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Dissolved Organic Matter Characterization of SAGD Produced Water

Effects on Produced Water Treatment

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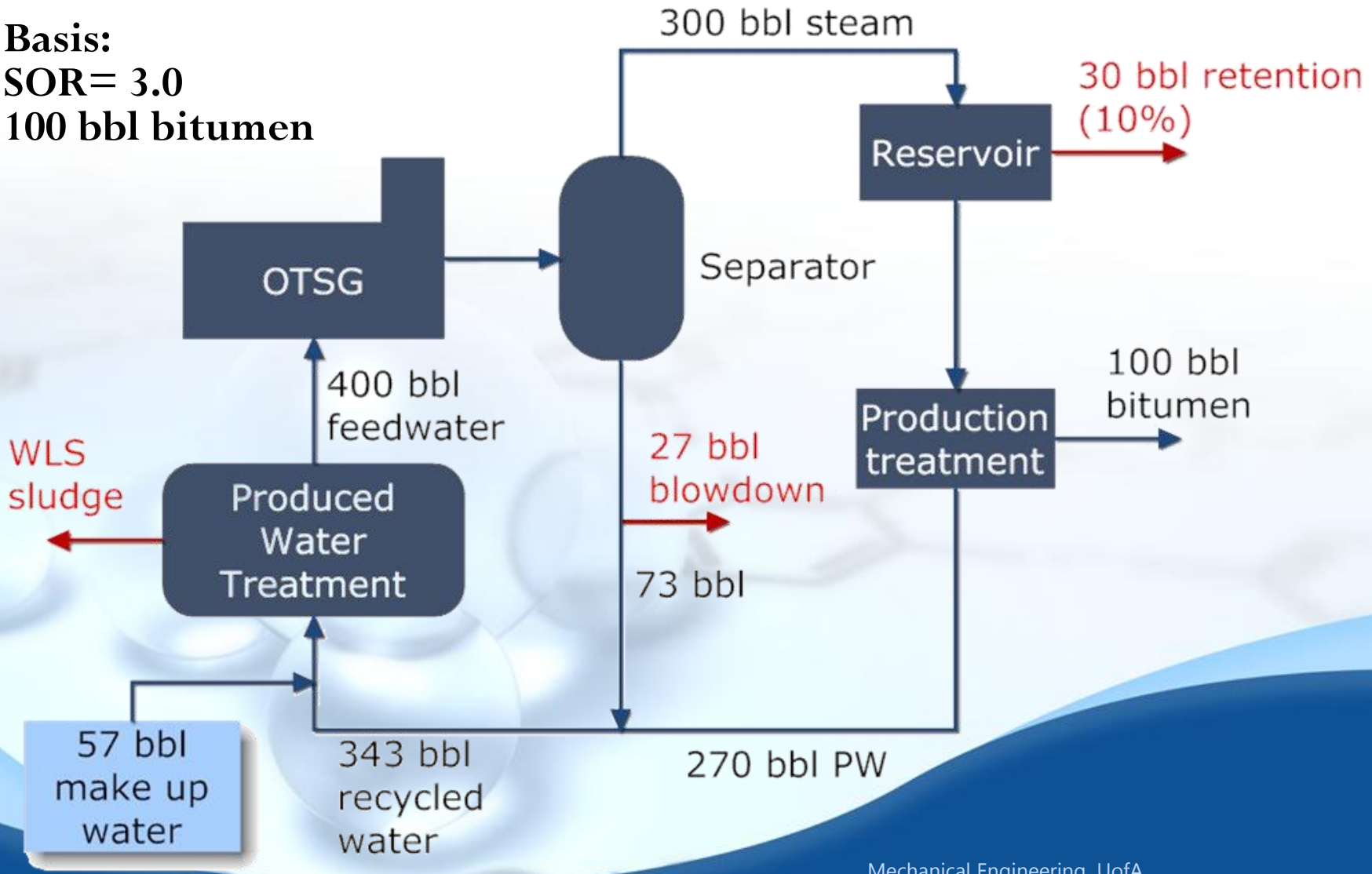
Outline

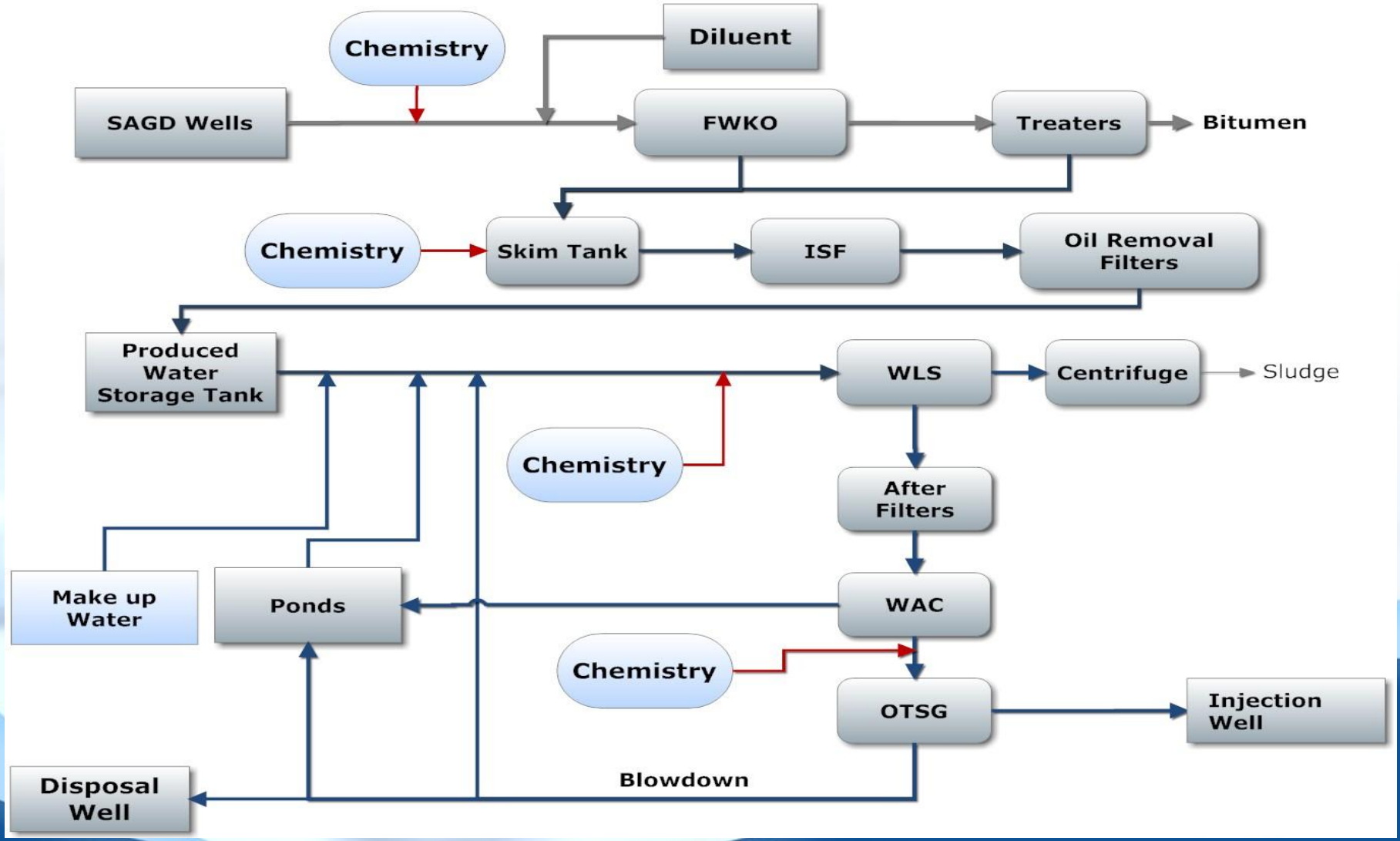
- Overview of SAGD produced water (PW) treatment
- Water chemistry management challenges:
  - Reduce blowdown water disposal
  - Reduce make up water
  - Improve reliability of treatment processes
- Knowledge of water chemistry
  - Snapshot of the chemistry of blow-down water
- Dissolved organic matter (DOM)
- Concluding remarks

Typical SAGD Surface Treatment

Basis:
SOR= 3.0
100 bbl bitumen



Schematic of Surface Treatment



Characteristics of Different Oil Field Produced Water and SAGD Blow-Down

Characteristics	Oil Field Produced Water[1]	Oil Sands Produced Water[2]	SAGD BBD (Our Study)
pH	7.4-8.5	7.11	11.2-10.3
Conductivity (µS/cm)	1400-5000	1540	10000-18000
TSS (mg/L)	97	-	25-65
TDS (mg/L)	700-2000	-	12000-17000
TOC (mg/L)	68-140	232	500-2500
Silica (mg/L as Si)	7-14	-	94-256

[1]Mondal, S., Wickramashingh, S. (2008) J. Membr. Sci. 322, 162-170

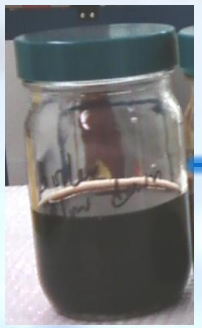
[2]Petersen, M.A., Grade, H. (2011) Ind. Eng. Chem. Res. 50, 12217-12224

UNDERSTANDING THE CHEMISTRY OF SAGD PW

Chemistry of the Blow Down Water

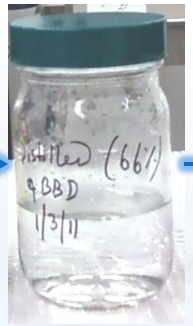
SAGD Blowdown Water Evaporation

"End of the pipe" water – represents cumulative effect of all chemistries.



