LC-OCD-OND analysis of sewage treatment steps

Your proj.-ID/ our proj.-ID:
Project Partner/ contact:
 # and type of samples: 3 (water)
Measuring conditions: column: 5032 / 006 flows: 1.0 / 0.3 / Ø buffer: STD

Sampling date:	2008-Feb-	**STD** ☐	**MC** ☐	**BC** ☒
Incoming date:	2008-Feb-22	**report:**	**Y** ☒	**N** ☐
Measuring date:	2008-Feb-22	**data processing:**	**Dr. M. Abert**	
Date of Report:	2008-Feb-25	**report:**	**Dr. M. Abert**	

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

Sewage

DOC is 17.2 ppm. Hereof 13 % are hydrophobic (fats, HCs etc.), 24% are Biopolymers, 20% are humic material (mainly humic substances from drinking water, but to some extent newly formed in the sewage plant), 18% are building blocks (degradation products of humics, “new pre-humic” material and biodegradable material co-eluting in this fraction, see below), and 26 % are low molecular weight neutral compounds. Free organic acids were not found, but it is possible that these were present in the fresh sample and were degraded (samples were pasteurized?).

Biopolymers contain 561 ppb of organic bound N. If we assume that proteins contain 18 % N (as mass) and if we assume that proteins contain 52 % C then we can say that biopolymers are 59 % polysaccharidic material and 41 % proteinic material.

Secondary effluent

DOC is 3.0 ppm, thus degradation is 83 %. This value is not very good but we have to consider that 62 % of DOC is refractory (humics + building blocks).

HOC is degraded by 93 %, biopolymers by 92 %, humics by 60 % (we assume that this is not due to degradation but adsorption on biomass), building bocks by 82 % (we assume that this is biodegradable material co-eluting with building blocks), and neutrals by 85 %.

Biopolymers contain 62 ppb of organic bound N. If we assume that proteins contain 18% N (as mass) and if we assume that proteins contain 52 % C then we can say that biopolymers are 55 % polysaccharidic material and 45 % proteinic material.

Permeate

DOC is 2.2 ppm.

HOC has increased from 194 ppb C to 306 ppb C. We assume that this is due to the release of HOC adsorbed on biomass due to shear stress at membrane surface.

Biopolymers are reduced from 340 ppb C to 64 ppb C. This is a rejection rate of 82 %.

Humics are rejected by 40 %.

For the low molecular weight fractions (building blocks and neutrals) there is almost no impact.

Biopolymers contain 8 ppb of organic bound N. If we assume that proteins contain 18 % N (as mass) and if we assume that proteins contain 52 % C then we can say that biopolymers are 85 % polysaccharidic material and 15 % proteinic material.

Ammonium, Nitrate and urea

Sewage contains no nitrate, but ammonium (eluting at 70 min). There also may be urea present, co-eluting with ammonium. For correct quantification of ammonium and urea a different mobile phase has to be used for a special analysis (we can measure ammonium and urea down to the low-ppb range).

Secondary effluent and **Permeate** contain nitrate (nitrification process). Due to overflow (peak is “cut”) quantification is not possible. (Note: Nitrate appears as a “double peak” due to competitive ionic interactions between nitrate, the mobile phase and the chromatographic column).

