Marine Waters and Membrane Autopsy

Your proj.-ID/ our proj.-ID: /
Project Partner/ contact:
 # and type of samples: 4 (water)
Measuring conditions: column: 570+5031 buffer: STDx2+STD

Sampling date:	**2007-Feb-05**	**STD** ☒	**MC** ☐	**BC** ☐
Incoming date:	**2007-Mar-02**	**report:**	**Y** ☒	**N** ☐
Measuring date:	**2007-Mar-03**			
Date of Report:	**2007-Mar-05**			

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.*

DOC (Dissolved OC): *Like for TOC, but a small 0.45 µm filter is inserted automatically in the sample stream.*

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

HOC (Hydrophobic OC): *Calculated as difference TOC - CDOC (CDOC= Chromatographic DOC). CDOC is the OC value obtained by area integration of the total chromatogram. Therefore, all OC retained on the column is defined as „hydrophobic".*

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.*

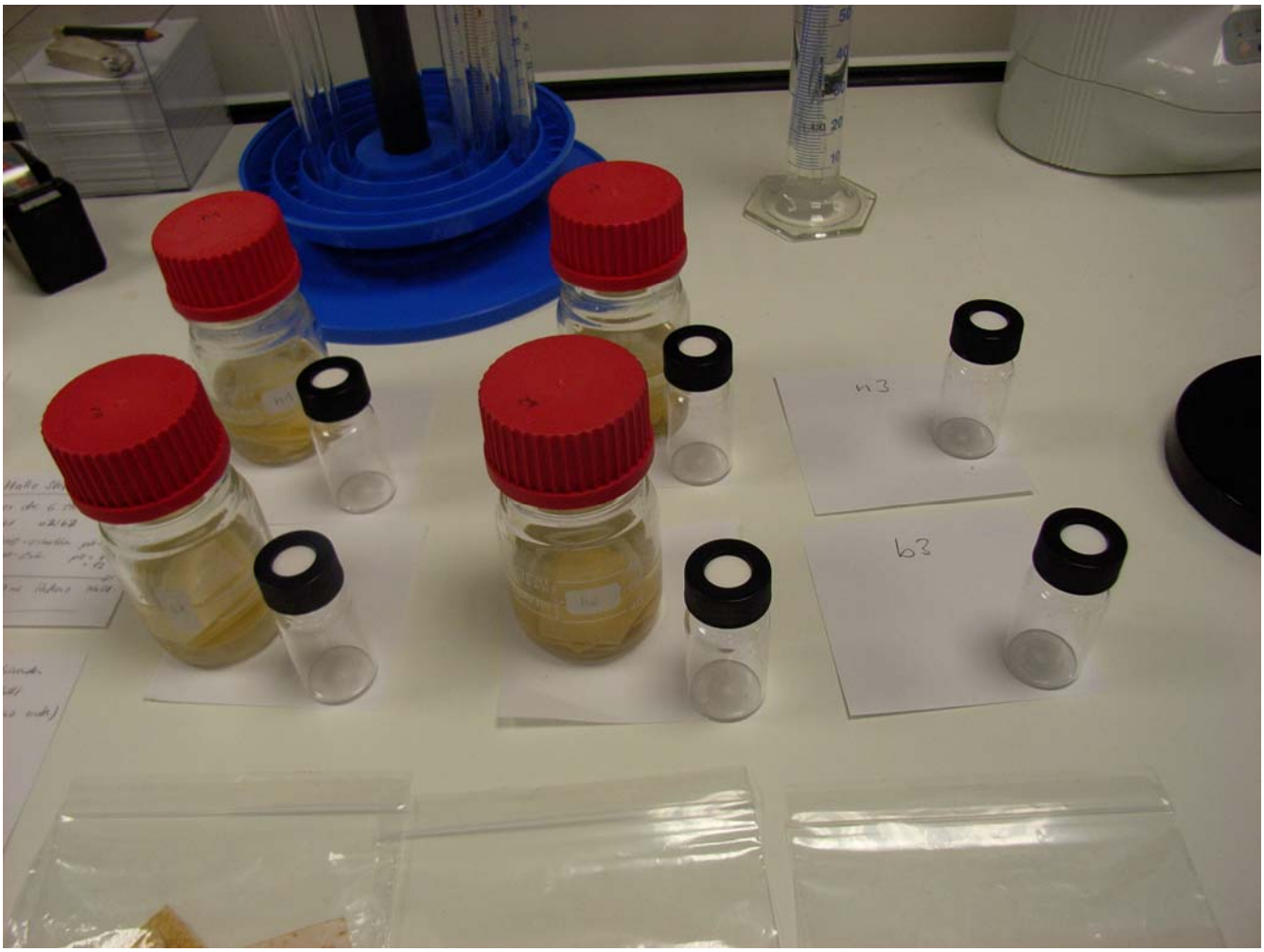
Inorganic Colloids (found only in UV-Chromatograms): *Negatively charged inorganic polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al or Si are present here and are detected by UV light-scattering (Rayleigh-effect).*

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 quite limited. Typical SOMs im water treatment are flocculant polymers, antiscalants, org. additives in water/steam cycles, resin leachables like polysulfonic acids and trimethyl amine.

