AgriAs- Risk assessment and risk management of Arsenic in the Tampere Region

Ecotoxicological test and purification methods

Isabel Jordan (G.E.O.S. Ingenieurgesellschaft mbH, Germany)
Hanna Valkama, Esa Turpeinen (University of Oulu, Finland)
Arslan Ahmad (KWR, Netherlands)
The AgriAs Project Team

Stakeholder Workshop
5th June 2018 in Tampere, Finland

STRUCTURE

I. **Ecotoxicological test methods** (G.E.O.S.)
II. **Purification methods for Soil** (G.E.O.S.)
III. **Investigations on soil treatment within AgriAs project** (G.E.O.S.)
IV. **Purification methods for Water** (UOULU)
V. **Investigations on water treatment within AgriAs project** (UOULU, KWR)
VI. **Sustainability assessment** (UOULU)

I. ECOTOXICOLOGICAL TEST METHODS

Ecotoxicological testing

- Determination of the effects of toxic chemicals on biological organisms, especially at the population, community, ecosystem, and biosphere levels
- Main goal is to be able to reveal and to predict the effects of pollution within the context of all other environmental factors
- Based on this knowledge suitable actions to prevent or remediate any detrimental effect can be identified

Bio-indicators

- Bio-indicators: any species or group of species whose function, population, or status can reveal the qualitative status of the environment
- Monitoring of bio-indicators for changes can show problems within their environment/ ecosystem
- Give information about effects of different pollutants and influencing factors of the ecosystem, which cannot be obtained by chemical testing

Ecotoxicological tests and Bio-indicators for As polluted soils

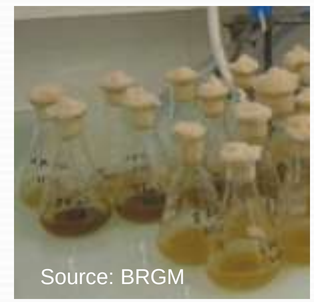
Soil organisms
e.g. Lumbricidae, Nematoda, Enchytraeidae, Collembola

Acute toxicity (mortality)
Reproduction (cocoons, descendants)

Terrestrial plants
e.g. winter wheat, spring barley, rape, lettuce

Inhibitory effect
(germination, growth)
Bio-indicators of availability
(Lipid peroxidation (Omega-3))

Microorganisms
e.g. bacteria, fungi, protozoa



Bio-indicators of availability
(abundance and activity)

Ecotoxicological tests and Bio-indicators for soil eluates

Water organisms
e.g. Cladocera

Source: Dieter Ebert, Basel, Switzerland
https://en.wikipedia.org/wiki/Daphnia_magna#/media/File:Daphnia_magna_asexual.jpg

Acute toxicity (mortality)
Reproduction (descendants)

Water plants
e.g. Lemna

Source: Kristian Peters
https://commons.wikimedia.org/wiki/File:Lemna_minor_detail.jpeg

Inhibitory effect (growth)

Microorganisms
e.g. Chlorella

Enzymatic in vitro test
e.g. RET with sub-mitochondrial particles

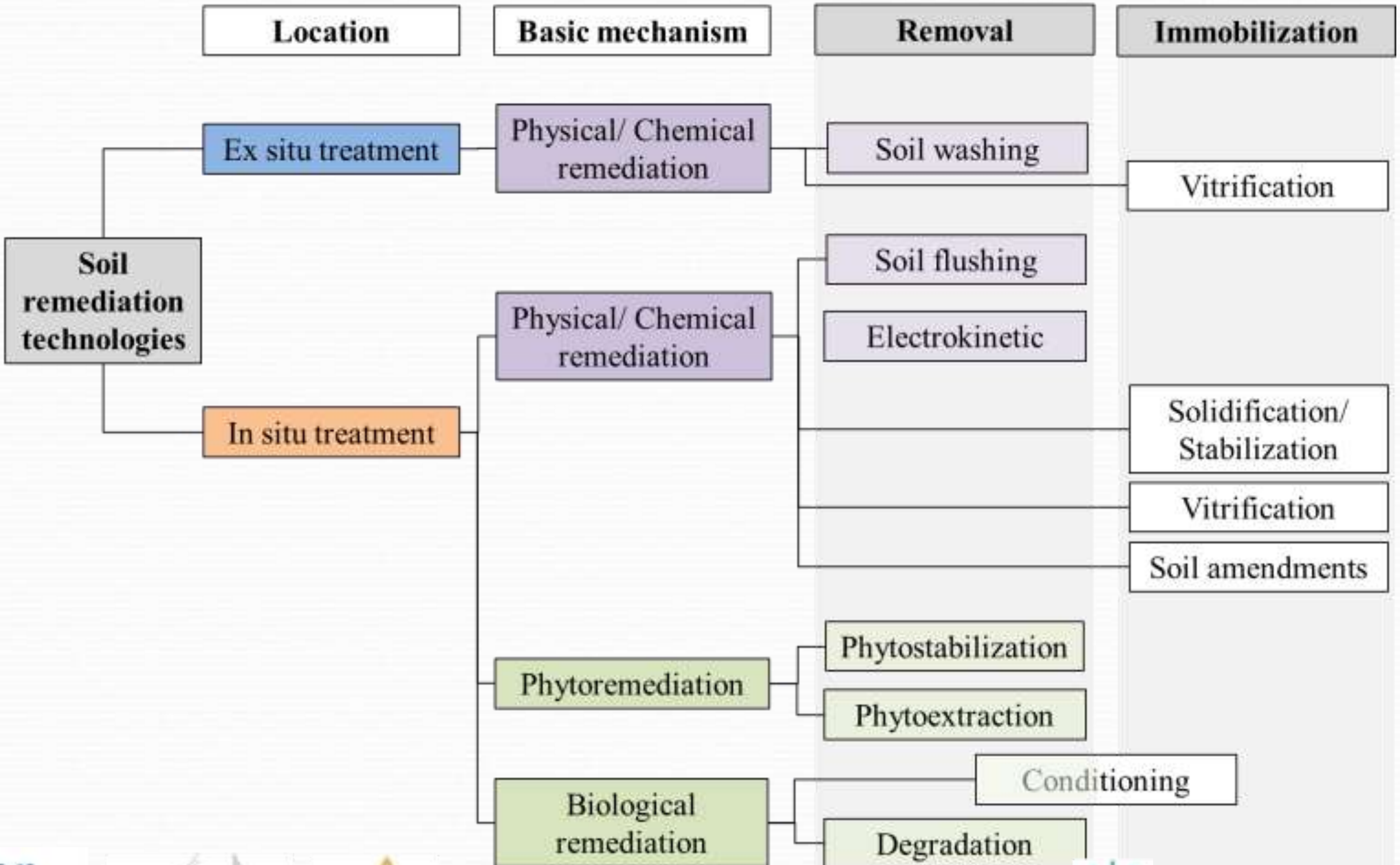
Source: https://algaeresearchsupply.com/products/algae-culture-kit-chlorella

