# LC-OCD Analyses of a power plant water treatment plant and steam cycle

**Your proj.-ID/ our proj.-ID:** /
**Project Partner/ contact:**
**# and type of samples:** 16 (water)
**Measuring conditions:** column: 5075 / 015 flows: 1.0 / 0.3 / Ø buffer: STD

| | | | | |
|---|---|---|---|---|
| **Sampling date:** | 2008-Jan-05 | STD ☐ | MC ☐ | BC ☒ |
| **Incoming date:** | 2008-Feb-01 | report: | Y ☒ | N ☐ |
| **Measuring date:** | 2008-Feb-01-03 | data processing: | | |
| **Date of Report:** | 2008-Feb-04 | report: | | |



***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

**WTP**

Raw Water: This is a surface water with moderate amounts in biogenic organic matter (biopolymers, part of neutrals, part of HOC and acids). If this is town water then the water was not – or not efficiently – treated by flocculation. This can be deduced from the HS-diagram: Humics are in the center of pedogenic FA and this shows that humics are still of relatively high molecular mass. Flocculation could remove more humics which would lead to a situation that remaining humics are in the left area of the diagram.

Organic Scavenger: The scavenger removes all humics and about 50% of building blocks and neutrals. Biopolymers break fully through. We do not know the precise way the scavenger functions but the results speak for themselves. Potential problems of the filter could be the precipitation of humic acids (these are still present due to incomplete flocculation, see above), but perhaps the filter has no problem to deal with these.

Anion outlet: The filter works fine. Biopolymers break partly through (obviously some biopolymers are sufficiently anionic in order to be removed). Organic acids are fully removed.

MB-outlet: When the anion filter works fine then the MB has no impact on DOC. In this case, however, we see a worsening of the situation: DOC rises slightly but significantly due to a compound X, eluting at about 75 min. What is it? We don't know. Should the MB-resin be regenerated only at long intervals, i. e. 6 month, then this compound X could be a microbial by-product from a microbially contaminated resin (cation or anion). However, it could also be a resin leachate. (Compound X will be discussed again below).

Demin Tank: The situation is almost identical to MB-outlet, except a slight increase in biopolymers. This may be due to microbial activity in the tank, i. e. biofilms which shed biopolymers. The impact is, however, minor.

**Conclusions WTP**: The performance of the WTP system in the light of a relatively "poor" raw water and a conventional set-up (no membrane systems) is quite good. The product water gives a water with DOC-values around 200 ppb, higher DOC-values may be expected during times when microbial activity in the surface water is stronger. The disadvantage of the system is the complete lack of an effective barrier for biopolymers.

**WSC**

Drum waters: We find TOC-values of around 1.6 ppm. Hereof, about 1 ppm are organic acids (measured as organic C). The source for these acids are - most likely – biopolymers and neutrals which are the dominating organics in the demin water. The typical breakdown product of biopolymers (and perhaps neutrals) is acetic acid. Thus, 1 ppm of acids as C would correspond to 3 ppm of acetic acid. There is no threshold value for how much organic acids can be tolerated in the drum. We had a case where 3 ppm of organic acid (as C) induced FAC despite of sufficient alkalisation. All we can say is that ppm-values of acids are a matter of concern: Apart from potential risk of corrosion there is the risk of insufficient alkalisation or the risks related to caustic dosing. We could imagine that caustic dosing could be ceased once organic acids go below a threshold of, say, 300 ppb C.

Condensates: We discuss all condensates together and highlight only specific aspects. In general, all condensates look good. Organic acids, which are the target compound for elevated cation conductivity (CC), are very low in all waters. This shows that alkalisation in the drum is sufficient, all acids are in the anion form and hence non-volatile. According to our findings for acids the CC should be below 0.2 µS/cm. There is one constraint to this statement: We cannot say *for sure* that organic acids are absent, because acetic acid may got lost after sampling.

Therefore we suggest to check for organic acids in the condensates by ion chromatography (IC). But perhaps this has already been done and the findings were in agreement with our findings that organic acids are practically absent?

