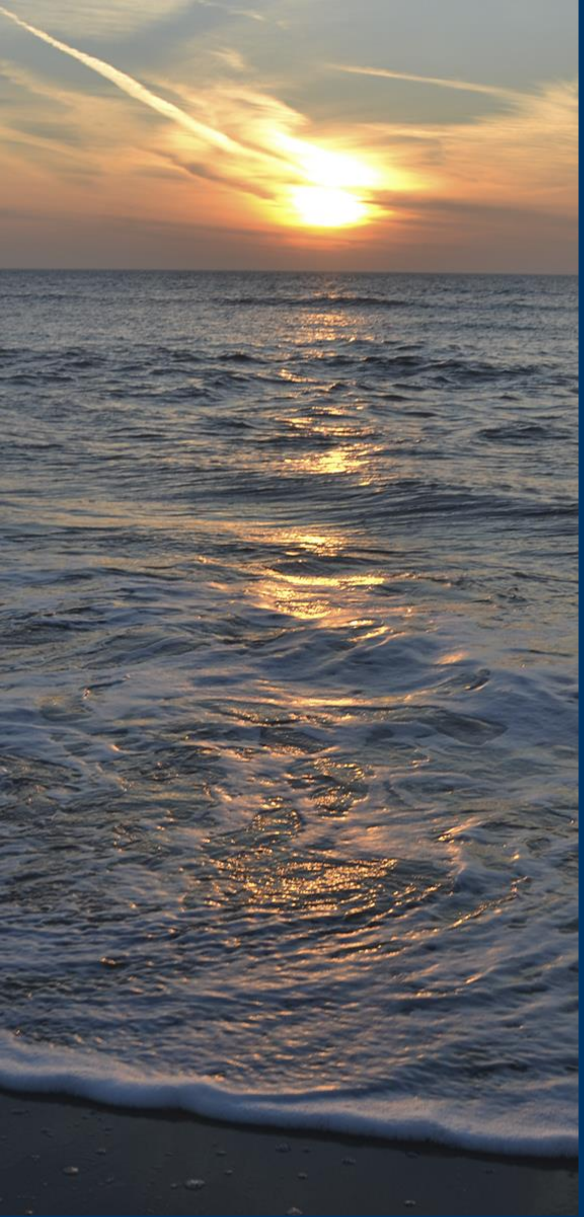


anion exchange brine treatment

Elisabeth Vaudevire

Interreg workshop 21-09-2016

Interreg
2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund

take home message

- anion exchange brine sometimes can not be discharged because of it's composition – treatment necessary
- in these cases separation and reuse of compounds could be seen as an opportunity to increase sustainability and create circular economy at affordable costs.

- value of humic substances depends on its proven efficiency, quantity required and purity

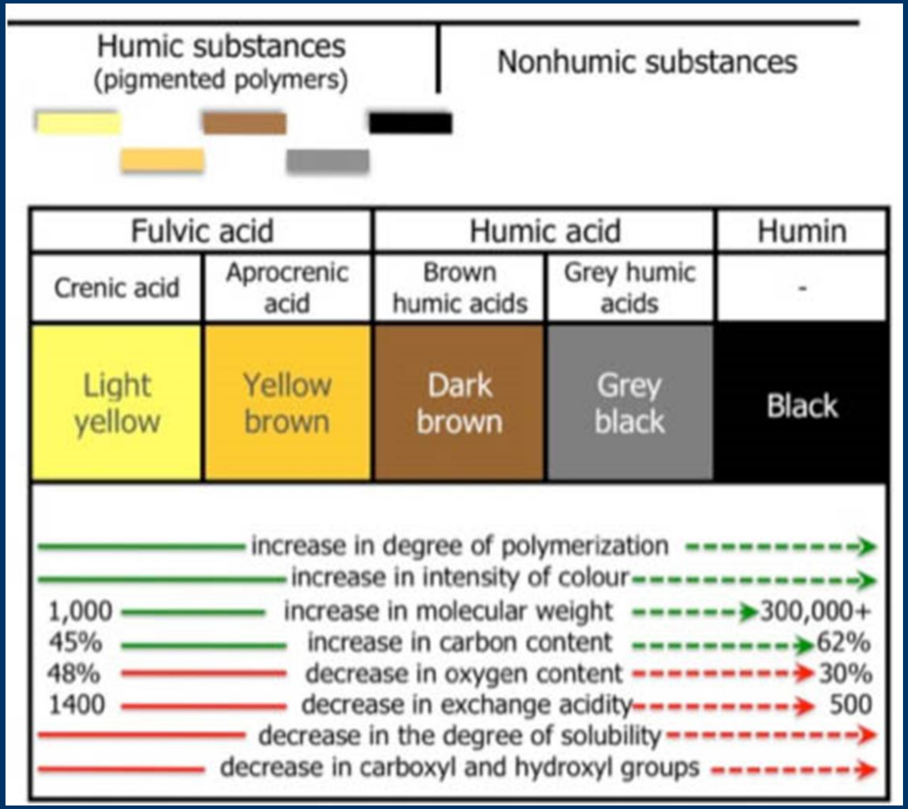
- ED was found performing better than NF for separation of NaCl
- separation of Na2SO4 from humic substances is more challenging

anion exchange contaminant removal

main driver to apply AIEX: increased removal of DOC to reduce DBP formation

- removal by adsorption onto resin beads

- organic matter
  - dissolved fraction - specifically anionic species with carboxylic groups (MW between 500 and 1500 Da)
- inorganic matter
  - sulphate, nitrate usually referred to as competitor to NOM adsorption
  - trace metal anions



Interreg 2 Seas Mers Zeeën DOC2C's European Regional Development Fund
PWNT WATER TECHNOLOGY
SOUTH WEST WATER
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

anion exchange brine generation

previously adsorbed compounds released in NaCl solution during resin regeneration

- desorption in concentrated NaCl solution
  - high conductivities
- organic matter
  - colorful
  - can not be discharged in surface water bodies
- inorganic matter
  - sulphate creates corrosion in pipes and sewage treatments
  - nitrate causes eutrophication in water bodies (infiltration or discharge)

TREATMENT MAY BE NEEDED

anion exchange brine generation

a source of potential by-products

- desorption in concentrated NaCl solution
  - reused in anion exchange process
- organic matter
  - humic acids
  - fulvic acids

