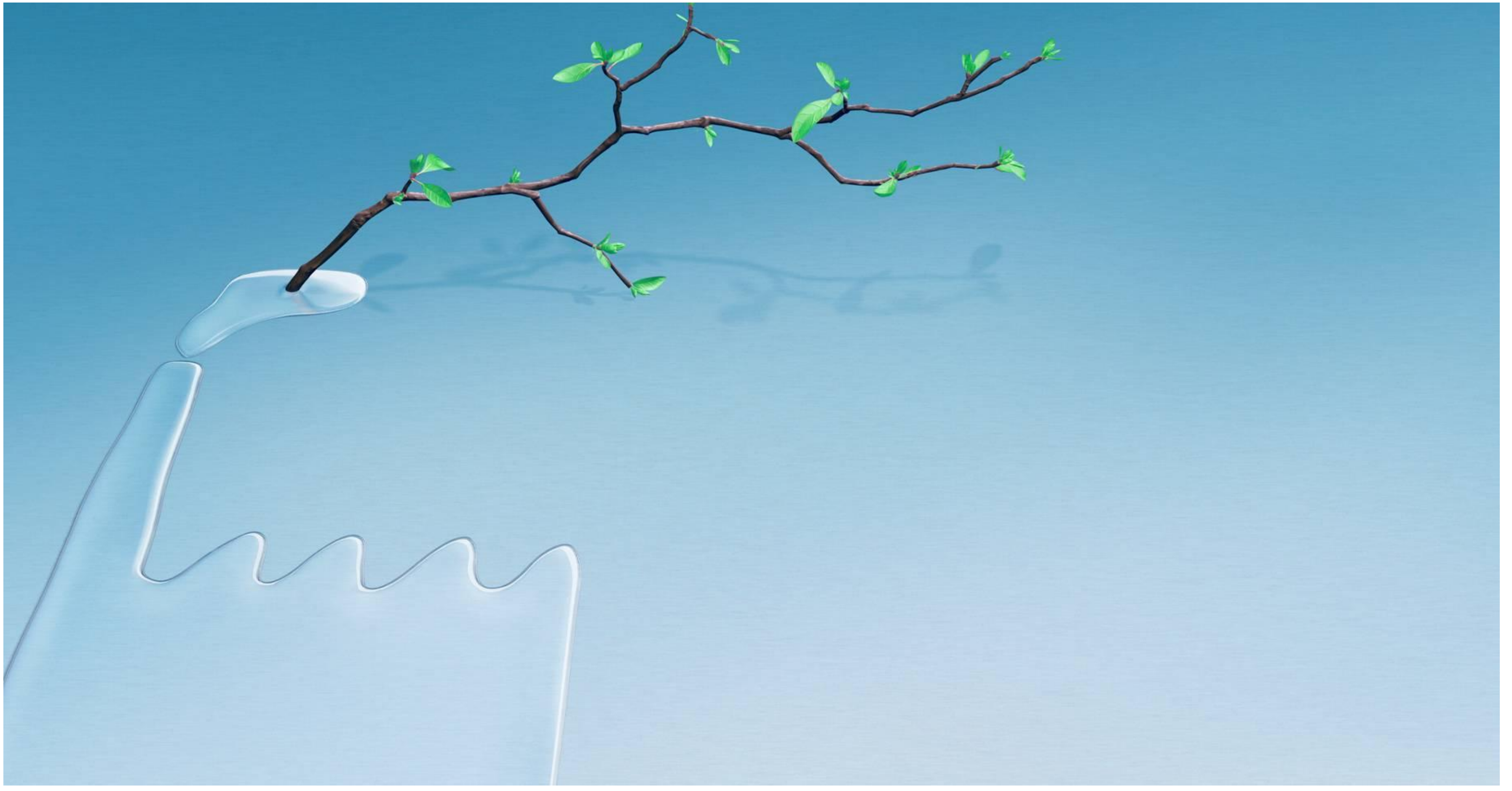


LC-OCD:n hyödyntämismahdollisuudet vesianalytiikassa.

Heli Vuorenpalo, Analytiikkapäivät Ketek 13.9.2011

Introduction- LC-OCD:n hyödyntämismahdollisuudet vesianalytiikassa

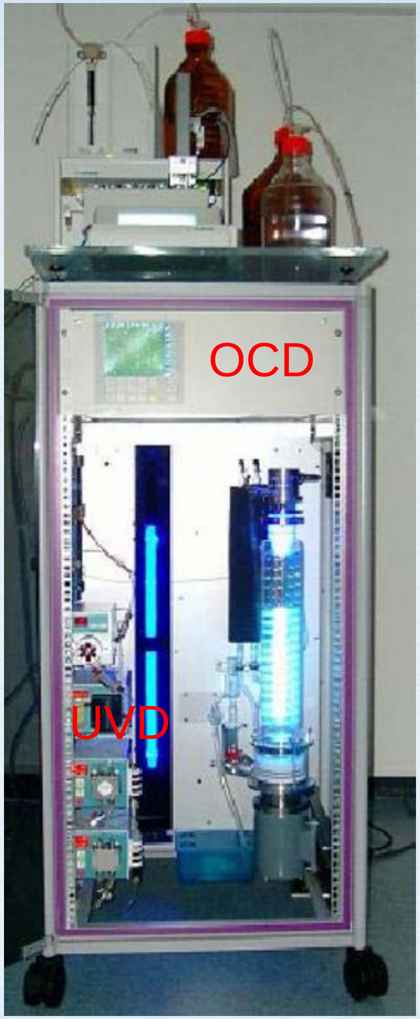
- What is LC-OCD, an overview
- The principles of LC-OCD
- What kind of results can be seen?
  - Characterization
  - Chromatograms
  - Results in numbers
- Examples

What is LC-OCD? – an overview

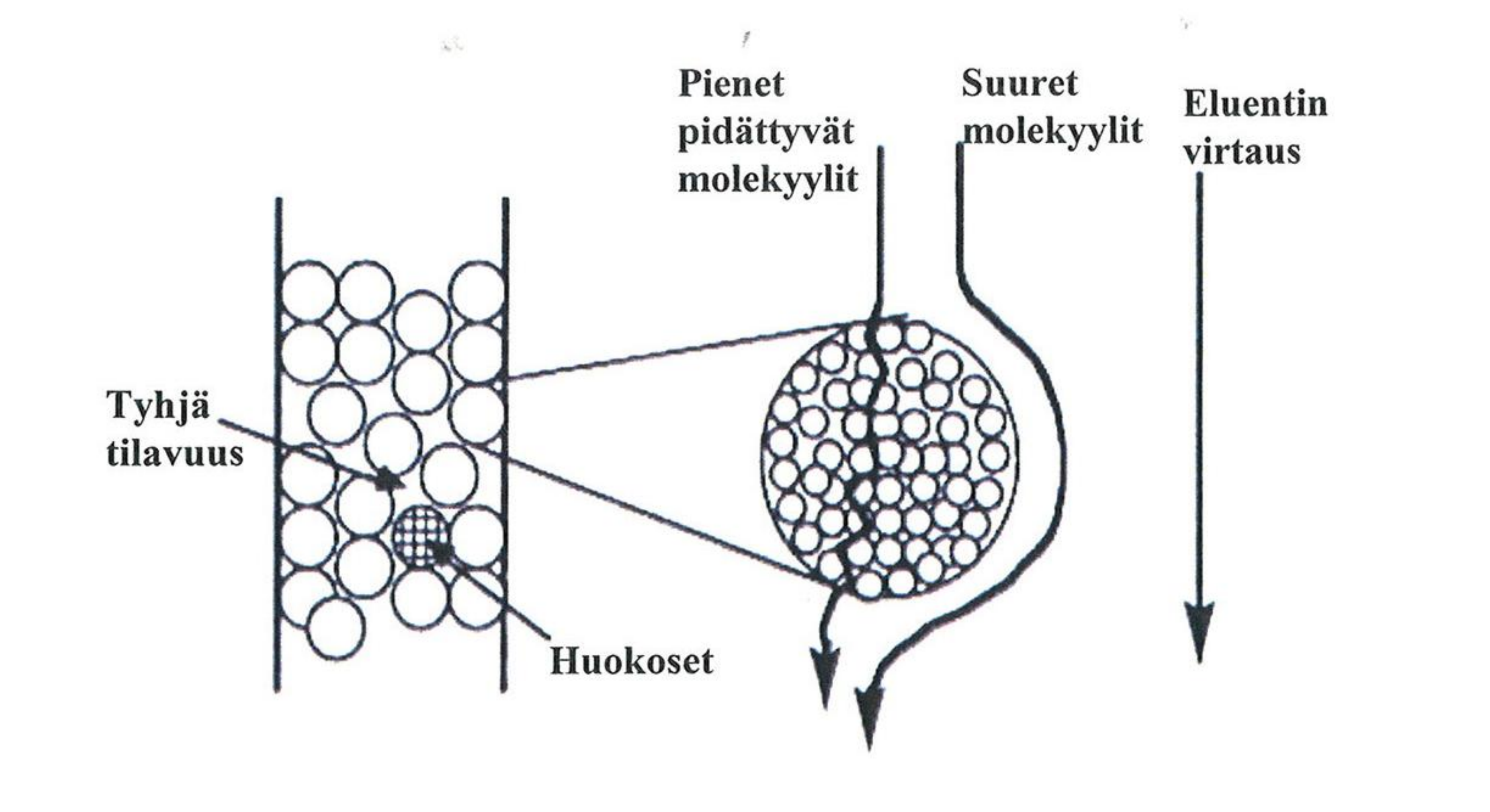
LC-OCD = Liquid chromatography - Organic carbon detector

