Fluorochemicals in AFFF Contaminated Sites:
Environmental Fate, Toxicity & Treatment

Montreal, April 26, 2016
National Workshop on Federal Contaminated Sites

Presented by:

SANEXEN ENVIRONMENTAL SERVICES INC.

Jean Paquin, Eng., CESA
Pierre Monnier , Jr. Eng.

McGill

Prof. Jinxia Liu, Ph.D.
Guowei Zhong, M.Sc.

Content of the presentation

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- Definitions
- Introduction on AFFFs and on fluorosurfactants
- Toxicity
- Challenges in adressing PFAS impacted sites
- NSERC Strategic Partnership Project
- Innovative characterization methods
- Case studies involving the large scale treatment of water and soil

Definitions

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- **AFFF** – *aqueous film-forming foam* (for fire fighting)
- **PFAS** – *poly/perfluoroalkyl substances*
- **PFOA** – *perfluorooctanoic carboxylic acid* ($C_7H_{15}CO_2H$)
- **PFOS** – *perfluorooctane sulfonic acid* ($C_8F_{17}SO_3H$)
- **POP** - persistent organic pollutant
- **TOP** – *Total oxidizable precursor*
- **TF** – *Total fluorine content*
- **ST** – Surface tension (force binding together the molecules on the surface of a liquid, dynes/cm)

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AFFF – *aqueous film-forming foam* (for fire fighting)

Note: fire practice sites were not always like this

Source: Chemical Engineering and Science. **2014**, 2(1), 11-14 doi:10.12691/ces-2-1-3

Introduction to AFFFs

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- A mixture of surfactants, water, solvents and other additives.
- Allows the formation of a layer that cuts the contact between combustible/flammable materials and oxygen from the air.
- Heat stability is important, which has led to the synthesis and use of strongly halogenated compounds, namely fluorosurfactants, in particular in military grades of fire fighting foams grades.
- Some AFFF were and are still based on PFAS compounds in locations such as military bases, petroleum refineries and airports.

Introduction to AFFFs

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- Since June 2013, the production and use of fire fighting foam containing PFOS is prohibited in Canada.
- PFOS has been added to the list of toxic substances of the Canadian Environmental Protection Act (1999).
- The world production of fire fighting foam does not use PFOS and PFOA any more (except in China et India).
- Producers now use other fluorosurfactants; the effects of these other compounds on human health and on the environment are however not adequately documented .

Introduction to fluorosurfactants

More powerful projection devices are now used

Pictures from the January 28, 2016 SERDP/ESTCP webinar on PFAS

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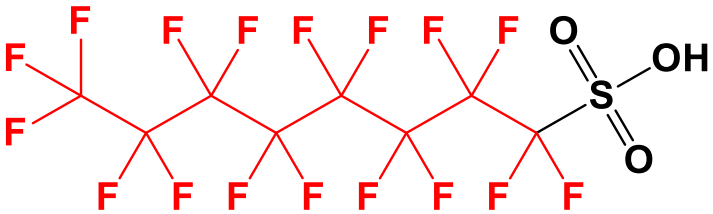
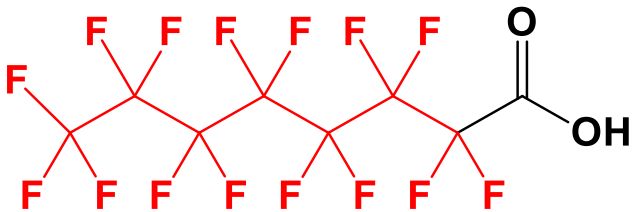
» **Fluorosurfactants** – Oleophilic and hydrophilic compounds used in some fire fighting foams.

PFOS



PFOA



» Fluorosurfactants in the PFAS family:

- **PFOA**: Perfluoro-octanoic carboxylic acid;

- **PFOS**: Perfluoro-octane sulfonic acid;

- About 200 other compounds with still little assessment.