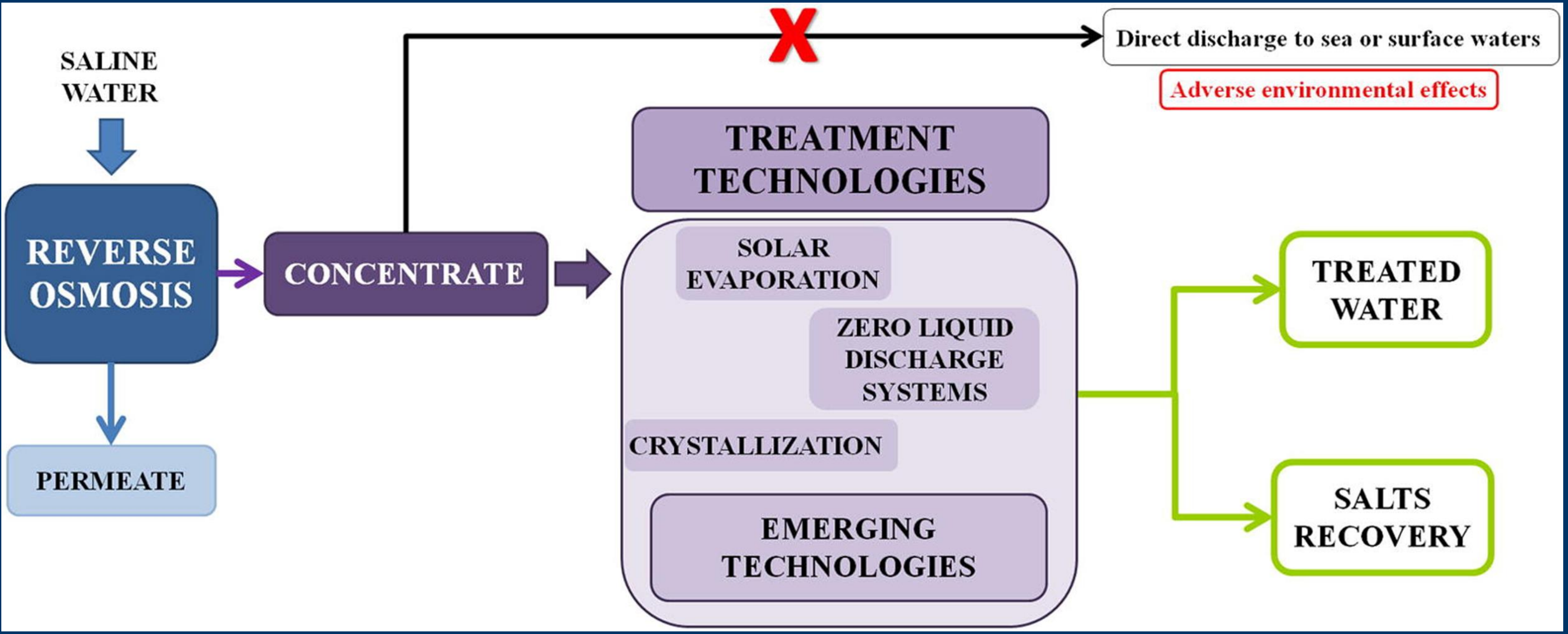
  with applications in:

  - agriculture
  -livestock feed
  - pharmaceuticals
  - food supplements
- inorganic matter
  - sulphate in glass industry

Interreg
2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
SOUTH WEST WATER
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

state of the art brine treatment

mastered in RO brine treatment with 2 goals: volume reduction & water recovery



Pérez-González, A.M. Urtiaga, R. Ibáñez, I. Ortiz

Water Research, Volume 46, Issue 2, 2012, 267–283

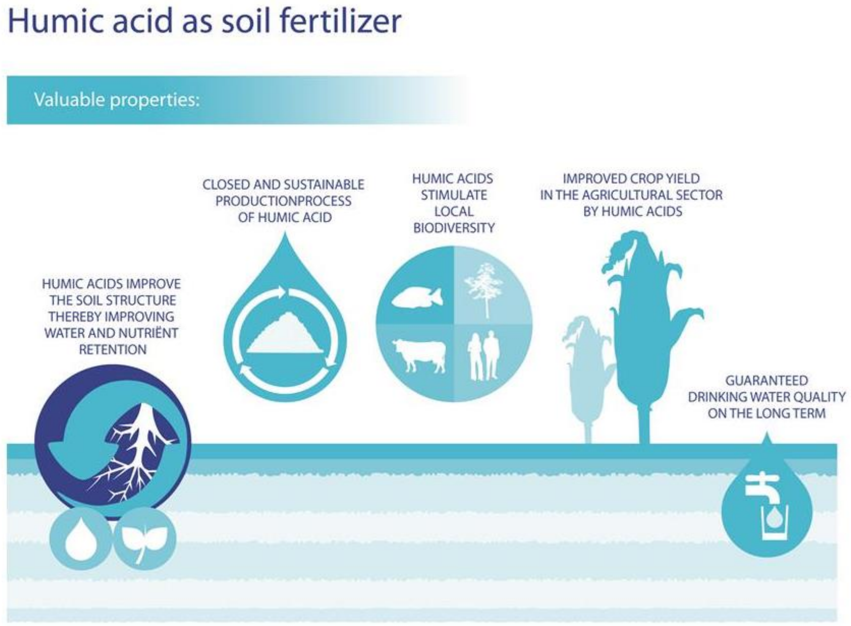
http://dx.doi.org/10.1016/j.watres.2011.10.046

a source of potential by products

state of the art resource recovery?

