HET WATERLABORATORIUM

Characterization of NOM by LC-OCD

Principle, Possibilities and Points of Attention

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Contents

- Natural Organic Matter (NOM)
- Methods of Measurement
- LC-OCD
  - History
  - Principles
- Application of LC-OCD
- Factors influencing measurements
- Conclusions

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Normal Organic Matter (NOM)

- Complex mix of molecules with a large variation
- Origin is from breakdown of material of animals, plants and micro-organisms present in nature (but also of anthropogenic nature)
- Components consists mainly of carbon, hydrogen, oxygen, nitrogen and sulphur
- Size variates from small acids and aminoacids (100 – 200 amu) to humic/fulvic acids and aggregates (1000 – 10.000 amu) till even biopolymers (proteins and polysacharides) (till 2.000.000 amu)
- Components are aliphatic, aromatic, polar, non polair of stucture and may have a colour (yellow/brown)

NOM influences

- Purification Proces
  - Advanced Oxydation
  - Membrane filtration
- Growth of bacteria in the distribution system (AOC)
- Corrosion

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Method of Analysis

- TOC, DOC (after filtration on 0.45 um), UV 254 (double bonds)
- XAD-4 and XAD-8 fractionation for polar, non-polar and hydrophobic NOM (Leenheer)
- Fluorescence Excitation Emission Matrices (humus like and protein like NOM)
- GC-MS
- MaldiTof
- Size Exclusion Chromatography

Analysis Method LC-OCD

- Liquid Chromatography based on Size-Exclusion Chromatography (SEC)
- Detection: OCD (Organic Carbon Detector, continue measurement with high sensitivity), continue UV-absorption (aromatics) and continue OND (Organic NitrogenDetector)

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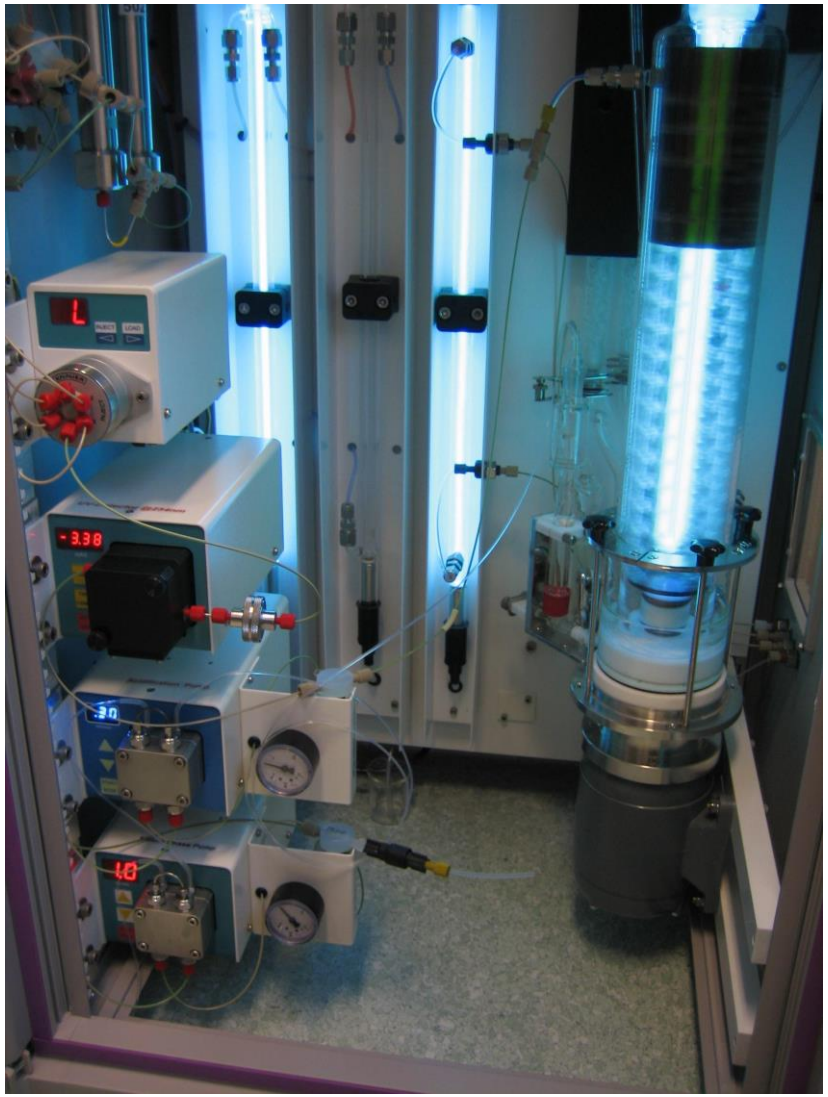
Principle LC-OCD



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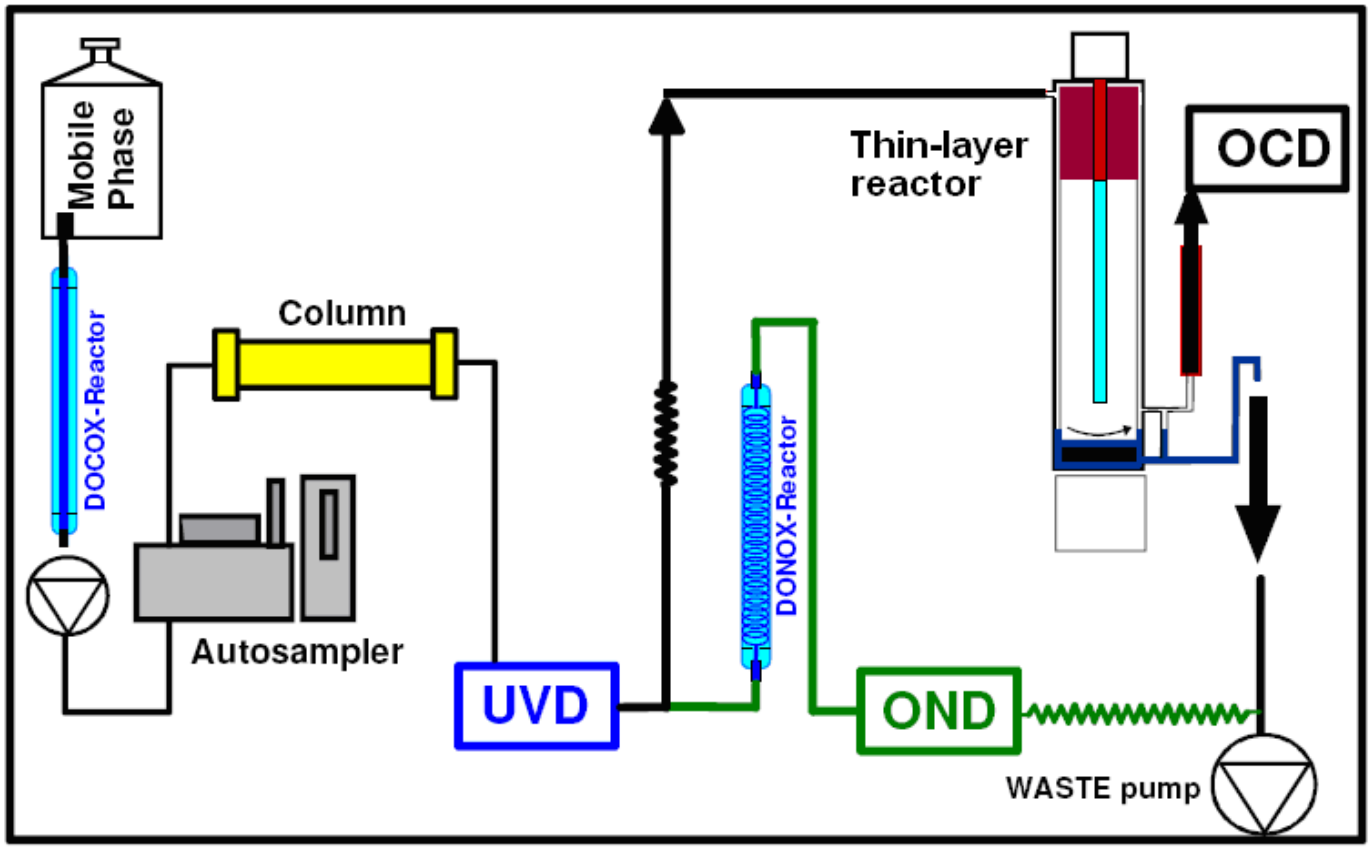