The LC-OCD-technique is an analytical technique to quantify total organic carbon (TOC) and dissolved organic carbon (DOC) in waters in the ”sub-ppm”-range (10 ppb-5 ppm). The method has been developed by DOC-Labor (Karlsruhe, Germany).

- LC-OCD in a liquid chromatography which uses SEC-column to separate the organic organic compounds (TOC) from water samples.
- Organic compounds are futher detected with UV-Detection (UVD) and Organic Carbon Detection (OCD).



Separation in SEC-column



OCD

OCD follows almost the scheme of classical TOC-analyzers, this being:

i) acidification with phosphoric acid

ii) purging of "inorganic" carbon dioxide,

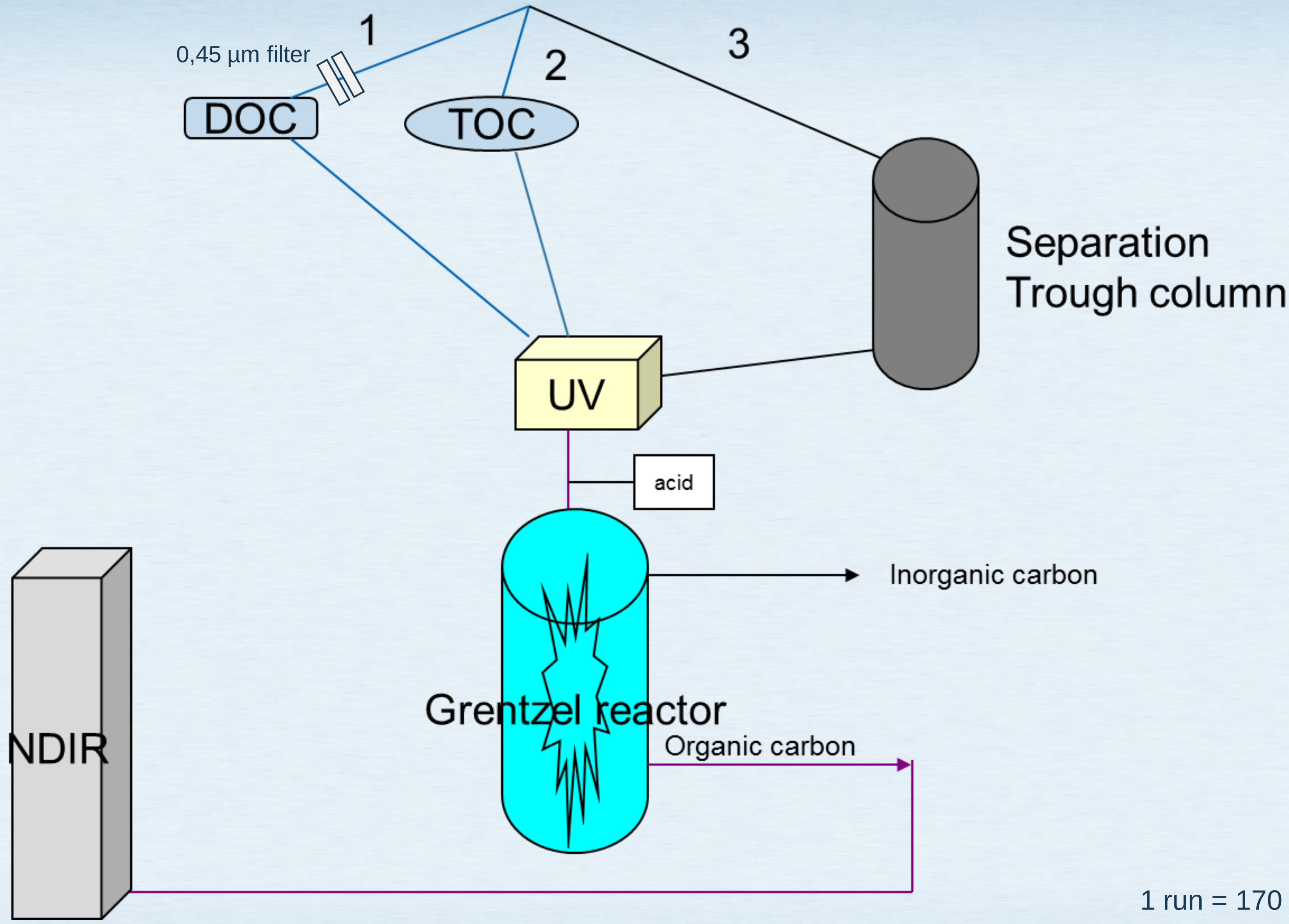
iii) oxidation of TOC to carbon dioxide,

iv) purging of "organic" carbon dioxide, and finally,

v) detection by NDIR (non dispersive IR).

In order to have all steps performed quantitatively and in short time, a thin film technique is used based on the so-called *Graentzel* thin film reactor (TFR). The measuring solution is spread out as a thin and mechanically stirred liquid film.

Prinsiples of LC-OCD



1 run = 170 min

14 place autosampler~40 h

Characterization

The instrument and the intelligent software are capable of classification of organic matter into following classes

TOC = Total organic carbon

DOC = Dissolved organic carbon

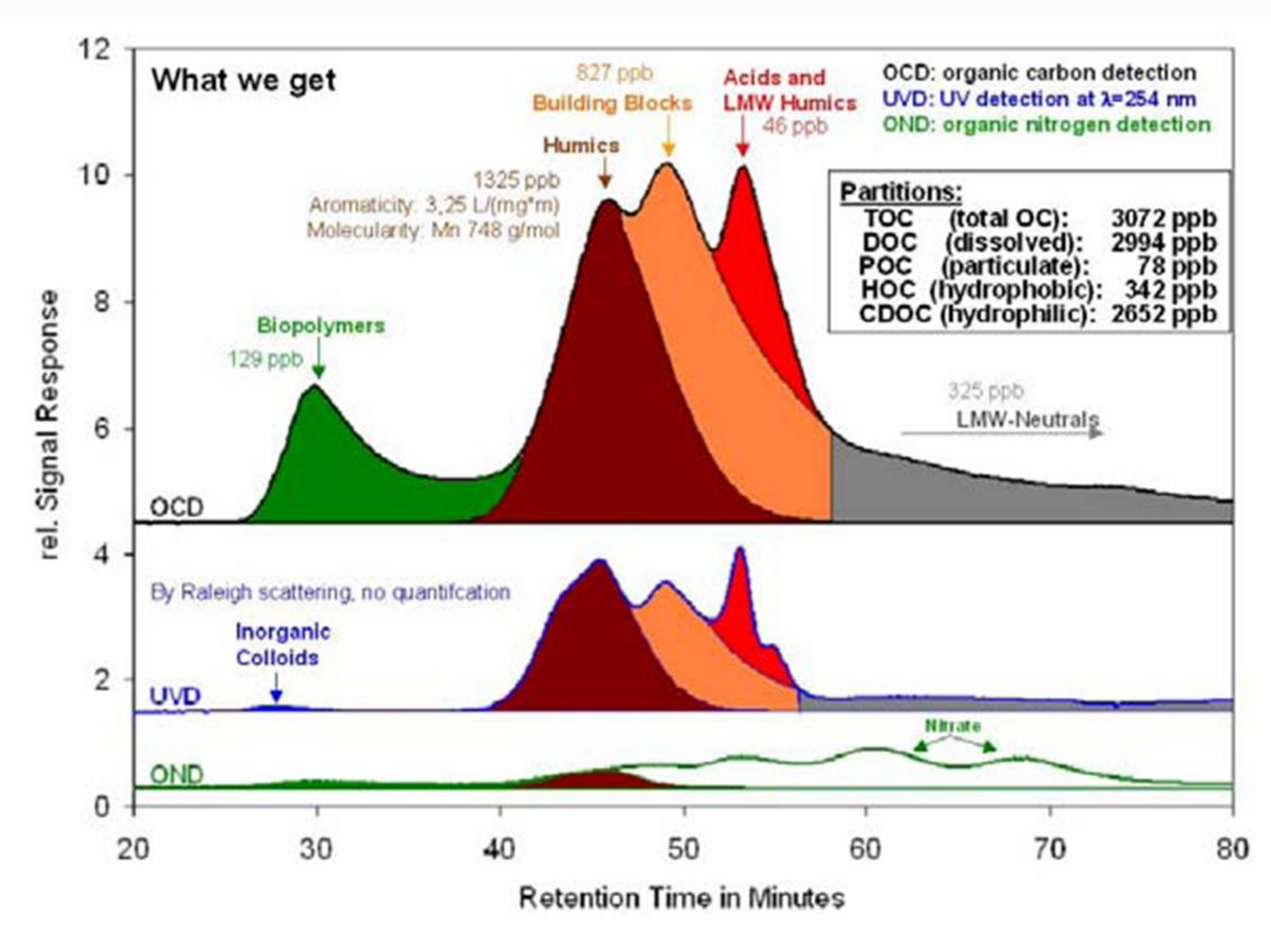
POC = Particles (TOC – DOC)