- anion exchange brine contains two resources:
  - NaCl for reuse
  - Humic substances for various applications

- state of the art separation & recovery of resources
  - NF for NaCl recovery: applied
  - other technologies : research (lab studies)
  - diafiltration: full scale at Vitens (ground water)



- if brine treatment is considered too expensive – can the production of by products reduce the bill?
- this research looks at the technical aspects of compounds separation in a view of by products creation

research goals
technologies & applications

- investigate the mass separation of compounds: organic / inorganic – monovalent / multivalent
    - valence
    - seize
    - crystallization properties
- Application in processes – long term operation
- lab & pilot work
- test the economical / environmental model of by product creation

- collaboration with specialized institute for application of humic substances
- crops growth trials (WUR)

- livestock feed trials (Denkavit)
- market studies and value of HS (aqua minerals)

Interreg 2 Seas Mers Zeeën DOC2C's European Regional Development Fund

PWNT Water Technology · South West Water · De Watergroep · Université de Lille · TU Delft

NaCl recovery for reuse in resin regeneration

a sustainability issue

Journal of Cleaner Production 104 (2015) 413–421

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Environmental and economic sustainability of ion exchange drinking water treatment for organics removal

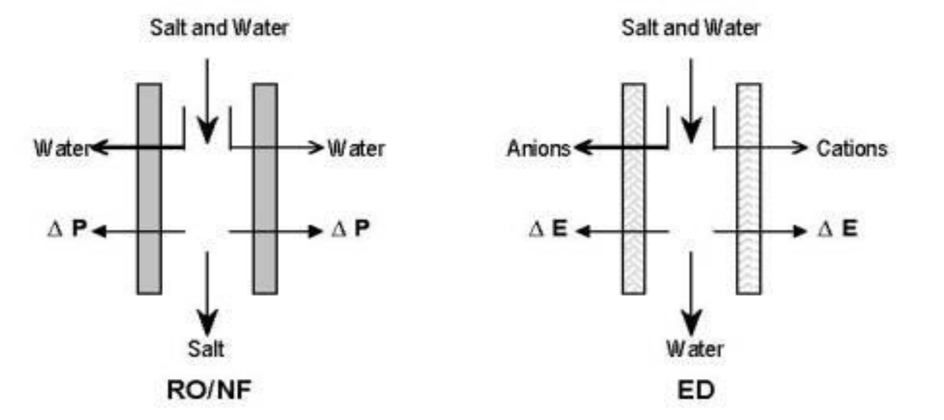
Adib Amini [a], Youngwoon Kim [a], Jie Zhang [a], Treavor Boyer [b], Qiong Zhang [a, *]

“the individuals impact contributors in life cycle inventory (I.e. electricity requirements, resins requirements, brine waste production, transport requirements, and salt requirements).”

NaCl recovery for reuse in resin regeneration

technical challenge and possible technologies

- technical challenge is the separation of monovalent ions from multivalent and organics
- nanofiltration
  - under pressure gradient
  - seize separation through pores (few nm in seize)



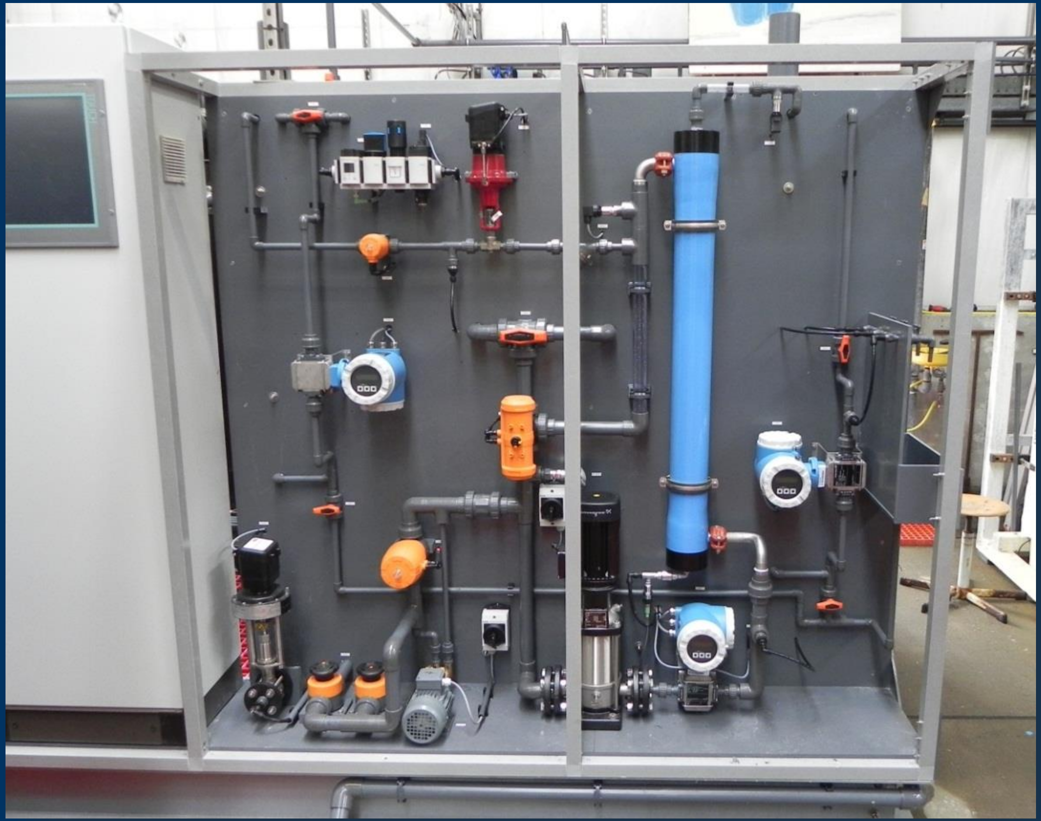
- electrodialysis
  - under electric potential gradient
  - extra layer increases perm selectivity for monovalent
    - highly cross linked (seize repulsion),
    - charged layer same sign as passing ion (charge repulsion)
    - hydrophobic layer (hydration repulsion)

Interreg 2 Seas Mers Zeeën DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
SOUTH WEST WATER
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

separation of monovalent ions – NaCl reuse

seize separation through nanofiltration

- pilot capacity: 80L/h
- optimization with frequent air flush
- membrane area: 7,6m^2
- flux: 6,6L/m^2/h - 80g Cl/h
- (salt) recovery goal: 80%,