Source:http://ww1.prweb.com/prfiles/2011/02/07/4447214/shakeflask.jpg.jpg

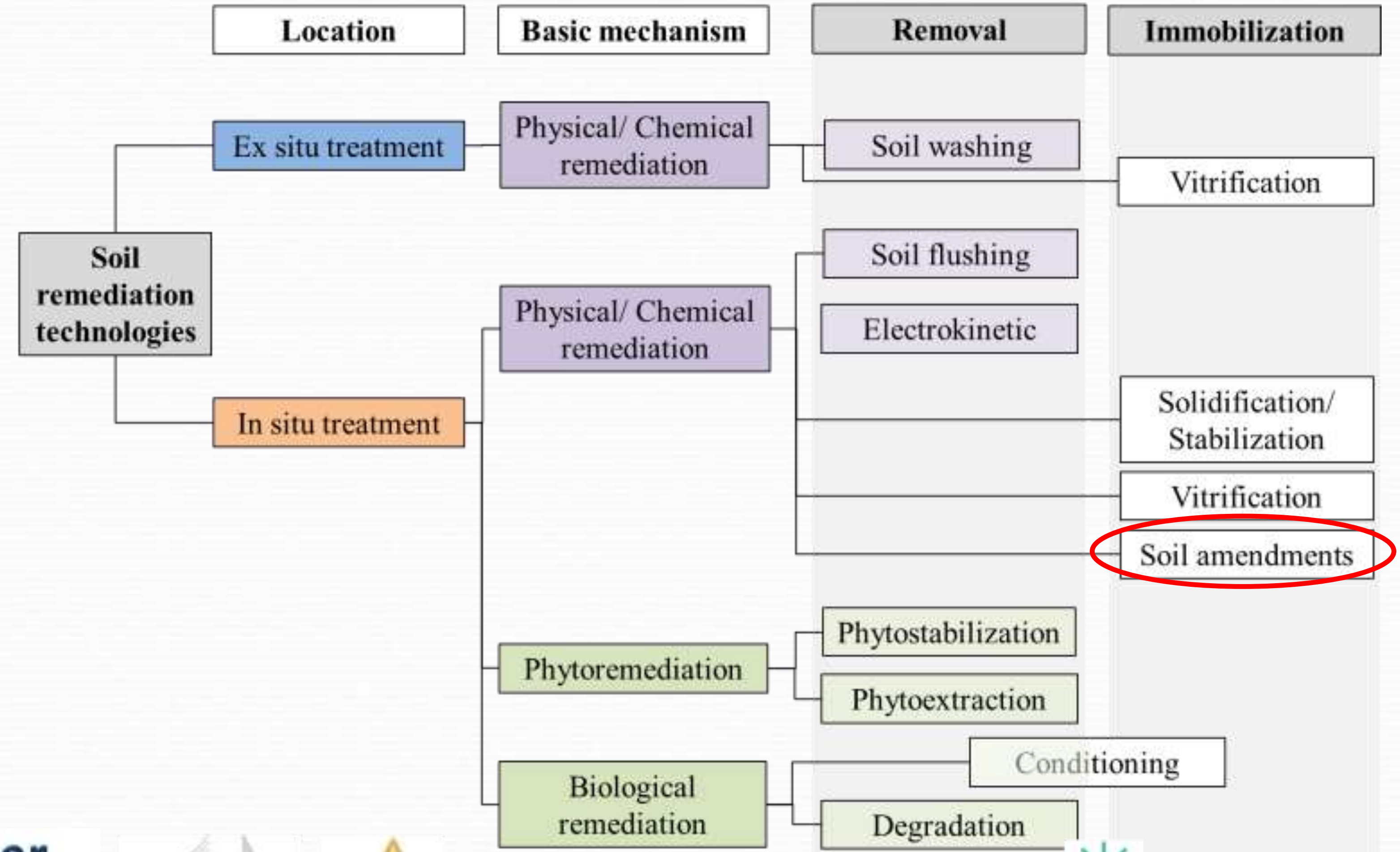
Inhibitory effect (activity)