Introduction to Fluorosurfactants

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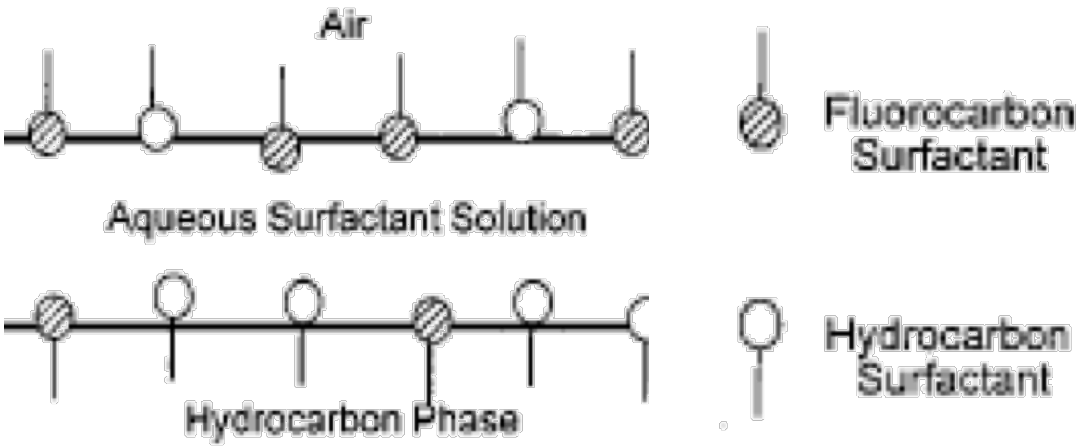
» Persistent compounds, with a potential for bioaccumulation and effects on human health



» POP/PBT

» **PFOA/PFOS**: Targeted as contaminants to be controlled in Canada.

» **PFOS et PFOA**: Banned in most countries and replaced by other fluorinated surfactants.

» **C-F bond**: The second strongest bond in organic chemistry .

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PFOS, PFOA and similar compounds

- Reproductive and developmental effects
  (e.g., mammary gland changes, obesity, neurodevelopmental effects);
- Endocrine and neuroendocrine effects
  (e.g., thyroid hormones disruption and estrogenic effects);
- Hepatic effects
  (e.g., changes in markers of liver activity, liver weight changes);
- Immune response alteration
  (e.g., changes in immune cells production);

Toxicity

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» Tumors in animals
(e.g., in the Leydig cells, liver, mammary glands, pancreas);

» Tumors in humans for PFOA
(i.e., testis, kidney);

» Carcinogenic potency:

- IARC (interim classification for PFOA):"possibly carcinogen to humans" (PFOS not assessed);

- U.S. EPA (draft): "suggestive evidence of carcinogenicity" for PFOA and PFOS;

- The NTP is currently performing additional research pertaining to the carcinogenicity of PFOA.

NTP: National (U.S.) Toxicology Program

Challenges in adressing AFFF impacted sites

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- Affinity with water and lipids, chemically stable, bioaccumulative.
- The fate and environmental behaviour of most compounds are not well known.
- Lack of treatment solutions that are efficient and economical to decontaminate water and soil.