separation of monovalent ions – NaCl reuse

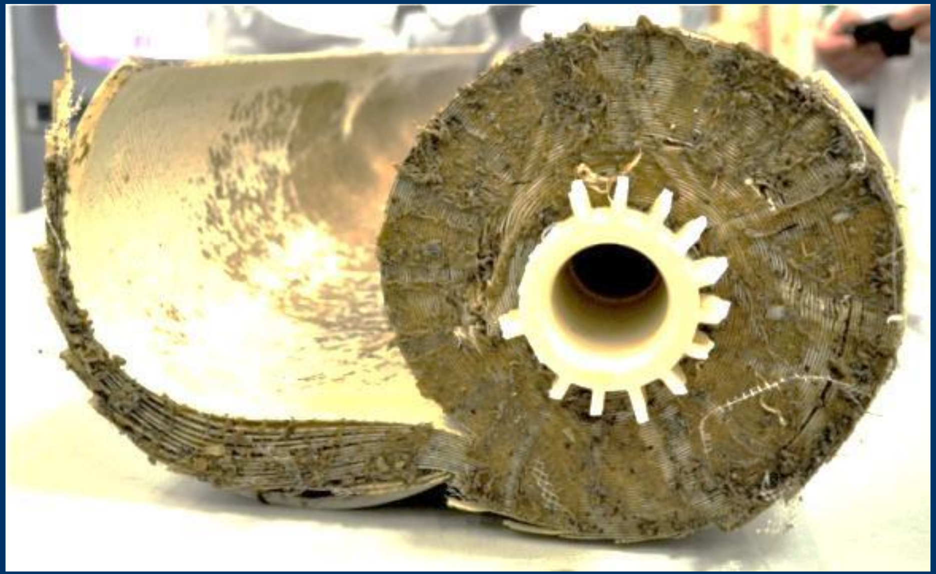
nanofiltration performances

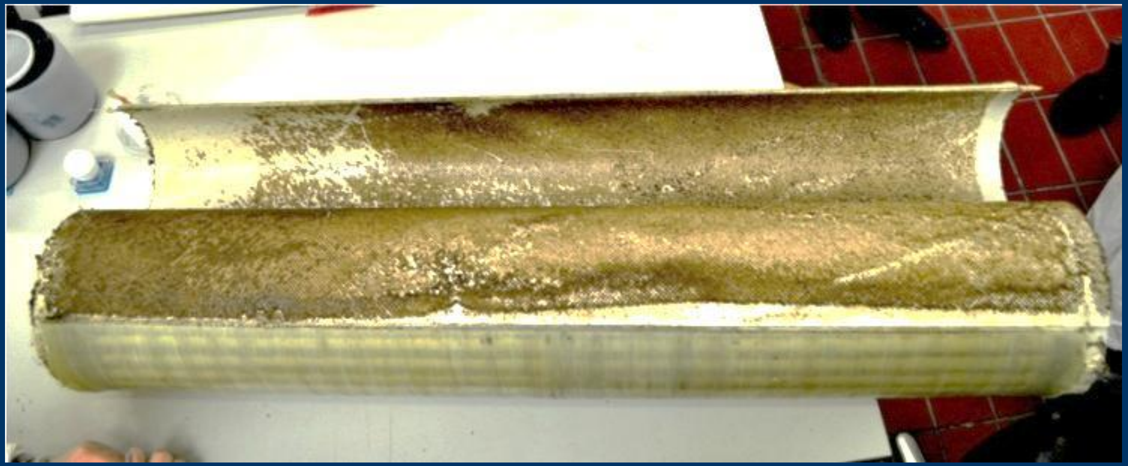
water soluble ions g/l	SIX® regenerant solution	NF permeate solution	NF concentrate solution
Na	15	9	14
Cl	10	12	8
SO_4	8	2	18
HCO_3	4	5	5
NOM	0,5	0,05	1,5
Volume	10-25 m^3/h	80%	20%

Interreg 2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT Water Technology
South West Water
De Watergroep
Université de Lille
TU Delft

separation of monovalent ions – NaCl reuse

fouling & clogging after 4 years un-continious operation





Interreg
2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund

PWNT WATER TECHNOLOGY
SOUTH WEST WATER
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

separation of monovalent ions – NaCl reuse

charge separation with electrodialysis and monoselective membranes

- pilot capacity 40L/h
- constant voltage 45V
- optimization with reversal
- membrane area: $3m^2$
- salt transfer: 100g Cl/h
- salt recovery 85%

separation of monovalent ions – NaCl reuse

permselectivity

		Chloride g/L	Bicarbonate g/L	Sodium g/L	TOC mg/L	Sulfate g/L	Conductivity mS/cm
3-6-16	Raw Diluate Feed	4	3	8	300	4	25
	Concentrate Final	32	11	26	10	0,4	84
9-6-16	Raw Diluate Feed	5	3	9	400	5	25
	Concentrate Final	32	12	30	17	0,5	84
23-6-19	Raw Diluate Feed	5	3	9	300	5	25
	Concentrate Final	35	9	29	10	0,3	84

separation of monovalent ions – NaCl reuse

permselectivity

		Chloride g/L	Bicarbonate g/L	Sodium g/L	TOC mg/L	Sulfate g/L	Conductivity mS/cm
3-6-16	Raw Diluate Feed	4	3	8	300	4	25
	Concentrate Final	32	11	26	10	0,4	84
9-6-16	Raw Diluate Feed	5	3	9	400	5	25
	Concentrate Final	32	12	30	17	0,5	84
23-6-19	Raw Diluate Feed	5	3	9	300	5	25
	Concentrate Final	35	9	29	10	0,3	84

Interreg
2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
SOUTH WEST WATER
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