Principle LC-OCD

3 Measurements:

- Small amount directly to detectors bypassing the colum -> TOC
- Small amount online filtered over 1,2 um glassfibre filter also directly to detectors bypassing the column -> DOC
- 5 ml sample chromatographed on colum and the entering the detectors -> CDOC

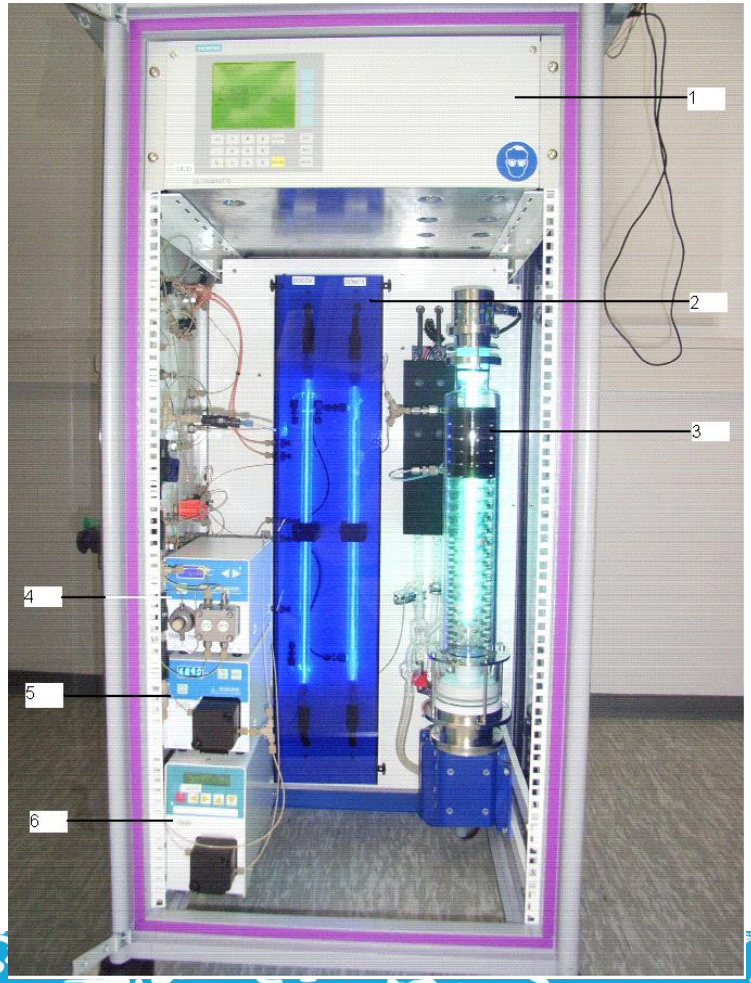
Column: GPC-kolom Toyopearl HW-50S, 30 µm (250 x 20) (hydroxylated methacrylic polymer)

Principle LC-OCD

Precautions:

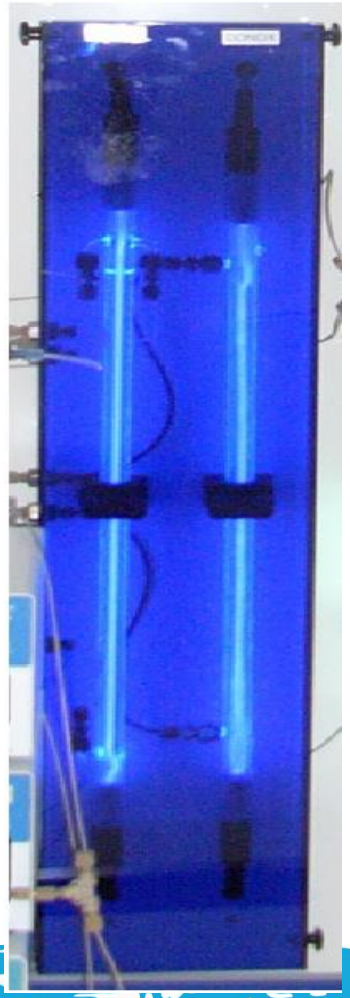
- Use special cleaned vials (available from HWL)
- Avoid fragrances (perfume, after shave) during sampling and handling

Principle LC-OCD



1. OCD-detector
2. DOCOX/DONOX
3. Thin layer reactor
4. Colums
5. UV-detector
6. OND-detector

Principle LC-OCD

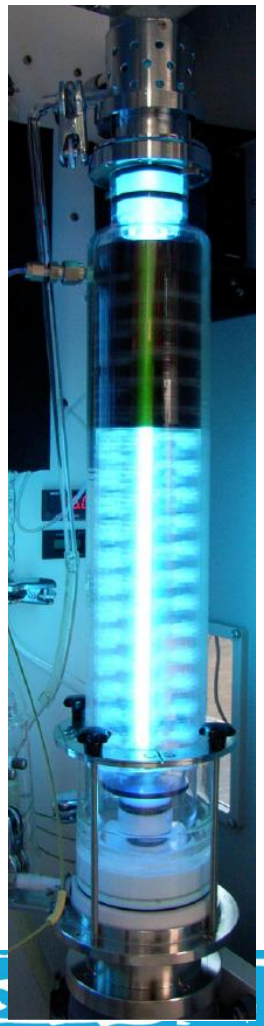


- Reactor consists of 2 UV lamps

- DOCOX (left)
- Eluent
- Organic Substances -> CO_2

- DONOX (right)
- Sample
- Nitrogen -> NO_3

Principle LC-OCD



- Removal of Inorganic Carbon (acidification, purging)

- Oxidation of Organic Carbon and Ureum

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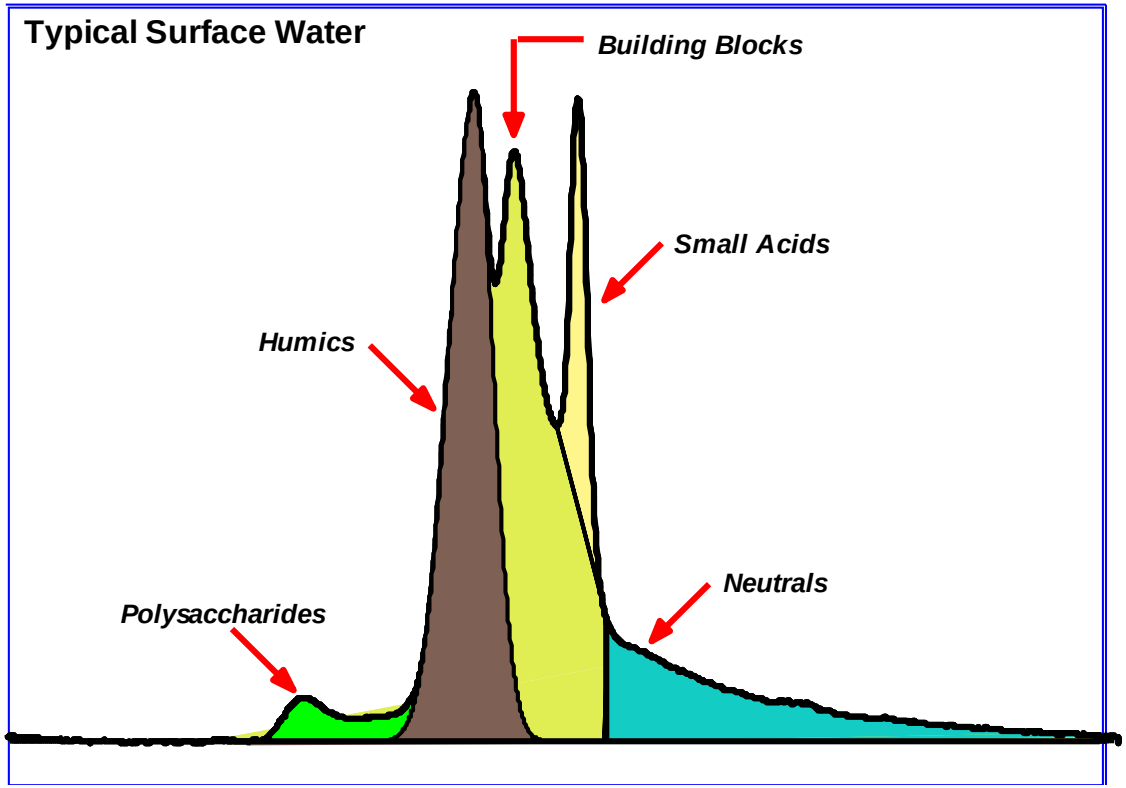
Chromatogram