HOC = Hydrophobic organic carbon

CDOC = Hydrophilic organic carbon

CDOC can be divided into humic substances, degradation products of humic substances (building blocks), biopolymers, low molecular weight organic acids and neutral substances.

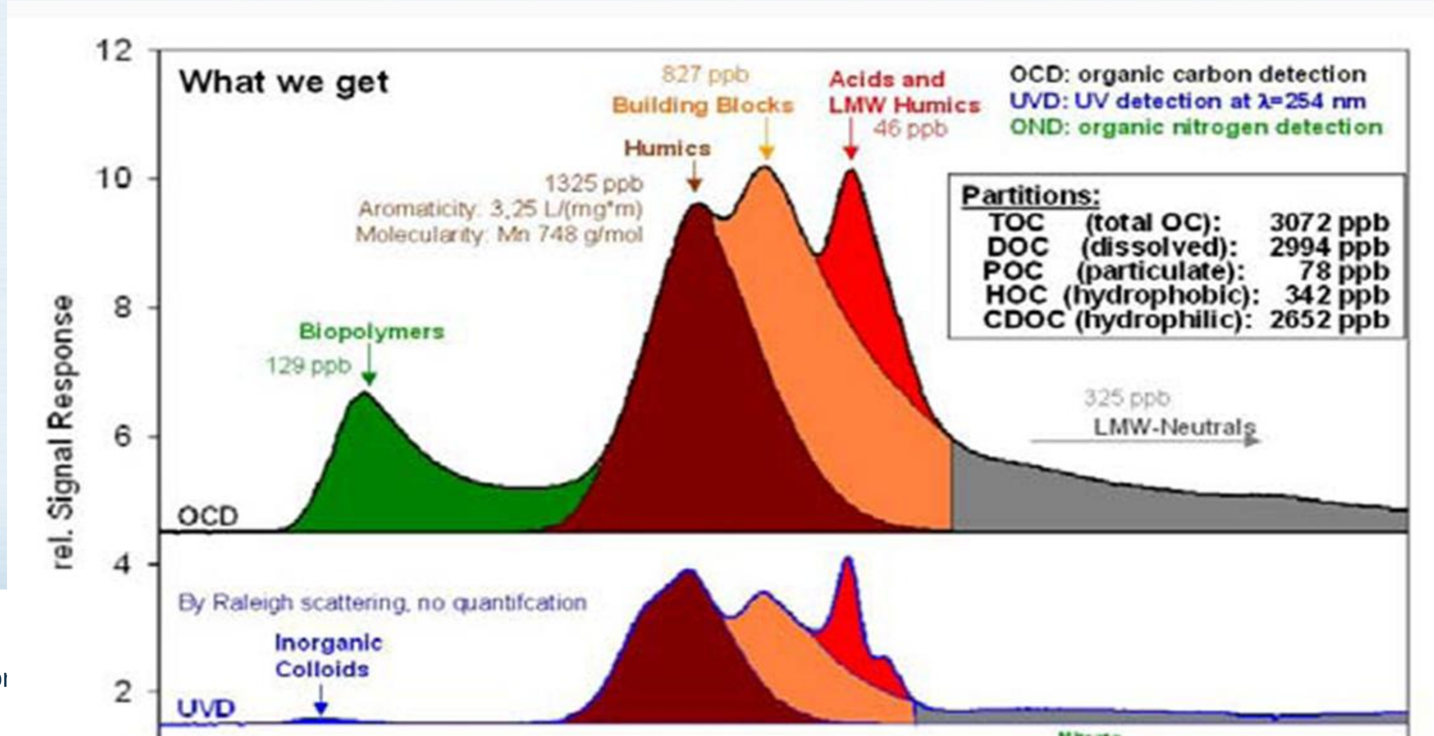
Chromatogram



Source: http://www.doc-labor.de

Results in numbers

	Partitioning of Organic Carbon (OC)												**(UV@254 nm)**	
	Approx. Molecular Weights in g/mol:				→	>>20.000	~1000 (see HS-Diagram)			300-500	<350	<350		
	TOC	**DOC**	**POC**	**HOC**	**CDOC**	**Bio-Polymers**	**Humic Subst. (HS)**	*Aromaticity (SUVA-HS)*	*Mol-Weight ($\overline{Mn}$)*	**Building Blocks**	**Neutrals**	**Acids**	**Inorg. Colloid.**	**SUVA**
	total OC	*dissolved*	*particul.*	*hydrophob.*	*hydrophil*								*SAC*	*(SAC/OC)*
	ppb-C	*ppb-C*	*ppb-C*	*ppb-C*	*ppb-C*	*ppb-C*	*ppb-C*	*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	--	--
0-sample	**1094043**	**1072340**	**21702**	**12426**	**1059915**	**5851**	**500770**	**6.18**	**929**	**226383**	**205851**	**121060**	**21.61**	**3.51**
	100	98.0	2.0	1.1	96.9	0.5	45.8	--	--	20.7	18.8	11.1	--	--
Kemira treatment	**283404**	**261447**	**21957**	**4596**	**256851**	**1915**	**122447**	**3.24**	**709**	**51966**	**53234**	**27289**	**10.43**	**2.05**
	100	92.3	7.7	1.6	90.6	0.7	43.2	--	--	18.3	18.8	9.6	--	--



SUVA

Specific UV absorbance (SUVA) is derived by measuring the absorbance of light at a wavelength of 254 nanometers (UVA) relative to the value to total organic carbon (TOC).

SUVA is a measure of the relative complexity of the organic molecules in the TOC pool. Complex man-made hydrocarbons such as those present in pesticides and pharmaceuticals, absorb more UV light than the simple, long-chain molecules of natural organic matter (NOM). Those complex molecules are not only indicative of contaminants in the water stream, but also more generally reactive, consuming more chemicals in flocculation and disinfection processes and increasing the rate of formation of disinfection byproducts (DBPs). Thus, SUVA is a valuable metric both in water quality monitoring and process control.

Reproducibility test

Source: http://www.doc-labor.de

Project:	0		Approx. Molecular Weights in g/mol:									
sampl.date	00.01.1900		>>20.000		~1000 (see separate HS-Diagram)				300-500	<350	<350	
		DOC	BIO-polymers	DON (Norg)	Humic Subst. (HS)	DON (Norg)	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Building Blocks	Neutrals	Acids	Inorg. Colloid. 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	--
	Sample 1	1474	259	9	435	11	0,68	494	162	500	117	0,00
		100,0	17,6	--	29,5	--	--	--	11,0	33,9	8,0	--
	Sample 2	1418	249	8	411	11	0,95	493	138	507	113	0,17
		100,0	17,6	--	29,0	--	--	--	9,7	35,7	8,0	--
	Sample 3	1394	255	9	393	9	1,07	495	136	497	112	0,13
		100,0	18,3	--	28,2	--	--	--	9,7	35,7	8,0	--
	Sample 4	1470	274	10	406	12	0,95	485	144	533	113	0,10
		100,0	18,6	--	27,6	--	--	--	9,8	36,2	7,7	--
	Sample 5	1454	272	11	400	15	0,94	472	146	524	113	0,17
		100,0	18,7	--	27,5	--	--	--	10,0	36,1	7,7	--
	Sample 6	1390	259	12	392	13	0,93	474	136	486	117	0,19
		100,0	18,6	--	28,2	--	--	--	9,8	35,0	8,4	--
	average	1434	261	10	406	12	0,92	486	144	508	114	0,13
	standard deviation	38	10	1	16	2	0,13	10	10	18	2	0
	half confidence interval											
	in ppb	40	10	1	17	2	0,14	11	11	18	3	0,07
	in %	2,8	3,9	14,3	4,2	18,7	14,9	2,2	7,4	3,6	2,2	57,6

A reproducibility test of a marine water showing the main important data obtained with LC-OCD.