separation of monovalent ions – NaCl reuse

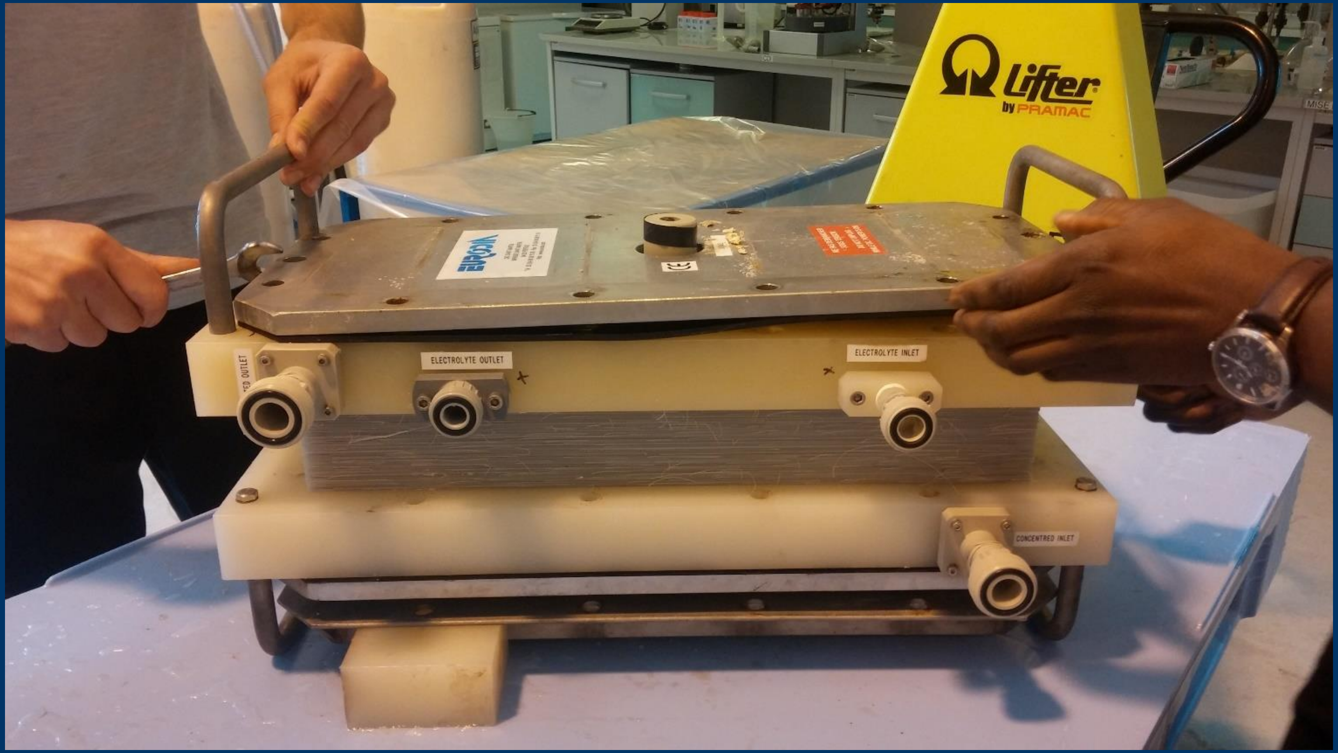
permselectivity

		Chloride g/L	Bicarbonate g/L	Sodium g/L	TOC mg/L	Sulfate g/L	Conductivity mS/cm
3-6-16	Raw Diluate Feed	4	3	8	300	4	25
	Concentrate Final	32	11	26	10	0,4	84
9-6-16	Raw Diluate Feed	5	3	9	400	5	25
	Concentrate Final	32	12	30	17	0,5	84
23-6-19	Raw Diluate Feed	5	3	9	300	5	25
	Concentrate Final	35	9	29	10	0,3	84

Interreg
2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund

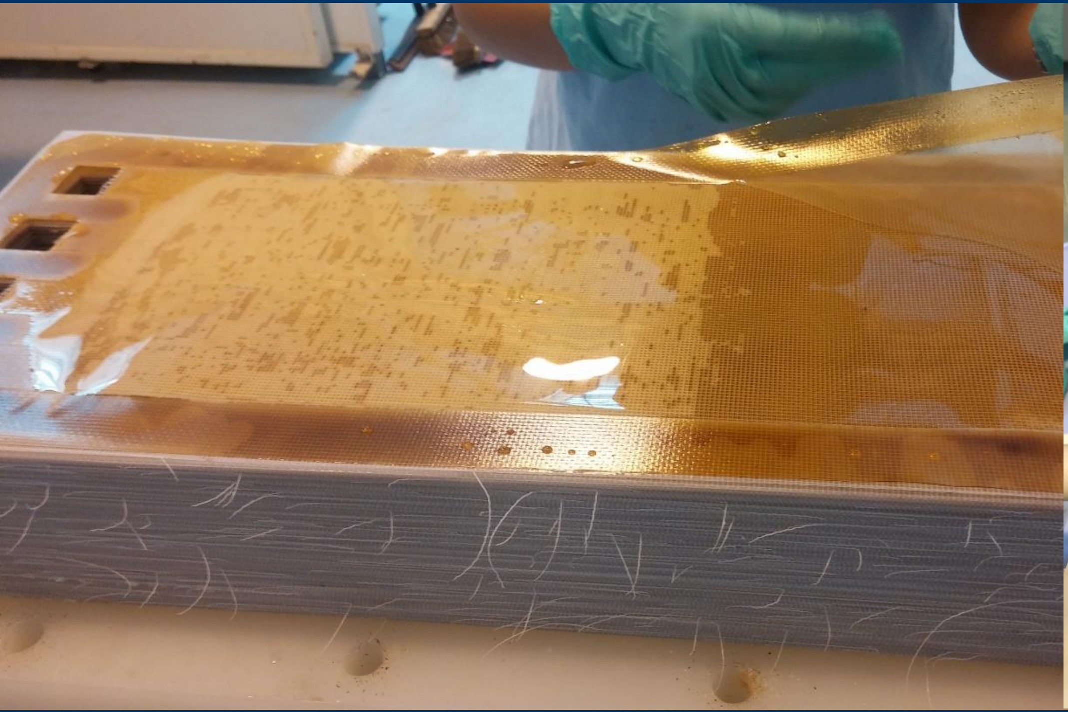
separation of monovalent ions – NaCl reuse

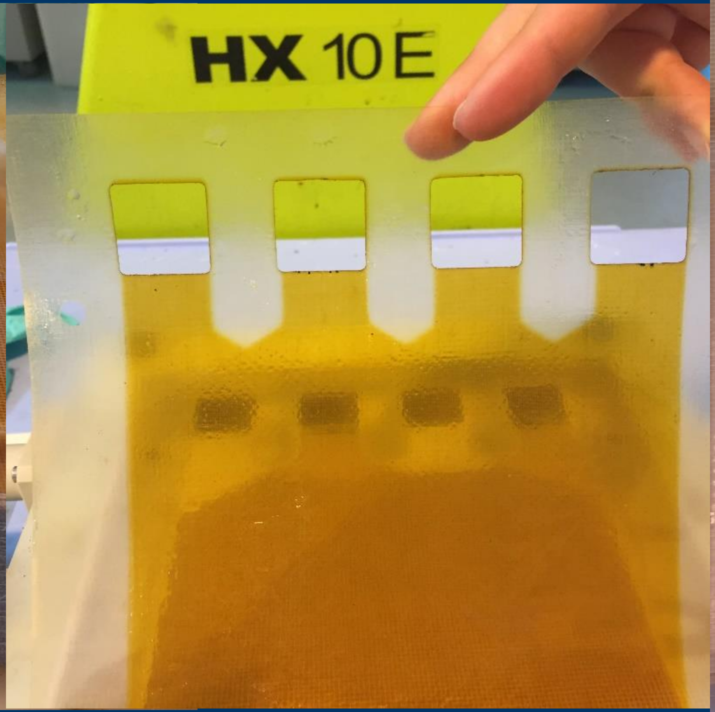
stack inspection after 870h of operation