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History

- 1969 Axt SEC-chromatography with thermal combustion C-detector
- 1986 Fuchs Gräntzel thin film detector with vacuum UV-detection
- 1991 Huber and Frimmel optimization of NOM analysis
- March 2006 HWL sign contract to obtain 7th NOM system from Doc Labor Karsruhe
- May 2006 system is placed and method validated
- August 2017 system is upgraded to work at least to 2020

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Performance

Performance	Demand	Result
Linearity	good	good
Robustness	good	good
Repeatability	-	< 10%
Reprodocubilily	< 25%	< 10%
Storage sample	-	8 days (refrigerated)
Reporting limit (fractions)	< 0,2 mg/l	0,03 - 0,15 mg C/l
Measurement range	-	< 12 mg/l

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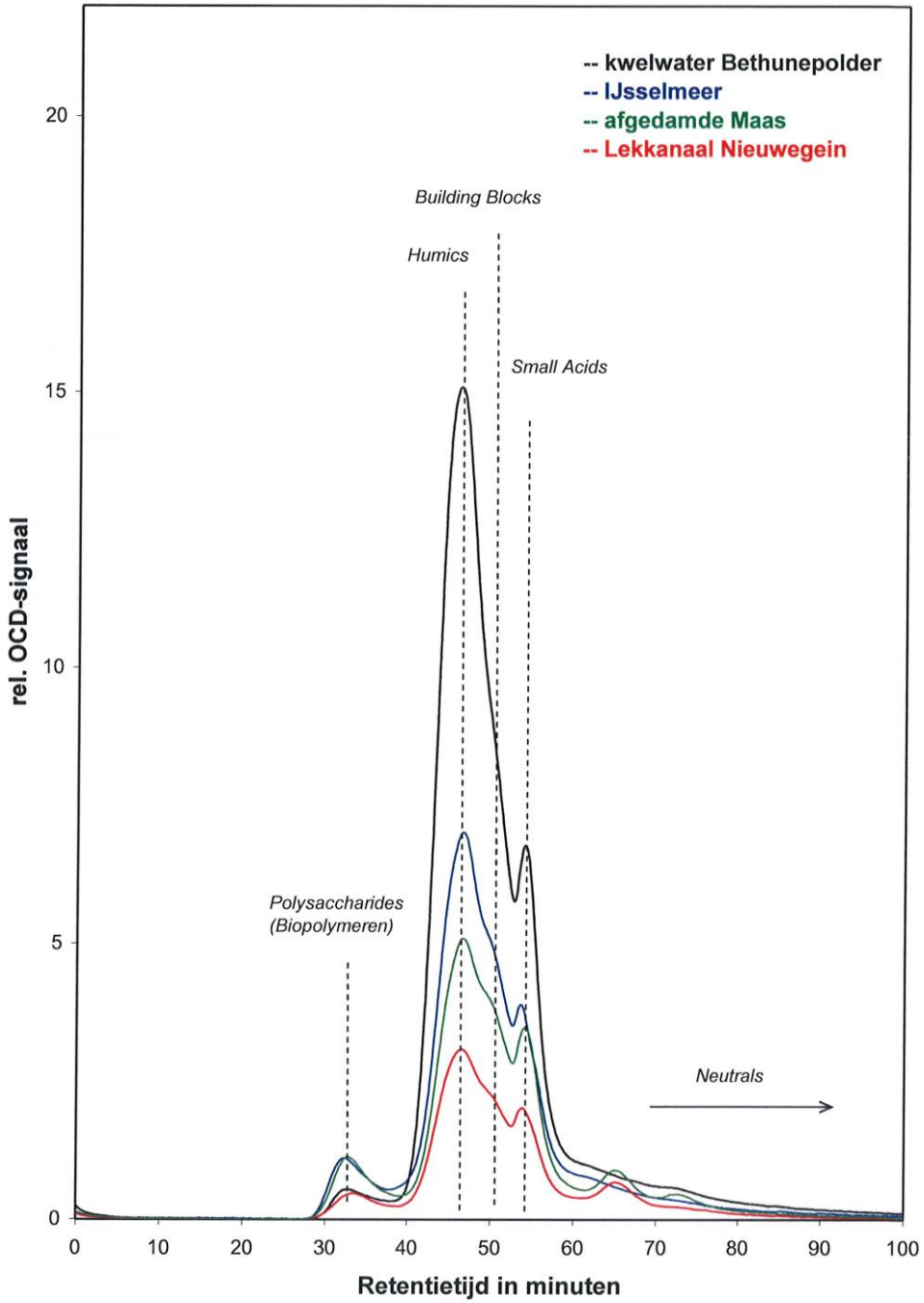
Typical Chromatograms