PURIFICATION METHODS FOR SOIL

Overview of Technologies



Overview of Technologies



INVESTIGATIONS ON SOIL TREATMENT WITHIN AGRIAS PROJECT

Soil amendments for Arsenic immobilization

Iron-based adsorbents

- Investigations on
  - Retention of As and PO_4^{3-}
  - Influence on plants growth
  - Optimized dosage

→ Pot trials with spring barley

  - 3 different concentrations of adsorbent
  - 3 modifications of adsorbent

Adsorbent material:

Experimental setup:

Test work on
Microbial bio-indicators

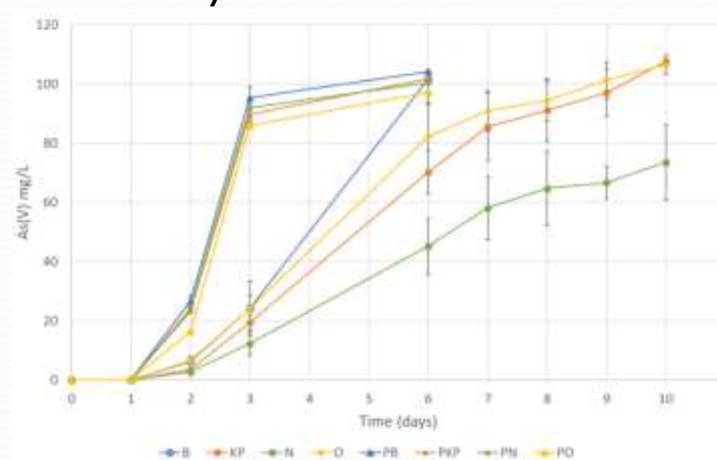
Activity test of As(III)-oxidation

- Specific medium
- Inoculated with of soil
- Aerobic incubation
- Sampling and analyse of As(V)

- Same type of method used for **As(V)-reduction**

Experimental setup:

Activity test for Verdun site:



WaterWorks 2015 · European Commission · AgriAs · brgm · G.E.O.S. Ingenieurgesellschaft mbH · University of Oulu · KWR · KTH · LEB Aquitaine Transfert

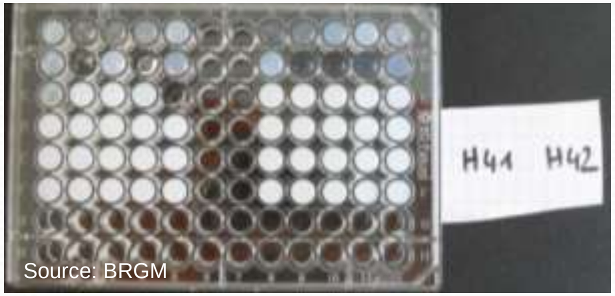
Test work on Microbial bio-indicators

Most probable number of As(III)-oxidizing microorganisms

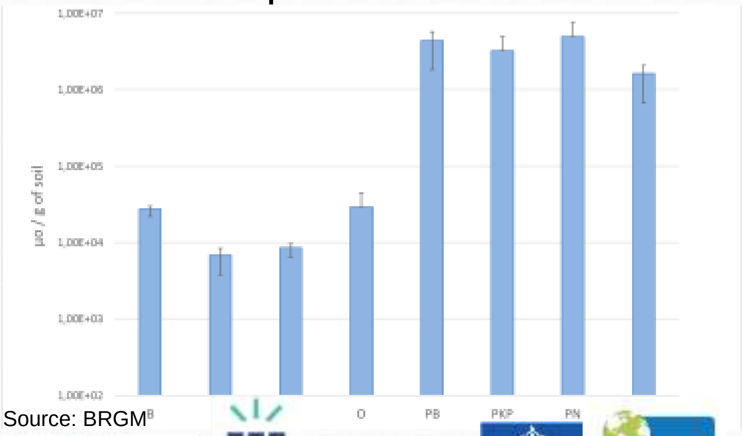
- Specific medium
- Dilutions of soil suspension
- Remaining As(III) revealed after 10 days incubation

- Same type of method used for **As(V)-reducing microorg.**

Experimental setup:



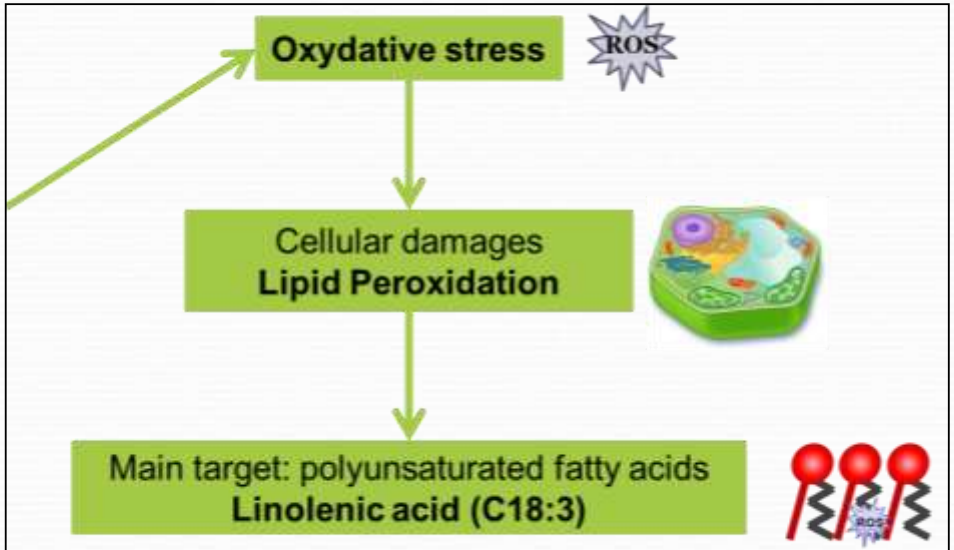
As(III)-oxidizing organisms at the end of the experiment:



Source: BRGM

Test work on Plants bio-indicator

Omega-3-Index



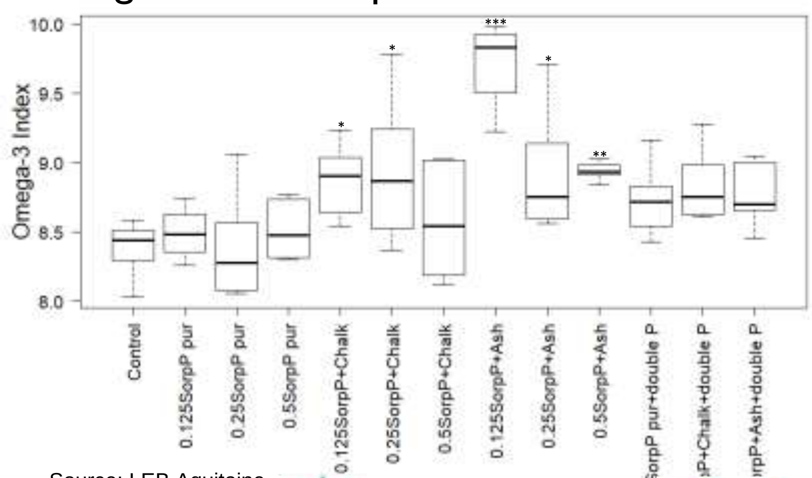
Plants exposed to soil contaminants

⇨ C18:3 decrease

Source: LEB Aquitaine

Experimental setup + leaf samples:

Omega-3-Index for pot tests with adsorbent:



Source: LEB Aquitaine

PURIFICATION METHODS FOR WATER

INVESTIGATIONS ON WATER TREATMENT WITHIN AGRIAS PROJECT

Remediation of Arsenic Contaminated Water

Arsenic Remediation

(1) Precipitation
- Iron/Manganese removal
- Coagulation-Filtration
- Softening

(2) Adsorption/Ion Exchange
- Activated Alumina
- Iron/nanomaterial-based sorbents
- Geological Materials

(3) Membrane Filtration
- Nanofiltration/Reverse Osmosis
- Ultrafiltration/Microfiltration
- Hybrid Processes

(4) Oxidation
- Air/chemical oxidation
- Photochemical oxidation
- *In-situ* oxidation

(5) Bioremediation
- Biosorbents
- Biological oxidation

(6) Source Substitution
- Lower arsenic groundwater
- Treated surface water
- Rain water

Advanced Oxidation—Coprecipitation—Filtration (AOCF)

Source: BRGM

$$3H_3AsO_3 + 2KMnO_4 \rightarrow 3HAsO_4^{-2} + 2MnO_2\,(s) + 2K^+ + 4H^+ + H_2O$$

$$3Fe^{+2} + KMnO_4 + 7H_2O \rightarrow 3Fe(OH)_3(s) + MnO_2\,(s) + K^+ + 5H^+$$

$$3Mn^{+2} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2(s) + 2K^+ + 4H^+$$

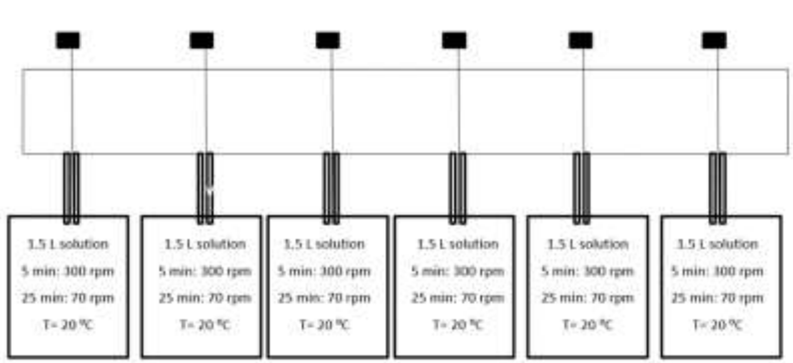
Scope

Performance of AOCF in removing arsenic from the polluted water from the contaminated sites (Verdun, Saxony) and optimal process conditions?