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

Results and Discussion



Membrane Extracts of inlet, center, outlet (left to right). Upper row: Neutral extraction; lower row: extraction pH 12.

Extraction conditions: 3 pre-cut pieces of membrane (total area between 25 cm² and 35 cm² , precise area on demand) were added to 50 mL of labwater or pH 12 water, ultrasonificated for 16 min, soaked for 24 hrs, neutralized with sulfuric acid. Thereafter, about 10 mL were filtrated over 0.45 µm and directly measured.

Results and Discussion

Marine Waters (see also fig .1 and table 1)

These waters were measured with a different chromatographic column and a stronger mobile phase after 1:2 dilution with labwater.

TOC of the RO feed water is 793 ppb. This is an extremely low TOC-value and suggests that this water is a “deep” water with little nutrients. However, the amount in biopolymers is relatively high (54 ppb C or 6.8% of TOC). Also the amount in LMW-neutrals is relatively high (266 ppbC or 33.5%). This suggests high amount in biogenic organic matter.

The Brine water is about F = 1.76 x the feed water. If we look at the enrichment factor for individual fractions we can say that humics were “lost” significantly (F = 1.67) while biopolymers seem to behave conservative (F = 2.09). Humics are very low in aromaticity, therefore there is almost no yellow colour.

Membrane Extracts (see also fig . 2 and table 2)

TOC-values were all quite low. Humics substances were found only in small amounts and these are low in aromaticity (like in the feed water). **Therefore it is clear that the yellow colour of the extracts (see photo) is of inorganic origin (e.g. very fine clay).** As to be expected, particulate organic carbon (POC) is a major component of all samples. All other TOC is practically hydrophilic

When we look at the qualitative composition we find a complex situation.

Aqueous extracts: The center extract consists almost exclusively of biopolymers. The inlet sample is also dominated by biopolymers, but humic material can also be found. In contrast to these the outlet sample is dominated by humics.

As far as OCD (organic carbon detection) is concerned there are only little differences in quantity and quality between aqueous extracts and caustic extracts. This suggests that we were able to remove almost all TOC by aqueous extraction. The caustic extracts are lower in biopolymers in Inlet and Outlet sample. We think that this is due to beginning of caustic hydrolysis of biopolymers.

The caustic extracts show significant response in the UV-range. These responses correspond to the fractions “humics”, “building blocks” and “acids” but the responses are much too high for aromatic structures (otherwise we would find these structures in the feed water). We therefore assume that caustic extraction released inorganic, yellow material which was associated with organic matter. This inorganic material could not be released by aqueous extraction.

<u>The question is: Where do biopolymers come from?</u> The comparison between feed and brine suggests that biopolymers were not retained in the modules. Therefore their existence is unclear. Were biopolymers produced on the membrane by microbial activity during operation? It is quite likely that biopolymers acted as a “glue” to fix inorganic material on the membrane.

It is suggested to investigate more deeply in the origin of the biopolymer fraction