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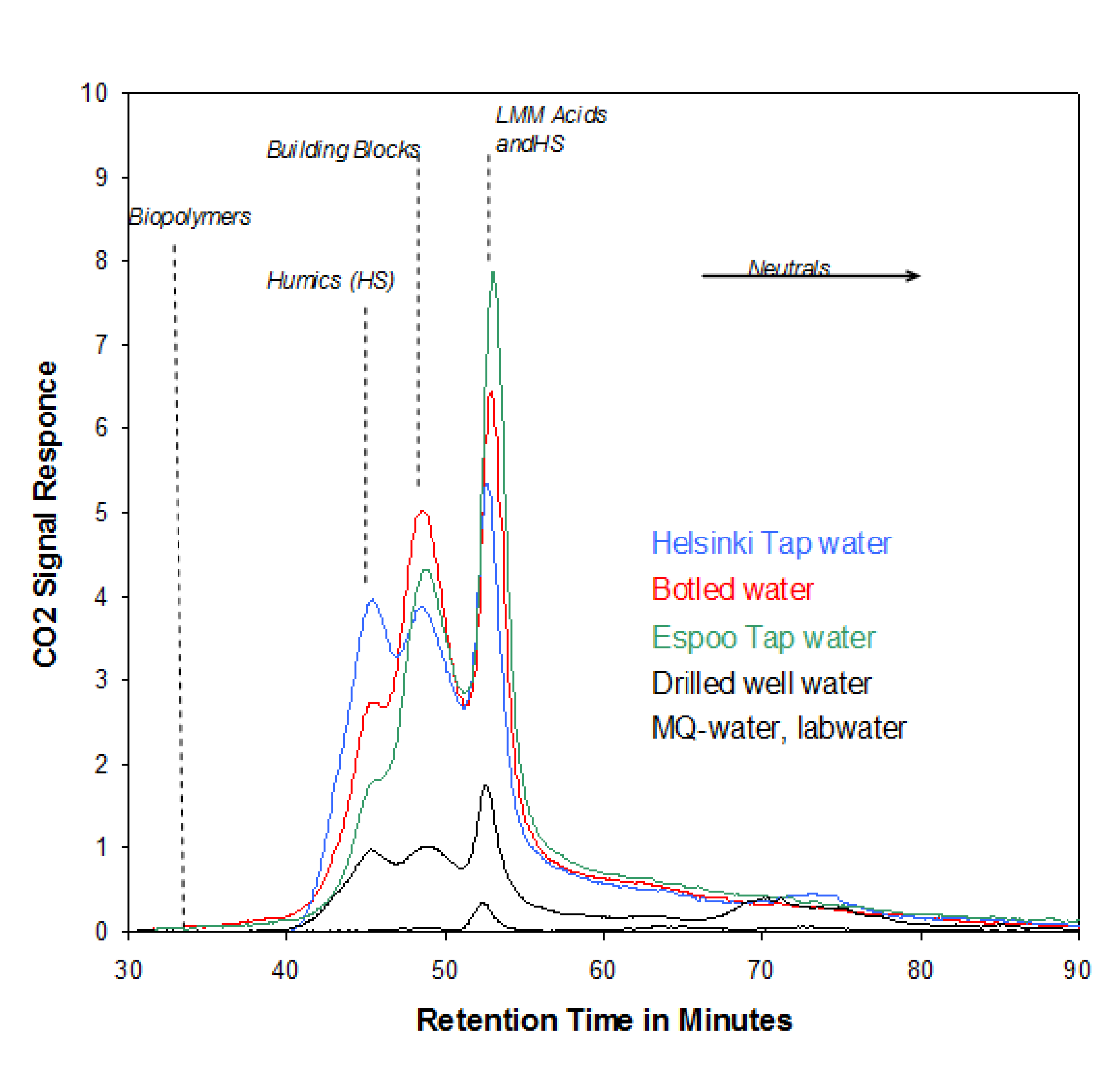
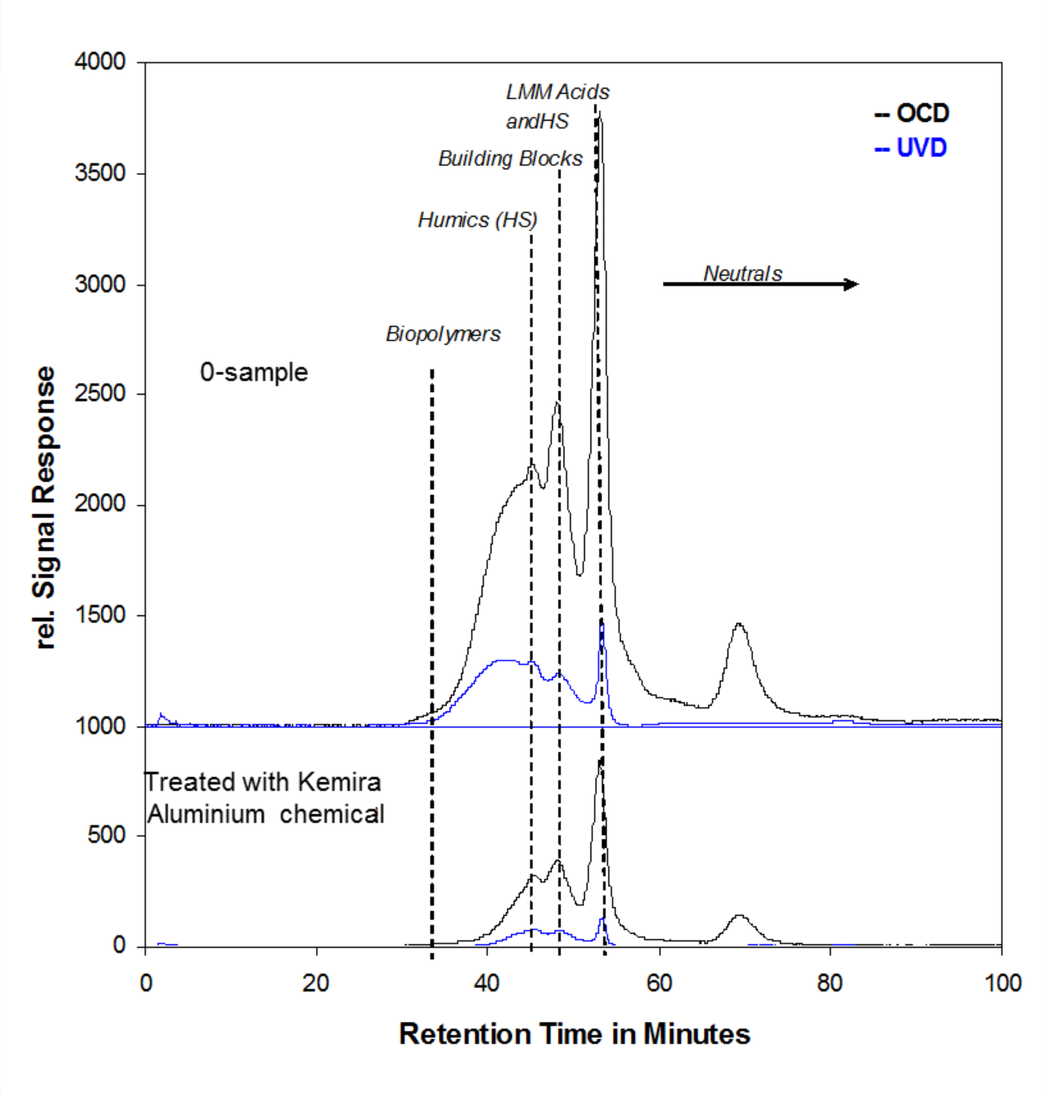
Water comparison



Process water caracterization (paper mill)



- The amounts of TOC, DOC, CDOC, humic substances, building blocks, neutrals and acids has decreased by about 75%.
- The amount of HOC and biopolymers has decreased by 65% (1-2% from TOC)
- The amount of aromatic substances (48%) and inorganic colloidal substances has also decreased compared to initial water.

