LC-OCD Analyses of ground water samples

Your proj.-ID/ our proj.-ID:
Project Partner/ contact:
 # and type of samples: 6 (water)
Measuring conditions: column: 5078 / 015 flows: 1.0 / 0.3 / Ø buffer: STD

Sampling date:	**2008-Dec-10**	**STD** ☐	**MC** ☒	**BC** ☐
Incoming date:	**2008-Dec-11**	**report:**	**Y** ☒	**N** ☐
Measuring date:	**2008-Dec-12-13**	**data processing:**	**Dipl.-Ing. A. Balz**	
Date of Report:	**2008-Dec-15**	**report:**	**Dr. S. Huber**	

Technical notes (see also our homepage): *LC-OCD stands for "Liquid Chromatography – Organic Carbon Detection". All values refer to "mass of* ***organic*** *bound* ***carbon*** *" (****OC****), not to total mass of compounds. As a „rule-of-thumb" compound mass is about twice (for acids threefold) the value of OC, only the molecular mass of humics refers to the total mass. Apart from OC, UV-absorbance at 254nm (SAC) is measured. Chromatograms are processed on the basis of area integration using the program FIFFIKUS. Recently, further detectors are available, like UV at 210 nm, 230 nm and 280 nm, and Dissolved Organic Nitrogen (DON). In many samples the acid fraction will contain low-molecular mass humic acids which are subtracted by FIFFIKUS on the basis of SAC//OC (HS) ratios.*

OCD = Organic Carbon Detector
UVD = UV-Detector (254 nm)
OND = Organic Nitrogen Detector (optional)

SUMMARIC PARAMETERS:

DOC (Dissolved OC): *Determined in the column bypass with an in-line 0.45 µm filter inserted into the sample stream.*

HOC (Hydrophobic OC): *Calculated as difference DOC minus CDOC (CDOC= Chromatographic DOC). Therefore, all OC retained on the column is defined as „hydrophobic". This could be either dissolved hydrocarbons etc. or microparticulate ("humins" in Ground waters).*

CDOC (Chromatographic DOC): *This is the OC value obtained by area integration of the total chromatogram. Subfractions of CDOC are either NOM or SOM (see below).*

INORGANIC COLLOIDS (determined in UV-Chromatograms): *Negatively charged inorganic polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al or Si are present here and are detected by UV light-scattering (Rayleigh-effect).*

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

NATURAL ORGANIC MATTER (NOM):

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).*

Building Blocks (HS-Hydrolysates): *The HS-fraction is overlain by broad shoulders. Shape, concentration and UV-activity varies. The shoulders can be produced from HS by ultrasonification or mild oxidation. This suggests that the shoulders are sub-units („building blocks") of HS with molecular weights between 300-450 g/mol. Building Blocks are perhaps weathering and oxidation products of HS, they cannot be removed in flocculation processes.*

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

LMW Neutrals: *According to theory, only low-molecular weight weakly charged hydrophilic or slightly hydrophobic ("amphiphilic") compounds appear in this fraction, like alcohols, aldehydes, ketones, amino acids. The hydrophobic character increases with retention time, e. g. pentanol at 120 min, octanol at 240 min. However, compounds eluting after 200 min are rated "hydrophobic" (HOC).*

Biopolymers (polysaccharides amino sugars, polypeptides, proteins; "EPS"): *This fraction is very high in molecular weight (100.000 - 2 Mio. g/mol), hydrophilic, not UV-absorbing. Polysaccharides exist only in surface waters.*

SYNTHETIC ORGANIC MATTER (SOM):

Basically any water-soluble synthetic organic compound can be quantified and identified (after comparison with compound) down to the low ppb-range. Sample composition should not be too complex however, as chromatographic resolution is limited. Typical SOMs im water are flocculant polymers, antiscalants, org. additives in water/steam cycles, resin leachables like polysulfonic acids or trimethyl amine.

Not measurable are hydrophobic SOMs like hydrocarbons, pesticides or long-chained tensides.

