Is found. The compound is released in UV-process.	Strong impact by UV on NOM. An new, inorganic UV-absorbing compound at 78 min. Is found. The compound is released in UV-process.
Treatment Aspects	If this water would be treated by Anion Exchange then DOC would be about 200 to 400 ppb.	If this water would be treated by Anion Exchange then DOC would be about 200 to 300 ppb	If this water would be treated by Anion Exchange then DOC would be around 100 ppb (mainly due to Comp. at 73 min.)	If this water would be treated by Anion Exchange a second time then DOC would be around 100 ppb (mainly due to Comp. at 73 min.)	If this water would be treated by Anion Exchange a second time then DOC would be around 100 ppb (mainly due to Comp. at 73 min.)

(Void boxes = no peculiarities)

End of Report

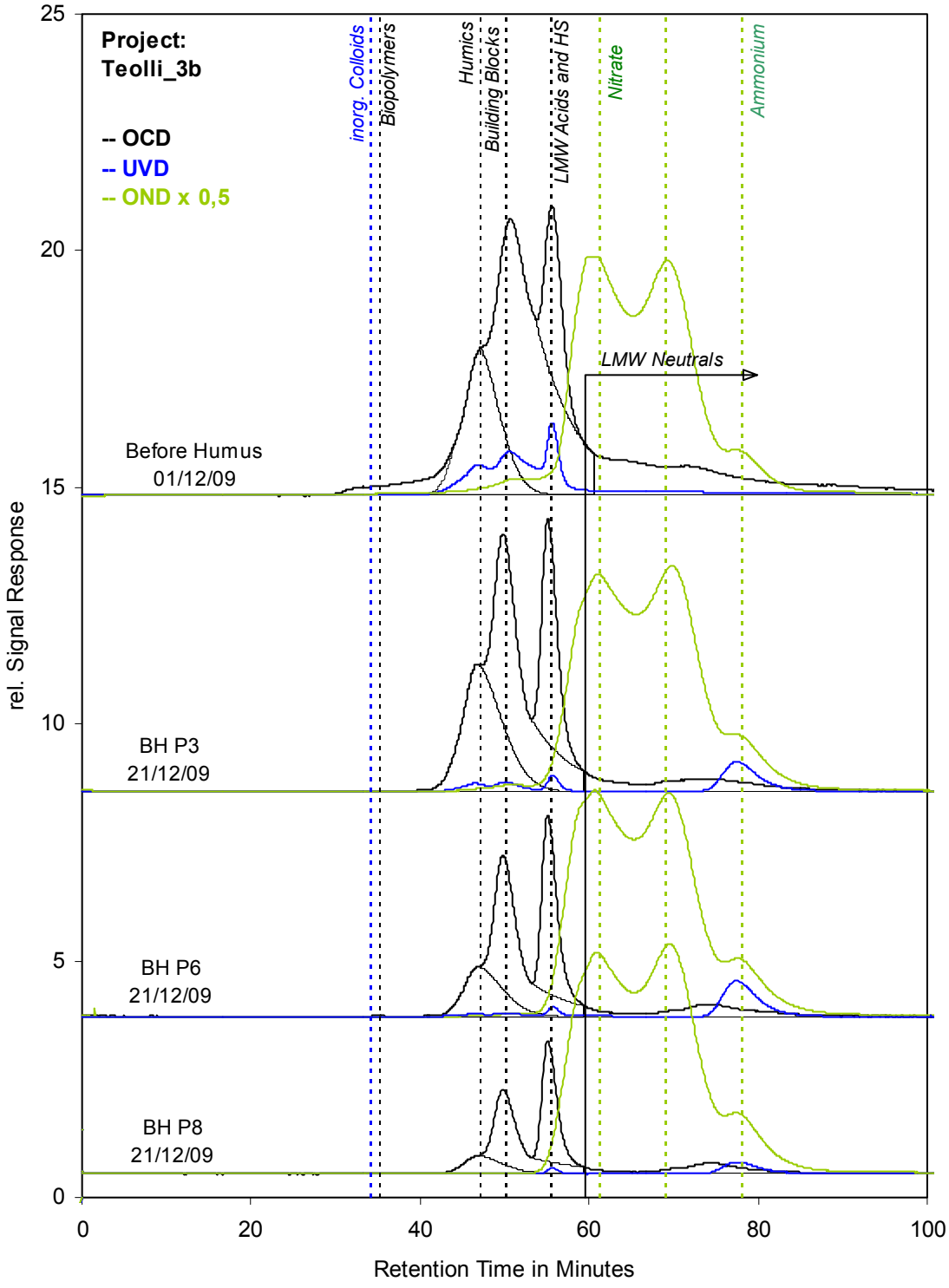

Fig. 1: LC-OCD chromatograms

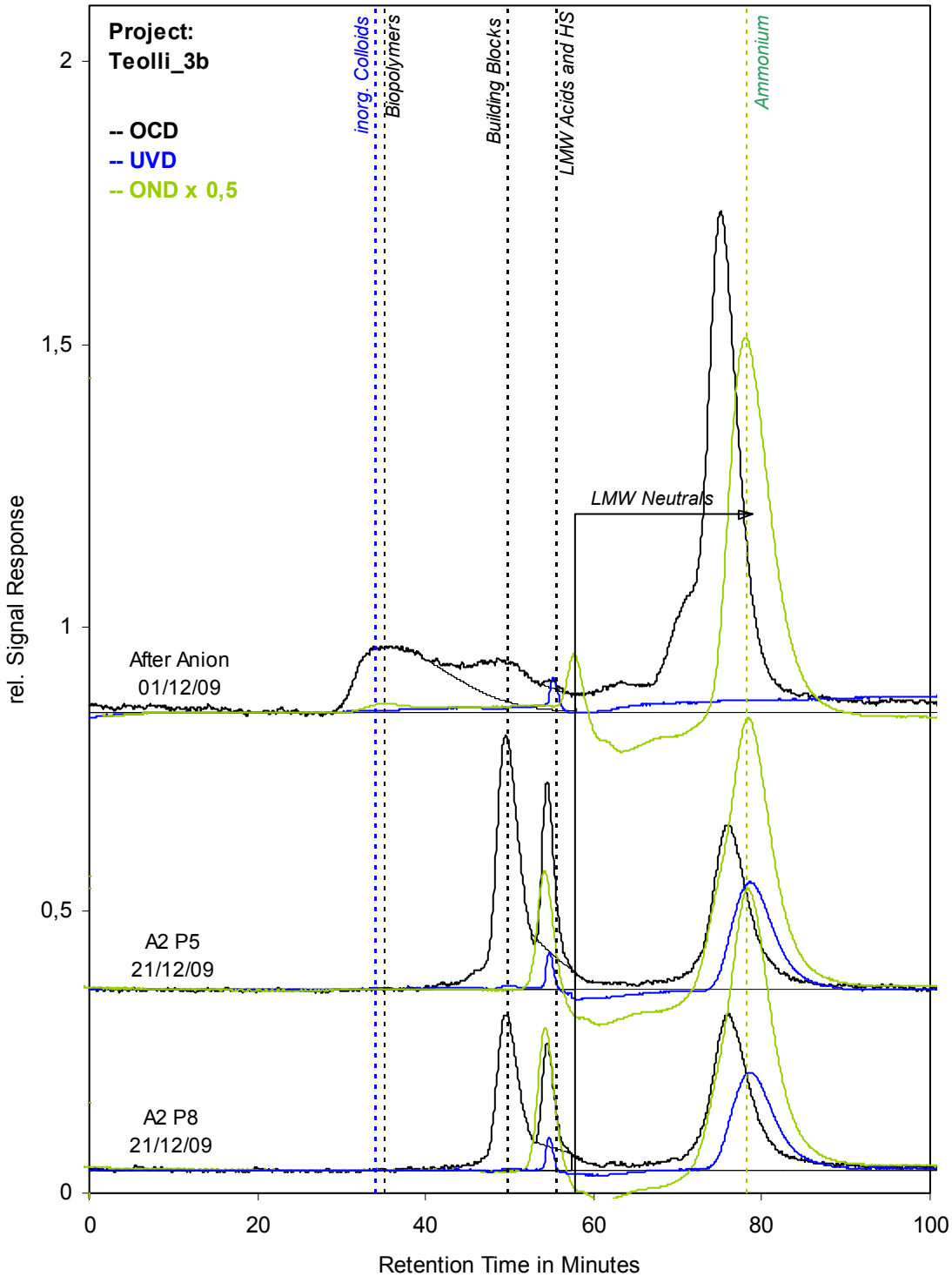

Fig. 2: LC-OCD chromatograms