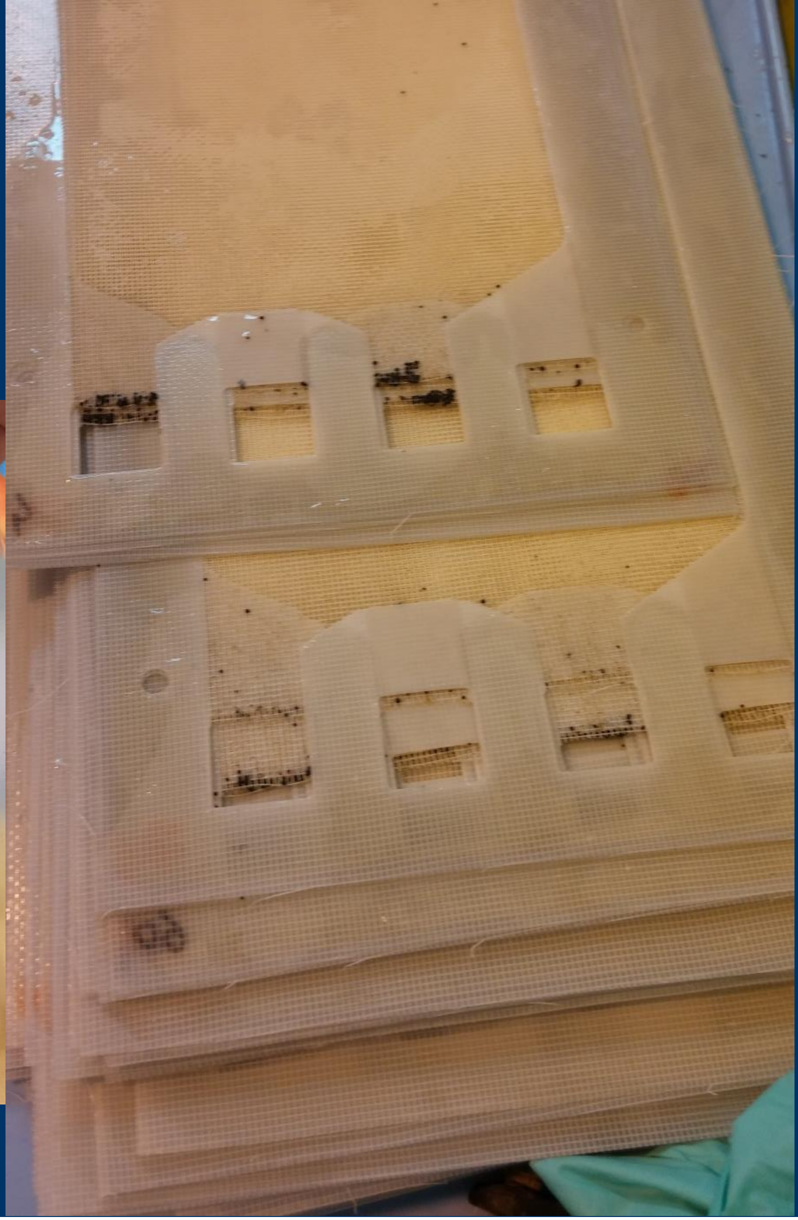


separation of monovalent ions – NaCl reuse

stack inspection after 870h of operation







separation of monovalent ions – NaCl reuse

assessment electrodialysis and nanofiltration

- sulphate passage: 20% with NF – 1,25% with ED
- TOC passage: 8% with NF – 0,4% with ED
- NaCl solution: not concentrated with NF 12g/L concentrated to 30g/L Cl- with ED
- salt transfer : 80g/L Cl with NF – 100g/L Cl with ED
- long term operation: to be directly compared

- overall 30% NaCl recovery
- energy consumption per m^3 of brine: 9,3 kWh for electrodialysis (+4 kWh for denitrification)

ion	% passage
Cl-	80-90%
HCO_3	60-70%
Na+	50-65%
SO_4^{2-}	<1%

results obtained in batch of 200L with a stack of 25 cells – 0,1 m2/cell PC MVA/ PC MVK

organic separation – humic as a byproduct

- multivalent ions separation from organics for products creation:
  - organics (humic substances) for agriculture and/ or animal feed
  - Na_2SO_4 used in glass industry

- trials with electrodialysis and non selective membranes

organic separation – humic as a byproduct

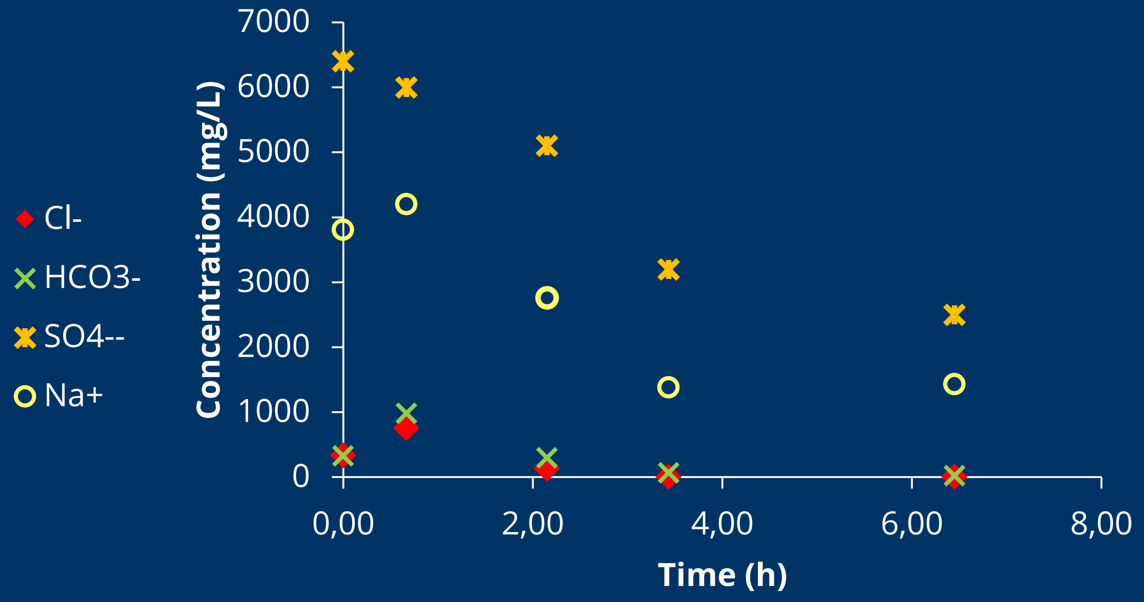
why the challenges are greater for electrodialysis