Results and Discussion

Pre-Note: All samples are high in nitrate (not quantified). It is possible that waters also contain ammonium (retention time is around 80 min and would be obstructed by peak for nitrate).

Samples 1-4

These 4 waters are very similar and can be discussed together.

DOC-values range from 1543 ppb to 2032 ppb.

All waters contain biopolymers, the concentrations range from 59 ppb C to 132 ppb C. Biopolymers are indicative for surface water input. Surface water input can be

a) meteoric (rain washes biopolymer from top soils into a shallow ground water aquifer), or

b) biopolymers from rivers or lakes penetrate into nearby ground water aquifers.

Should neither a) nor b) be applicable then a high microbial activity must be inferred.

The protein content of biopolymers is around 33 %. This suggests a microbial origin of biopolymers. Biopolymers produced from algae are lower in protein content. *#2* has the highest relative content of proteins in biopolymers (40 %), *#4* the lowest (22 %).

Humic substances range from 941 ppb C to 1191 ppb C. The quality (aromaticity and molecularity) is identical which suggests an identical history for these waters. Humics are fulvic acids of pedogenic origin. In the HS-diagram they are positioned at the upper end in the center. Thus, humics are quite high in aromaticity, or colour. Nevertheless, molecularity is moderate which suggests that removal of humics by flocculation is perhaps not as efficient as one would expect. Removal rates > 40 % should however be feasible.

HOC is very low in all waters and – except for *#4* (2.3 %) – below the limit of detection (< 1 %). Thus, hydrophobic compounds, like humins, are practically absent.

Building blocks are breakdown products of humics. Building blocks are around 19 % of DOC which is a typical figure for ground waters.

LMW-neutrals are around 15 %, which is also a typical value. There are no maxima found in the chromatograms, which suggests that also LMW-neutrals – together with humics and building blocks - are largely refractory.

Traces of free, saturated LMW-acids are found in all samples. This finding is rather unusual and suggests microbial activity It is possible that these LMW-acids contribute to AOC-parameters.

Samples 5-6

Also these waters are high in nitrate but they differ in the composition of NOM drastically.

a) DOC-values are around 500 ppb only.

b) Biopolymers are absent. The few traces found (< 10 ppb C) are ubiquitous in natural waters and are not significant.

c) Humics are of low aromaticity and molecularity and resemble aquagenic FA. The low DOC-content and the low aromaticity “would” suggest an in-situ flocculation process but this is unlikely because the ratio of humics to building blocks is typical for non-flocculated waters (in flocculation building blocks are not removed, only humics and biopolymers).

d) No traces of free LMW-acids are found.

Comments

In respect to NOM the ground waters (#5 and #6) are excellent waters for use as drinking water. We would think that no special treatment is required.

The other four waters are also quite good. Humics are such that a flocculation process is perhaps not mandatory but would be of advantage. Biopolymers are a matter of concern. These could cause biofilm formation and bacterial regrowth in distribution systems. We were told that all waters are “ground waters”. If this is correct then the origin of biopolymers should be studied in more detail.