Challenges in adressing AFFF impacted sites

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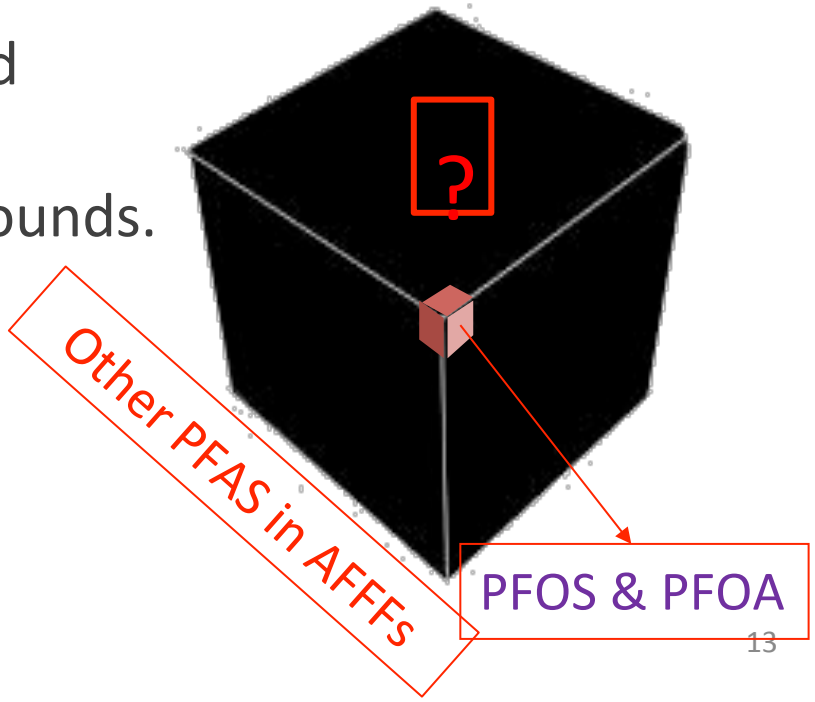
- Information on the extent and migration of PFAS contamination on sites where AFFF were/are used is sparse.
- Identification of PFOS and PFOA as compounds to be controlled, but these compounds constitute only a small fraction of the PFAS family.
- A risk weighted index of toxicity and of undesirable effects could be developed based on all PFAS compounds.
- Development of tools to assess risks and help determine when mitigation or remediation is justified or not.



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Research collaboration since 2013

- Engage projects at McGill with a participation from Sanexen as an industrial partner.
- Treatment tests and development of methods for the characterization and environmental remediation of water and soil.
- Participation to conferences and other events, national and international to exchange with site managers and researchers.

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Partenariat stratégique avec le NSERC CRSNG

Fluorochemicals in AFFF Contaminated Sites
- Environmental Fate, Toxicity and Treatment

- Collaboration between McGill University and Université de Montréal, Sanexen, Transport Canada and CEAEQ.
- Generation of scientific knowledge to assist reaching contamination risk mitigation goals .
- Development of new technical expertise on PFAS remediation.
- Contribution to scientifically informed policy development by regulatory agencies with respect to AFFF use, disposal, risk assessment and remediation.

CEAEQ: Centre d'excellence en analyse environnementale du Québec

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Objectives :

(1) Perform detailed characterization of PFAS contamination in AFFF impacted sites in Canada.

(2) Conduct investigation on environmental fate and behaviors (multi-phase partitioning and transformation processes) of PFAS in soil and groundwater.

(3) Assess biotransformation and bioaccumulation potential of major PFAS species.

(4) Develop innovative nanoscale zero valent iron based reductive defluorination processes for *in situ* or *ex situ* remediation.

Characterization of PFAS

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- Liquid chromatography and mass spectrometry can be used to analyze a number of individual compounds.
- New characterization methods for fluorosurfactants indicate however that the direct analysis of individual compounds such as PFOA and PFOS is insufficient.
- This can greatly underestimate the quantity of compounds of significance and underestimate the risk of exposure.
- An indirect quantification is possible with the TOP method.