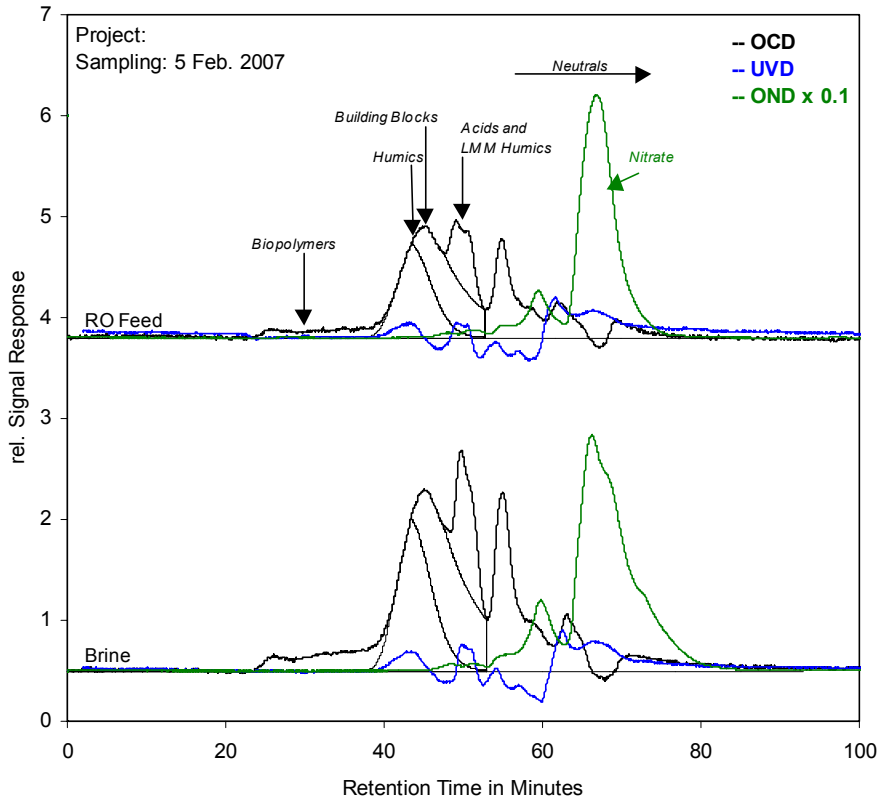


Fig. 1

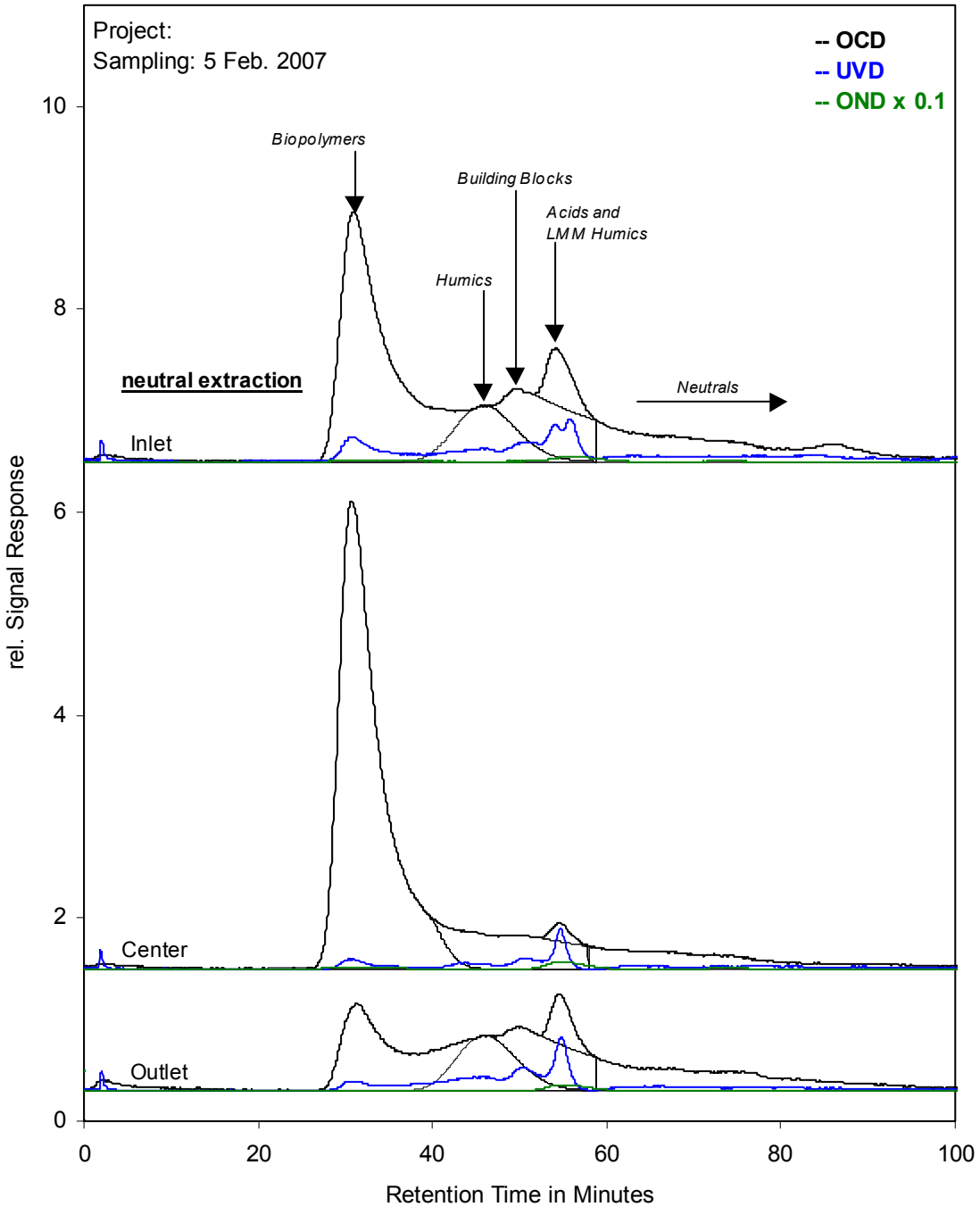

Project:
Sampling: 5 Feb. 2007
-- OCD
-- UVD
-- OND x 0.1
Biopolymers
Building Blocks
Acids and
LMM Humics
Humics
neutral extraction
Neutrals
Inlet
Center
Outlet
rel. Signal Response
Retention Time in Minutes
0
2
4
6
8
10