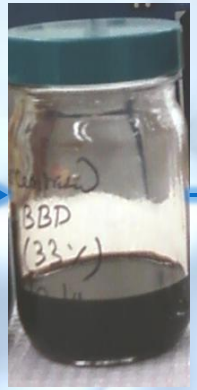
100 ml BBD

Evaporation



67% condensate

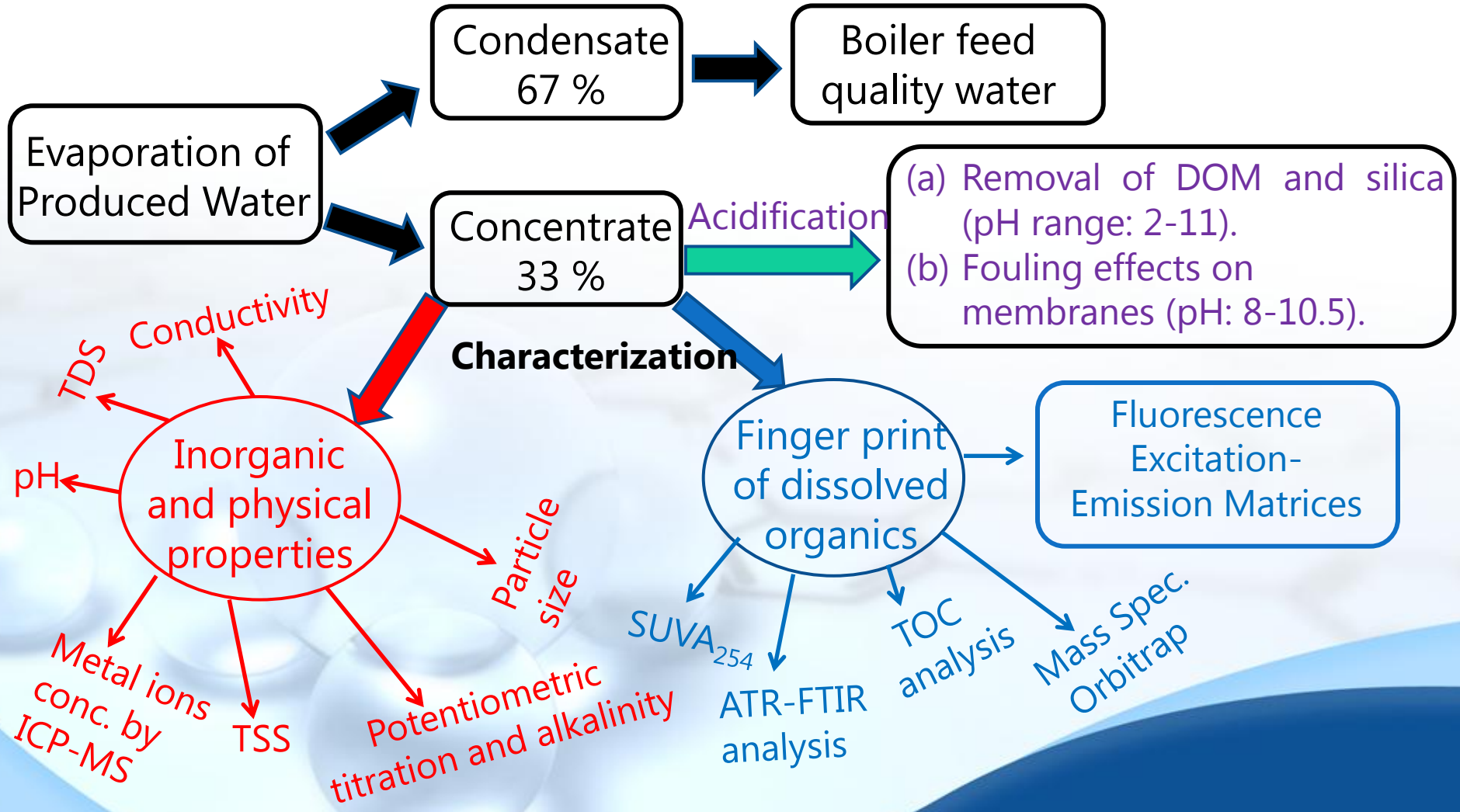
Analysis as potential BFW



33% concentrate

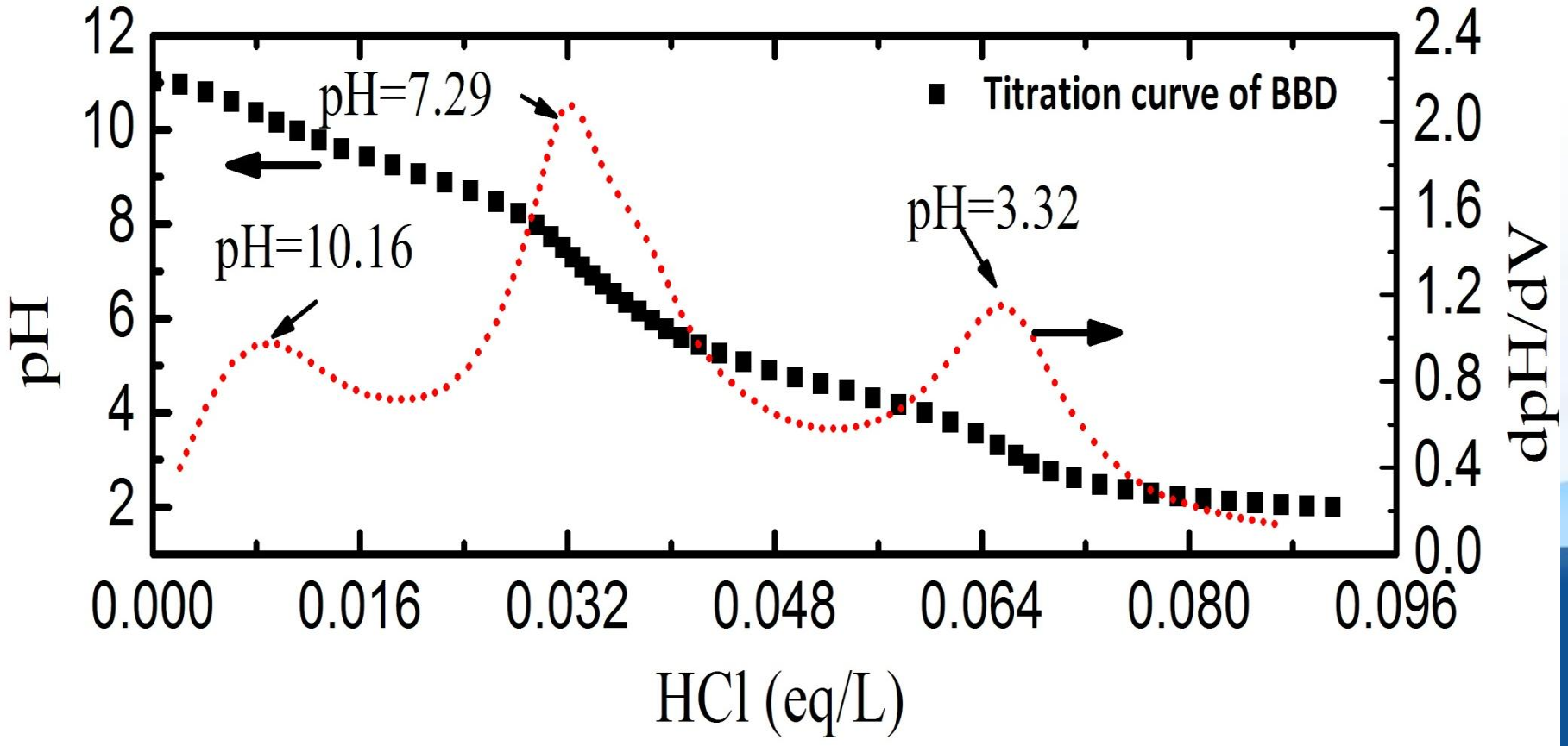
Detailed analysis of chemistry

Characterization Methods

