LC-OCD Analysis of raw water for demineralisation

Your proj.-ID/ our proj.-ID:
Project Partner/ contact:
 # and type of samples: 1 (water)
Measuring conditions: column: 5031 flows: 1.0 / 0.3 / 0.3 buffer: STD

Sampling date:	**2007-Aug-07**	**STD** ☒	**MC** ☐	**BC** ☐
Incoming date:	**2007-Aug-15**	**report:**	**Y** ☒	**N** ☐
Measuring date:	**2007-Aug-15**	**data processing:**	**Dipl.-Ing. A. Balz**	
Date of Report:	**2007-Aug-16**	**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:

TOC (Total OC): *Determined in the column bypass. TOC-values slightly too low are possible for samples rich in particulate bound OC (POC) due to incomplete oxidation in the Vacuum UV process (exposure time too low to destroy particles from "outside in").*

DOC (Dissolved OC): *Like for TOC, but an in-line 0.45 µm filter is inserted into the sample stream.*

POC (Particulate OC): *Calculated as difference TOC minus DOC.*

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

TOC is very high, around 8-10 ppm (there were flocs of humic acids in the sample which were not analyzed).

Refractory organic matter (Humics, Building Blocks, most of Neutrals, POC) make up about 96 % of TOC. Only 4 % of NOM can be attributed to biogenic organic matter (biopolymers). Biopolymers are very low in DON which suggests that this are polysaccharides produced by algae in the water body.

Humics are of pedogenic fulvic acid type. This means that humics were not produced in the water body but originate from soils or bogs.

Despite of very high TOC this water can be used for demineralisation processes because of the low amount in biogenic organic matter. By acidic flocculation up to 80 % of humics and 50 % of biopolymers should be removable, by caustic flocculation perhaps 60 % of humics and 80 % of biopolymers.

After demineralisation (SAC, SBA, MB) TOC should be around 200 ppb, this depends on how much biopolymers were removed in flocculation and SBA.

For TOC-values < 100 ppb a full rejection of biopolymers (UF or RO) is recommended.

Interestingly, this water is free of nitrate, thus there is obviously no agriculture in the neighbourhood!