Characterization of PFAS
TOP (Total Oxidizable Precursors)

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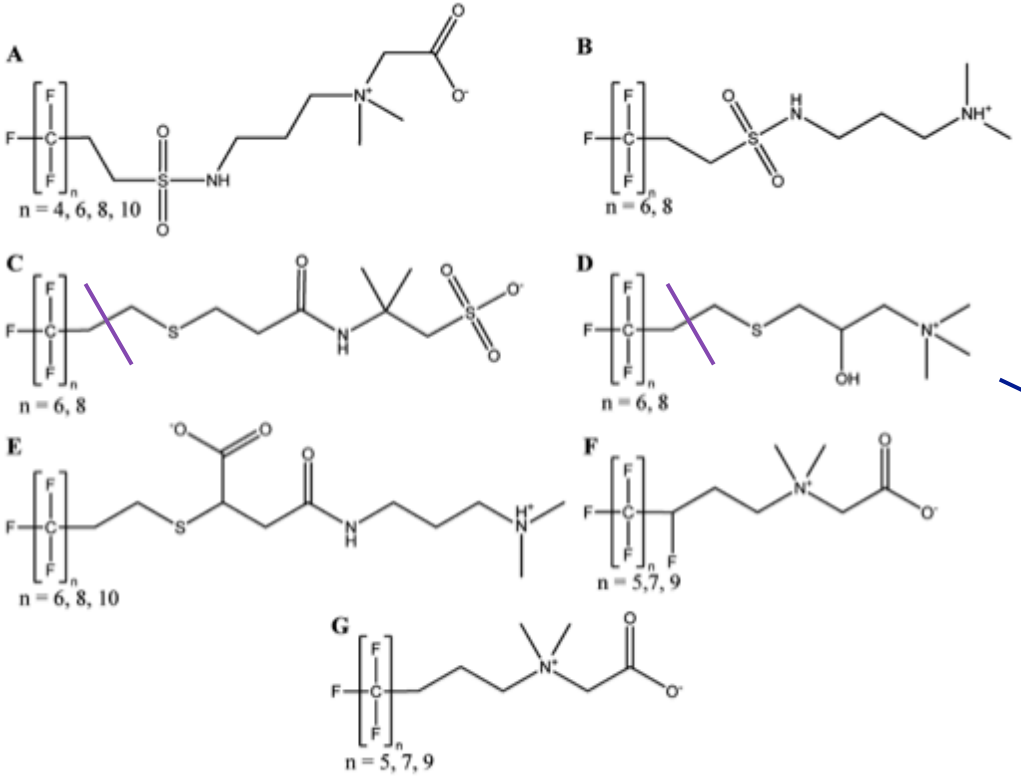
Chemical oxidation eliminates the polar part of precursors and allows to quantify fluorosurfactants.

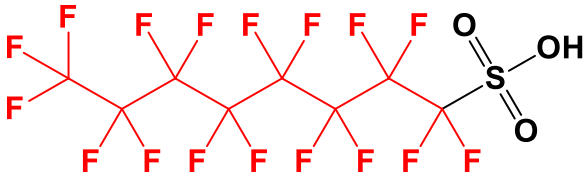
Biological or chemical degradation of newer surfactants can generate a discontinued compound (PFOA).

Some currently used compounds

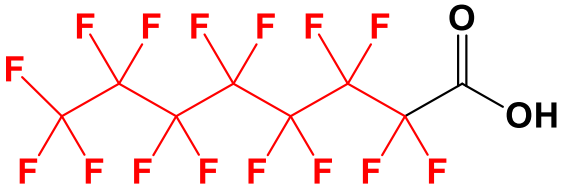


(Place and Field 2012, ES&T)

