LC-OCD Analysis of organics in seawater TP

Your proj.-ID/ our proj.-ID:
Project Partner/ contact:

# and type of samples:	**7 (water)**		
Measuring conditions:	**column: 5075 / 015**	**flows: 1.0 / 0.3 / Ø**	**buffer: STD**

Sampling date:	**2008-Feb-19/25**	**STD** ☐	**MC** ☐	**BC** ☒
Incoming date:	**2008-Mar-07**	**report:**	**Y** ☒	**N** ☐
Measuring date:	**2008-Mar-07-09**	**data processing:**	**Dipl.-Ing. A. Balz**	
Date of Report:	**2008-Mar-10**	**report:**	**Dr. S. Huber**	

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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

Site A

Raw Water

DOC of Raw water is 890 ppb. Hereof, 55 ppb C belong to the most critical fraction of biopolymers. This value is very low for a coastal seawater which is of advantage for demineralisation. From this it maybe concluded that:

1) there is no influence from terrestrial surface waters,

2) sea water comes perhaps from a deep water source (no or only narrow continental shelf).

The shape of the biopolymer fraction is also quite favourable. In contrast to Site B (see below) there is no accumulation of biopolymers at the column exclusion limit at about 30 min. This shows that the molecular weight distribution of biopolymers does not extent to more than about 100.000 g/mol and decreases uniformly to a molecular weight of about 5.000 g/mol (incept of humic substances peak).

The other fractions of DOC are not unusual. It may be noted that the amount in low molecular weight neutrals is relatively high (33%). This fraction contains also (as the biopolymer fraction) biodegradable organic matter. We still have little experience in interpreting this fraction in respect to RO-fouling. Should fouling be experienced at this site then the neutrals fraction is considered to be mainly responsible for this.

RO-feed

This water is almost identical to the raw water. It is difficult to say whether the observed small differences in individual fractions are significant both in terms of analytical reproducibility and/or natural fluctuations in sea water composition.

It may be argued that – owing to the favourable composition of the raw water – there cannot be a major impact for pretreatment.

RO-brine

Values are – as to be expected – significantly higher and range from 140 % (biopolymers) to 184 % (building blocks). For DOC, the increase is 172 %. The low value for biopolymers may reflect a “loss” of biopolymers at the membrane surface. Nevertheless, the effect is little and has perhaps no negative impact on performance.

Site B

Raw Water

Despite of similarly low DOC (1095 ppb), the qualitative composition is worse, mainly in respect to biopolymers and neutrals. For biopolymers we find that 8 ppb C elute with the exclusion limit and reflect molecular weights in excess to 100.000 g/mol. In the neutrals fraction we find 2 marked peaks at around 70 min.

Penetrated sea water

Pre-treatment has a clear positive impact on DOC-composition. The biopolymer fraction has decreased by about 50%, the high-molecular weight fraction of 8 ppb C has completely disappeared. Also for the other fractions we find significant reduction, except for organic acids (perhaps due to an oxidation process).

RO-feed

This water is almost identical to “penetrated sea water”, the differences are presumably not significant.

RO-Brine

Increases range from 152 % (biopolymers) to 339 % (building blocks). For biopolymers and humics the increase is lowest which suggests that some of this material is “lost” in the RO modules. For DOC, the increase is 239 %. This finding may reflect a fouling problem of the RO at this site.