Methodology

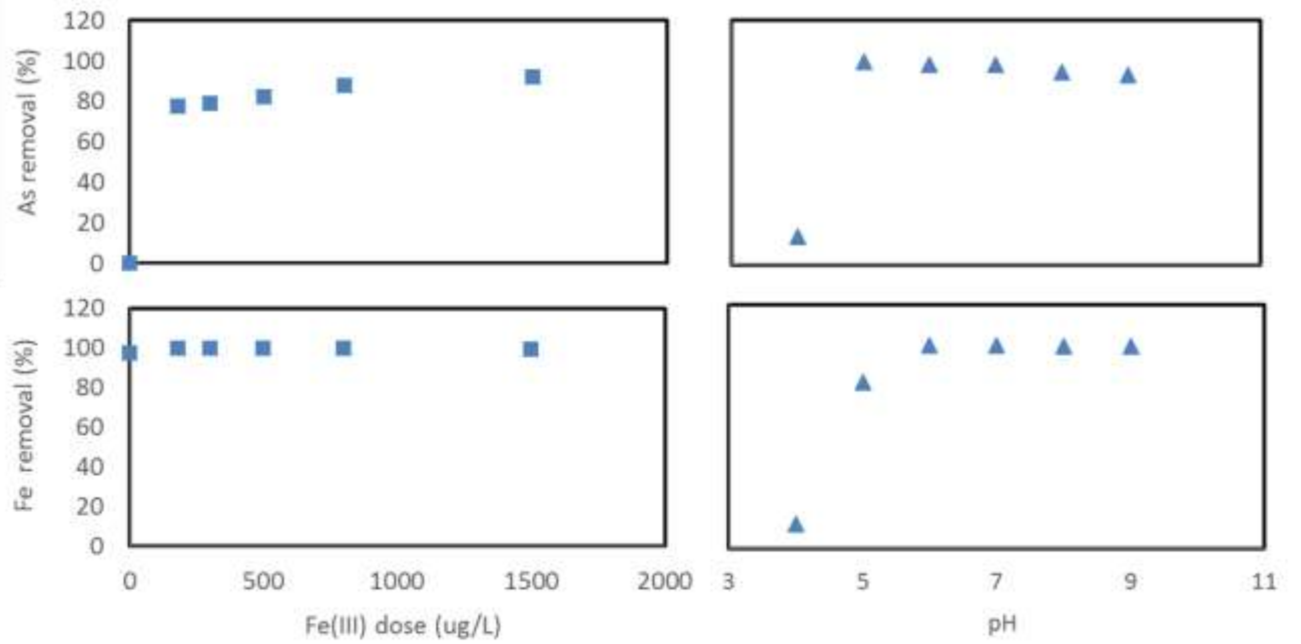
Saxon (Kleine Biela)
Verdun (Pond water)

pH	7.5	
Alkalinity	150	mg HCO_3/l
As III	30	µg/l
As V	100	µg/l
Total As	130	µg/l
DOC	3	mg/l
Ca	50	mg/l
Fe	70	µg/l
Mg	4	mg/l
Mn	50	µg/l
Si	2	mg SiO_2/l
P	0.05	mg PO_4/l
N	2	mg NO_3/l
Na	6	mg/l
S	20	mg SO_4/l



Experimental conditions
Initial As concentration :145-750 µg/l
pH=4, 5, 6 ,7, 8, 9
Coagulant dose : $FeCl_3$=0, 2, 3, 5, 8, 12,7 mg/l
Ionic strength: 0.1 M NaCl, 0.05 M NaCl and 0.01 M NaCl.
Oxidant: 1 mg/l $KMnO_4$
Filtration : 0.45 µm disc filters
Determination of coagulant dose: with the use of Visual Minteq 3.1
Analysis of the results
Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Results

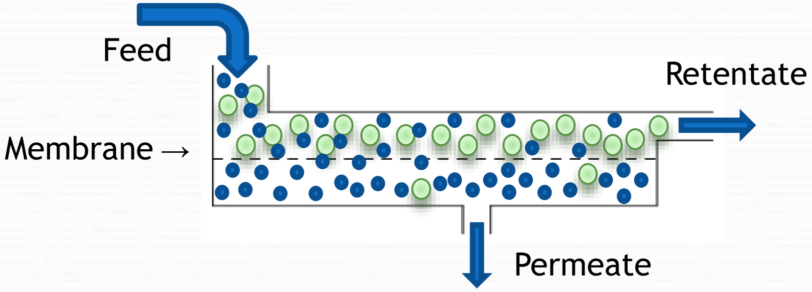


As removal (%)
Fe removal (%)
120
100
80
60
40
20
0
0
500
1000
1500
2000
Fe(III) dose (ug/L)
3
5
7
9
11
pH

PURIFICATION OF WATER BY MEMBRANE TECHNOLOGY

Objective

- To efficiently remove As and other contaminants from water by nanofiltration and low pressure reverse osmosis (LPRO).
- Membrane technologies are promising methods for arsenic removal
  - + selectivity
  - + high quality water as the product.
- Low pressure was preferred to minimize the energy costs of the process.