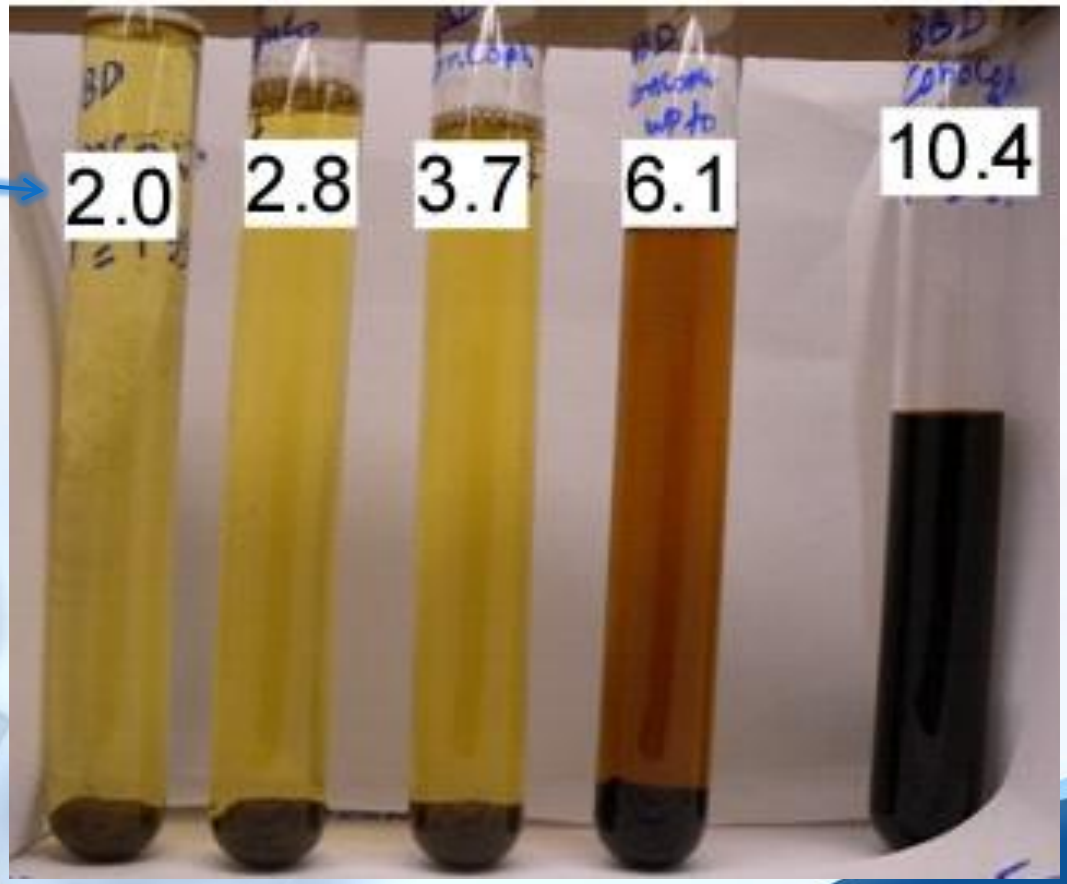


Potentiometric Titration of BBD

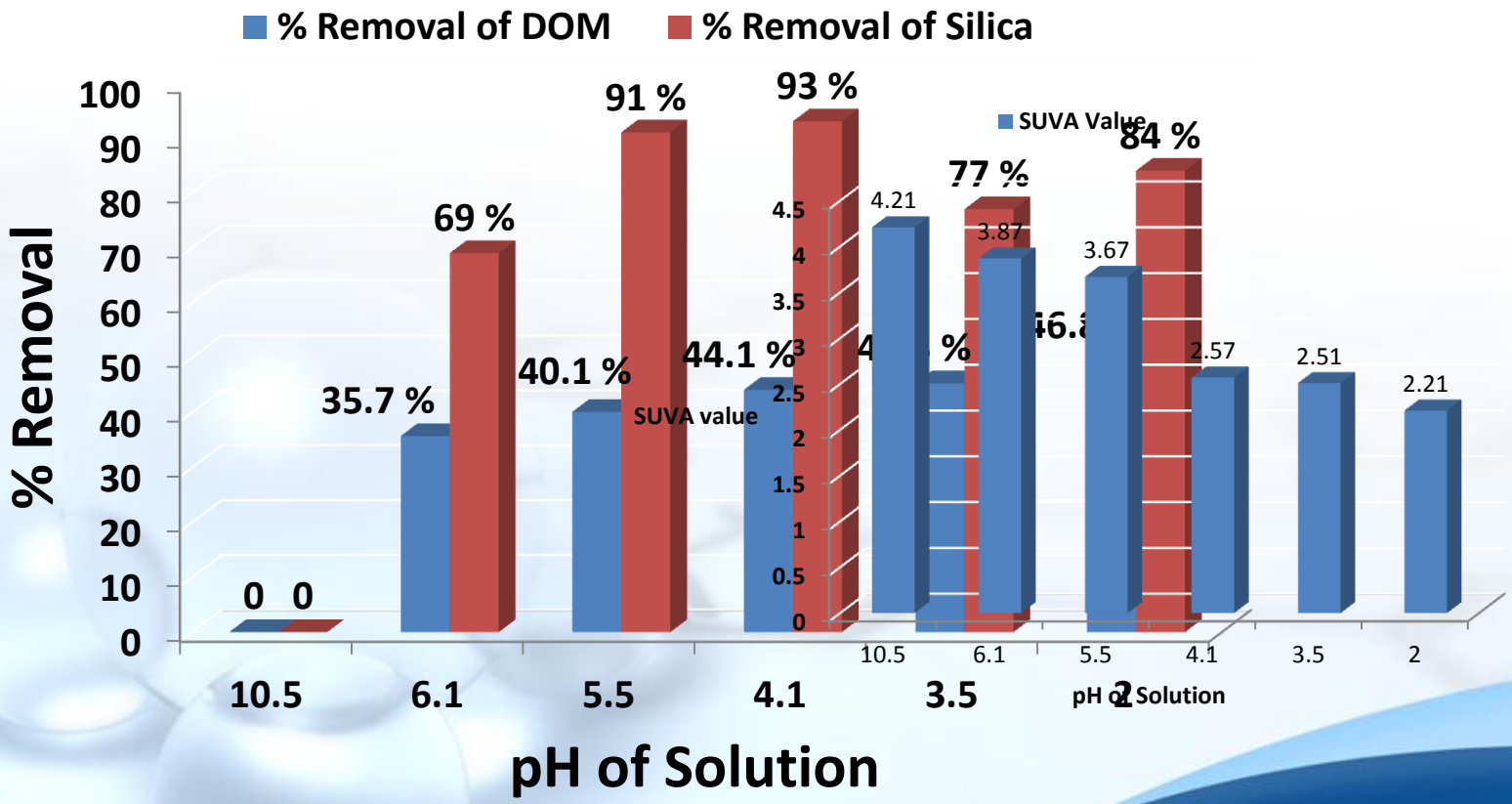
Acid-titration of BBD water performed to different end-points using a potentiometric "true equilibrium" auto-titrator (QC-Titrate)



