LC-OCD analyses of pilot drinking water treatment plant

Your proj.-ID/ our proj.-ID: /
Project Partner/ contact: /
 # and type of samples: 4 (water)
Measuring conditions: column: 50710 / 015 flows: 1.0 / 0.3 / Ø buffer: STD

Sampling date: 2009-Jul- STD ☒ MC ☐
Incoming date: 2009-Jul-17 report: Y ☒ N ☐
Measuring date: 2009-Jul-17 data processing: Dr. M. Abert
Date of Report: 2009-Jul-20 report: Dr. M. Abert

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

	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	N/C	% Proteins	Humic Subst.	DON	N/C	Aromaticity	Mol-Weight	Position in	Building Blocks	LMW Neutrals	LMW Acids	Inorg. Colloid.	SUVA
					(Norg)		in BIOpol.*	(HS)	(Norg)		(SUVA-HS)	$\overline{(Mn)}$	HS diagram				SAC	(SAC/DOC)
Project:	*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	--	--
1: Raw Water	**3291**	**132**	**3159**	**127**	**11**	**0,09**	**27**	**1785**	**62**	**0,03**	**3,27**	**655**	**A**	**659**	**563**	**26**	**n.q.**	**2,75**
	100%	4,0%	96,0%	3,9%	--	--	--	54,2%	--	--	--	--	--	20,0%	17,1%	0,8%	--	--
2: after sand filtration	**3029**	**70**	**2960**	**115**	**9**	**0,08**	**25**	**1605**	**49**	**0,03**	**2,49**	**559**	**B**	**603**	**637**	**n.q.**	**n.q.**	**2,41**
	100%	2,3%	97,7%	3,8%	--	--	--	53,0%	--	--	--	--	--	19,9%	21,0%	--	--	--
3: ground water	**903**	**38**	**865**	**n.q.**	**n.q.**	**--**	**--**	**354**	**9**	**0,03**	**1,85**	**570**	**C**	**227**	**283**	**n.q.**	**n.q.**	**2,18**
	100%	4,2%	95,8%	--	--	--	--	39,2%	--	--	--	--	--	25,2%	31,4%	--	--	--
4: after CAG	**1560**	**n.q.**	**1560**	**41**	**3**	**0,07**	**21**	**913**	**28**	**0,03**	**1,50**	**560**	**D**	**321**	**284**	**n.q.**	**n.q.**	**1,55**
	100%	--	100,0%	2,6%	--	--	--	58,6%	--	--	--	--	--	20,6%	18,2%	--	--	--

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	Sample 1	Sample 2	Sample 3	Sample 4
Treatment Scheme	*Raw water*	*Chlorination, flocculation, sedimentation, sand filtration*	*Raw water II (Ground Water added)*	*After ozonation and CAG treatment*
Humics (HS) quantitative	Relative percentage of HS is 54 % and therefore within the typical range for natural (untreated) waters.	Relative percentage of HS remains at 53 %. HS concentration decreases by 10 % after flocculation, sedimentation and sand filtration. This is an extraordinary low value.	Concentration of HS is low, which is typical for an older ground water.	HS concentration is halved compared sample 1 (River caption).
Humics (HS) qualitative	HS belong to the class of pedogenic fulvic acids (FA).	Remaining HS can be assigned to the class of aquagenic FA.	HS are of aquagenic FA origin.	After dissolution with ground water (sample 3) and bleaching of remaining HS in sample 2 by ozonation mixture of HS can be assigned to aquagenic FA with a low aromaticity.
Building Blocks (BB)		Concentration of BB is reduced by 8.5 %. After flocculation a relative enrichment of BB is expected, which is not the case here.		
Biopolymers (BP)	BP content is in the low range for a surface water (4 %). Calculated protein content in BP fraction is 27 %.	Concentration of BP is reduced by 9 %. Assuming a flocculation under acidic conditions (with no or small impact on BP concentration) slight decrease might be due to biological degradation in sand filter.	No BP found as expected for ground water.	Should reflect the mixture of sample 2 and sample 3 as mild ozonation is not expected to alter the BP concentration dramatically.
Neutrals (NEU)	Baseline in NEU fraction is a little bit bumpy, therefore fraction may contain some biodegradable material.	Baseline in NEU fraction is a little bit bumpy, therefore fraction may contain some biodegradable material.	Baseline in NEU fraction is a little bit bumpy, therefore fraction may contain some biodegradable material.	
LMW Acids	Traces of free LMW acids are found.	All LMW Acids can be assigned to (low molecular weight) HS.	All LMW Acids can be assigned to (low molecular weight) HS.	All LMW Acids can be assigned to (low molecular weight) HS.
Other Compounds	Contains traces of nitrate and ammonium (not quantified).	Contains traces of nitrate and ammonium (not quantified).	Contains nitrate (not quantified), but no ammonium.	Contains nitrate (not quantified), but no ammonium.
Comments	See below	See below	See below	See below

(Void boxes = no peculiarities)

Discussion

The river raw water is a well suited raw water for treatment. BP concentration is in the lower range for surface waters (but may vary with season) and HS are of pedogenic FA type, which generally allows a good decrease by flocculation. The decrease in HS concentration of 10 % found here (sample 2) is unexpected low. Even though, remaining HS are of aquagenic FA type (which are difficult to remove by flocculation in general) flocculation should perform a little bit better. Flocculation removes predominantly HS with high molecular weight (compare fig. 3) and high aromaticity. Therefore, a shift in position of HS peak maximum is seen in OCD chromatogram (see fig. 1) as well as in position of HS in HS-diagram (see fig. 2).