Materials and Methods

Materials and Methods

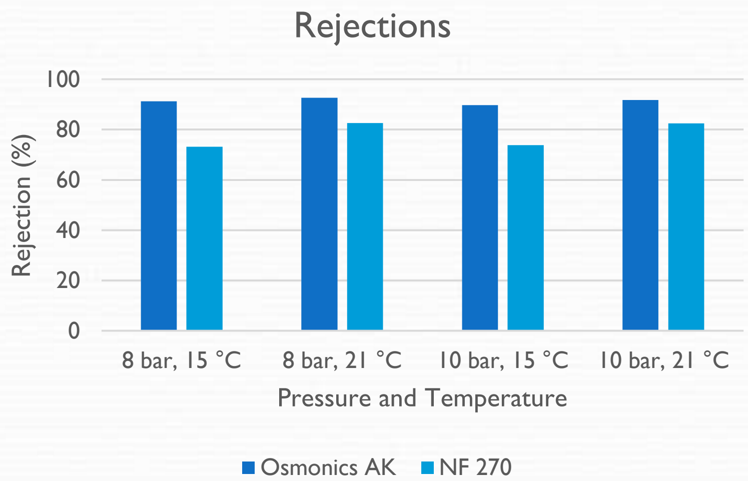
- Model water mimicking contaminated natural waters from France and Germany was used.
- The initial total arsenic concentration was 130 µg/l, containing both As(III) and As(V).
- The combined effect of other compounds was studied.
- Flat sheet membranes:
  - Nanofiltration membrane NF270 from Dow Filmtec
  - Reverse osmosis membrane Osmonics AK from GE Osmonics.
- Pressures of 8 and 10 bars
- Temperatures of 15 and 21 °C.
- pH close to neutral, 6.76–7.57.

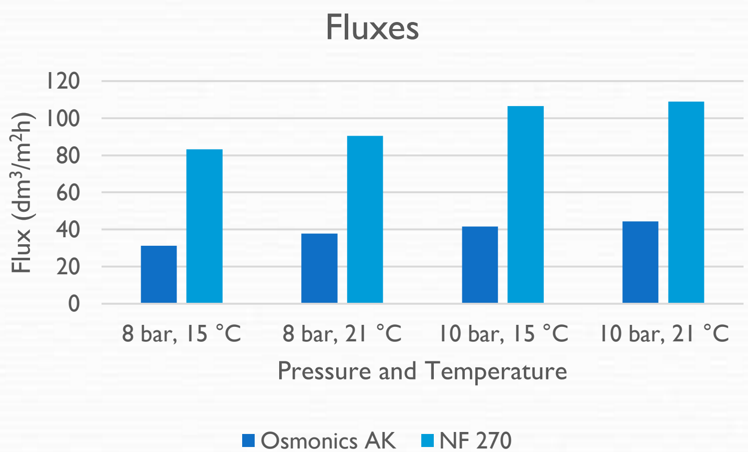
Sepa CF cross-flow membrane unit

- Effective membrane area A = 0.014 m^2.
- Wanner Hydra-Cell diaphragm pump.
- Cooling with VWR digital temperature controller, model 1156D.

Results

- An increase in temperature was observed to enhance the rejection more than an increase in the operation pressure.
- The fluxes remained constant during each experiment with both membranes.
- Higher pressure and temperature
  → higher fluxes.
- The flux in NF 270 was higher
  vs.
- The arsenic removal of Osmonics AK was higher.





Conclusions

- Both membranes were able to separate arsenic in relatively low pressure
  - Savings to energy costs.
- Arsenic concentration of the water purified with the Osmonics AK membrane was between 9–13.4 µg/l.
  - **The lowest value of 9 µg/l was below the WHO guidelines for drinking water, 10 µg/l.**
- Arsenic concentration (22.9–34.3 µg/l) of the water purified with NF 270
  - Still meets the looser limits of e.g. of Bangladesh drinking water standard of 50 µg/l.