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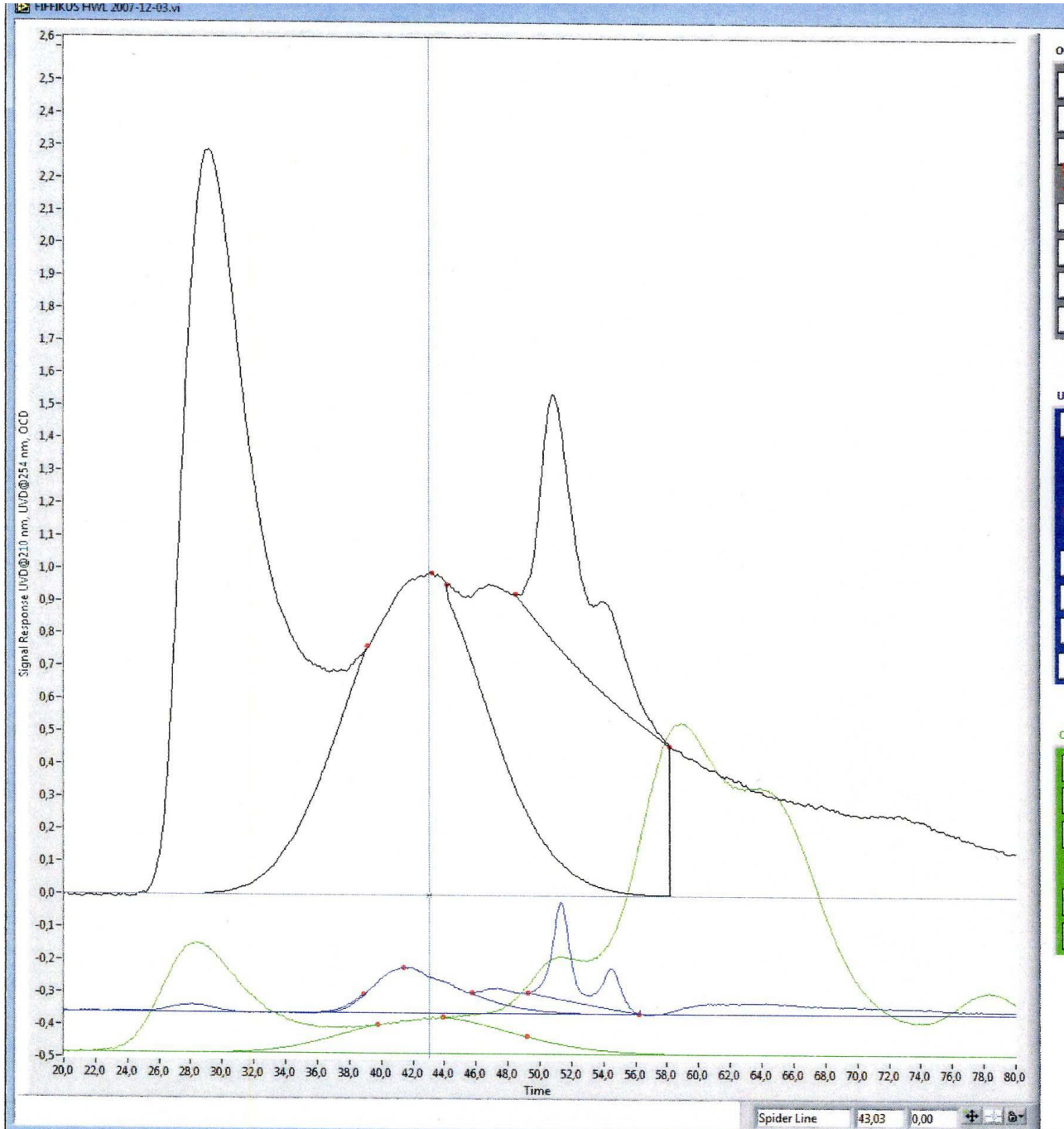
Deconvolution



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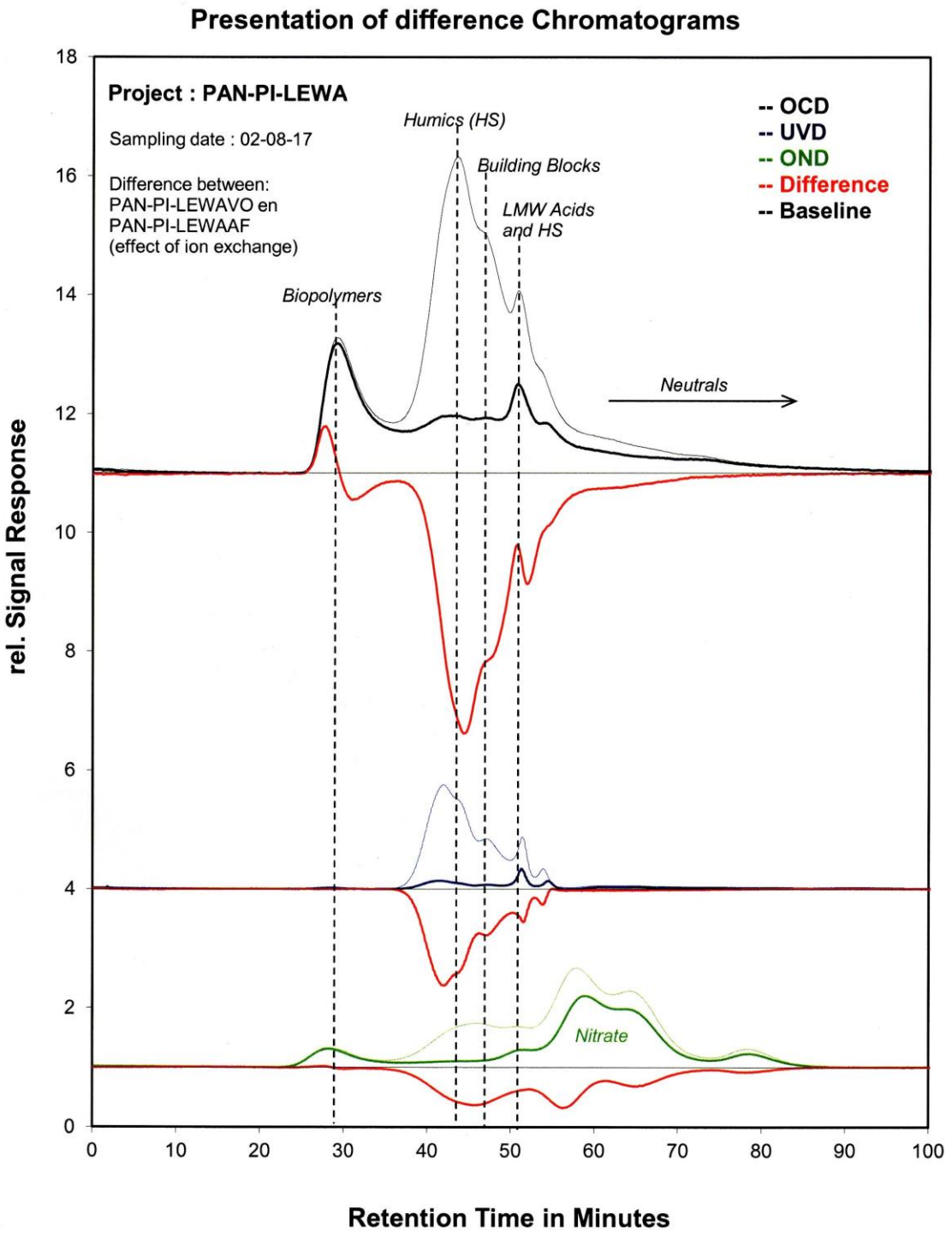
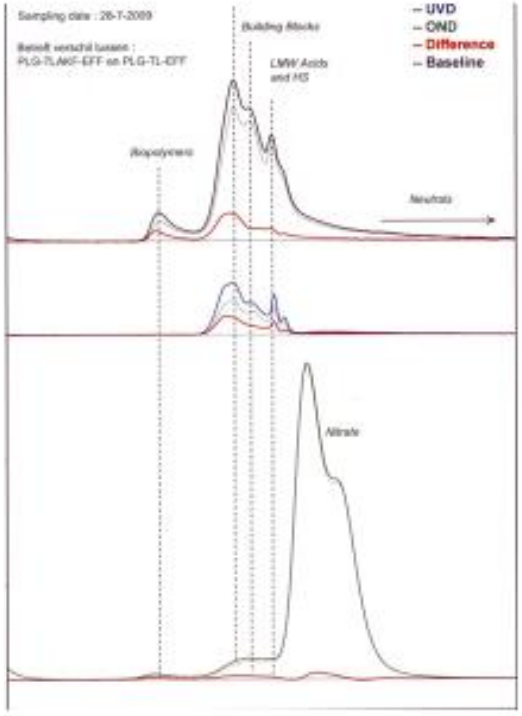
Typical Chromatograms