Discontinued compounds



PFOS



PFOA

PFAS: Poly/perfluoroalkyl substances

Characterization of PFAS

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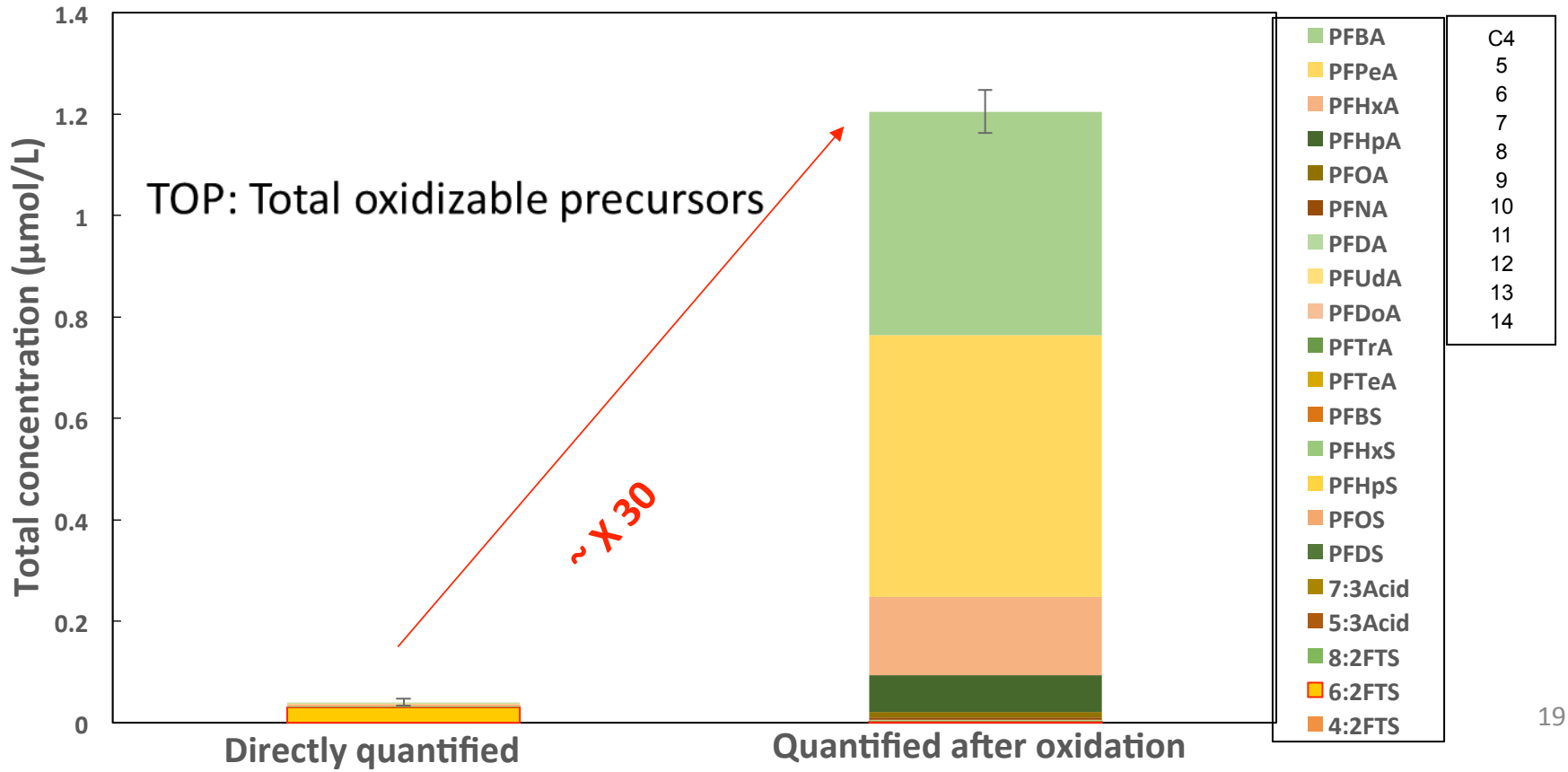
- Most PFAS in water are not directly measurable.
- An oxidation with persulfate (TOP) can be used for a quantification; in a case studied, the PFAS were present at 30 times the concentrations of directly quantified PFAS.
- These precursors can can constitute or form PFAS with harmful effects on health and the environment.