Future objectives

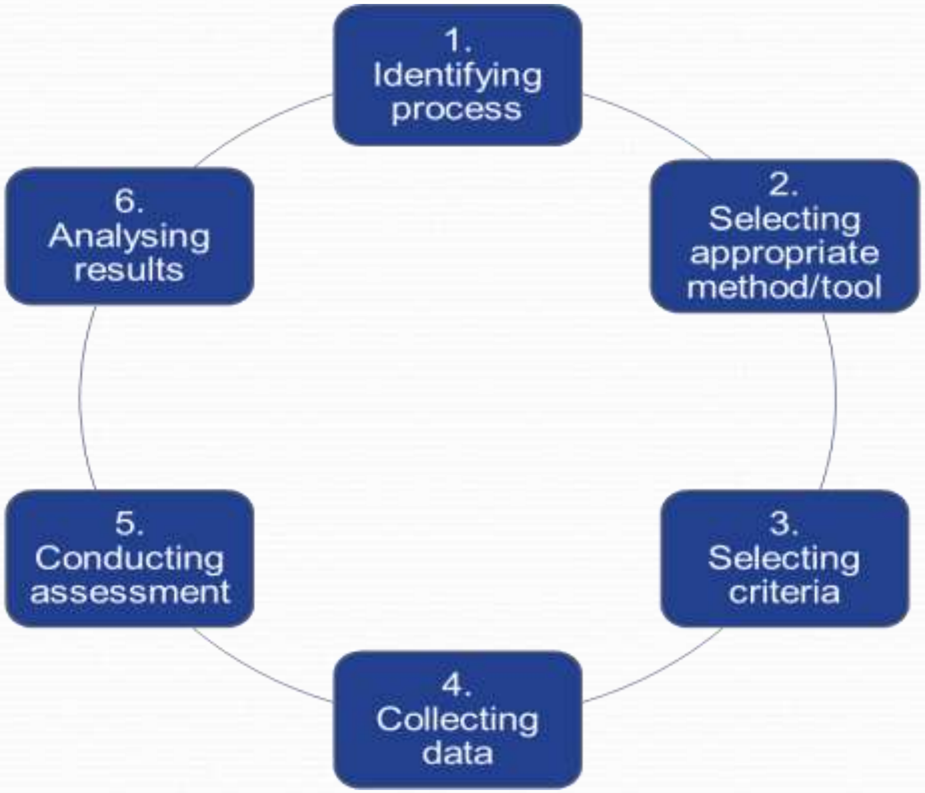
- Real water samples and optimization of the purification process
- Combining the membrane technologies with adsorption and/or photocatalysis as a hybrid process.
- To design and develop a sustainable As removal process by taking into account environmental, economic and social aspects.

SUSTAINABILITY ASSESSMENT

Sustainability assessment

- Sustainability assessment will be conducted to evaluate arsenic removal technologies
- Helps to compare and choose among several design possibilities
- Considers technological, economic, environmental, health and social sustainability issues

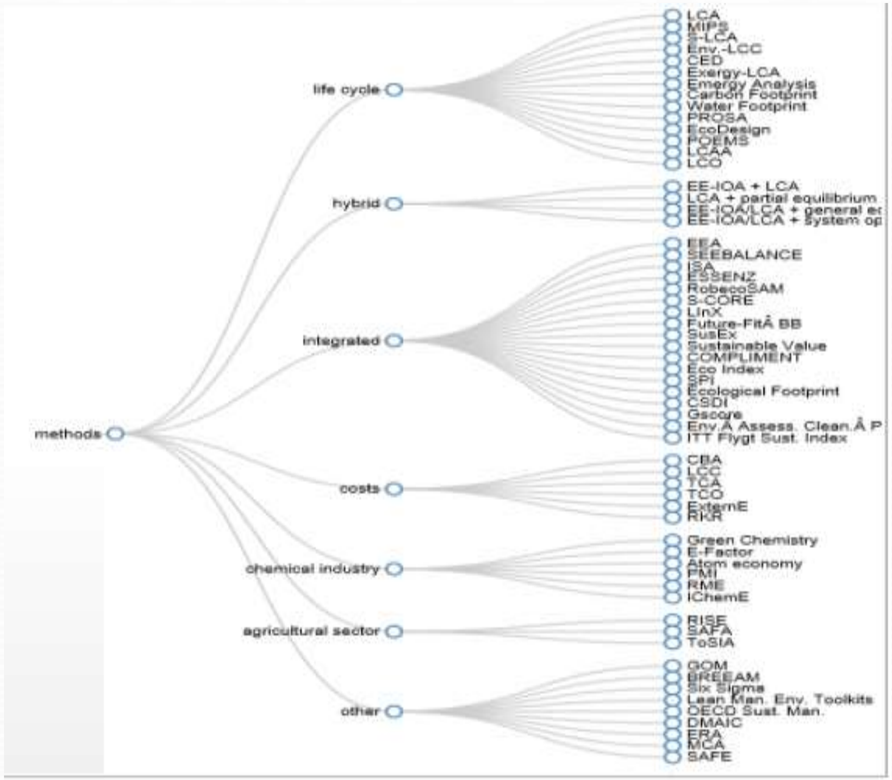
General sustainability assessment procedure