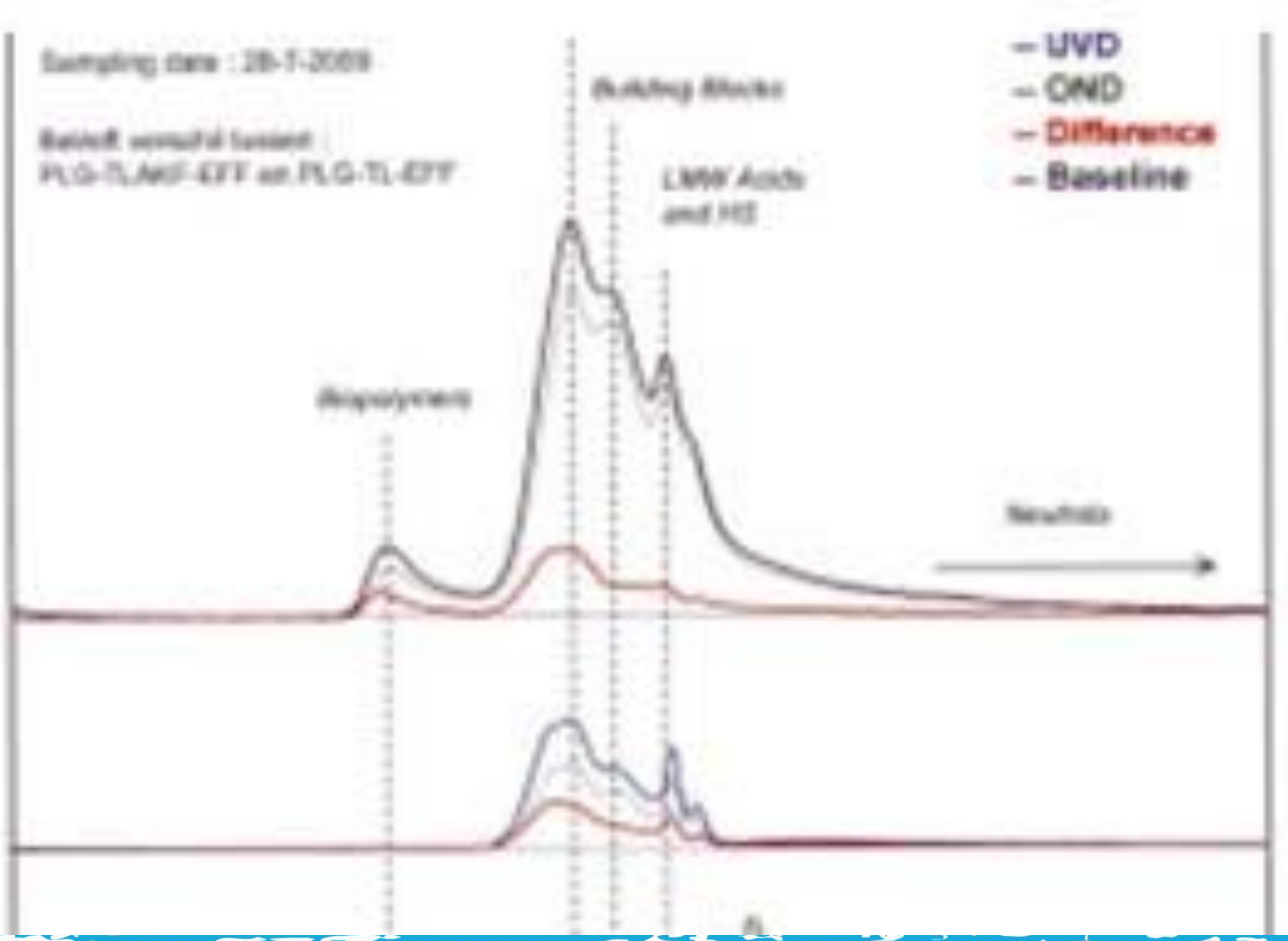


Typical Chromatogram UV-Peroxyde (1)

Verschilchromatogram



Typical Chromatogram UV-Peroxyde (2)



Typical Chromatograms

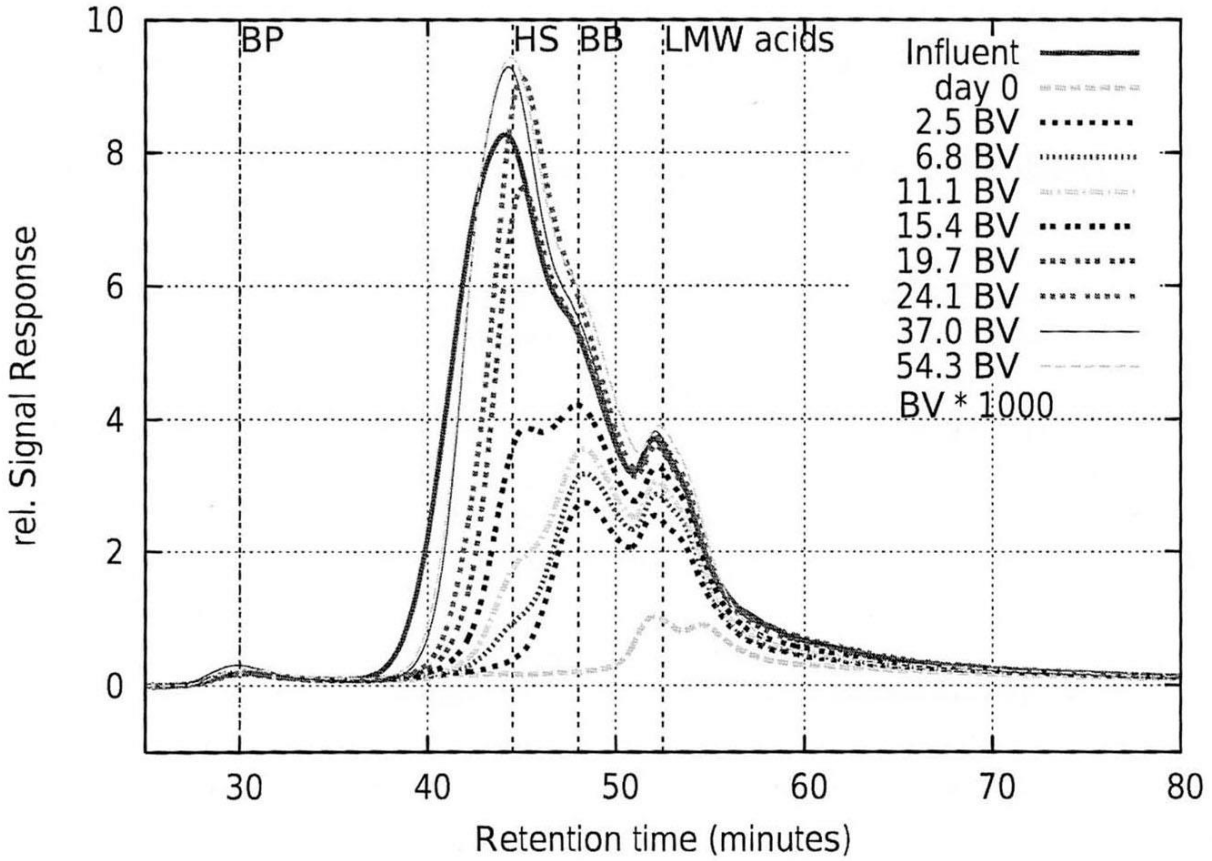
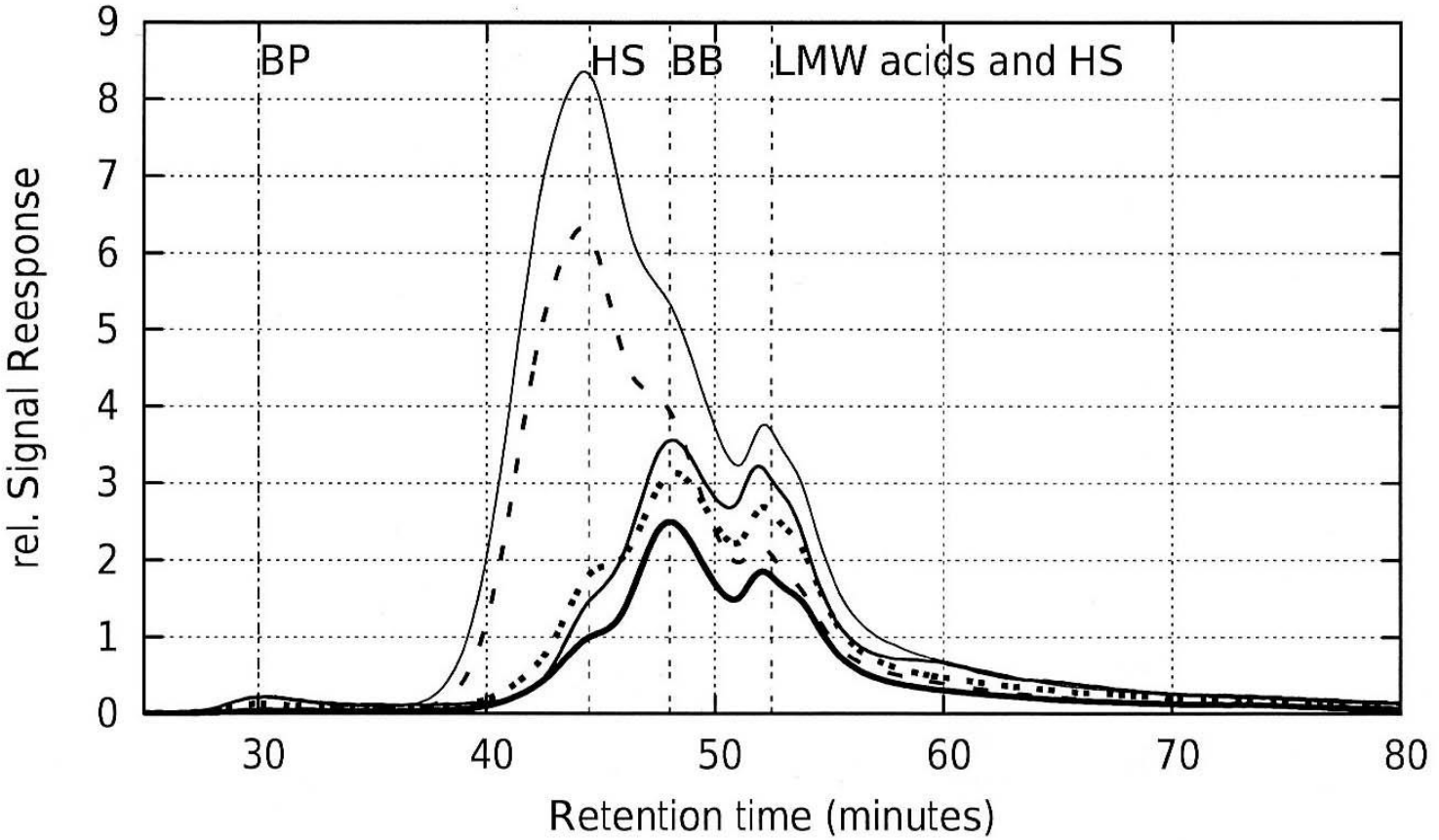