Results (paper mill-filtrate)

	Partitioning of Organic Carbon (OC)												(UV@254 nm)	
	Approx. Molecular Weights in g/mol:				→	>>20.000	~1000 (see HS-Diagram)			300-500	<350	<350		
	TOC	DOC	POC	HOC	CDOC	Bio-Polymers	Humic Subst. (HS)	Aromaticity (SUVA-HS)	Mol-Weight ($\overline{Mn}$)	Building Blocks	Neutrals	Acids	Inorg. Colloid. SAC	SUVA (SAC/OC)
	total OC	dissolved	particul.	hydrophob.	hydrophil									
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	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	--	--
0-sample	**1094043**	**1072340**	**21702**	**12426**	**1059915**	**5851**	**500770**	**6.18**	**929**	**226383**	**205851**	**121060**	**21.61**	**3.51**
	100	98.0	2.0	1.1	96.9	0.5	45.8	--	--	20.7	18.8	11.1	--	--
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	100	92.3	7.7	1.6	90.6	0.7	43.2	--	--	18.3	18.8	9.6	--	--

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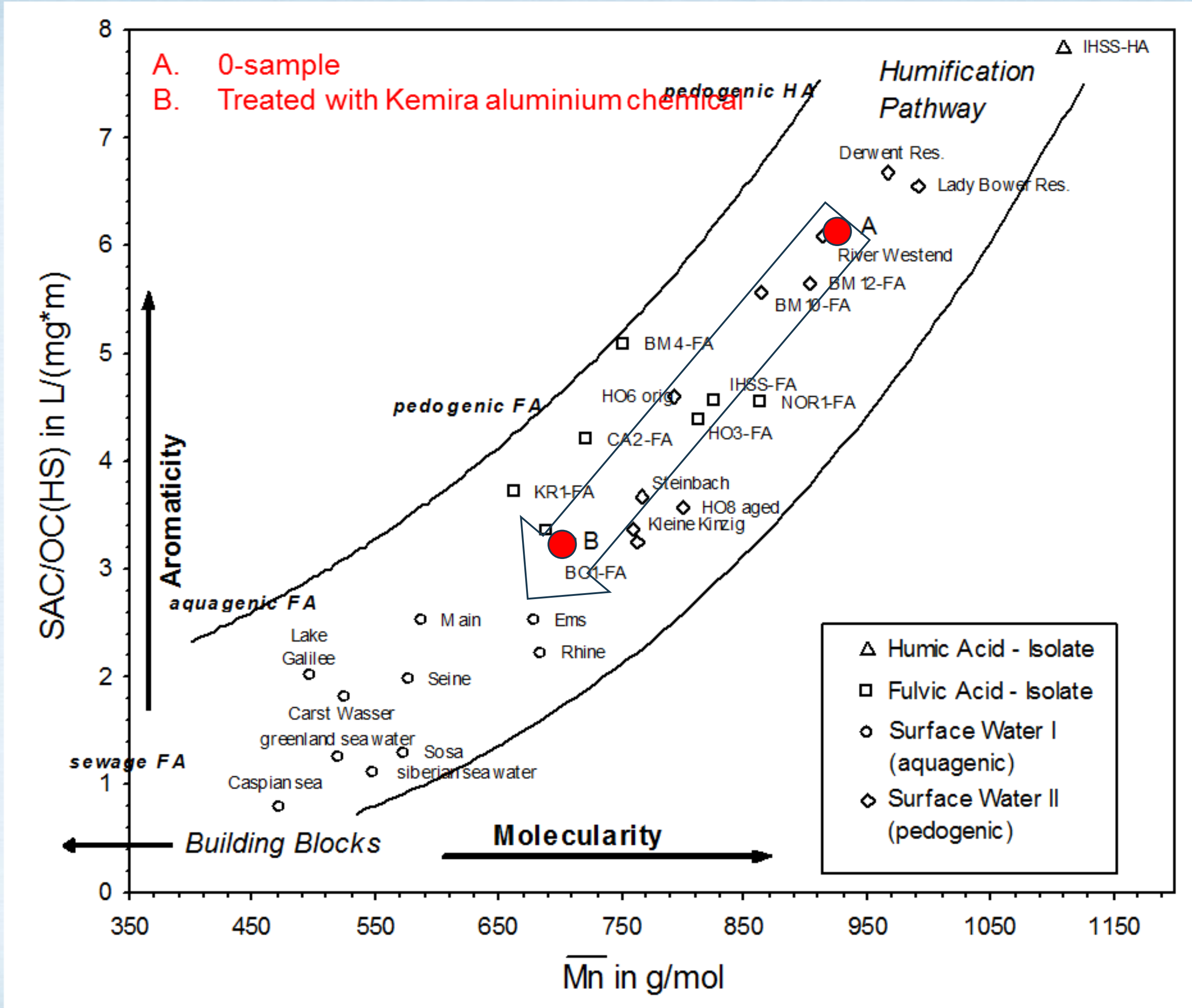
HS-diagram (paper mill-filtrate)

Humic Subst. (HS)	Aromaticity (SUVA-HS)	Mol-Weight (Mn)
ppb-C	L/(mg*m)	g/mol
% TOC	--	--
500770	6.18	929
45.8	--	--
122447	3.24	709
43.2	--	--

Finally the humification pathway will reveal information about the maturity and origin of organic matter.

Selection aid for treatment method.



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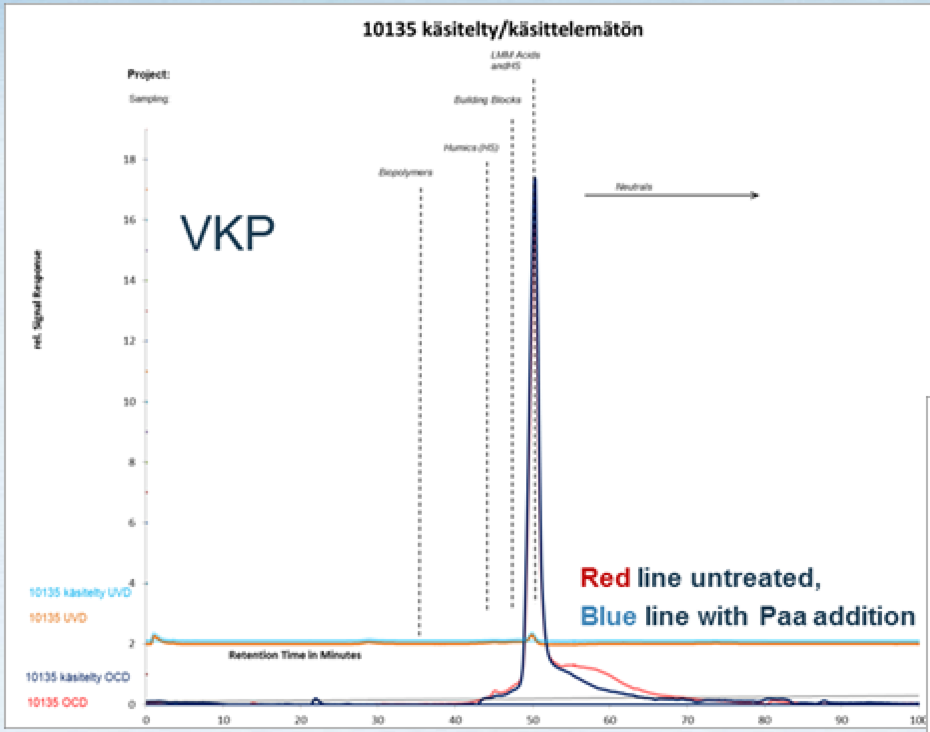
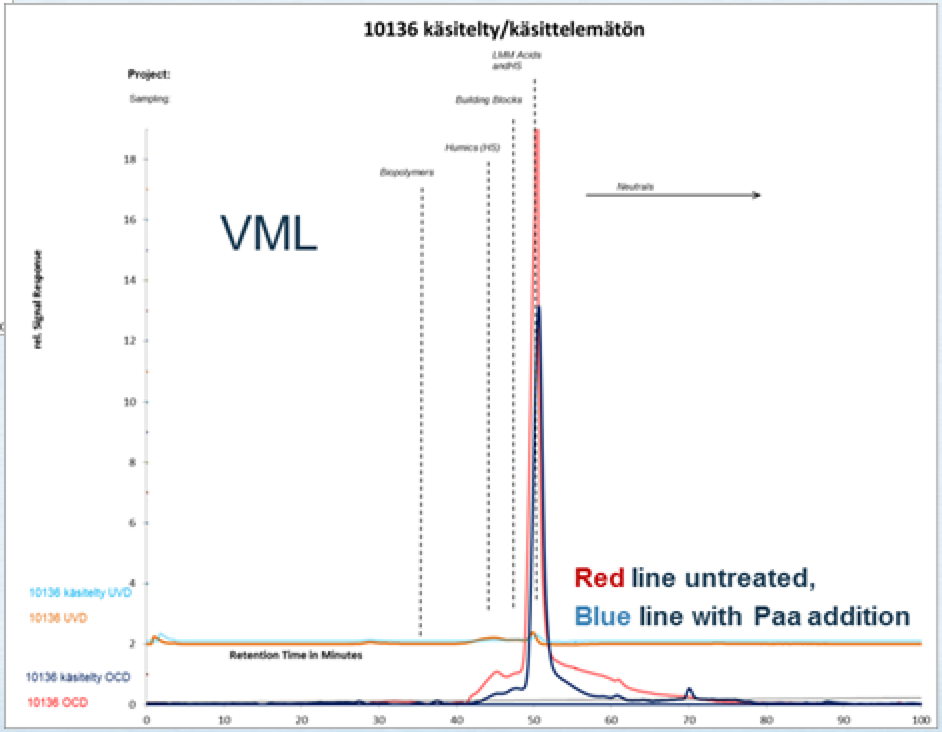