Sustainability assessment methods and tools

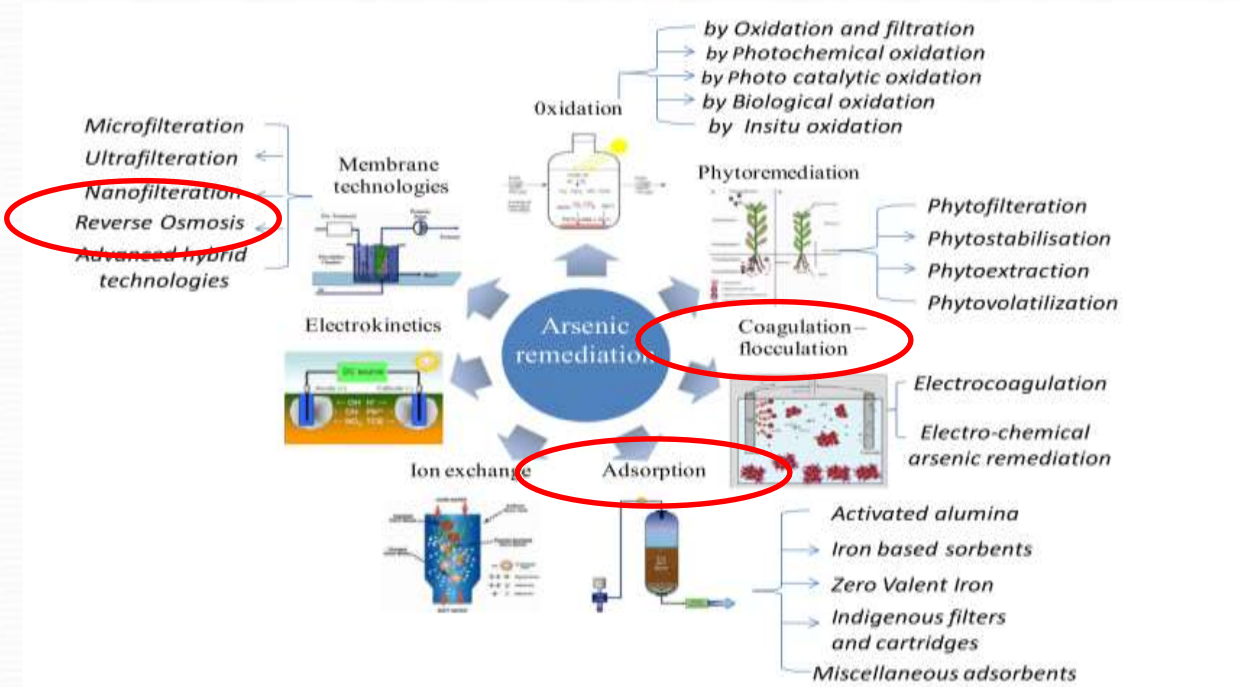
Methods:

- Life cycle related methods
- Hybrid methods
- Integrated methods
- Methods focusing on costs
- Methods spesific to the chemical industry
- Methods spesific to the agricultural, forestry and food sectors
- Other methods



López A., Mabe L., Sanchez B., Tapia C. and Alonso A., (2015). Best practice solutions: Methods for sustainability assessment within the process industries. Sustainability assessment methods and tools to support decision-making in the process industries (SAMT)

Removal technologies to be assessed



Source: Sing R. (2015) Ecotoxicology and Environmental Safety, 112, 247–270

Assessment criteria

- **Qualitative and quantitative assessment using multi-criteria approach**
- **Assessment is based on the most suitable and essential criteria**

	Assessment criteria			
Process alternatives	Technological criteria	Economic criteria	Environmental criteria	Societal criteria
Membrane separation	Suitability	Capital costs	Manufacturing emissions	Acceptability
Adsorption	Flexibility/Scalability	Operating costs	Liquid waste generation	Innovativeness
Coagulation-filtration	Robustness, Reliability	Maintenance costs	Solid waste generation	Operator skill requirements
Hybrid process	Removal efficiency, (As (III), As (V))	Operating life	Used materials	Safety issues
	Removal rate	Commercialization potential		Usability
	Pre-treatment need			
	Maturity level			
	Capability to remove other impurities			

- **Each alternatives will be assessed against these criteria and rated**
- **Data will be gathered through laboratory experiments and from the literature and experts**

Sustainability assessment for typical removal technologies

Qualitative assessment, HOX! Just an example

Basis: groundwater, high capacity, low final arsenic concentration

Qualitative analysis:	
+++	very positive
++	positive
+	neutral

	Weighting	Membrane Process	Adsorption Process	Precipitative Process	Hybrid Process
Technological aspects					
Suitability		+	++	+++	
Flexibility/Scalability		+	+++	++	
Robustness, Reliability		++	++	+++	
Removal efficiency, (As (III), As (IV))		+++	++	+	
Removal rate		+++	++	+	
Pre-treatment need		+++	++	+	
Maturity level		++	+++	+++	
Total		15	16	14	
Economic aspects					
Capital costs		+	++	+++	
Operating costs		+	++	+++	
Maintenance costs		++	+++	++	
Operating life		+++	++	++	
Commercialization potential		++	++	++	
Total		9	11	12	

Sustainability assessment for typical removal technologies

	Weighting	Membrane Process	Adsorption Process	Precipitative Process	Hybrid Process
Environmental aspects					
Manufacturing emissions		+	++	++	
Liquid/sludge waste generation		++	+++	+	
Solid waste generation		+++	+	++	
Used materials		++	++	++	
Total		8	8	7	
Societal and health aspects					
Acceptability		++	++	++	
Innovativeness		++	++	++	
Operator skill requirements		++	+	++	
Safety issues		++	++	++	
Usability		+++	++	++	
Total		11	9	10	
Total points		**43**	**44**	**43**	


Foto: V. Scherer (G.E.O.S.)

Thank you for your attention!

The authors would like to thank the ***EU and National funders AKA, ANR, BMEL and FORMAS*** *for funding, in the frame of the collaborative international consortium AgriAs financed under the ERA-NET Cofund WaterWorks2015 Call. This ERA-NET is an integral part of the 2016 Joint Activities developed by the Water Challenges for a Changing World Joint Programme Initiative (Water JPI)*

Water JPI

SUOMEN AKATEMIA
FINLANDS AKADEMI
ACADEMY OF FINLAND

Bundesministerium
für Ernährung
und Landwirtschaft

AGENCE NATIONALE DE LA RECHERCHE
ANR

FORMAS

European Commission