Figure 3.5: LC-OCD Chromatograms after different run times FIX


BP
HS
BB
LMW acids and HS
rel. Signal Reesponse
0
1
2
3
4
5
6
7
8
9
30
40
50
60
70
80
Retention time (minutes)
WPK feed water
MIEX before ozonation
FIX before ozonation
SSF
MIEX after SSF

Restrictions

Rapportcode: 2017-104

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Deze rapportage is geen vervanging van het formele analyserapport en geeft geen inzicht in eventuele disclaimers die betrekking hebben op het monster of analyseresultaten. Deze zijn op aanvraag beschikbaar.

Berekening zonder Humics!

Project: PAN-PI-LEWA
sampl.date: 9-8-2017

	Partitioning of Organic Carbon (OC)					Chromatographic Fractionation of Organic Carbon (CDOC)								(UV@254 nm)	
	Approx. Molecular Weights in g/mol: →					>>20.000		~1000 (see separate HS-Diagram)				300-500	<350	<350	
	TOC=DOC+POC DOC=CDOC+HOC														
	Note: POC, hence TOC may be too low														
	TOC	DOC	POC	HOC	CDOC	Bio-Polymers	DON	Humic Subst. (HS)	DON	Aromaticity	Mol-Weight	Building Blocks	Neutrals	Acids	Inorg. Colloid.	SUVA
	total OC	dissolved	particul.	hydrophob.	hydrophil.		(Norg)		(Norg)	(SUVA-HS)	$\overline{(Mn)}$				SAC	(SAC/OC)
	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})	L/(mg*m)
	% TOC	% TOC	% TOC	% TOC	% TOC	% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--	--
PAN-PI-LEWAAF	2815	2674	142	236	2438	734	45	n.n.	n.n.	--	n.n.	1090	463	151	0,11	1,22
1025341	100	95,0	5,0	8,4	86,6	26,1	--	--	--	--	--	38,7	16,4	5,3	--	--

Humic and Fulfic Acids

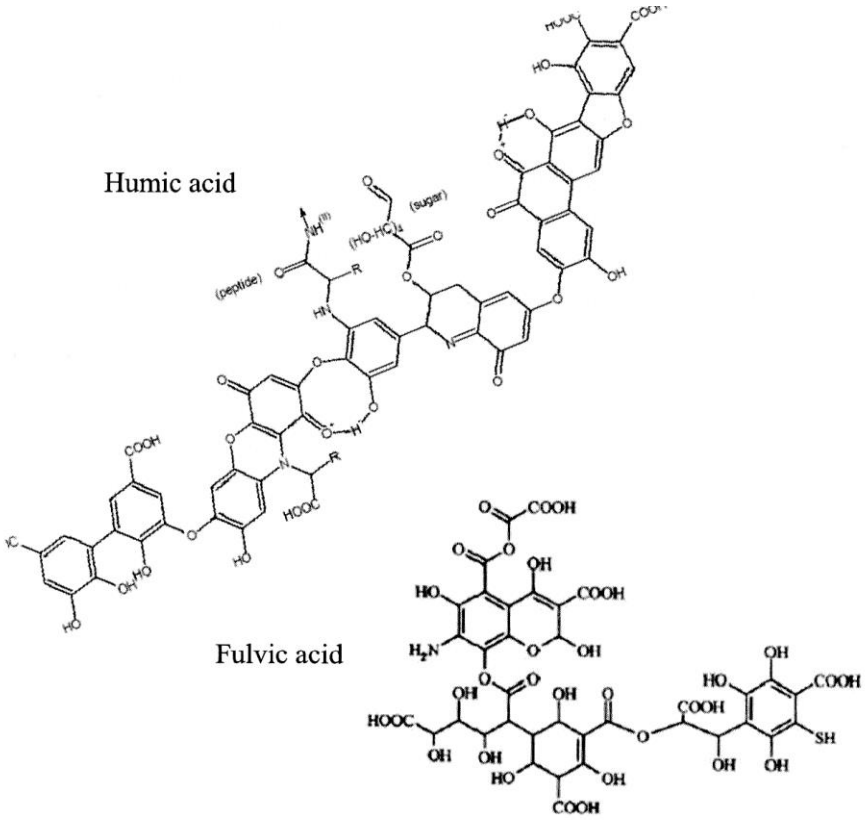

Figure 2.1 Proposed model molecular structure of humic and fulvic acids (Stevenson, 1982, Alvarez-Pueblaa et al., 2006).