0
20
40
60
80
100

Fig.2

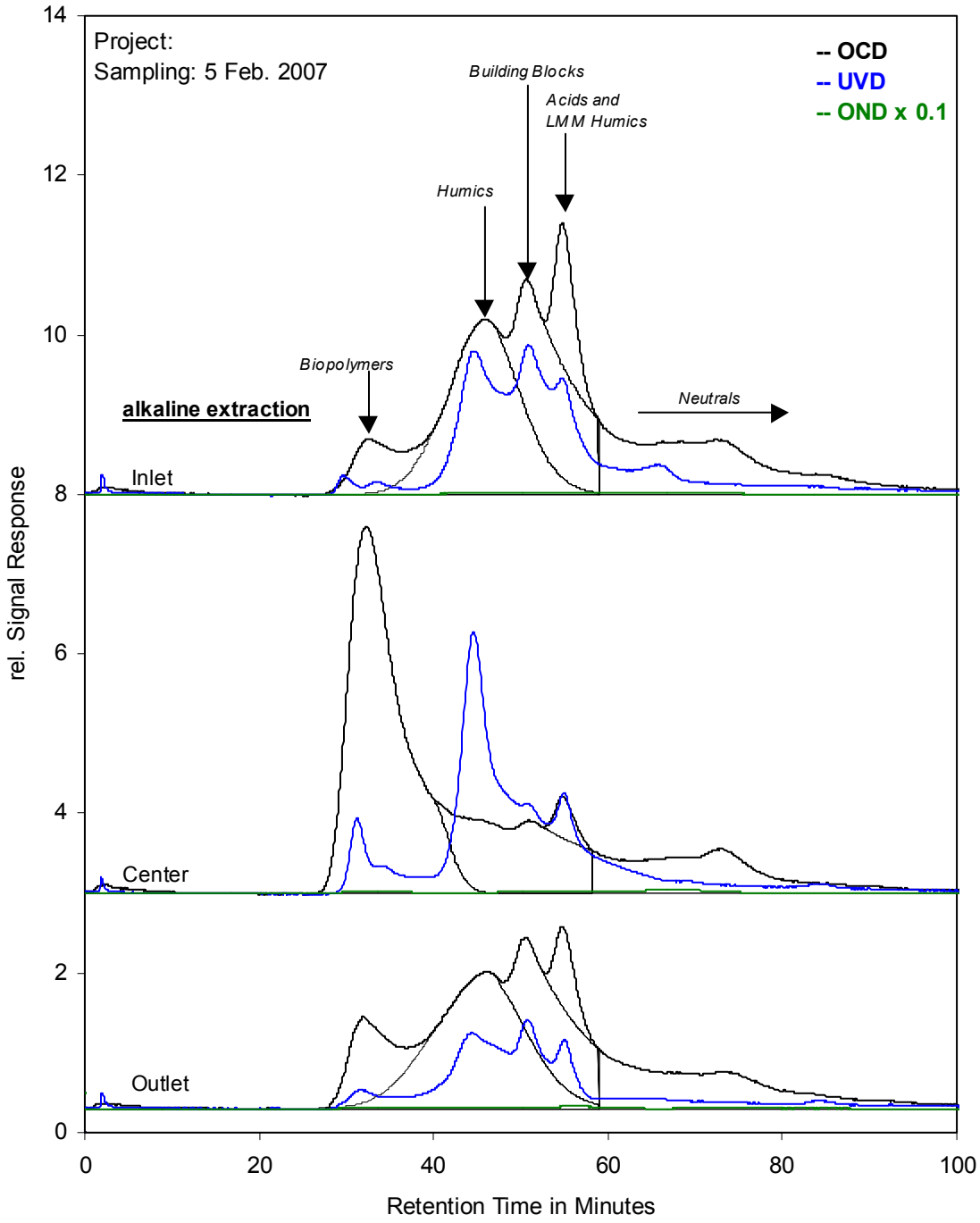

Project:
Sampling: 5 Feb. 2007
-- OCD
-- UVD
-- OND x 0.1
Building Blocks
Acids and
LMM Humics
Humics
Biopolymers
Neutrals
alkaline extraction
Inlet
Center
Outlet
rel. Signal Response
Retention Time in Minutes
0
2
4
6
8
10
12
14
0
20
40
60
80
100