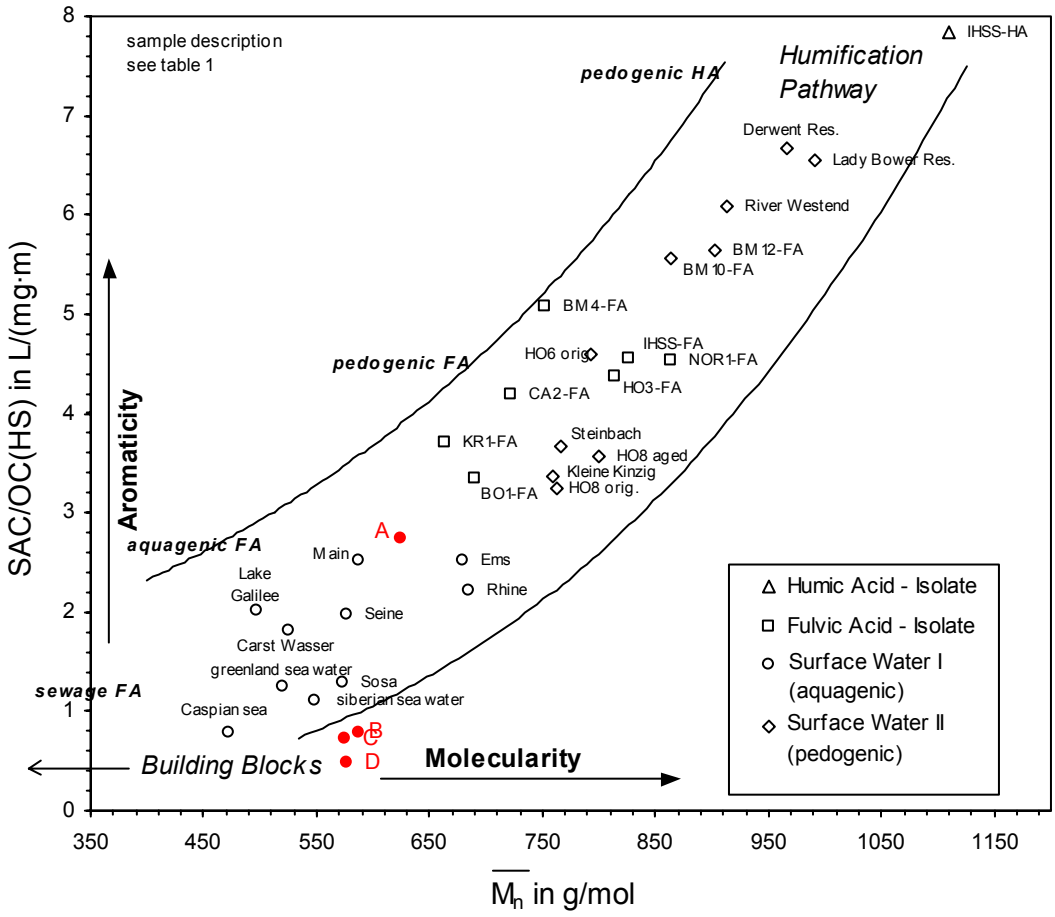

Fig. 3: HS diagram

Teollisuuden Vesi

Menetelmä	Periaate	TOC-poistoaste	Muut huomiot ja kommentit
Kemiallinen saostus	Kiintoaineen ja humuksen saostaminen rauta- ja alumiinisuolojen avulla.	70…75 %	Perinteinen menetelmä. Käsitteenä tuttu “kemiallisesti puhdistettu vesi”.
Humus-suodatin, scavenger-suodatin	Humuksen poisto vahvalla ioninvaihtohartsilla. Elvytetään suolalla ja lipeällä.	0…80 %	Humussuodattimen toiminta on verrattavissa vahvaan anionivaihtimeen. Perinteisesti humussuodattimella vaadittu vain noin 50 % poistumaa mitattuna $KMnO_4$-luvulla. Kykenee parempaan.
Ioninvaihto	Perustyö liuenneiden suolojen poisto. Orgaaninen kuorma häiritsee perustyötä.	75…95 %	Orgaanisen aineen poisto lähes yhtä tärkeässä osassa lisäveden laadun kannalta kuin suolojen poisto. Kiinnitettävä huomiota elvytykseen ja orgaanisen aineen poistumiseen hartsista. Tämä koskee erityisesti pakattuja petejä. Hartsivalinnoilla voidaan parantaa tilannetta.