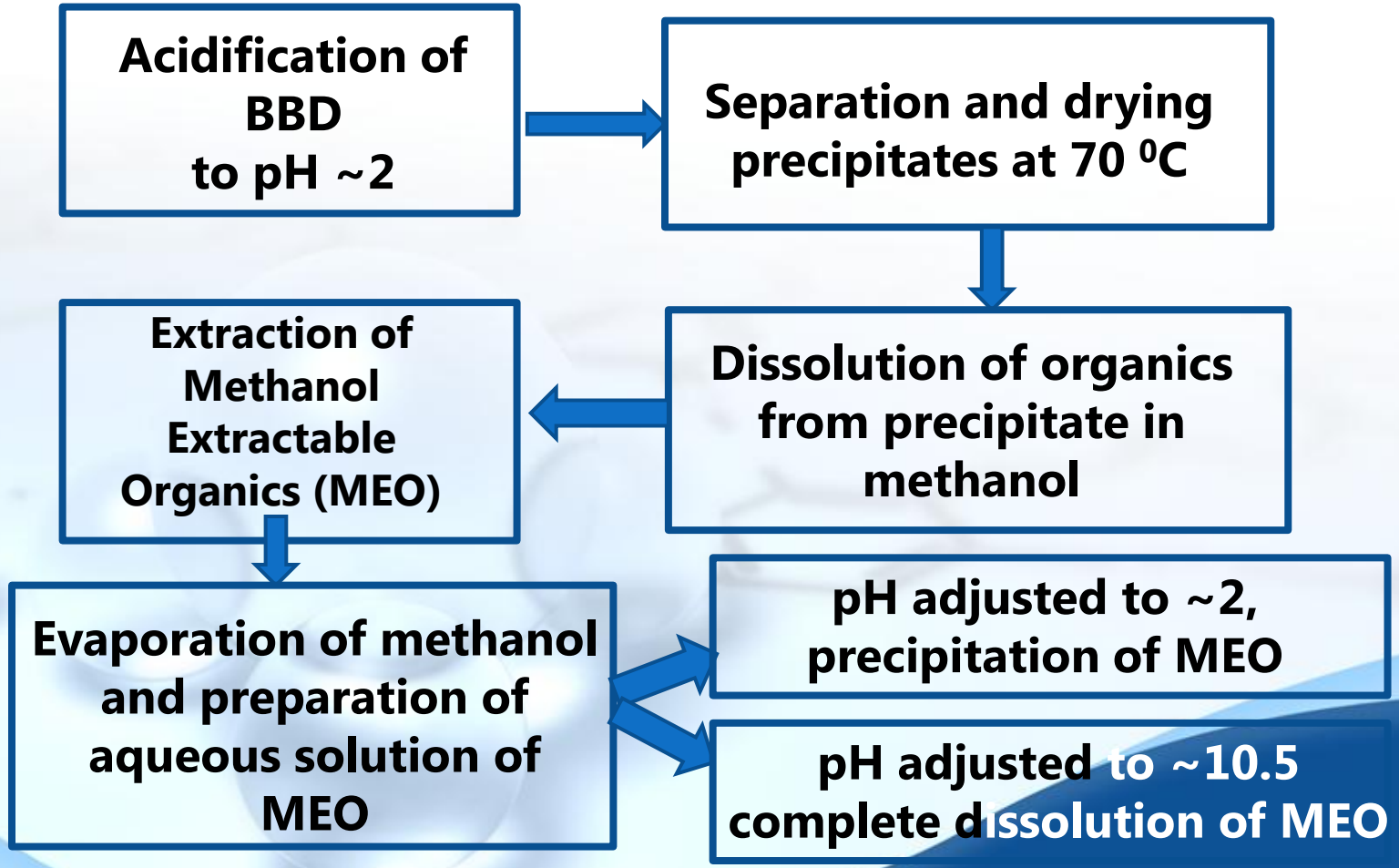
Acidification of Blow-Down



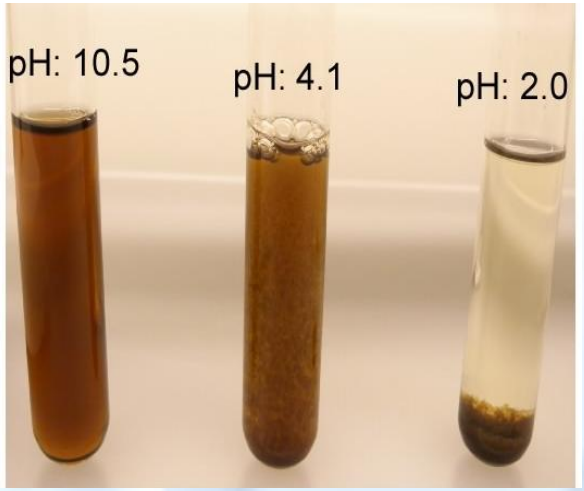
Silica and DOM Removal on Acidification



Methanol Extracted Organics (MEO)



Effects of pH on Aqueous Methanol Extracted Organics

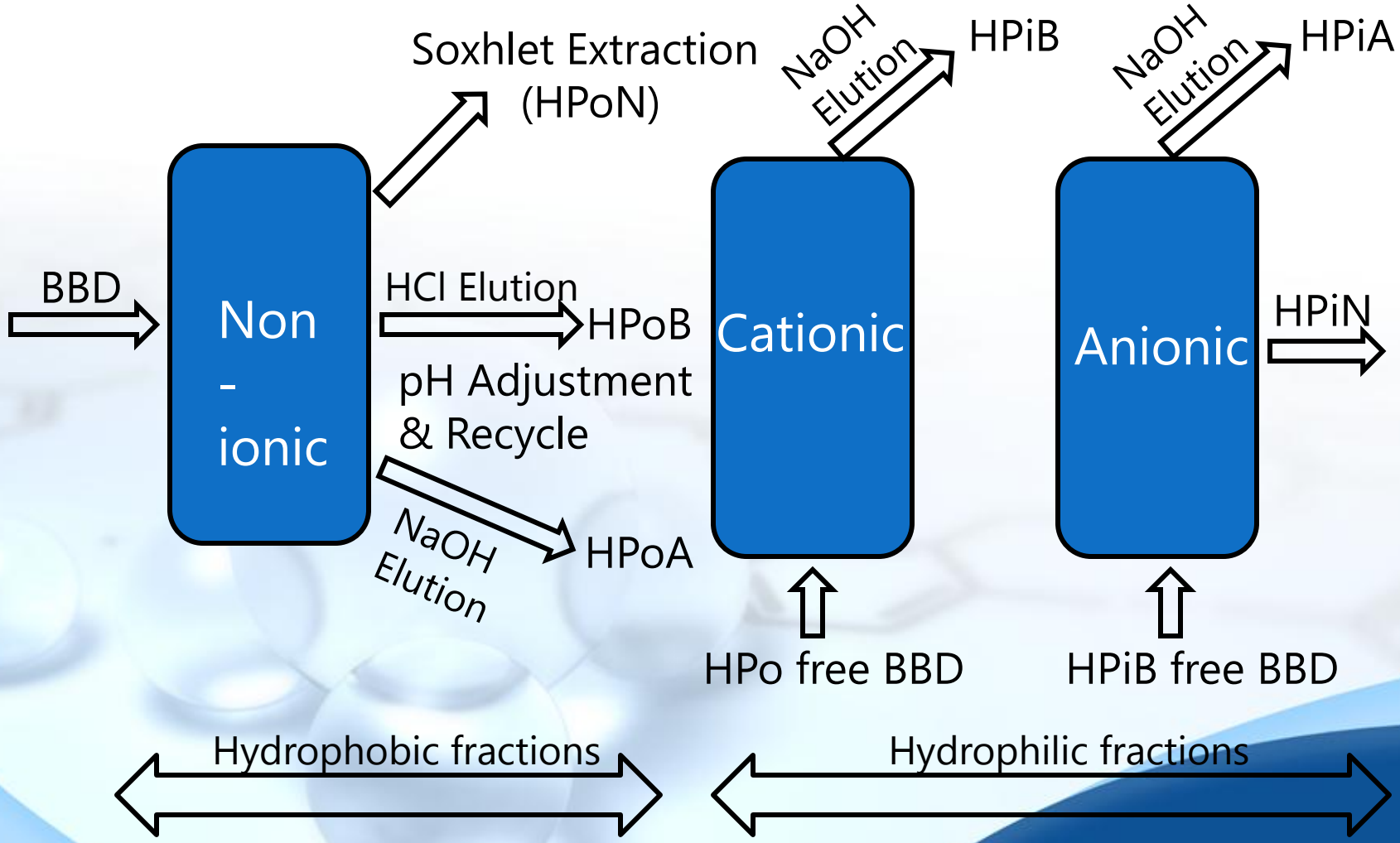


CHNS analysis of acid precipitated organics

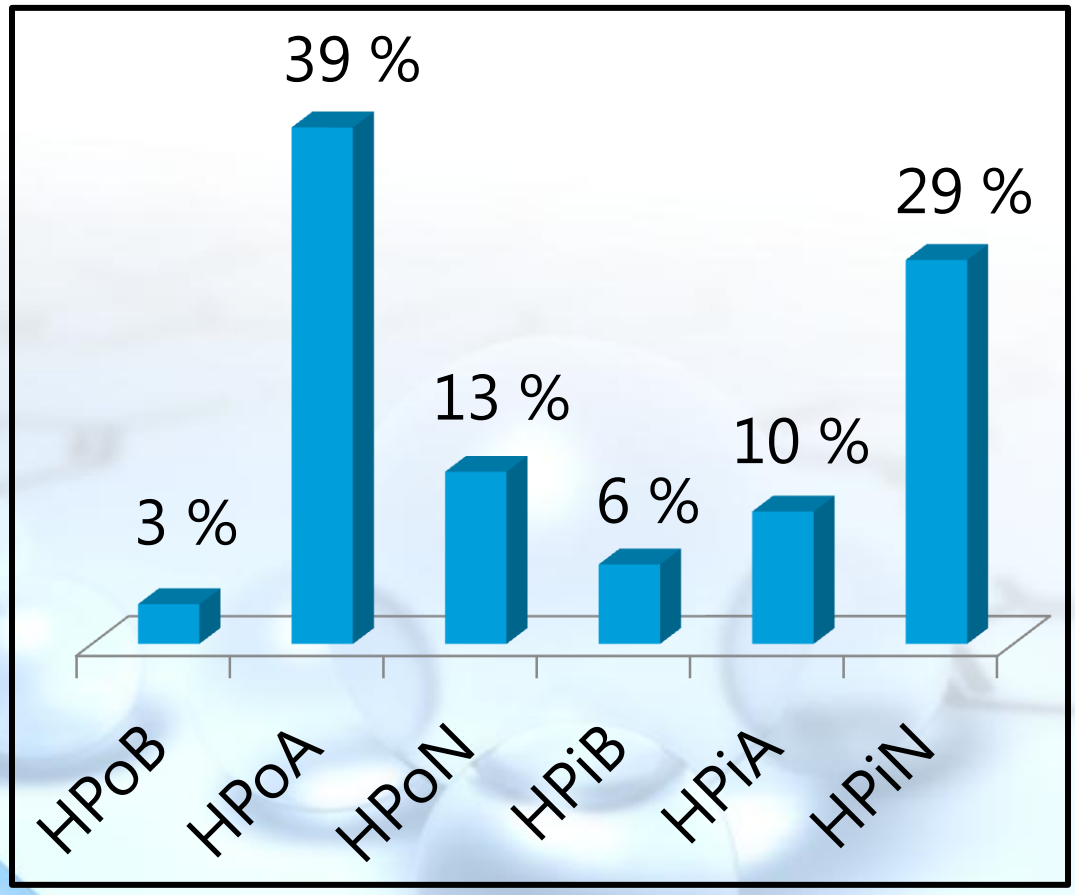
C (Wt %)	H (Wt %)	N (Wt %)	S (Wt %)
18.08	2.23	0.25	0.29

- The MEO fraction of DOM precipitates independently with acidification
- This behavior can be attributed to the protonation of organic acid salts to a free acid form, which become insoluble in aqueous media and precipitate at low pH

Ion-Exchange Fractionation



DOM Fractions in BBD



- Hydrophobic acid and hydrophilic neutral are the major fractions
- Hydrophobic neutral is the next major fraction

Analytical Techniques

Excitation-emission matrix (Fluorescence spectroscopy)