End of Report

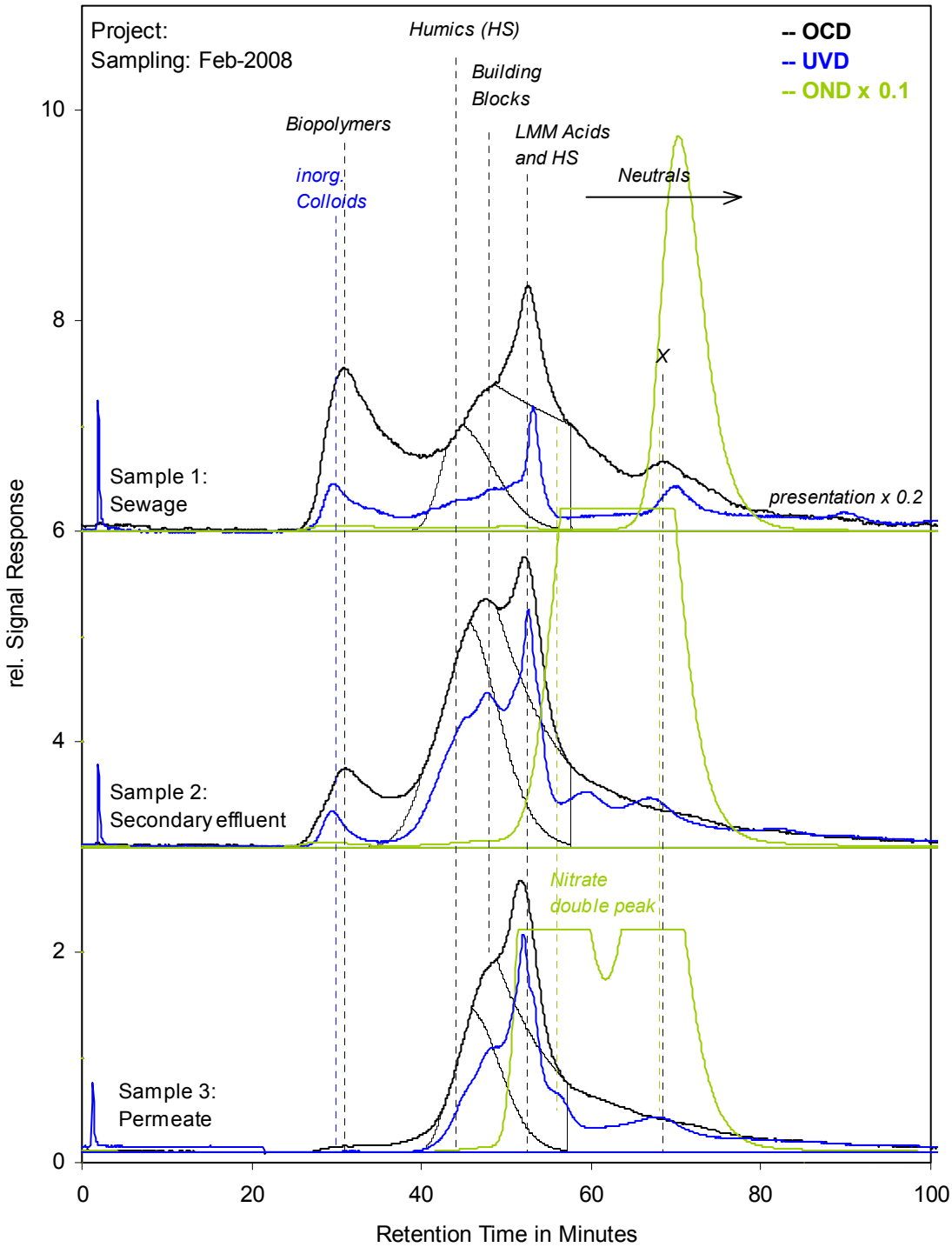

Fig. 1: LC-OCD chromatograms

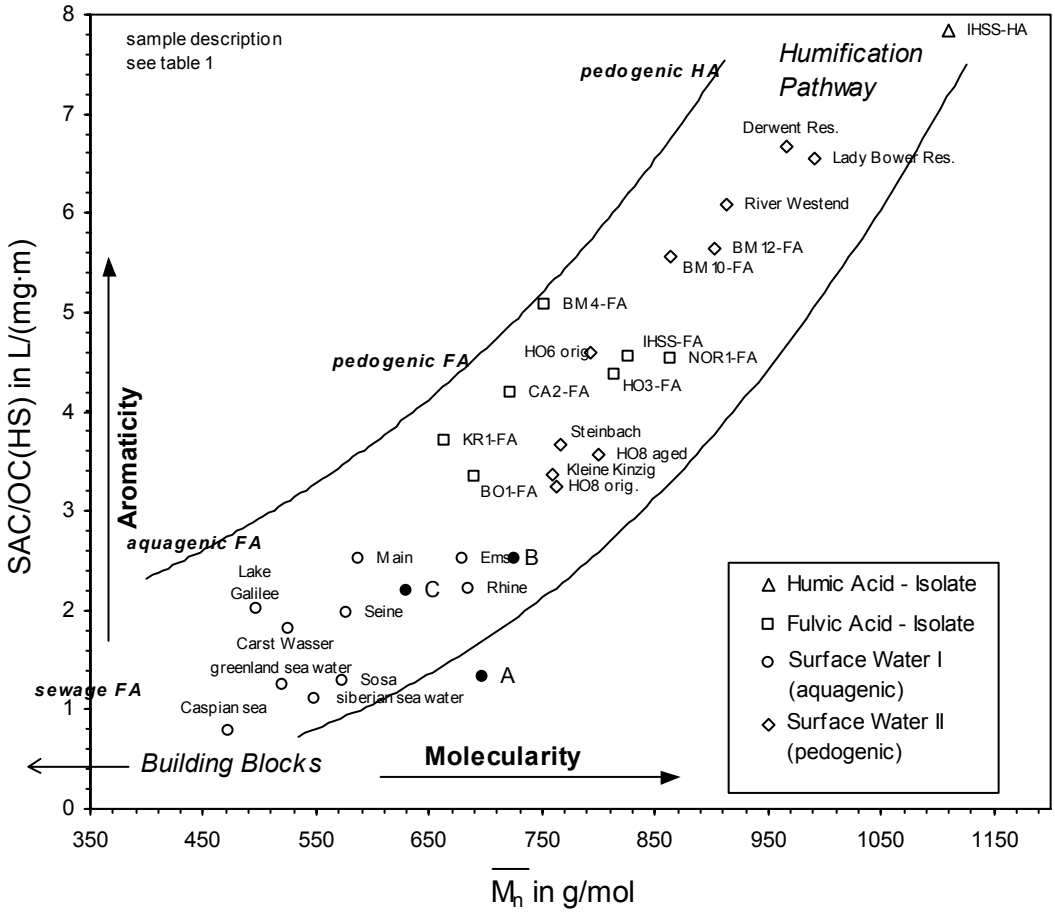

Fig. 2: Humic substances diagram

Table 1

Project:		DOC	HOC	CDOC	Approx. Molecular Weights in g/mol: >>20.000			~1000 (see separate HS-Diagram)					300-500	<350	<350		
sampl.date	Feb 2008				BIO-polymers	DON (Norg)	N/C	Humic Subst. (HS)	DON (Norg)	N/C	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Position in HS diagram	Building Blocks	Neutrals	Acids	Inorg. Colloid.	CSUVA
		Dissolved	Hydrophob.	Hydrophil.	ppb-C	ppb-N	µg/µg	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	--	ppb-C	ppb-C	ppb-C	SAC (m^{-1})	(CSAC/CDOC) L/(mg*m)
		% DOC	% DOC	% DOC	% DOC	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC	--	--
Sample 1:		**17246**	**2231**	**15015**	**4176**	**561**	**0,13**	**3354**	**237**	**0,07**	**1,33**	**697**	**A**	**3046**	**4438**	**1**	**4,46**	**1,75**
Sewage		100%	12,9%	87,1%	24,2%	--	--	19,5%	--	--	--	--	--	17,7%	25,7%	0,0%	--	--
Sample 2:		**3074**	**194**	**2881**	**340**	**62**	**0,18**	**1334**	**77**	**0,06**	**2,52**	**725**	**B**	**566**	**641**	**n.q.**	**0,42**	**3,19**
Secondary effluent		100%	6,3%	93,7%	11,1%	--	--	43,4%	--	--	--	--	--	18,4%	20,8%	--	--	--
Sample 3:		**2236**	**306**	**1930**	**64**	**8**	**0,13**	**797**	**42**	**0,05**	**2,19**	**630**	**C**	**499**	**569**	**n.q.**	**0,10**	**3,23**
Permeate		100%	13,7%	86,3%	2,9%	--	--	35,7%	--	--	--	--	--	22,3%	25,5%	--	--	--

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