Fig. 3

Project:

sampl.date 5 Feb. 2007

Approx. Molecular Weights in g/mol:

	TOC	Hydrophil.	>>20.000 BIO-polymers	DON (Norg)	~1000 (see separate HS-Diagram) Humic Subst. (HS)	DON (Norg)	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	300-500 Building Blocks	<350 Neutrals	<350 Acids	UV(254 nm) Inorg. Colloid.
	ppb-C	ppb-C	ppb-C	ppb-N	ppb-C	ppb-N	L/(mg*m)	g/mol	ppb-C	ppb-C	ppb-C	SAC (m^{-1})
	% TOC	% TOC	% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--
RO Feed	**793**	**54**	**4**	**302**	**4**	**0,75**	**783**	**171**	**266**	**bdl**	**0,00**	
	100,0	6,8	--	38,1	--	--	--	21,6	33,5	--	--	
Brine	**1402**	**113**	**bdl**	**505**	**6**	**0,60**	**785**	**311**	**472**	**bdl**	**bdl**	
	100,0	8,1	--	36,1	--	--	--	22,2	33,7	--	--	

Project:

sampl.date 5 Feb. 2007

Approx. Molecular Weights in g/mol:

	TOC	Total OC	POC Particul.	DOC Dissolved	HOC Hydrophob.	CDOC Hydrophil	>>20.000 BIO-polymers	DON (Norg)	~1000 (see separate HS-Diagram) Humic Subst. (HS)	DON (Norg)	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	300-500 Building Blocks	<350 Neutrals	<350 Acids	(UV@254 nm) Inorg. Colloid.	SAC	SUVA
	ppb-C	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	SAC (m^{-1})	SAC (m^{-1})	(SAC/DOC) L/(mg*m)
	% TOC	% TOC	% TOC	% TOC	% TOC	% TOC	% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--	--	--
Inlet	**2739**	**1105**	**1634**	**78**	**1555**	**703**	**21**	**297**	**6**	**1,04**	**579**	**216**	**339**	**bdl**	**0,28**	**6,81**	**2,49**	
neutral extraction	100	40,4	59,6	2,9	56,8	25,7	--	10,8	--	--	--	7,9	12,4	--	--	--	--	
Inlet	**3897**	**770**	**3128**	**401**	**2727**	**186**	**2**	**1098**	**28**	**2,24**	**597**	**601**	**739**	**103**	**0,26**	**10,09**	**2,59**	
alkaline extraction	100	19,7	80,3	10,3	70,0	4,8	--	28,2	--	--	--	15,4	19,0	2,6	--	--	--	
Center	**2193**	**580**	**1613**	**bdl**	**1613**	**1163**	**34**	**bdl**	**bdl**	**--**	**--**	**224**	**205**	**21**	**0,08**	**0,62**	**0,28**	
neutral extraction	100	26,5	73,5	--	73,5	53,0	--	--	--	--	--	10,2	9,3	0,9	--	--	--	
Center	**3990**	**1339**	**2650**	**bdl**	**2650**	**1518**	**58**	**bdl**	**bdl**	**--**	**--**	**569**	**503**	**61**	**0,44**	**41,97**	**10,52**	
alkaline extraction	100	33,6	66,4	--	66,4	38,0	--	--	--	--	--	14,3	12,6	1,5	--	--	--	
Outlet	**1442**	**323**	**1119**	**110**	**1008**	**302**	**8**	**265**	**5**	**1,13**	**570**	**177**	**265**	**bdl**	**0,15**	**0,96**	**0,66**	
neutral extraction	100	22,4	77,6	7,7	69,9	20,9	--	18,4	--	--	--	12,3	18,4	--	--	--	--	
Outlet	**3546**	**979**	**2568**	**206**	**2362**	**258**	**16**	**1084**	**23**	**1,66**	**585**	**430**	**590**	**bdl**	**0,30**	**3,66**	**1,03**	
alkaline extraction	100	27,6	72,4	5,8	66,6	7,3	--	30,6	--	--	--	12,1	16,6	--	--	--	--	

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