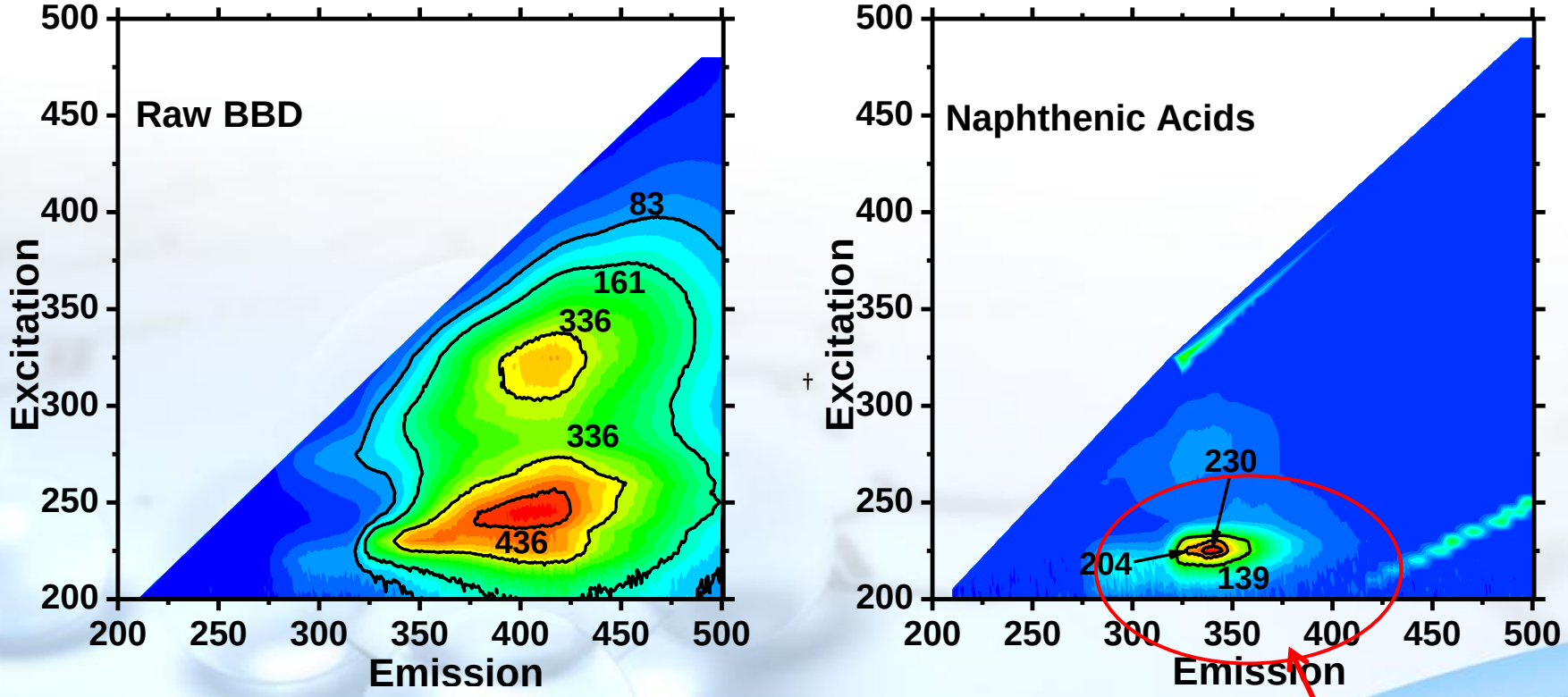
- Ex/Em ranges: 200 to 500 nm

  Step sizes: 10 nm for excitation

  5 nm for emission

- Other analytical techniques used are TOC analysis, $SUVA_{254}$, ATR-FTIR spectroscopy

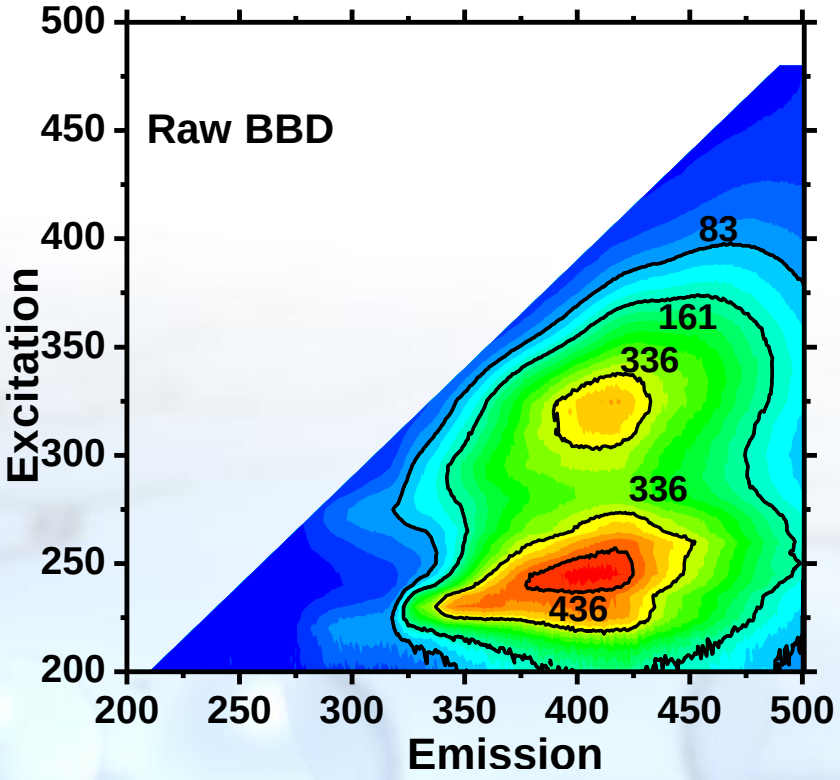
EEMs of BBD- Organics and Naphthenic Acids

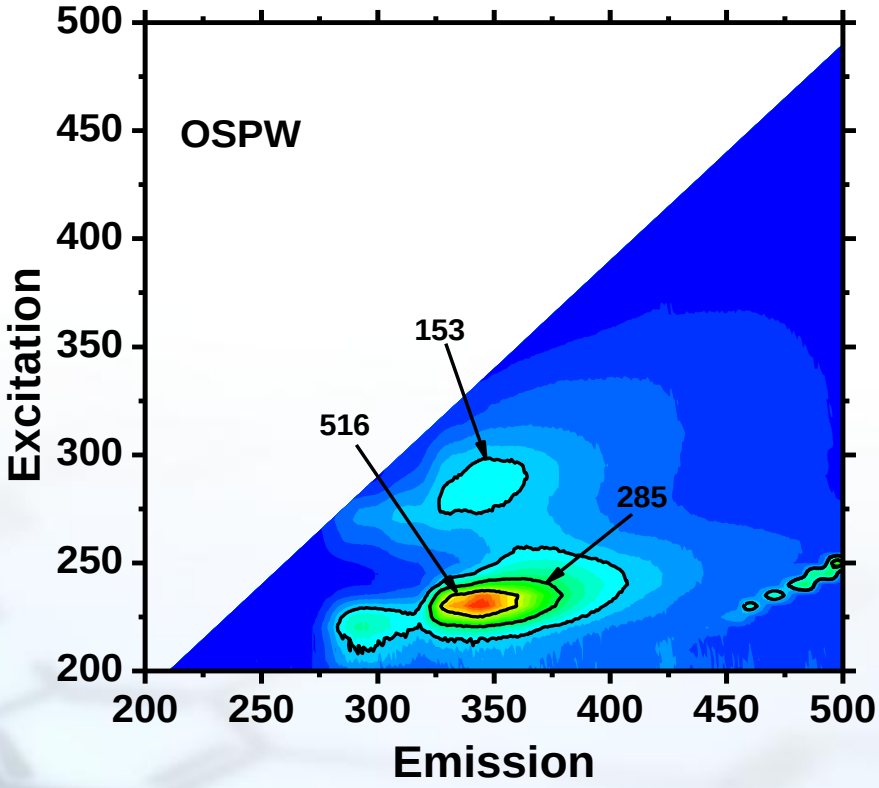


Signature of commercial Naphthenic acid (NA) not observed in BBD

Ex/Em 230/350

BBD v/s OSPW

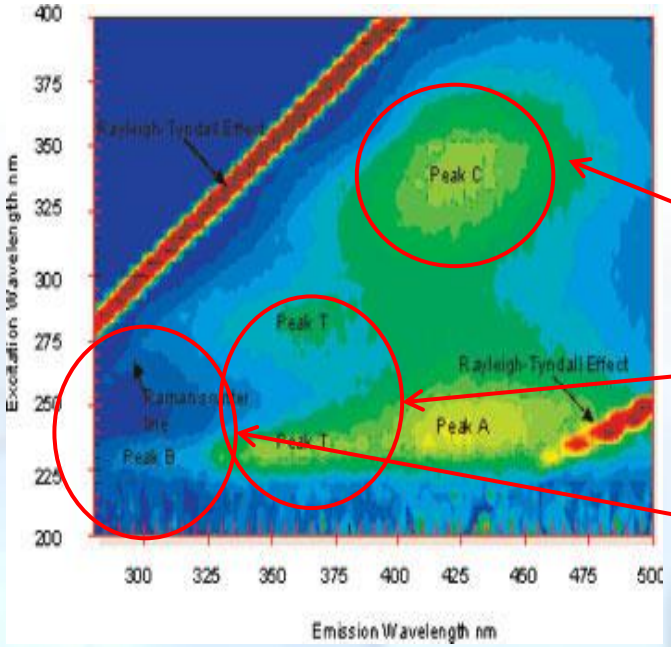




- The BBD does not contain NA signatures
- NA is a principal DOM component in OSPW