- sulphate are large and very hydrated ions
  - membrane choice to extract them not too cross linked – retention of organics may be lower
  - carries water molecules during ion exchange
- osmosis force
  - diluate 15→3mS/cm
  - concentrate : up to 80mS/cm

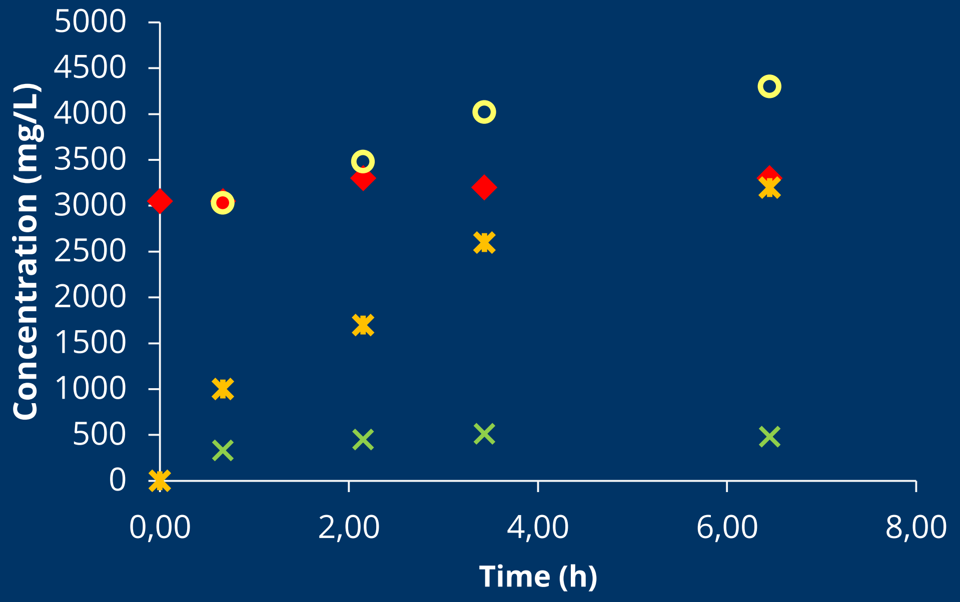
Interreg
2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund

organic separation – humic as a byproduct

batch trials non selective electrodialysis



brine

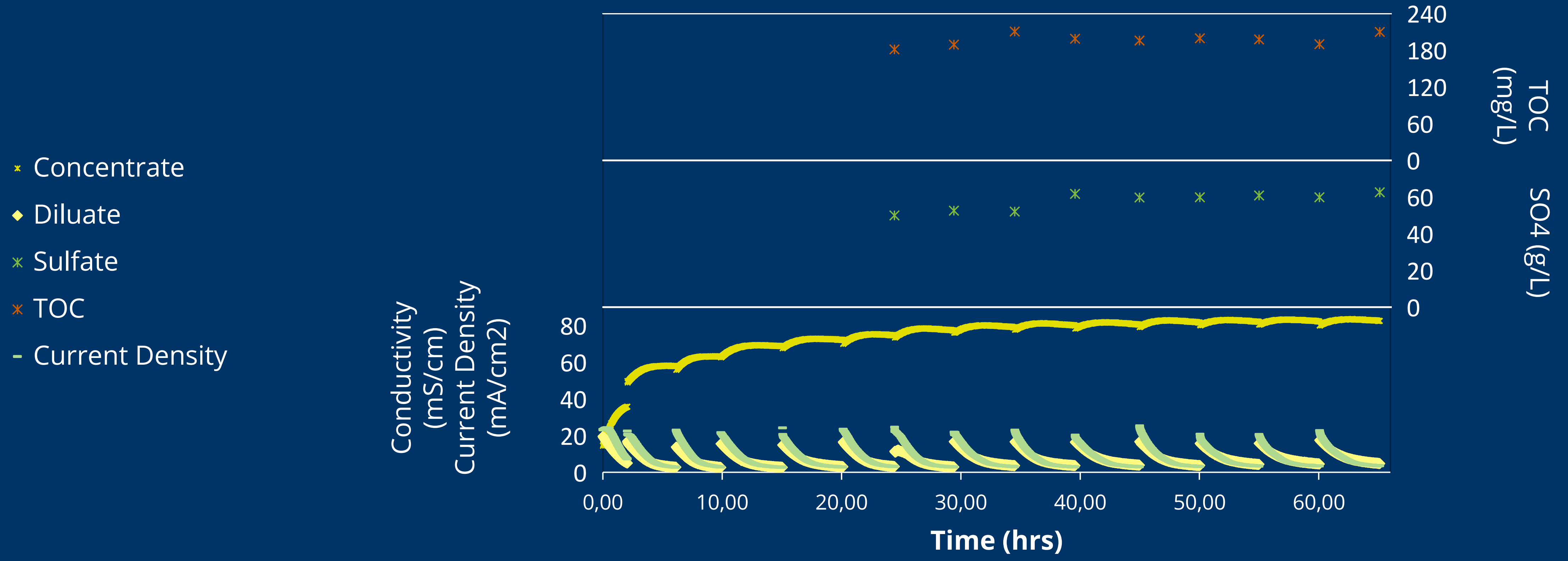


concentrate

Interreg
2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund
PWNT WATER TECHNOLOGY
SOUTH WEST WATER
De Watergroep
Université de Lille
TU Delft

organic separation – humic as a byproduct

limitations non-selective separation



•non-selective separation

- average exchange per batch

Average transfer per batch		
Sulphate	TOC	Water
640g	3,4g	15L
43g/L	188mg/L	

- concentrate has a upper limit at 70mS/cm and 43mg/L SO_4
- tradeoff between sulfate passage and NOM contamination
- need for optimization or alternative technology?