End of Report

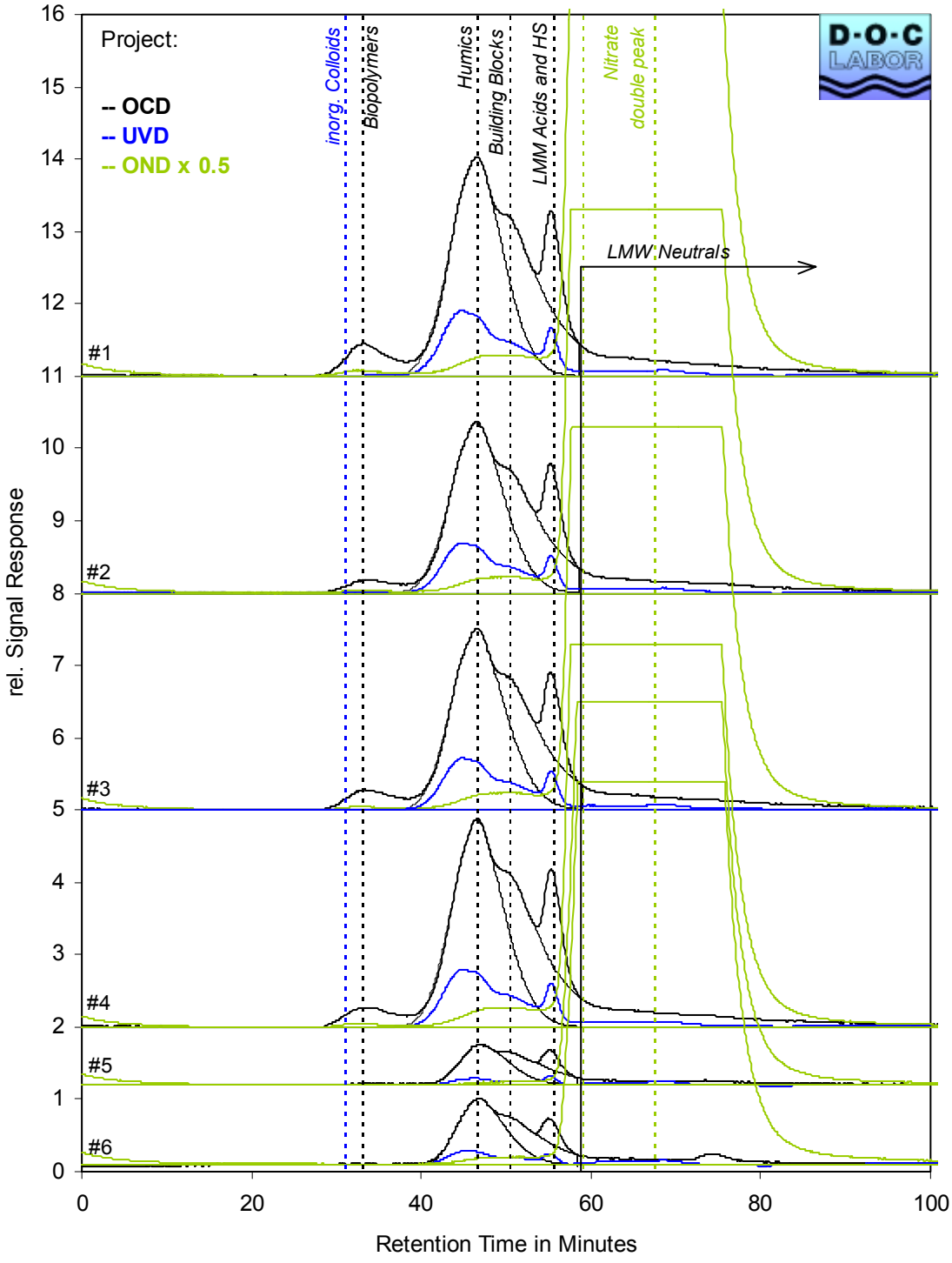

Fig. 1: LC-OCD chromatograms

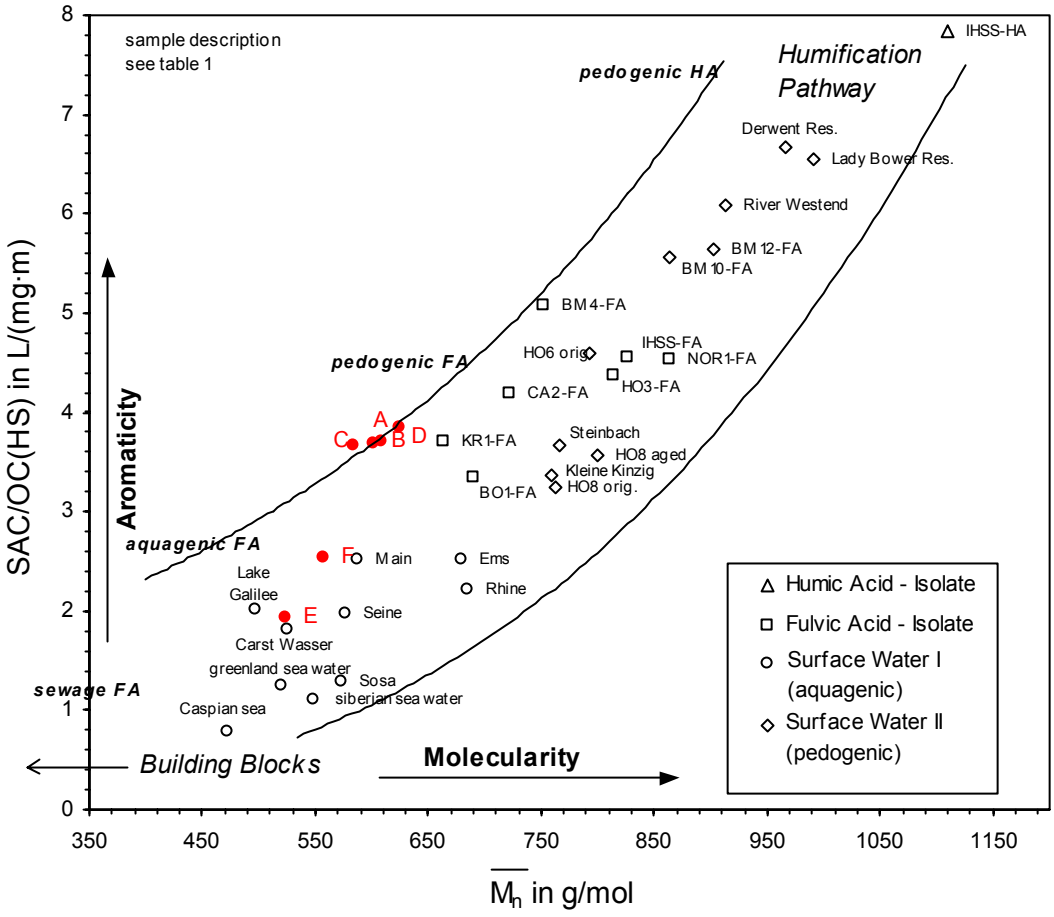

Fig. 2: Humic substances diagram

Table 1

Project:		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})	(SAC/DOC) L/(mg*m)
		% DOC	% DOC	% DOC	% DOC	--	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC	--	--
	#1	2032	12	2020	132	14	0,11	33	1191	50	0,04	3,85	625	A	379	296	21	0,06	3,28
		100%	0,6%	99,4%	6,5%	--	--	--	58,6%	--	--	--	--	--	18,7%	14,6%	1,0%	--	--
	#2	1543	7	1536	59	8	0,13	40	941	37	0,04	3,71	609	B	282	238	16	0,02	3,34
		100%	0,5%	99,5%	3,8%	--	--	--	61,0%	--	--	--	--	--	18,3%	15,4%	1,0%	--	--
	#3	1679	10	1669	93	9	0,10	29	1008	40	0,04	3,66	584	C	291	260	16	0,02	3,21
		100%	0,6%	99,4%	5,5%	--	--	--	60,1%	--	--	--	--	--	17,3%	15,5%	1,0%	--	--
	#4	1922	44	1878	91	7	0,07	22	1125	42	0,04	3,69	602	D	359	279	24	0,03	3,09
		100%	2,3%	97,7%	4,8%	--	--	--	58,5%	--	--	--	--	--	18,7%	14,5%	1,2%	--	--
	#5	413	45	368	8	n.q.	--	--	208	5	0,03	1,94	523	E	75	77	n.q.	0,00	2,95
		100%	10,8%	89,2%	1,9%	--	--	--	50,4%	--	--	--	--	--	18,2%	18,7%	--	--	--
	#6	577	33	544	4	n.q.	--	--	329	16	0,05	2,53	557	F	104	107	n.q.	n.q.	3,19
		100%	5,7%	94,3%	0,6%	--	--	--	57,0%	--	--	--	--	--	18,1%	18,5%	--	--	--

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 originates from proteins**