Chemically purified raw water (VKP) did not consume Paa. Mechanically purified raw water on the other hand reduced the amount of Paa in the test. SEC showed that it contained humic substances which consumed Paa.



Difference Surface Water – Ground Water ?

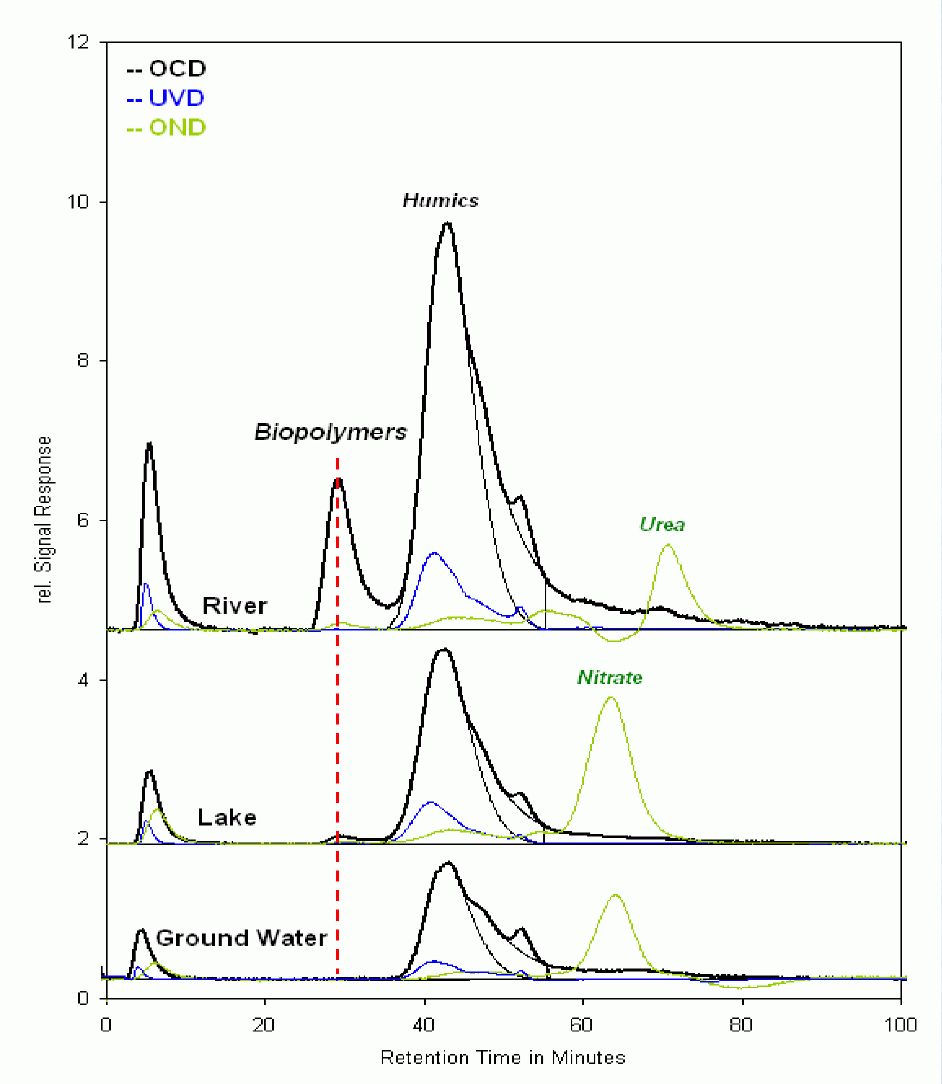
Source: http://www.doc-labor.de

The fundamental difference is the absence of biopolymers in ground waters.

In river waters biopolymers originate from diffuse run-off from top soils or sewage effluents. A high N/C ratio, thus a high amount in proteinic matter is typical.

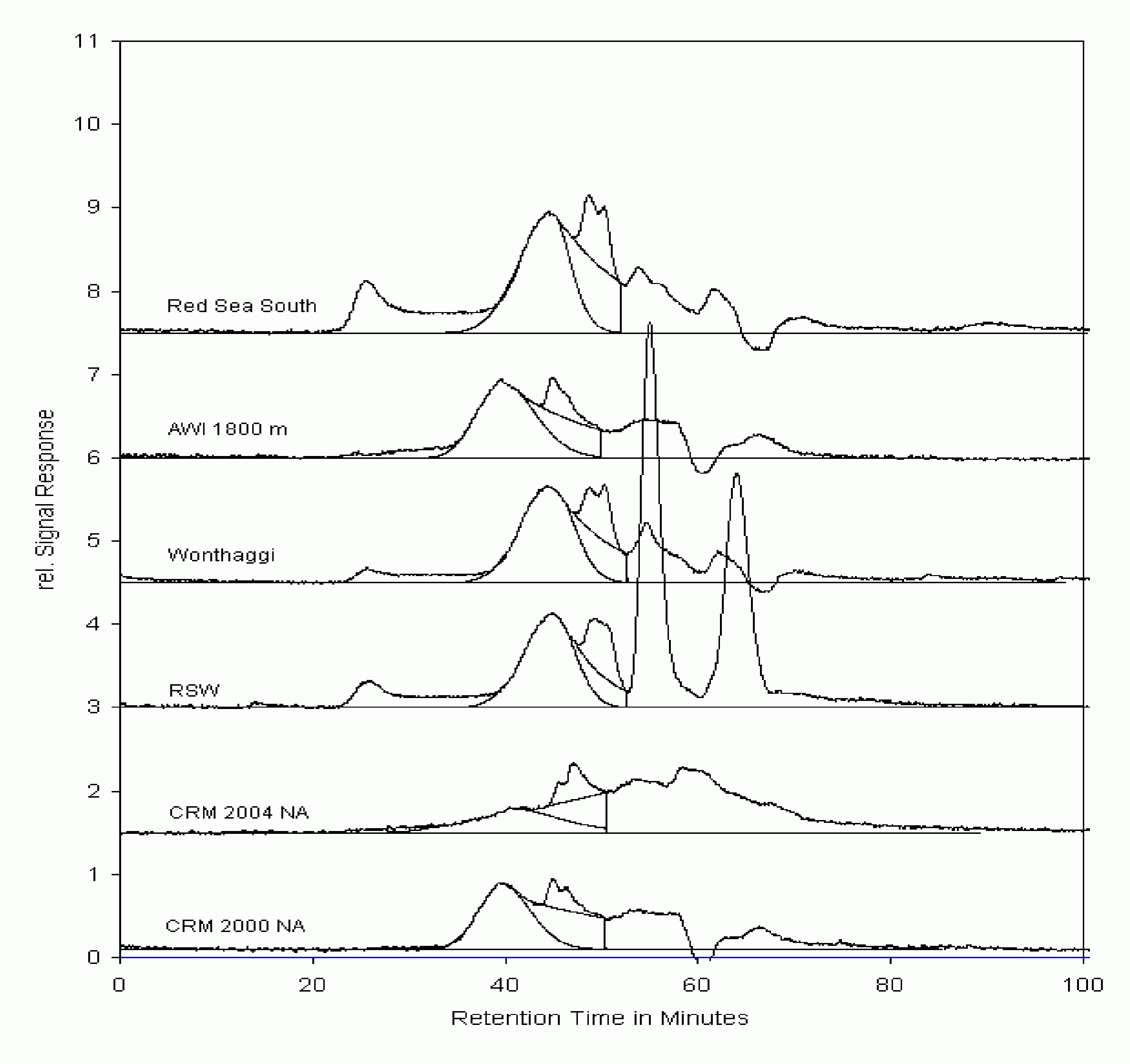
In lakes, biopolymers originate from algae and exhibit a low N/C ratio. This material is primarily polysaccharidic.