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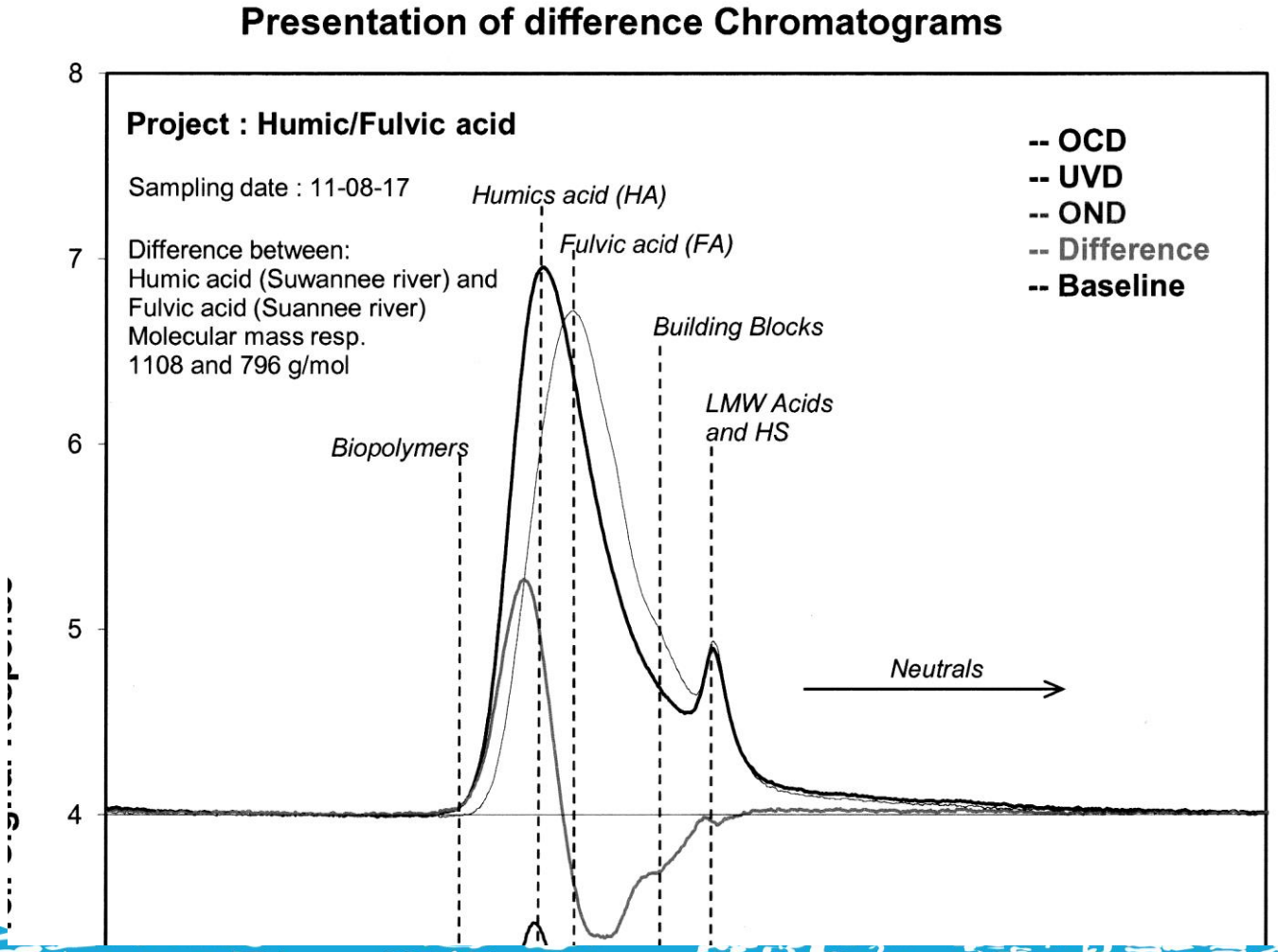
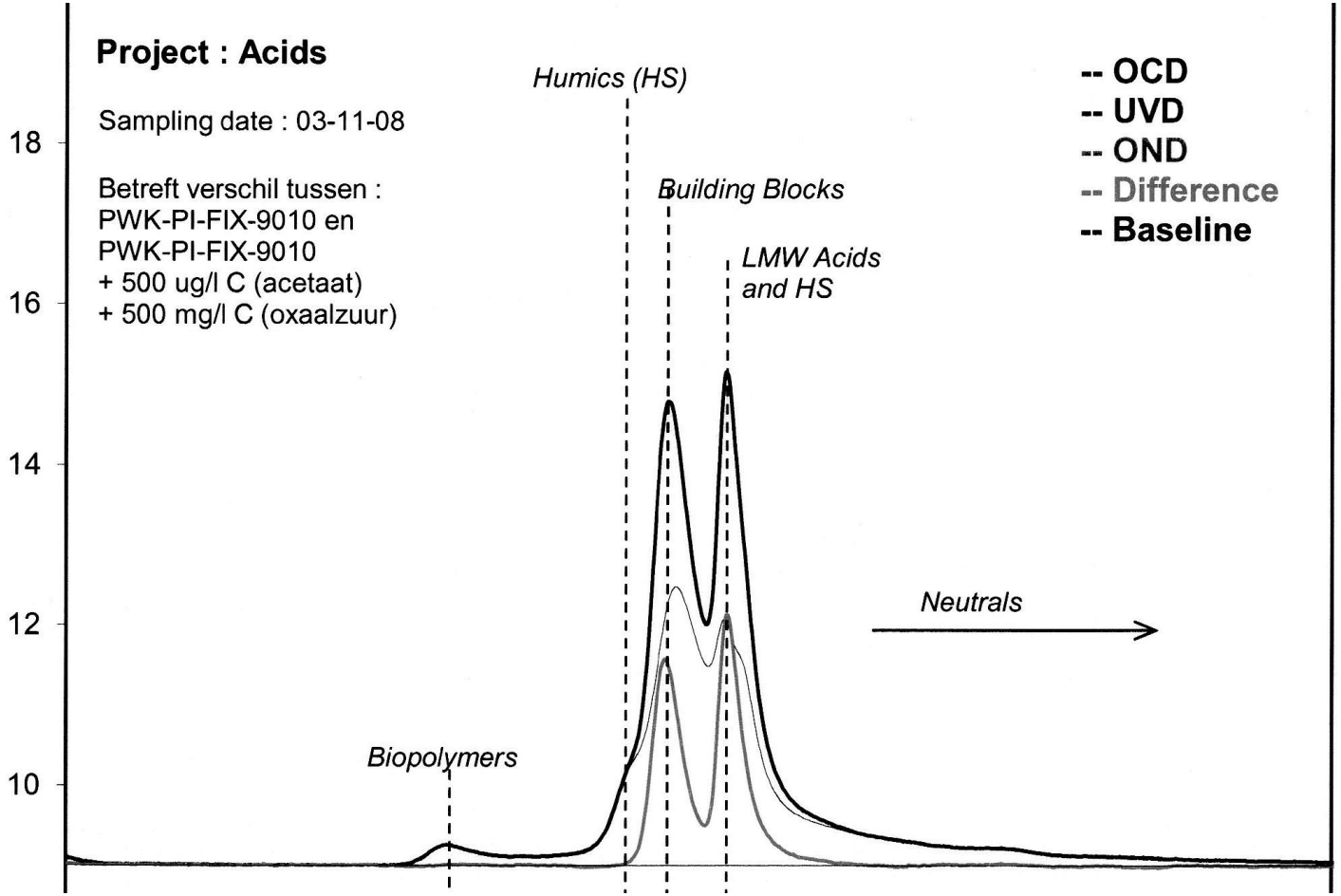
Restrictions

- Particulate Organic Matter
- Hydrophobic Organic Matter
- Inorganic Colloids
- Apparent Molecular Weight Humics

Humic and Fulvic Acids



Acids are not always acids



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Retention Time of Acids

- Formic Acid : 53 minutes (= LMW Acid Peak)
- Acetic Acid: 53 minutes (= LMW Acid Peak)
- Oxalic Acid: 47.5 minutes (= Building Blocks)
- Citronic Acid: 46 minutes (= Building Blocks)

Humics are not always humics

The peak

Humics are not always humics

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(UV@254 nm)