End of Report

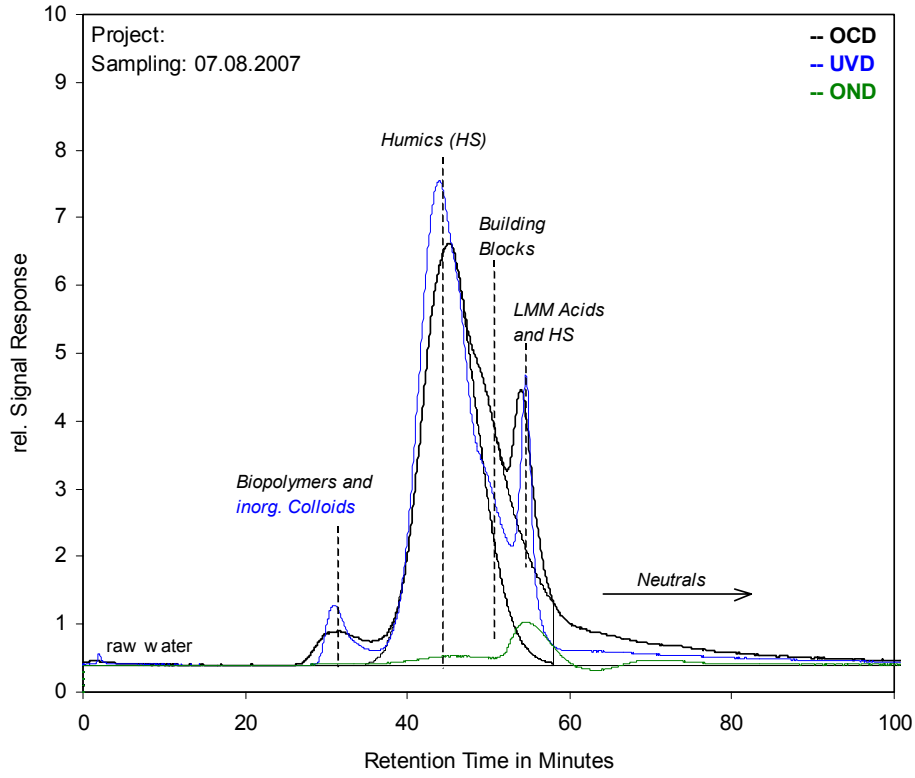

Fig. 1: LC-OCD chromatograms

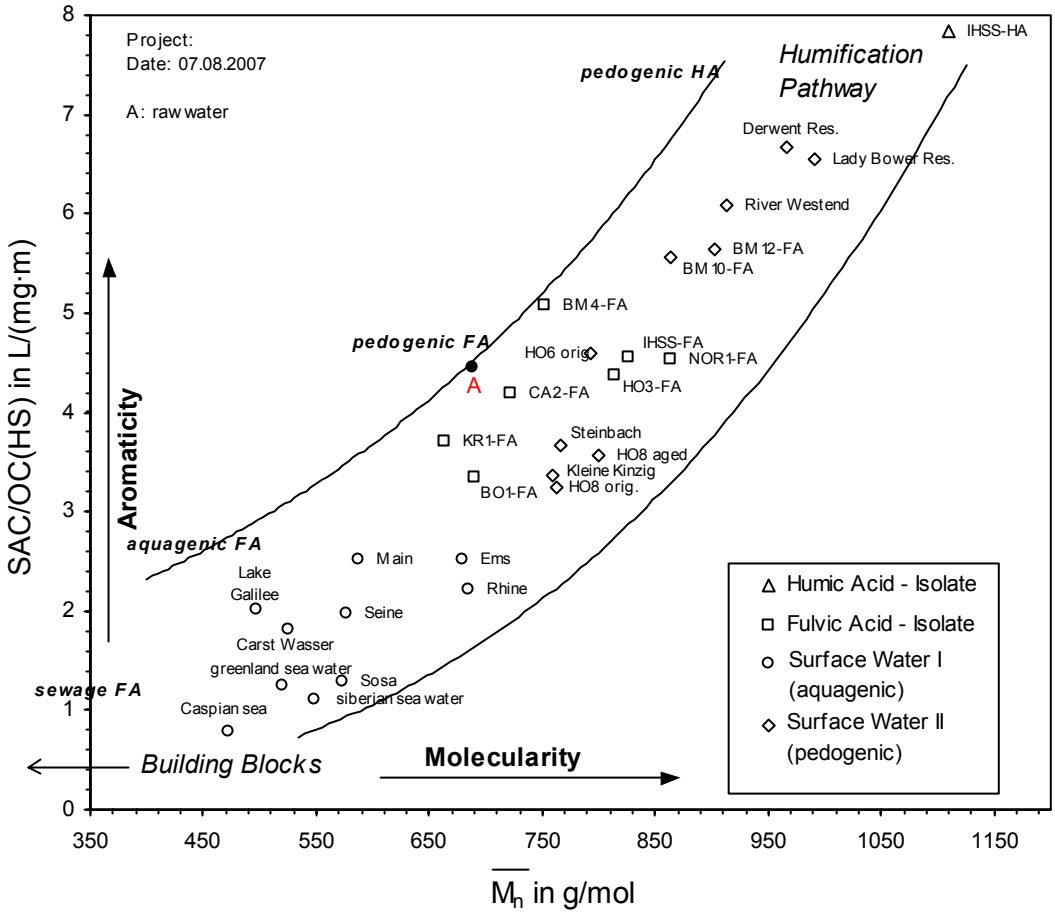

Fig. 2: Humic substances diagram

Table 1

Project:	TOC	POC	DOC	HOC	CDOC	Approx. Molecular Weights in g/mol:									(UV@254 nm)		
sampl.date 07.08.2007						>>20.000		~1000 (see separate HS-Diagram)				300-500	<350	<350			
	Total	Particul.	Dissolved	Hydrophob.	Hydrophil.	BIO-polymers	DON (Norg)	Humic Subst. (HS)	DON (Norg)	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Building Blocks	Neutrals	Acids	Inorg. Colloid. SAC	SAC	SUVA (SAC/DOC)
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	ppb-C	ppb-N	L/(mg*m)	g/mol	ppb-C	ppb-C	ppb-C	(m^{-1})	(m^{-1})	L/(mg*m)
	% TOC	% TOC	% TOC	% TOC	% TOC	% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--	--	--
raw water	**8073**	**252**	**7821**	**21**	**7801**	**334**	**6**	**5162**	**53**	**4,45**	**688**	**1250**	**1031**	**24**	**1,37**	**31,28**	**4,00**
	100	3,1	96,9	0,3	96,6	4,1	--	63,9	--	--	--	15,5	12,8	0,3	--	--	--

POC, thus TOC may be too low for some surface waters
LMW = low-molecular weight
DON = Dissolved organic nitrogen
bdl = below detection limit
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