In this case we offer a 2$^{nd}$ hypothesis: We find "compound X" in all condensates, in particular in the LP regime, and most pronounced in LP steam 14. As mentioned above the compound is released form the MB filter. The compound is volatile as it is not found in the drum waters. Thus it is apt to contribute to CC in 2 ways: a) If it is anionic then it should be only slightly anionic because otherwise volatility would be low. It is well possible that our system does not identify slightly anionic compounds as "acids" (neither IC would do); b) The compound travels with the steam and decomposes to carbon dioxide with a very short half life for acids.

Basically, this latter process can also apply  for traces of acids carried over from the drum.

**Conclusions WSC**: Should elevated CC be observed as a novel, rather episodic situation then we would suspect a contamination of the MB-filter. Should elevated CC be observed as a slow increase then we would suspect the adding-up of acids in the drum.

End of Report

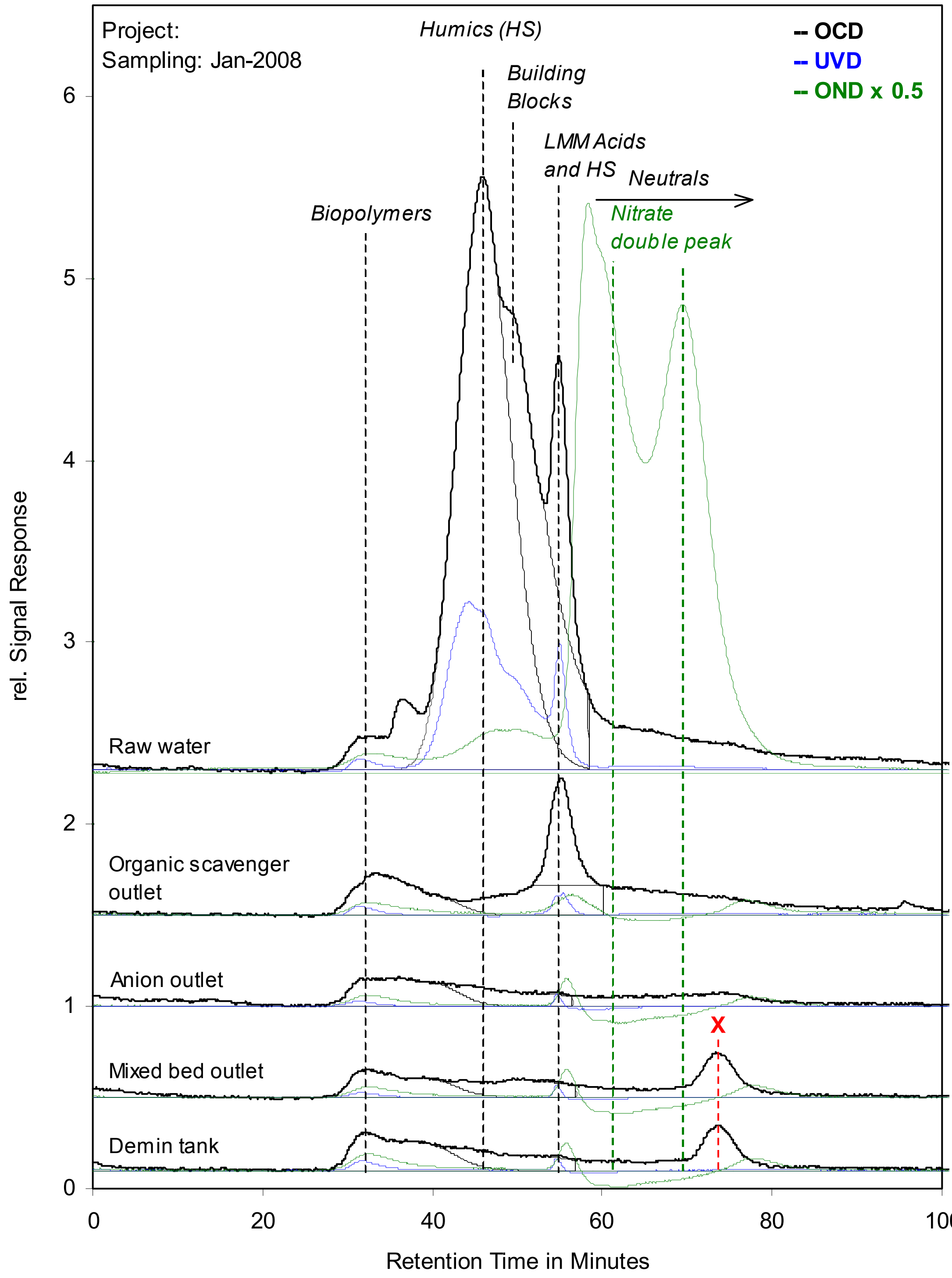


Fig. 1a: LC-OCD chromatograms

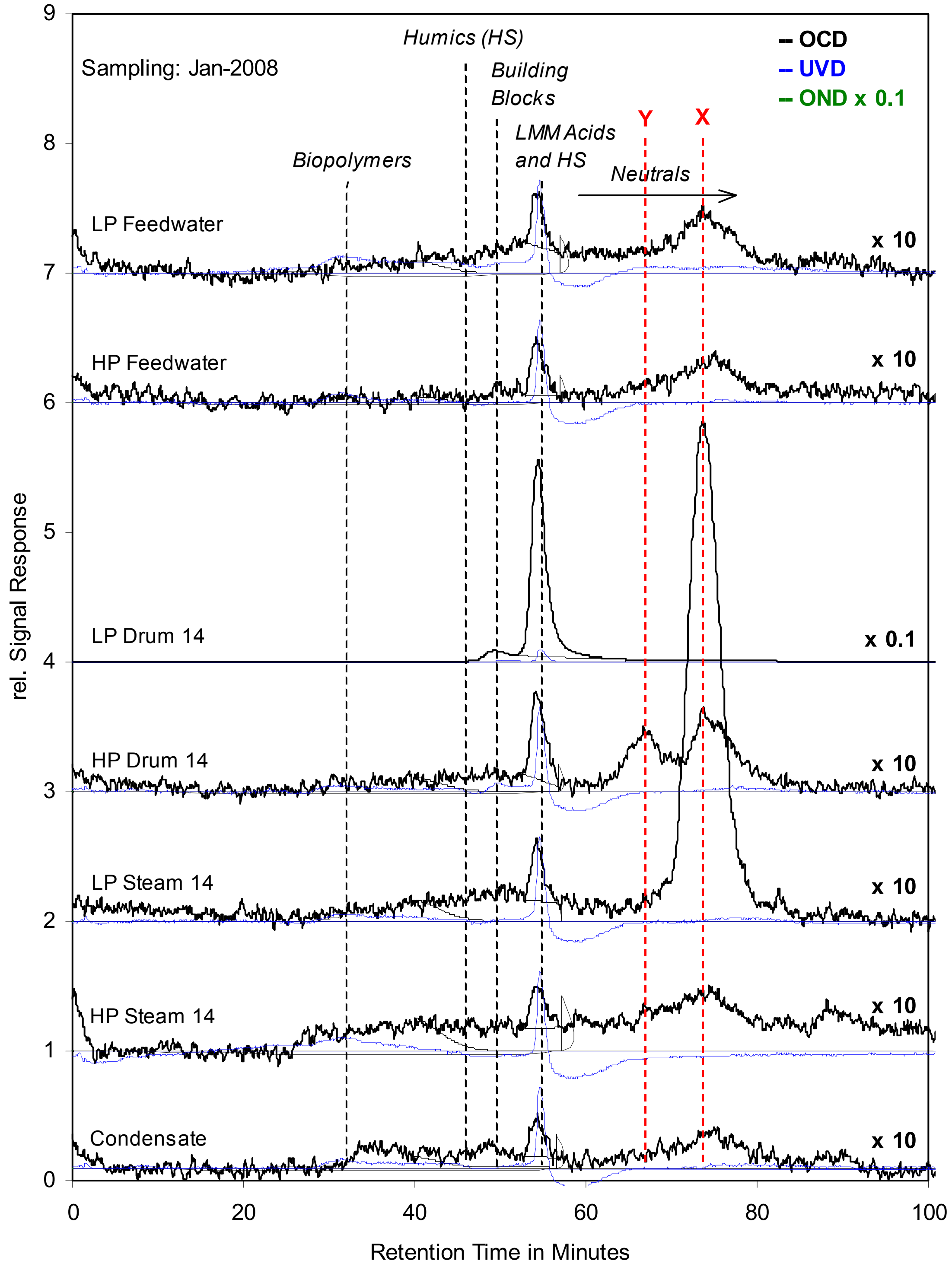


Fig. 1b: LC-OCD chromatograms

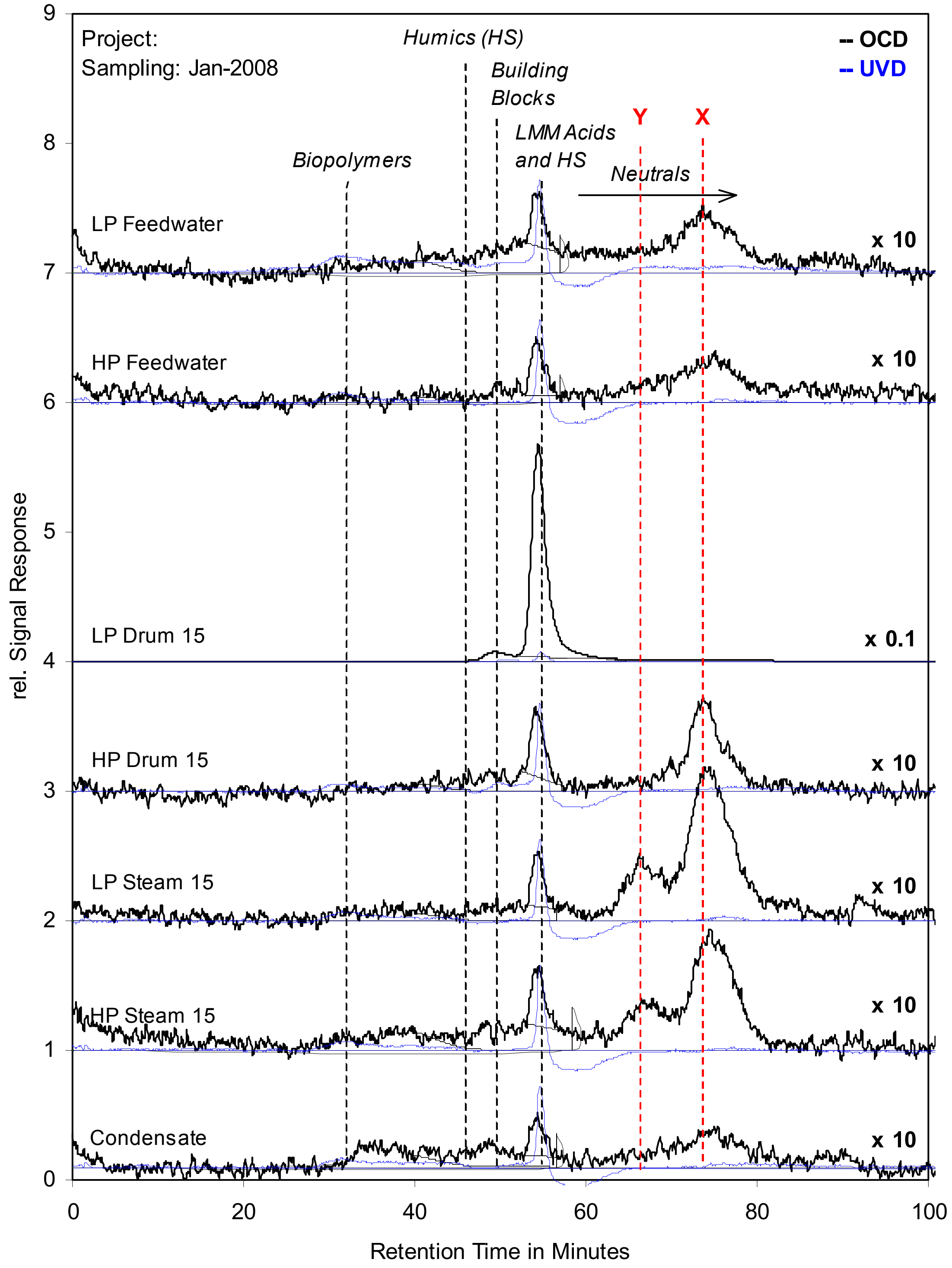


Fig. 1c: LC-OCD chromatograms

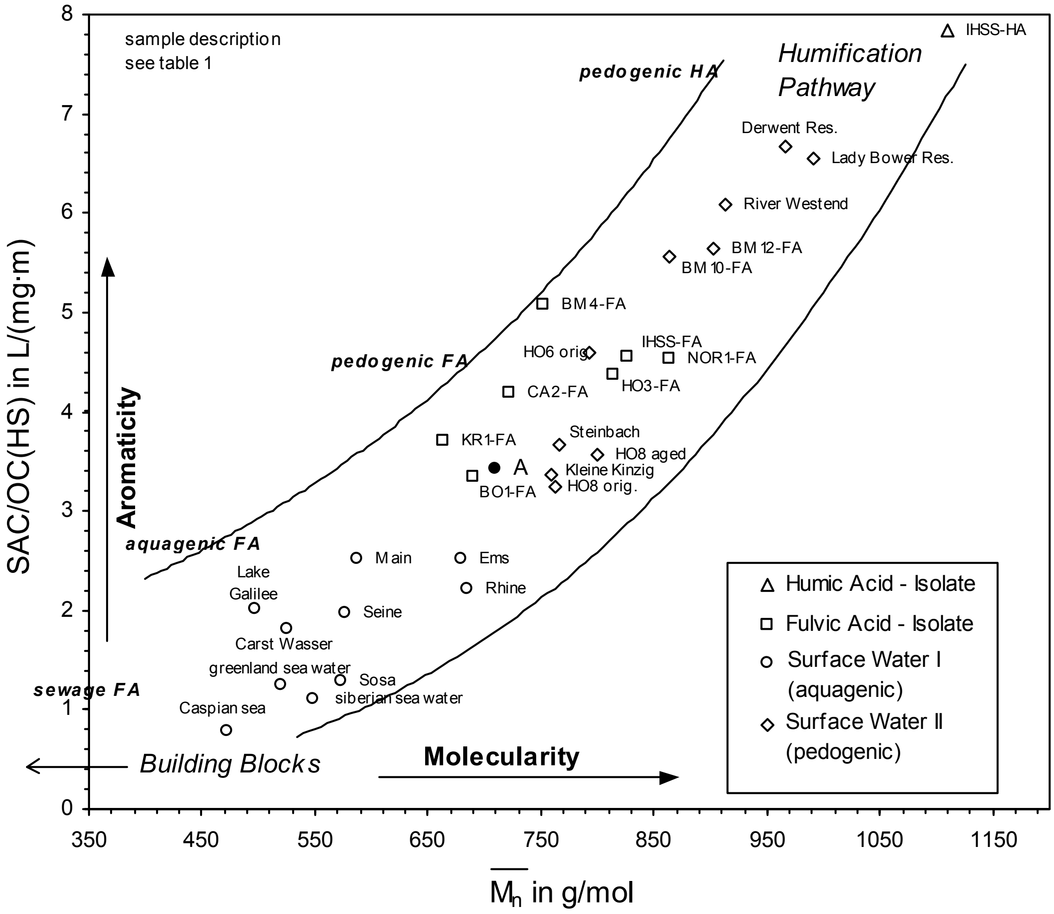


Fig. 2: Humic substances diagram

Table 1:

**Project:**

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Approx. Molecular Weights in g/mol: >>20.000 (Biopolymers); ~1000 (see separate HS-Diagram) (Humic Subst.); 300-500 (Building Blocks); <350 (Neutrals); <350 (Acids)

| | DOC Dissolved | HOC Hydrophob. | CDOC Hydrophil. | 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. SAC | CSUVA (CSAC/CDOC) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ppb-C | ppb-C | ppb-C | ppb-C | ppb-N | µg/µg | ppb-C | ppb-N | µg/µg | L/(mg*m) | g/mol | -- | ppb-C | ppb-C | ppb-C | ($m^{-1}$) | L/(mg*m) |
| | % DOC | % DOC | % DOC | % DOC | -- | -- | % DOC | -- | -- | -- | -- | -- | % DOC | % DOC | % DOC | -- | -- |
| **Raw water** | **2277** | **143** | **2135** | **108** | **32** | **0,30** | **1332** | **34** | **0,03** | **3,43** | **709** | **A** | **397** | **295** | **3** | **0,14** | **2,73** |
| | 100 | 6,3 | 93,7 | 4,7 | -- | -- | 58,5 | -- | -- | -- | -- | -- | 17,4 | 13,0 | 0,1 | -- | -- |
| **Organic scavenger outlet** | **674** | **186** | **489** | **119** | **15** | **0,13** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **103** | **176** | **91** | **0,12** | **1,10** |
| | 100 | 27,5 | 72,5 | 17,7 | -- | -- | -- | -- | -- | -- | -- | -- | 15,3 | 26,1 | 13,4 | -- | -- |
| **Anion outlet** | **172** | **20** | **153** | **62** | **8** | **0,12** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **32** | **58** | **bdl** | **0,05** | **0,69** |
| | 100 | 11,4 | 88,6 | 36,2 | -- | -- | -- | -- | -- | -- | -- | -- | 18,3 | 33,6 | -- | -- | -- |
| **Mixed bed outlet** | **203** | **35** | **168** | **53** | **7** | **0,14** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **36** | **78** | **bdl** | **0,04** | **0,68** |
| | 100 | 17,4 | 82,6 | 25,9 | -- | -- | -- | -- | -- | -- | -- | -- | 17,9 | 38,4 | -- | -- | -- |
| **Demin Tank** | **206** | **14** | **192** | **79** | **11** | **0,14** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **36** | **76** | **bdl** | **0,08** | **0,82** |
| | 100 | 6,9 | 93,1 | 38,4 | -- | -- | -- | -- | -- | -- | -- | -- | 17,3 | 37,0 | -- | -- | -- |
| **LP Feedwater** | **79** | **41** | **38** | **6** | **bdl** | **--** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **8** | **22** | **2** | **0,05** | **4,47** |
| | 100 | 51,4 | 48,6 | 8,0 | -- | -- | -- | -- | -- | -- | -- | -- | 9,6 | 28,1 | 2,9 | -- | -- |
| **HP Feedwater** | **49** | **16** | **33** | **5** | **9** | **1,67** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **3** | **23** | **3** | **0,01** | **1,61** |
| | 100 | 31,8 | 68,2 | 11,1 | -- | -- | -- | -- | -- | -- | -- | -- | 5,8 | 46,1 | 5,2 | -- | -- |
| **LP Drum 14** | **1696** | **322** | **1373** | **6** | **2** | **0,28** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **232** | **107** | **1027** | **0,01** | **0,80** |
| | 100 | 19,0 | 81,0 | 0,4 | -- | -- | -- | -- | -- | -- | -- | -- | 13,7 | 6,3 | 60,6 | -- | -- |
| **LP Drum 15** | **1697** | **284** | **1413** | **10** | **3** | **0,28** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **200** | **104** | **1098** | **0,02** | **0,65** |
| | 100 | 16,7 | 83,3 | 0,6 | -- | -- | -- | -- | -- | -- | -- | -- | 11,8 | 6,1 | 64,7 | -- | -- |
| **HP Drum 14** | **92** | **52** | **40** | **8** | **4** | **0,54** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **5** | **24** | **4** | **0,01** | **1,75** |
| | 100 | 56,1 | 43,9 | 8,3 | -- | -- | -- | -- | -- | -- | -- | -- | 4,9 | 26,2 | 4,5 | -- | -- |