Mild ozonation attacks only unsaturated carbon-carbon bounds as well as aromatic moieties whereas molar mass of HS is not altered as can be seen in vertical change of position from “B” to “D”; also taking into account that addition of ground water (“C”) with a nearly similar characteristic to “D” has also a small impact.

BP are generally not affected by a flocculation under acidic conditions (as assumed here). An alkaline flocculation or a biological activated sand filter (with low filter flow rates) should decrease BP concentration to a larger extend. However, remaining BP concentration of 115 ppb C is diluted by addition of BP-free ground water and resulting BP concentration of 41 ppb C is not expected to cause serious problems with membrane fouling on RO membrane.

Addition of ground water is a big advantage for water quality in course of the current water treatment. Performance of RO membrane depends on the behaviour of LMW Neutrals fraction.

End of Report

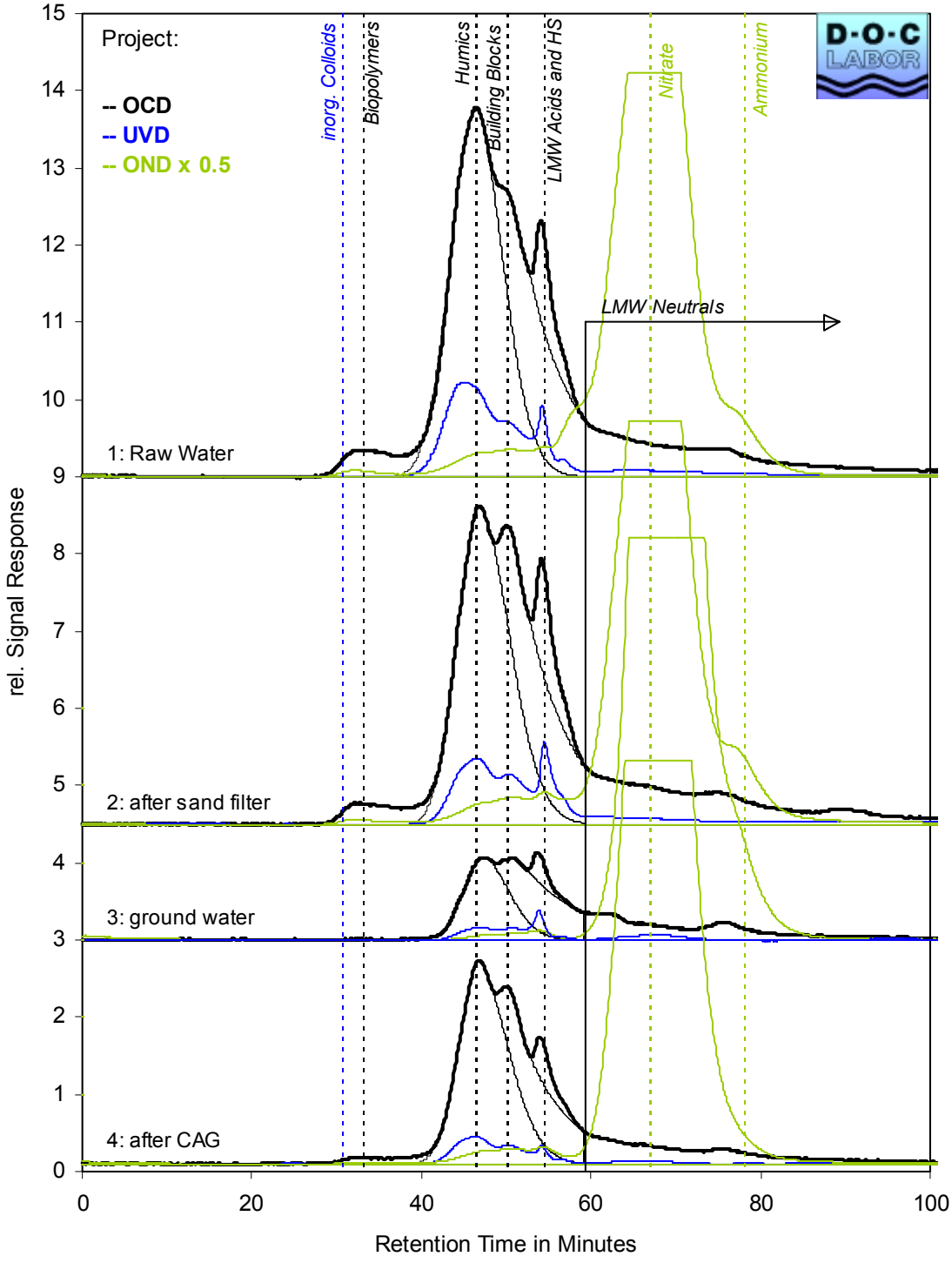

Fig. 1: LC-OCD chromatograms

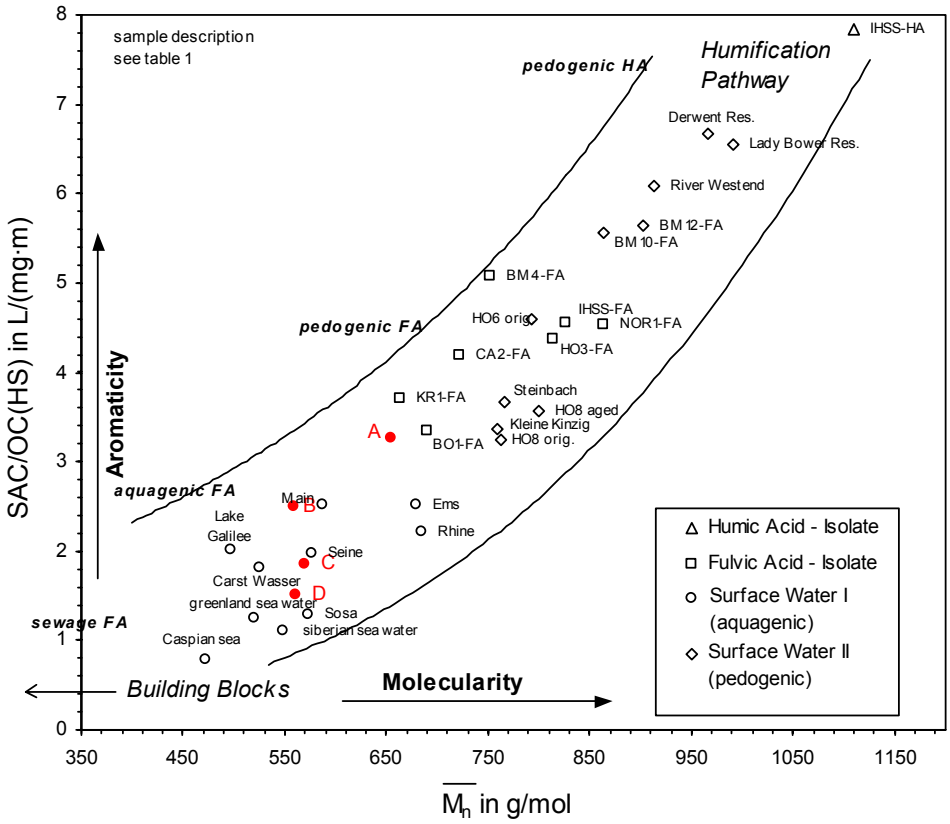

Fig. 2: Humic substances diagram

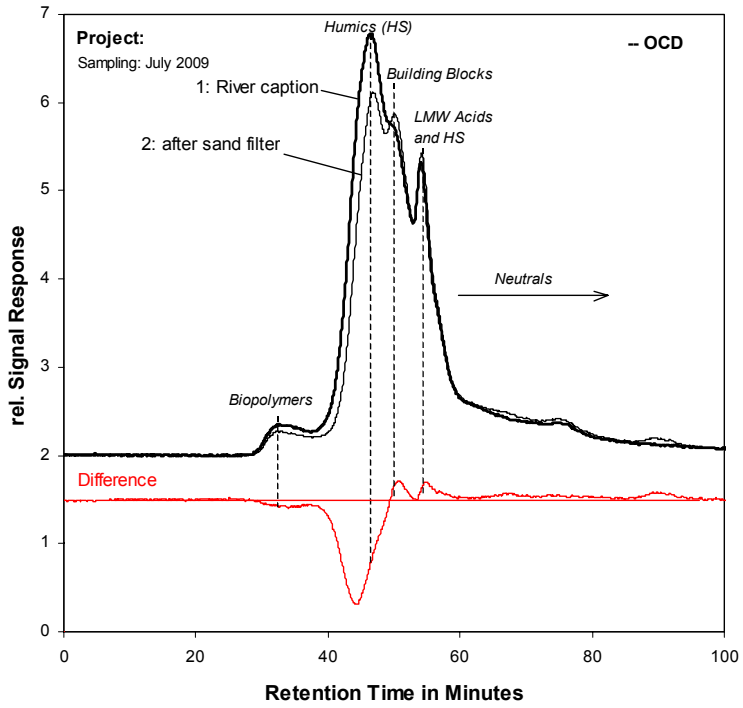

Fig. 3: Difference chromatogram of sample 1 and sample 2 (OCD signal only).