Aktiivihiili-suodatus	Poistaa aluksi erittäin hyvin orgaanista ainetta, mutta ehtyessään muuttuu biologisesti aktiiviseksi suodattimeksi.	20…80 % 50 % biologisesti aktiiviselle suodattimelle	Toimiakseen hyvin tarvitsee eteen esim. otsonaattorin orgaanisen aineen poiston tehostamiseksi. Käytetään laajasti juomavesilaitoksilla. Tuotetun veden laatu voi vaihdella ja puhdas vesi voi kontaminoitua ajoittain suodattimesta irtoavista bakteereista. Massan ehdyttyä sitä voidaan regeneroida tai hankkia uutta massaa.

Teollisuuden Vesi

Menetelmä	Periaate	TOC-poistoaste	Muut huomiot ja kommentit
UV-tekniikat/UV-AOP	Hajottavat tehokkaasti varauksettomia molekyylejä OH-radikaalien avulla. Hajoamistuotteet ovat edelleen poistettavissa esim. ioninvaihtotekniikalla.	50 % > 50 % ioninvaihto-tekniikaan yhdistettynä	Toimii hyvin ioninvaihtotekniikkaan yhdistettynä. Voidaan asentaa joko ennen humussuodatinta tai sarjan jälkeen ennen sekavaihdinta. Muutamia laitoksia asennettu TOC:n poistamiseksi ioninvaihdon yhteyteen takuurajan 0,2 mg/l TOC saavuttamiseksi.
Nanosuodatus	Poistaa tehokkaasti tiettyä molekyylikokoa (> 300…500 g/mol) suuremmat orgaaniset aineet.	80…90 %	Vaihtoehtoinen menetelmä kemialliselle saostukselle. Käytössä suuressa mittakaavassa esim. Norjassa. Ei vastaavassa käytössä Suomessa.
Käänteisosmoosi	Poistaa erittäin tehokkaasti suurimman osan kaikesta orgaanisesta aineesta, kun molekyylikoko > 100 g/mol.	> 95 %	Paras käytettävissä oleva tekniikka varauksettomien biopolymeerien ja neutraalien pienimolekyylisten orgaanisten aineiden poistamiseen. Tarvitsee tehokkaan esikäsittelyn, vähintään orgaanisten aineiden poiston sekä raudan, mangaanin ja alumiinin poiston.
MIEX-prosessi	Poistaa humuksen ja muut varaukselliset yhdisteet	60…70 %	Mielenkiintoinen vaihtoehtoinen menetelmä kemialliselle saostukselle. Käytössä Australiassa. Vaatii jälkisaostuksen kiintoaineen poistamiseksi.