In ground waters biopolymers should be absent. If not, then either a hydraulic contact to a surface water or a high microbial activity in the aquifer can be inferred.



Heterogeneity of marine NOM

Source: http://www.doc-labor.de

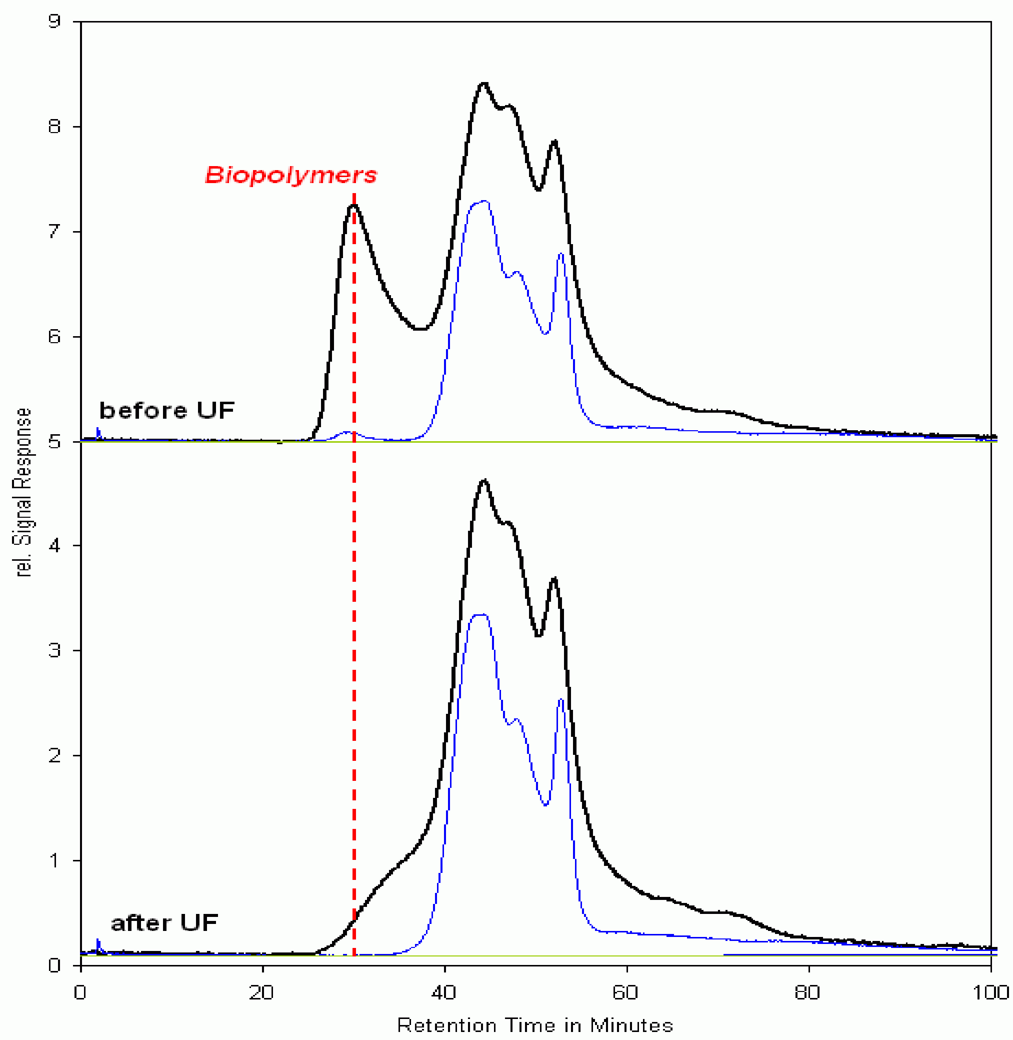


- An illustrative figure showing how complex and heterogeneous marine NOM can be.

Municipal waste water and MBR

Source: http://www.doc-labor.de

MBR systems are gaining increasing recognition. The membrane selectively removes particulate biologic matter and dissolved biopolymers to some extent. This makes the membranes also prone to fouling. The example shows a typical performance of an MBR system: Biopolymers are removed by about 80 %.



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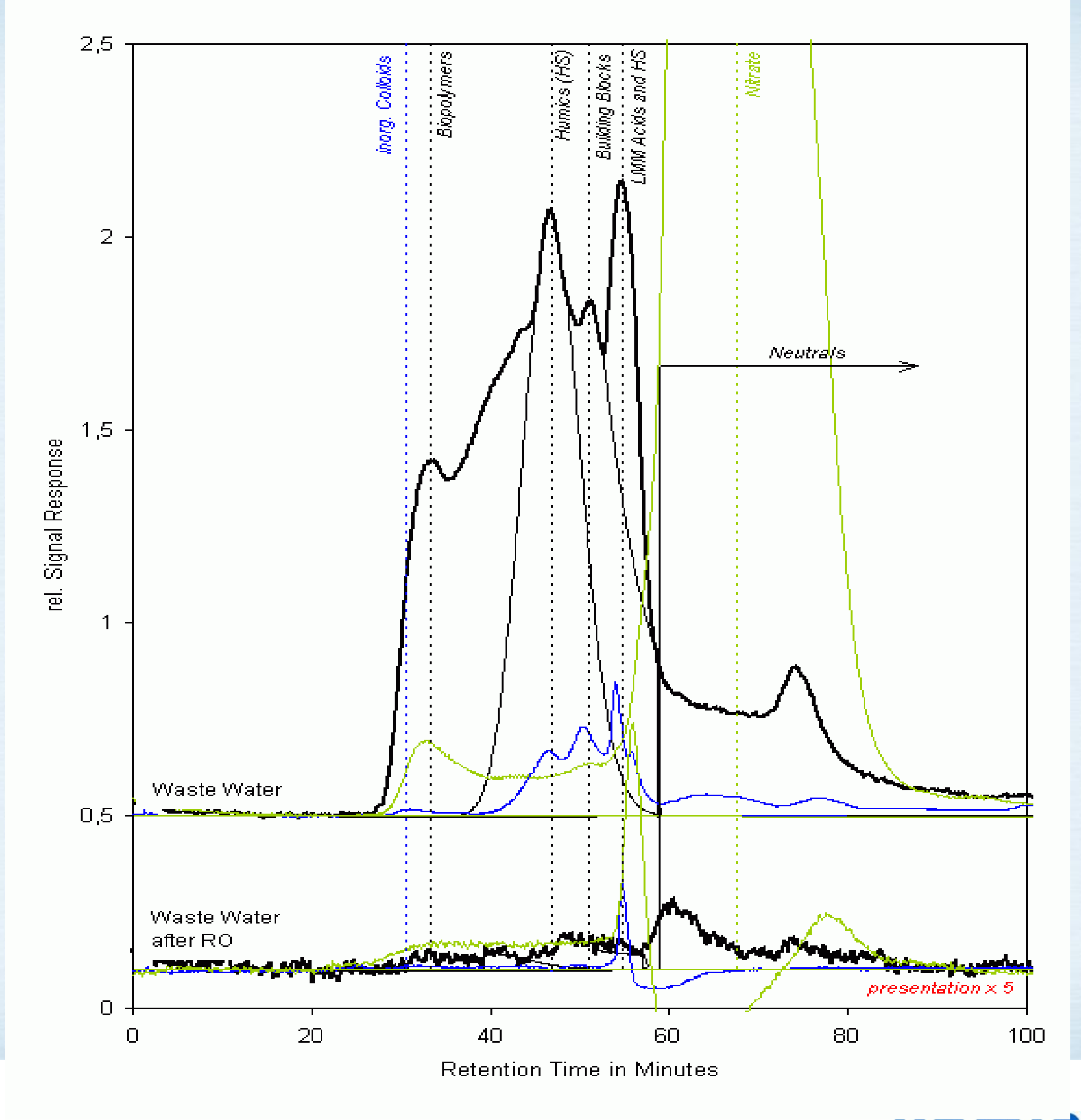
Ultrapure water from waste?