FLUORESCENCE SIGNATURES OF DOM FRACTIONS OBTAINED FROM ION-EXCHANGE FRACTIONATION

Typical NOM EEMs

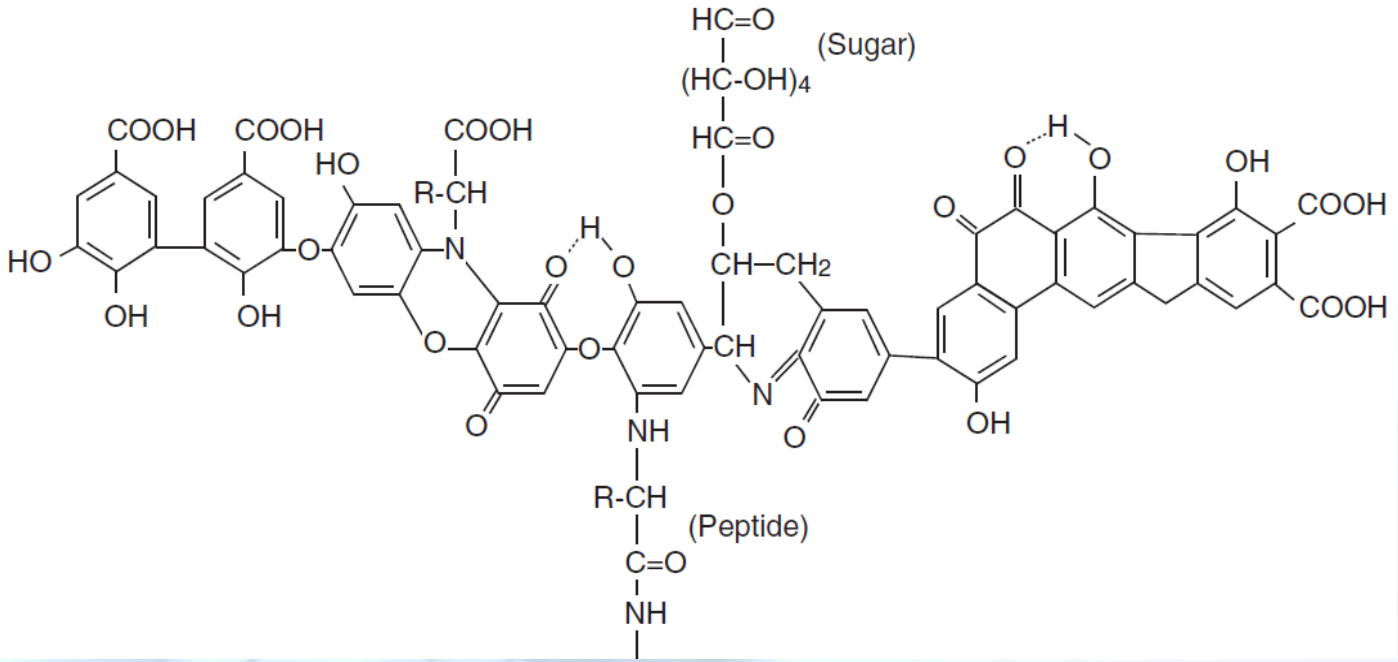


Fluorophore type	Excitation-emission wavelength (nm) fluorescence peaks
Humic like	300-370/400-500
Tryptophan	225-237/340-381 and 275/340
Tyrosine	225-237/309-321 and 275/310

Hudson, N.; Baker, A.; Reynolds, D. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters-a review. River Research and Applications 2007, 23, 631–649.

Structures of Humic Acid

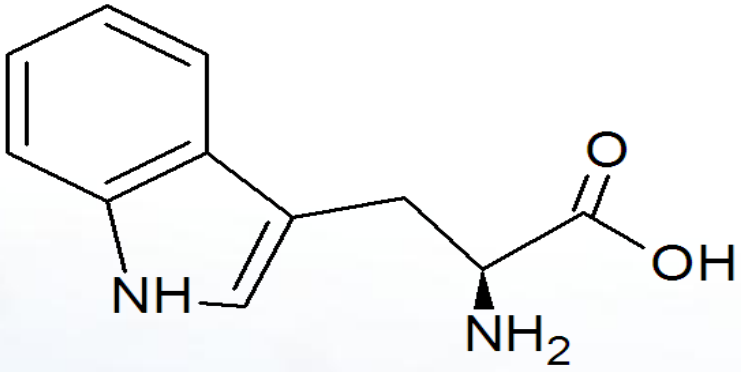
Model Structure:



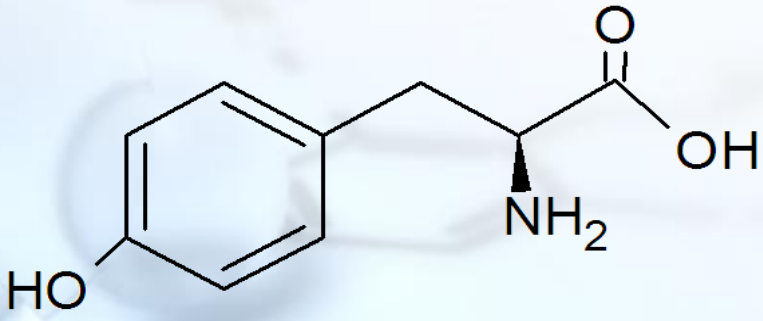
Aiken GR, McKnight D,Weshaw RL, MacCarthy P. 1985. An introduction to humic substances in soil, sediment and water. Humic Substances in Soil, Sediment and Water, John Wiley & Sons: New York; 203.

Structures of Tryptophan and Tyrosine

Tryptophan

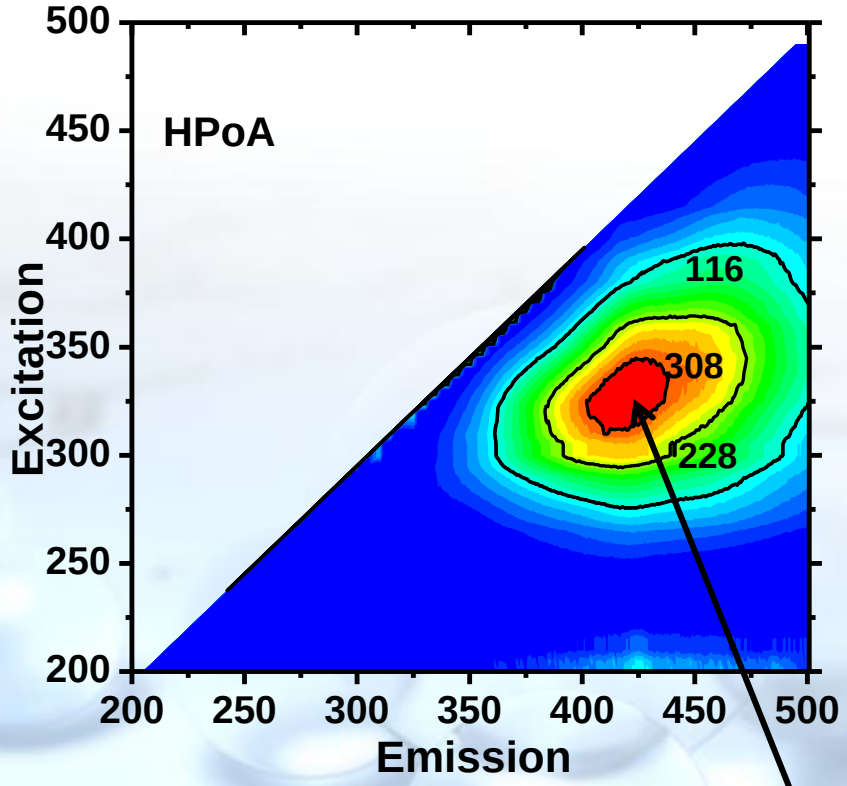


Tyrosine

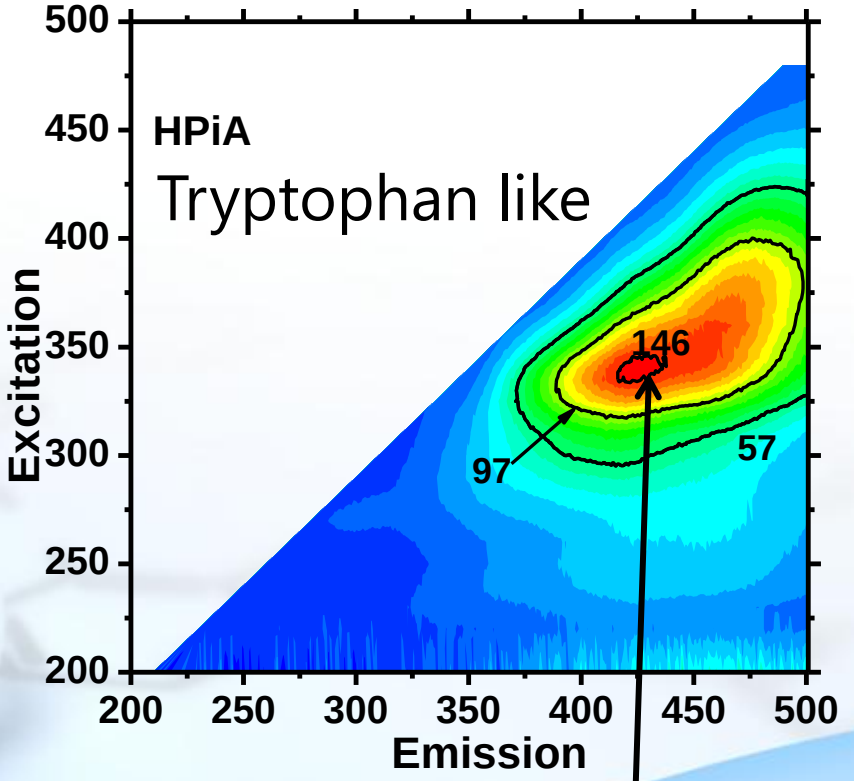


Hudson, N.; Baker, A.; Reynolds, D. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters-a review. River Research and Applications 2007, 23, 631–649.