**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*

Table 1 (continued):

| Project: sampl.date 01.2008 | DOC | HOC | CDOC | BIO-polymers | DON | N/C | Humic Subst. (HS) | DON | N/C | Aromaticity | Mol-Weight | Position in | Building Blocks | Neutrals | Acids | Inorg. Colloid. | SUVA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Approx. Molecular Weights in g/mol: | | | | >>20.000 | | | ~1000 (see separate HS-Diagram) | | | | | | 300-500 | <350 | <350 | | |
| | Dissolved | Hydrophob. | Hydrophil. | | (Norg) | | | (Norg) | | (SUVA-HS) | (Mn) | HS diagram | | | | SAC | (SAC/DOC) |
| | ppb-C | ppb-C | ppb-C | ppb-C | ppb-N | µg/µg | ppb-C | ppb-N | µg/µg | L/(mg*m) | g/mol | -- | ppb-C | ppb-C | ppb-C | $(m^{-1})$ | L/(mg*m) |
| | % DOC | % DOC | % DOC | % DOC | -- | -- | % DOC | -- | -- | -- | -- | -- | % DOC | % DOC | % DOC | -- | -- |
| **HP Drum 15** | **76** | **49** | **27** | **2** | **4** | **1,56** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **4** | **17** | **3** | **0,01** | **2,96** |
| | 100 | 64,2 | 35,8 | 3,2 | -- | -- | -- | -- | -- | -- | -- | -- | 5,6 | 22,9 | 4,1 | -- | -- |
| **LP Steam 14** | **136** | **50** | **85** | **10** | **9** | **0,97** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **7** | **66** | **3** | **0,01** | **0,65** |
| | 100 | 37,2 | 62,8 | 7,1 | -- | -- | -- | -- | -- | -- | -- | -- | 5,4 | 48,4 | 1,9 | -- | -- |
| **LP Steam 15** | **91** | **38** | **52** | **6** | **9** | **1,38** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **4** | **40** | **2** | **0,02** | **1,29** |
| | 100 | 42,3 | 57,7 | 6,9 | -- | -- | -- | -- | -- | -- | -- | -- | 4,4 | 44,0 | 2,3 | -- | -- |
| **HP Steam 14** | **82** | **19** | **64** | **12** | **9** | **0,74** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **7** | **42** | **2** | **0,01** | **0,69** |
| | 100 | 22,5 | 77,5 | 14,9 | -- | -- | -- | -- | -- | -- | -- | -- | 9,1 | 50,8 | 2,6 | -- | -- |
| **HP Steam 15** | **89** | **33** | **57** | **14** | **9** | **0,68** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **7** | **34** | **3** | **0,03** | **1,24** |
| | 100 | 36,6 | 63,4 | 15,2 | -- | -- | -- | -- | -- | -- | -- | -- | 7,7 | 37,6 | 2,9 | -- | -- |
| **Condensate** | **54** | **24** | **29** | **6** | **8** | **1,43** | **bdl** | **bdl** | **--** | **--** | **--** | **--** | **5** | **17** | **2** | **0,03** | **2,81** |
| | 100 | 45,2 | 54,8 | 11,1 | -- | -- | -- | -- | -- | -- | -- | -- | 8,9 | 31,4 | 3,4 | -- | -- |

**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*
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