organic separation – humic as a byproduct

crystallization as an alternative

- at evaporation temperature, solubility limit of Na_2SO_4 is 30g Na_2SO_4/100g water
- concentrating further CF 40 leads to crystal formation removable with DVR
- crystal salts preferred by glass industry
- humics gain in potential application as they are further concentrated

- energy requirements 25 – 35kWh.m^3 brine

further define the product

0,05% humics

desalted

irrigation water

feed - drinking water

1,2% humics

desalted
dewatered
agriculture

>20% humics

desalted
more dewatered
feed - supplement

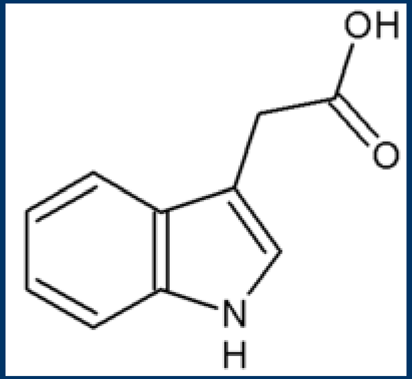
Interreg
2 Seas Mers Zeeën
DOC2C's
European Regional Development Fund

PWNT WATER TECHNOLOGY
SOUTH WEST WATER
De Watergroep WATER. VANDAAG EN MORGEN
Université de Lille
TU Delft

humic substances properties in agriculture

- fulvic acids carry Ca, Mg, P, Fe, Zn and Cu into the plant (chelating agent and metal carrier)
- humic acids improve rooting capacity

- important parameters for growth effect:



  - auxin like molecules used by plants as growth hormon - detected by gas chromatography mass spectrometry (GC MS)
  - carboxilic group have the ability bound with cations; binding with metals brings several COO- close together and is responsible for the 3D structure of the molecule

tests on brine

agricultural / horticultural purpose

- brine composition for trial after extensive desalination :

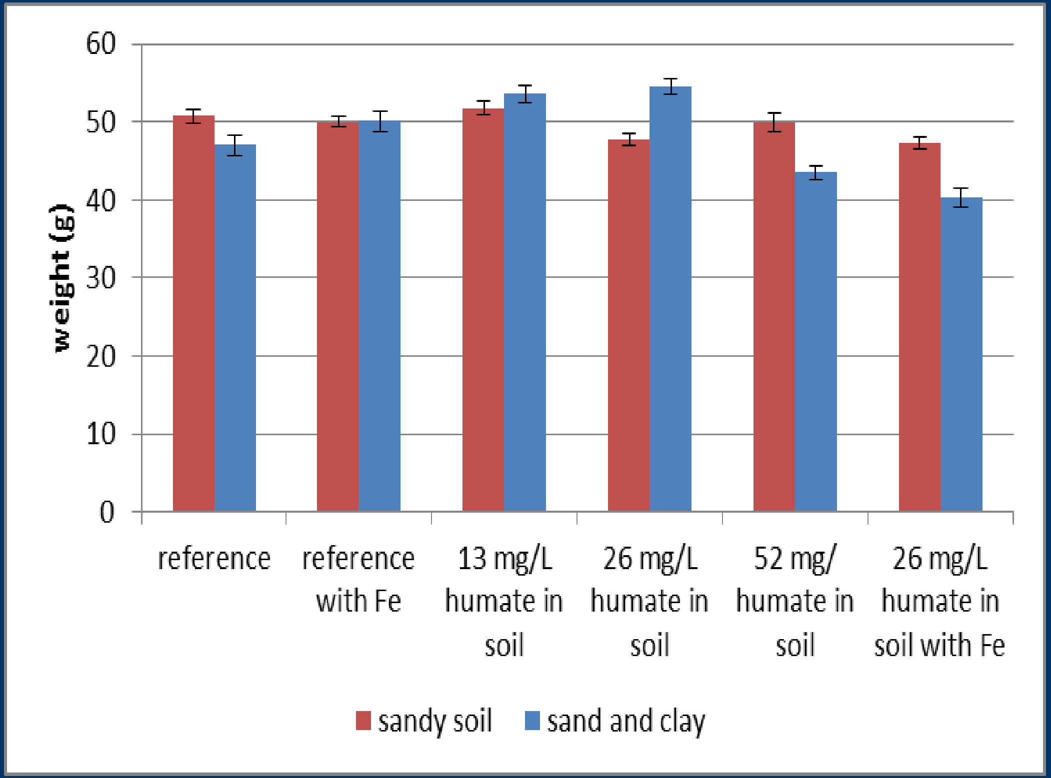
NOM	1g/L
Na	2g/L
Cl	0,02g/L
SO_4	3g/L

- set up:
  - 2 types of soil
  - 3 concentration of brine 13, 26, 52 mg/L
  - one reference no addition
  - one reference 5µmole/L iron chelate
  - one treatment 26mg/l + 5µmole ion chelate

Figure 3.1 The start of the experiment on 13th May

tests on brine

agricultural / horticultural purpose



ref | ref +iron | 13mg/L brine | 26mg/L brine | 52mg/L brine | 26mg/L brine + iron

sandy soil

clay soil

tests on brine

- low concentration of brine increased growth about 10% over the reference and over the addition of iron chelate.
- possible toxic effect of sodium at 52 g decreased growth about 10%- further desalination needed
- because of Na acceptance limit of the soil tests were not possible at higher humic concentration
- need for further desalination

- alternative application in animal feed, instead of anti microbial growth promoter

overview benefice brine treatment

feature	benefits
NaCl recovery	- reduce chemical costs - reduce NaCl production and transportation (positive impact on LCA)
zero discharge	- no transporation of waste - no discharge permit / fees
humic substances recovery as fertilizers	- create circular economy - benefits from sale - answer the need of the local horticultural industry

take home message

- anion exchange brine sometimes can not be discharged because of it's composition – treatment necessary
- in these cases separation and reuse of compounds could be seen as an opportunity to increase sustainability and create circular economy at affordable costs.

- value of humic substances depends on its proven efficiency, quantity required and purity

- ED was found performing better than NF for separation of NaCl
- separation of Na_2SO_4 from humic substances is more challenging