End of Report

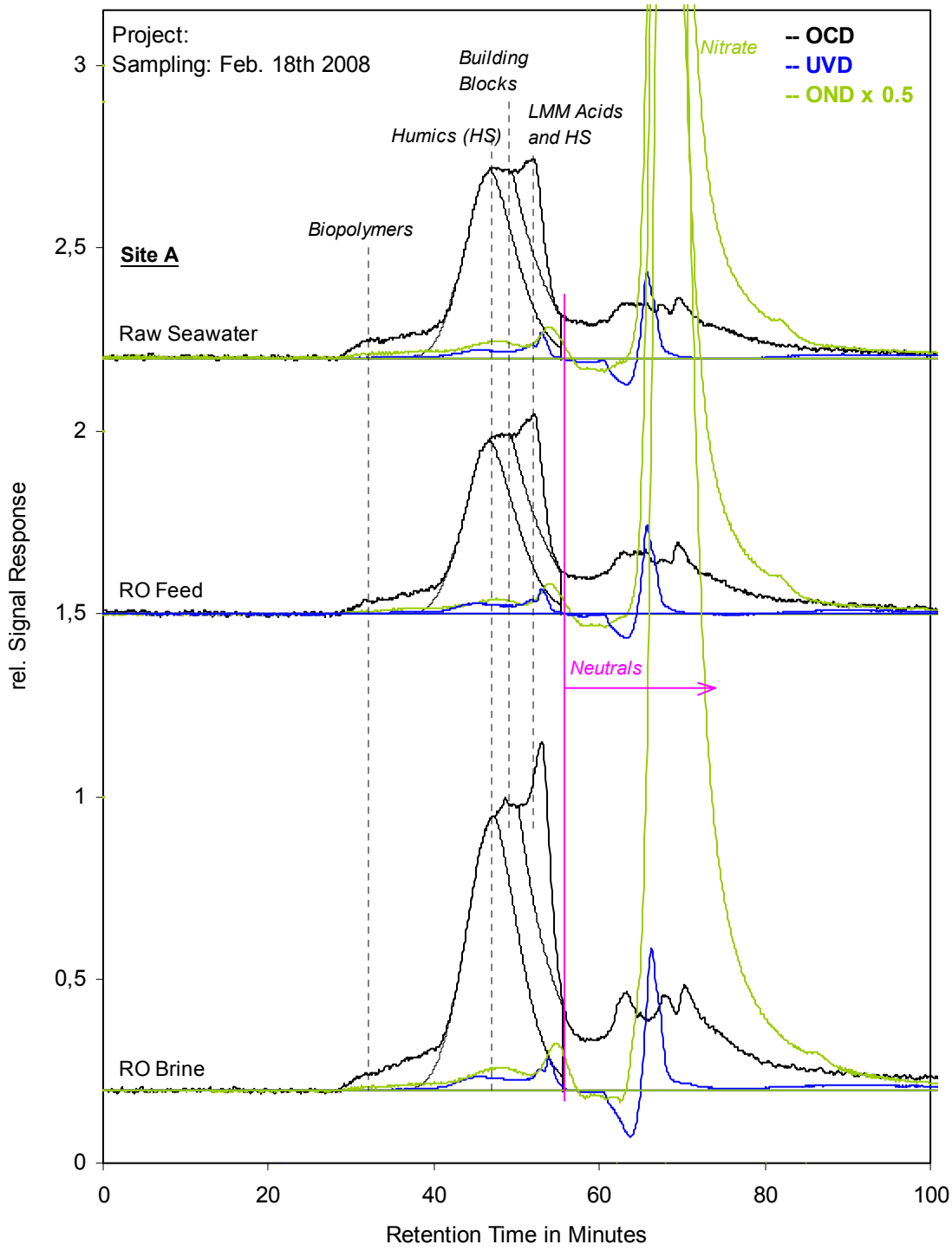

Fig. 1: LC-OCD chromatograms Site A

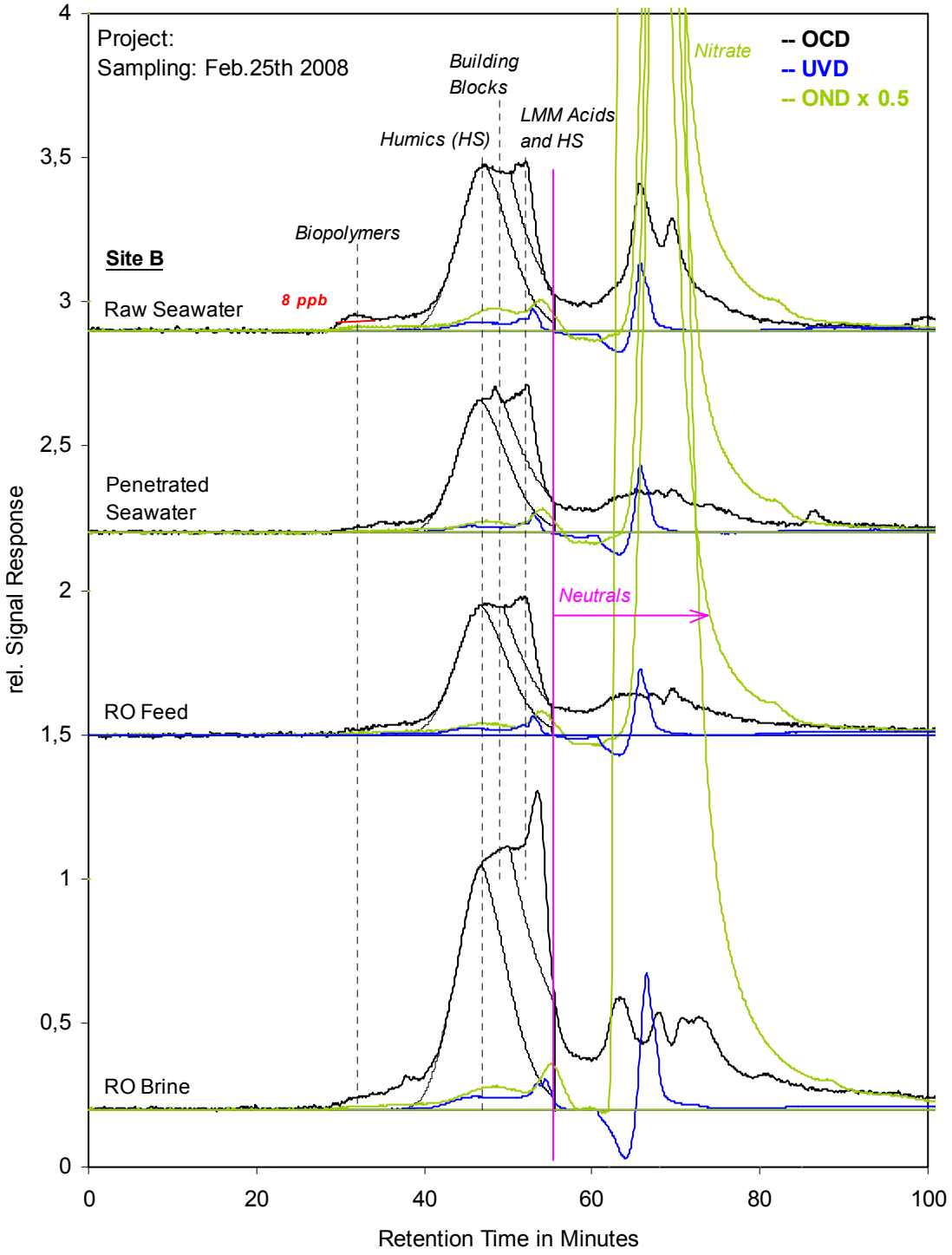

Fig. 2: LC-OCD chromatograms Site B

Table 1

Project:			Approx. Molecular Weights in g/mol:								UV(254 nm)
sampl.date Feb. 2008			>>20.000		~1000 (see separate HS-Diagram)				300-500	<350	<350	
	DOC		BIO-polymers	DON	Humic Subst. (HS)	DON	Aromaticity	Mol-Weight	Building Blocks	Neutrals	Acids	Inorg. Colloid.
	Hydrophil.			(Norg)		(Norg)	(SUVA-HS)	(Mn)				SAC
	ppb-C		ppb-C	ppb-N	ppb-C	ppb-N	L/(mg*m)	g/mol	ppb-C	ppb-C	ppb-C	(m^{-1})
	% TOC		% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--
Site A	**890**		**55**	**7**	**375**	**18**	**0,46**	**656**	**96**	**297**	**66**	**0,02**
Raw Seawater	100,0		6,2	--	42,1	--	--	--	10,8	33,4	7,5	--
Site A	**918**		**46**	**6**	**346**	**15**	**0,74**	**657**	**101**	**355**	**71**	**0,03**
RO Feed	100,0		5,0	--	37,7	--	--	--	11,0	38,6	7,7	--
Site A	**1536**		**65**	**5**	**553**	**21**	**0,52**	**640**	**186**	**602**	**129**	**0,01**
RO Brine	100,0		4,2	--	36,0	--	--	--	12,1	39,2	8,4	--
Site B	**1095**		**50**	**8**	**412**	**23**	**0,52**	**631**	**108**	**474**	**50**	**0,02**
Raw Seawater	100,0		4,6	--	37,6	--	--	--	9,9	43,3	4,6	--
Site B	**828**		**29**	**4**	**324**	**14**	**0,57**	**644**	**99**	**312**	**65**	**0,02**
Penetrated Seawater	100,0		3,5	--	39,1	--	--	--	11,9	37,7	7,8	--
Site B	**809**		**31**	**4**	**319**	**14**	**0,54**	**649**	**83**	**315**	**61**	**0,01**
RO Feed	100,0		3,9	--	39,5	--	--	--	10,2	38,9	7,5	--
Site B	**1936**		**73**	**7**	**606**	**27**	**0,56**	**648**	**282**	**829**	**146**	**0,01**
RO Brine	100,0		3,8	--	31,3	--	--	--	14,6	42,8	7,5	--

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