EEMs Contour of Acidic DOMs

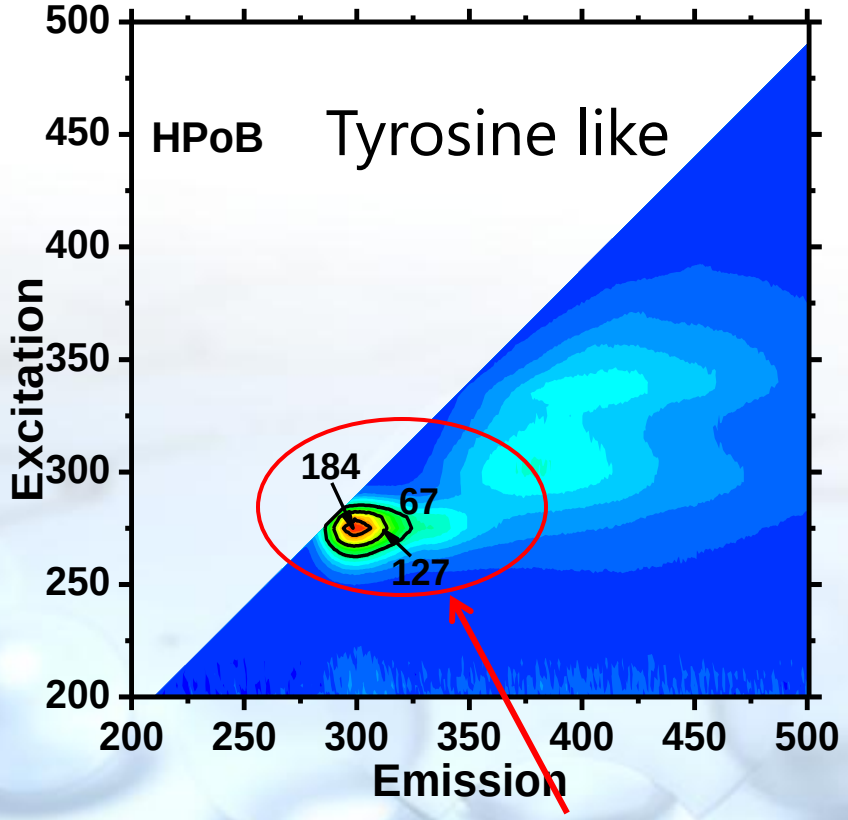


Humic like Ex/Em: 325/420

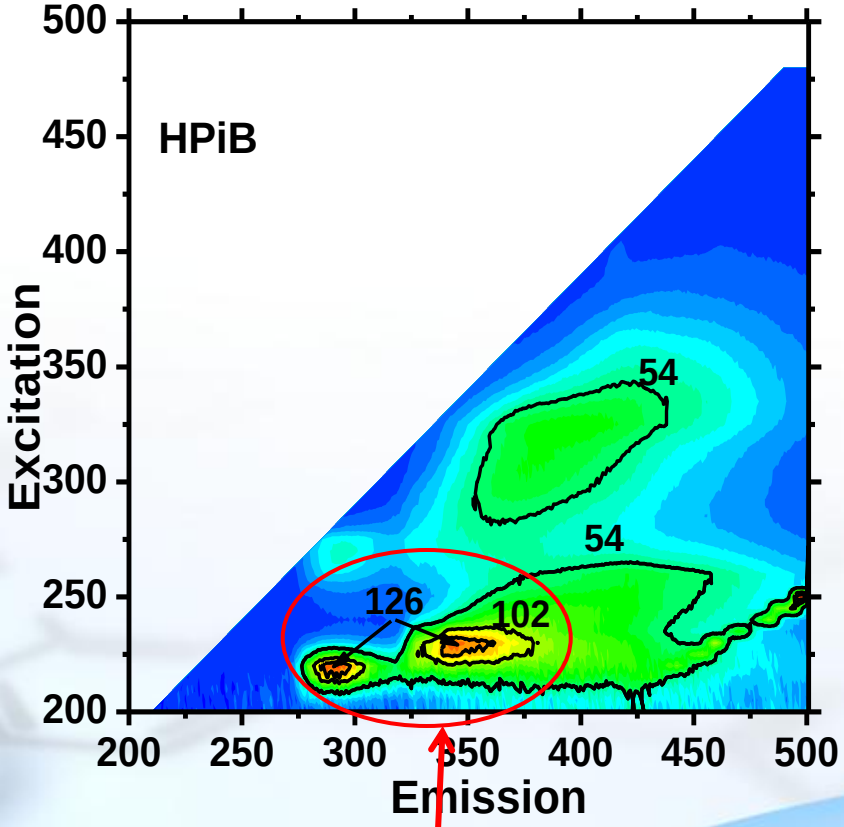


Ex/Em: 340/425

EEMs Contour of Basic DOMs

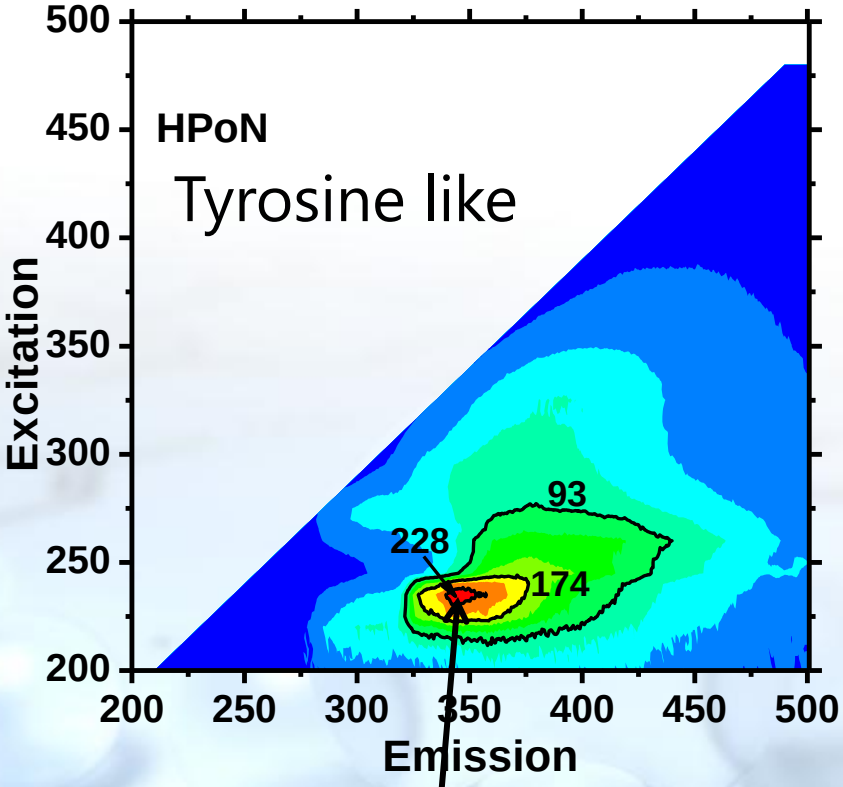


Ex/Em:260-290/280-320

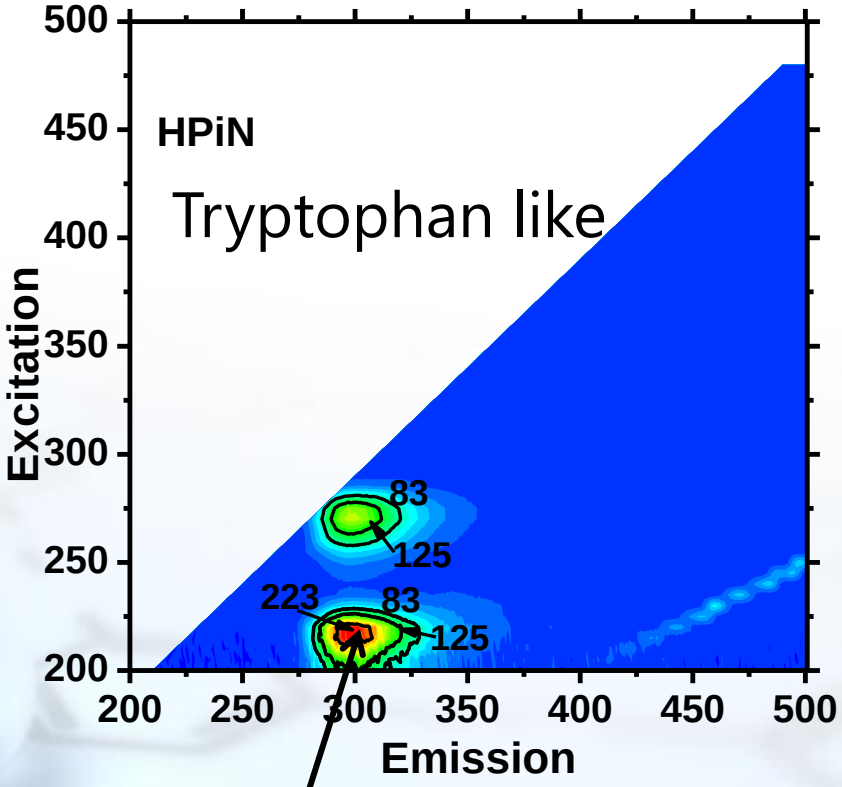


Ex/Em:210-225/310,350

EEMs Contour of Neutral DOMs



Ex/Em: 240/350



Ex/Em: 220/300

$SUVA_{254}$

$SUVA_{254}$ value of DOM fractions:

Fractions	$SUVA_{254}$
HPoB	0.61
HPoA	**3.62**
HPoN	**3.95**
HPiB	1.11
HPiA	2.03
HPiN	0.18

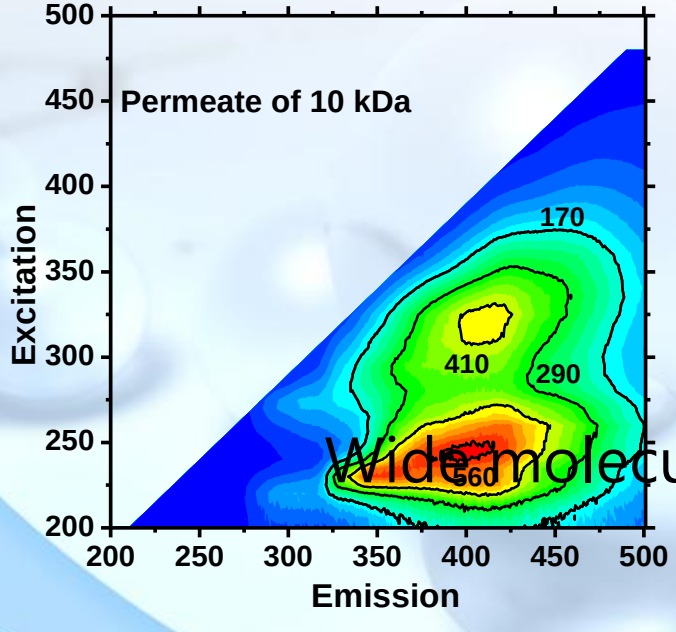
$SUVA_{254}$ = (UV Abs_{254}/ TOC) *100

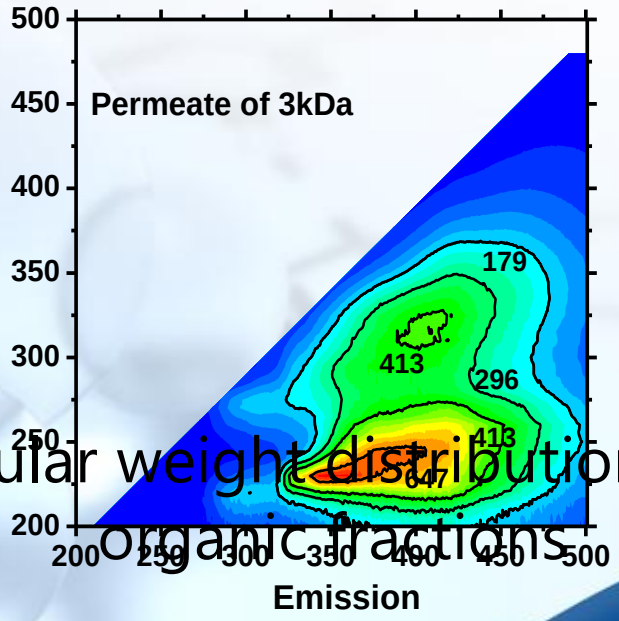
Presence of aromatic content in the HPoA and HPoN

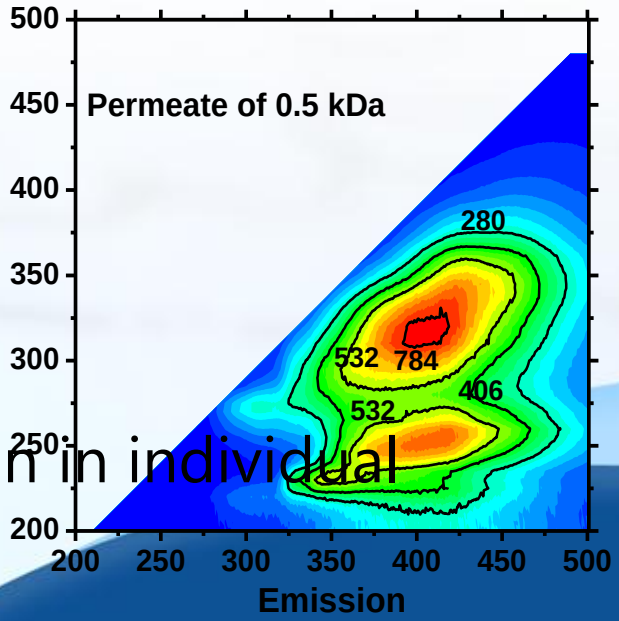
Lower aromatic content in the other fractions

Membrane Fractionation

BBD → YM10 (Cutoff: 10 kDa) → Permeate → YM3 (Cutoff: 3 kDa) → Permeate → YC05 (Cutoff: 500 Da)







Wide molecular weight distribution in individual organic fractions

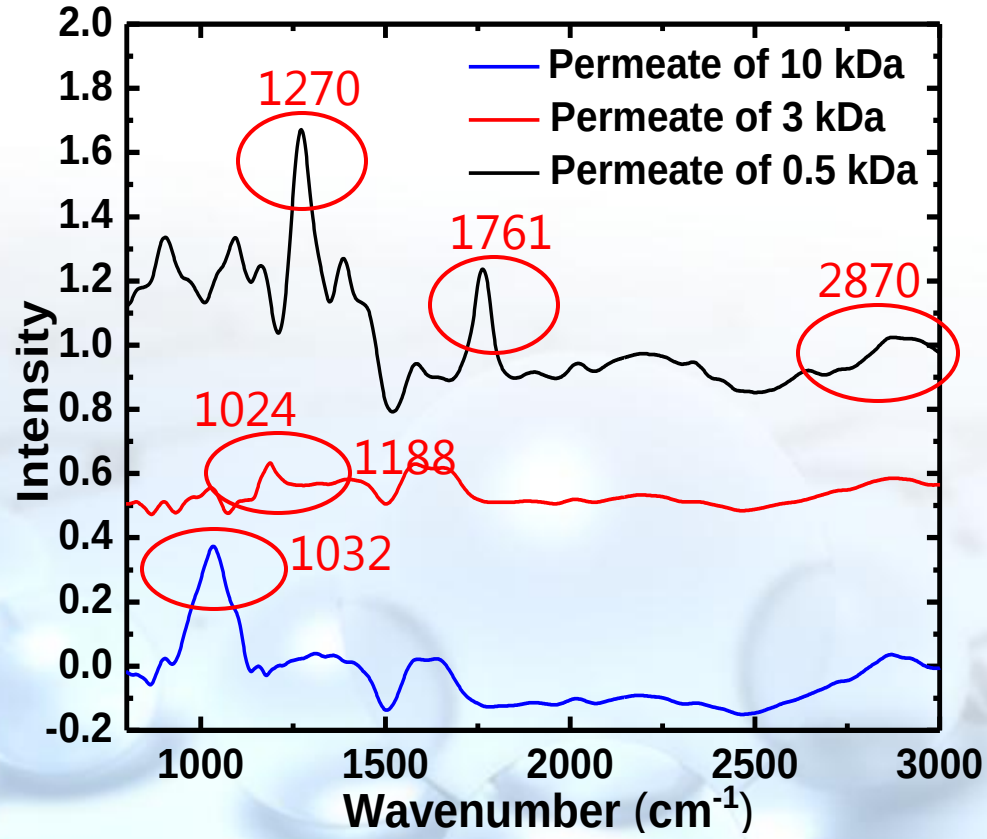
Molecular Weight Distribution

Molecular weight range	Percentage DOM in permeate
> 10 kDa	8 %
> 3 kDa – 10 kDa	19 %
> 0.5 kDa – 3 kDa	33 %
< 0.5 kDa	40 %

Nanofiltration (500 Da) retains 60% of DOM; a significant fraction is too small for NF removal

40% of organic matter in BBD is of molecular weight less than 500 Da

FTIR Results



10 kDa: Silica peaks at 1032 cm^{-1}

3 kDa: Very weak peaks obtained at 1024 and 1188 cm^{-1}

0.5 kDa: Peaks

- At 2870 cm^{-1} C-H stretching
- At 1761 cm^{-1} for C=O
- At 1270 cm^{-1} for C-O

Concluding remarks

- DOM in SAGD blow-down water consists of low molecular weight compounds
- Hydrophobic acids and hydrophilic neutrals are the major fractions in the SAGD blow-down water
- Membrane filtration is unable to separate the DOM fractions based on size exclusion
- Knowledge of physico-chemical characteristics of SAGD fluids is the first step toward building a program for treatment

NSERC Industrial Research Chair in

Water Quality Management for Oil Sands Extraction

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