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	total OC	*dissolved*	*particul.*	*hydrophob.*	*hydrophil.*		*(Norg)*		*(Norg)*	*(SUVA-HS)*	*(Mn)*				*SAC*	*(SAC/OC)*
	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})*	*L/(mg*m)*
	% TOC	% TOC	% TOC	% TOC	% TOC	% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--	--
PAN-PI-LEWAAF	2824	2654	170	248	2405	764	50	770	30	0,89	695	418	453	0	0,06	1,22
1025341	100	94,0	6,0	8,8	85,2	27,1	--	27,3	--	--	--	14,8	16,0	0,0	--	--

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	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})*	*L/(mg*m)*
	% TOC	% TOC	% TOC	% TOC	% TOC	% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--	--
PAN-PI-LEWAAF	2815	2674	142	236	2438	734	45	n.n.	n.n.	--	n.n.	1090	463	151	0,11	1,22
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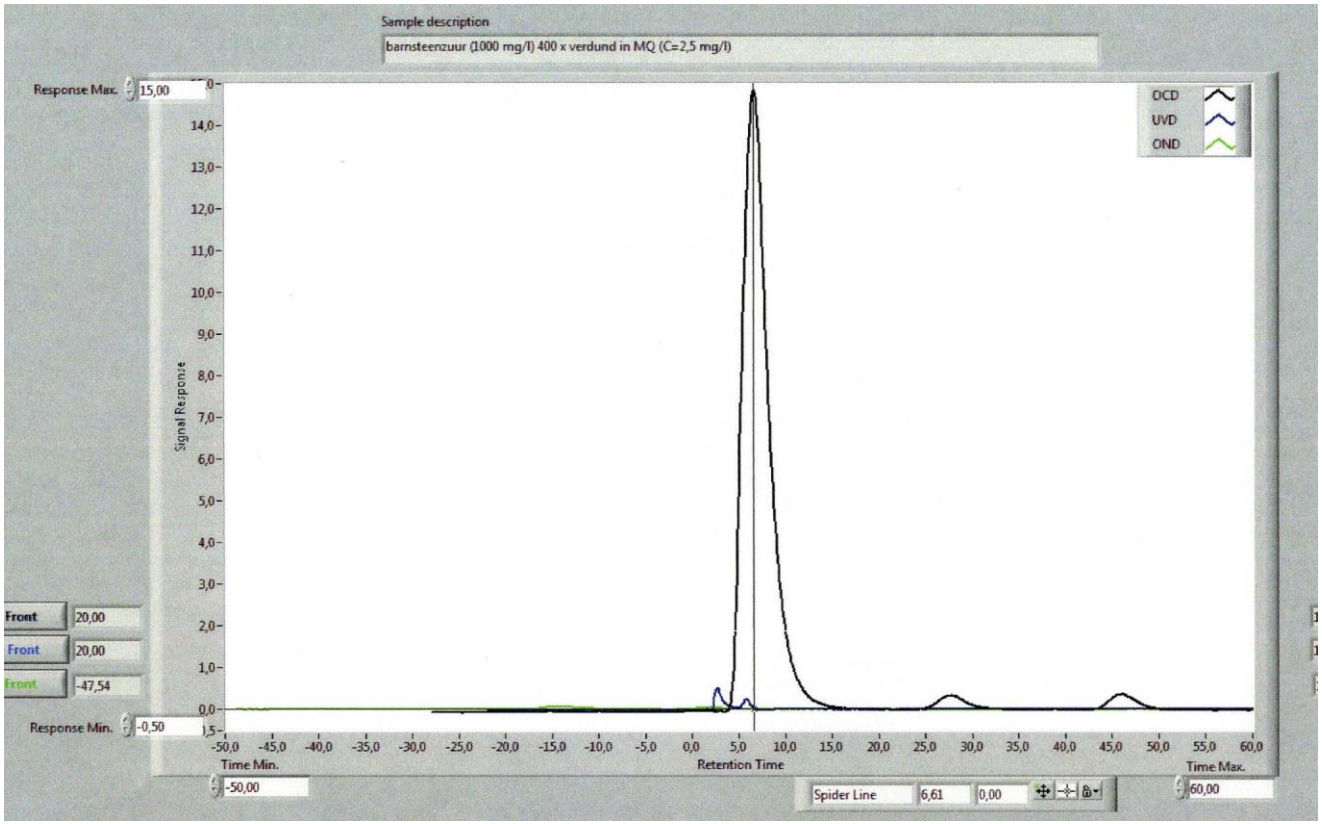
Finally: It's not always you expect



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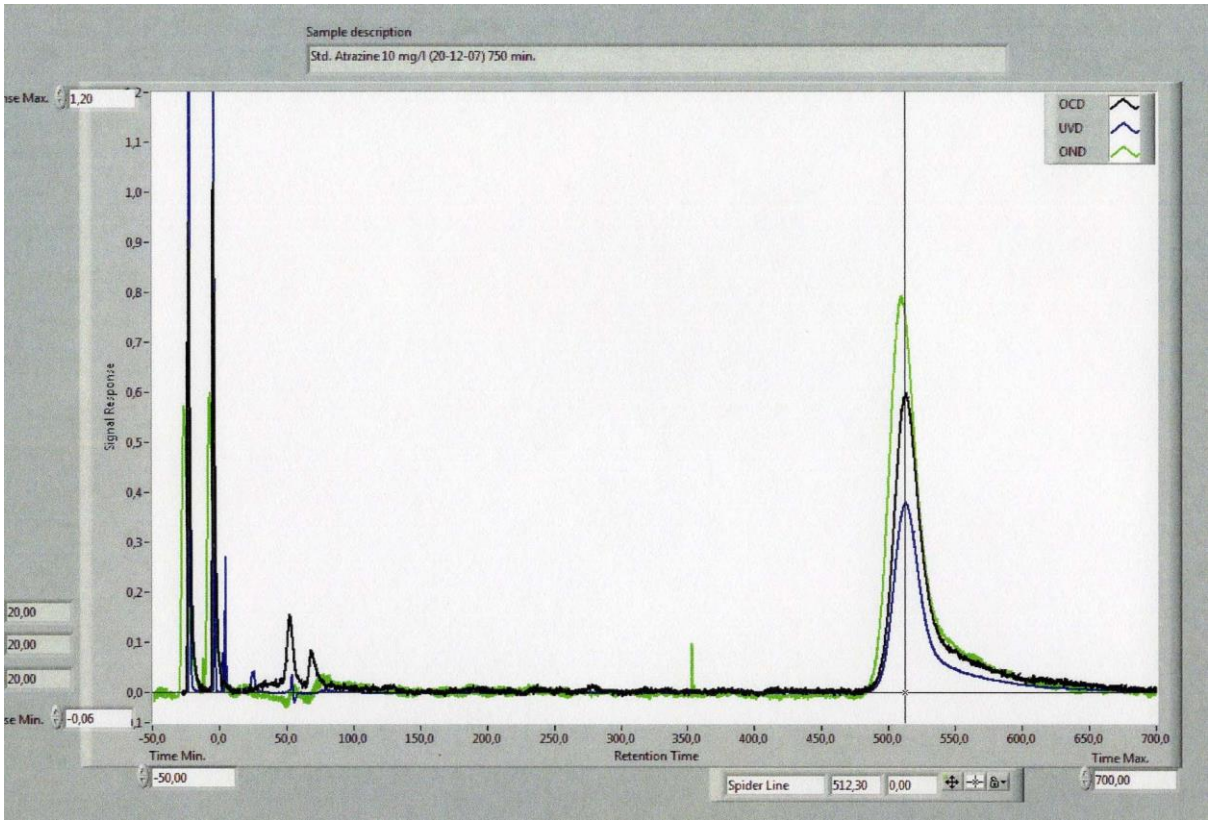

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Questions…