Source: http://www.doc-labor.de

Here, a municipal waste water was directly fed to a single stage RO-unit. The permeate water had a TOC-value of only 10 ppb and – interestingly – fouling issues were negligible.



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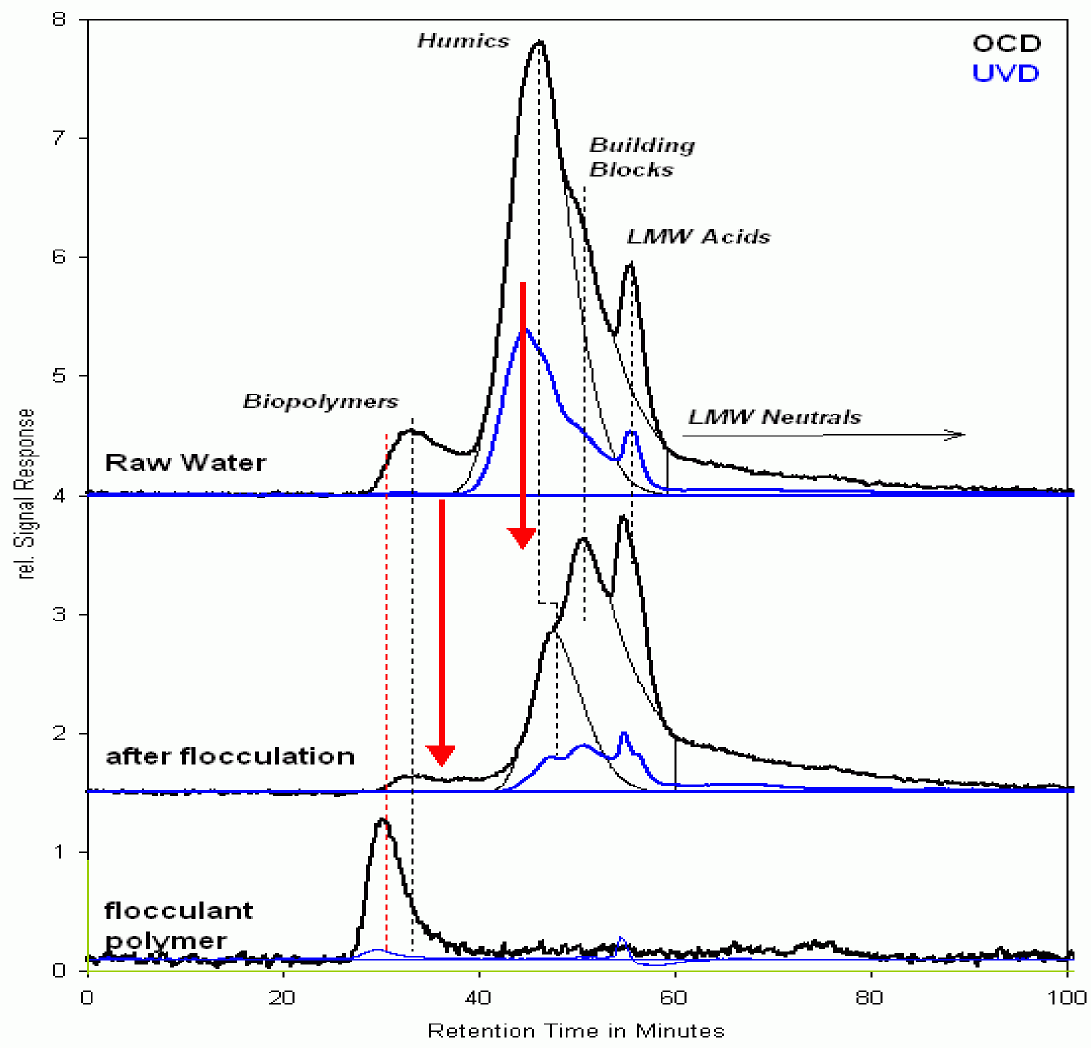
Impact of flocculation on NOM

Source: http://www.doc-labor.de

A flocculant polymer was added and question was risen whether flocculant polymer was still present after flocculation. Results suggest that this is not the case (residual polymer < 5 ppb).



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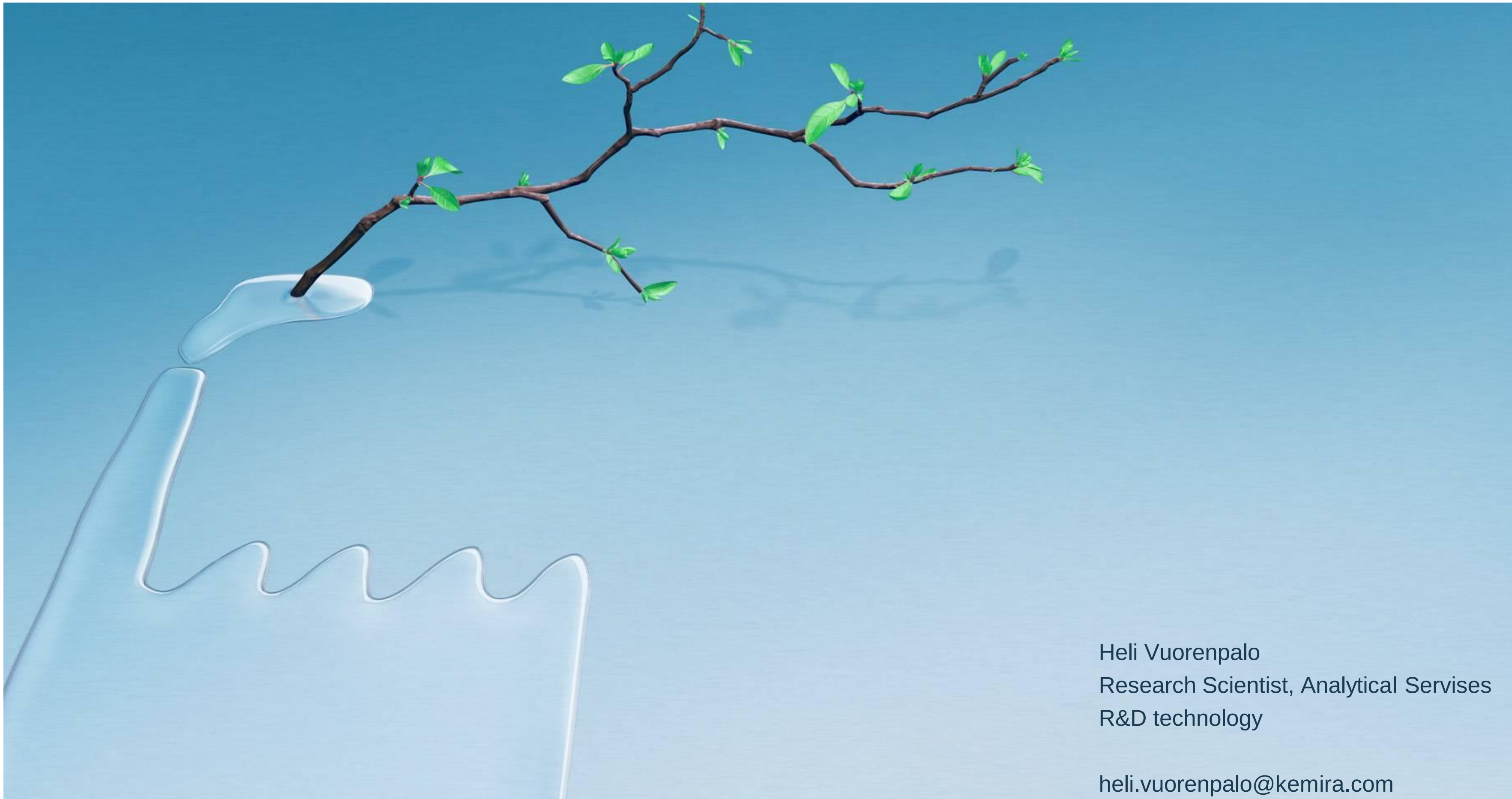
Summary

- LC-OCD is a great tool to characterize different types of waters in µg/l level.
- The core of the system is the organic carbon detector (OCD) which is also the only OCD commercially available world-wide. Additional detectors include UV-absorption (UVD), organic and inorganic bound nitrogen (OND), and, optionally, fluorescence (FLU).
- The system is currently used by about 20 research groups world-wide. Applications include studies on MBR performance and optimisation, causes for UF and RO membrane (bio)fouling, pre-treatment optimisation in sea water desalination, monitoring of city water quality and others more.



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Thank you!