Characterization of PFAS
Quantification by LC-MS/MS Individual PFAS compounds

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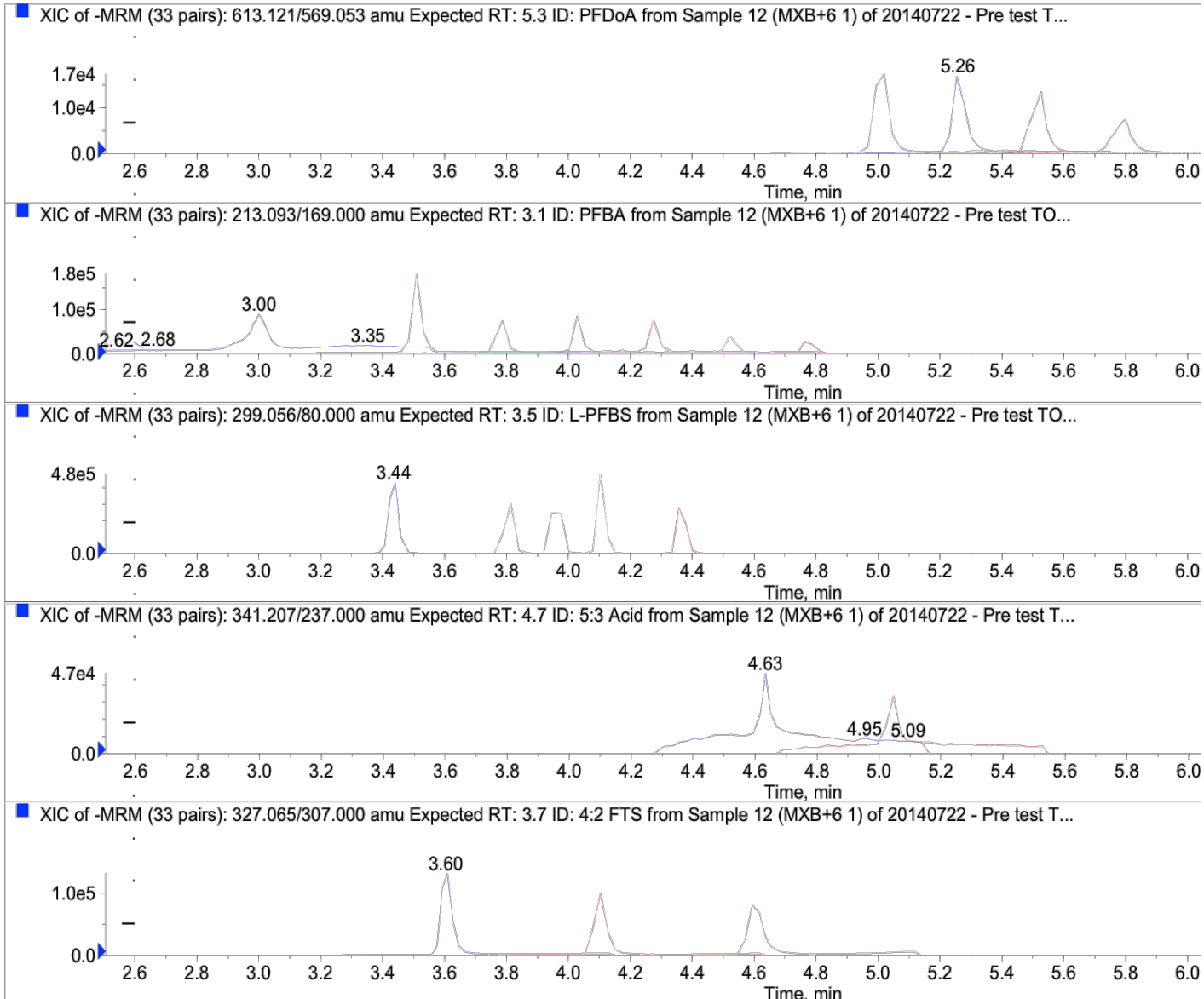
- » A standard solution at 1 ng/ml was used to show the resolution of the 21 targetted compounds.
- » These results were obtained with a same elution.



Surface tension

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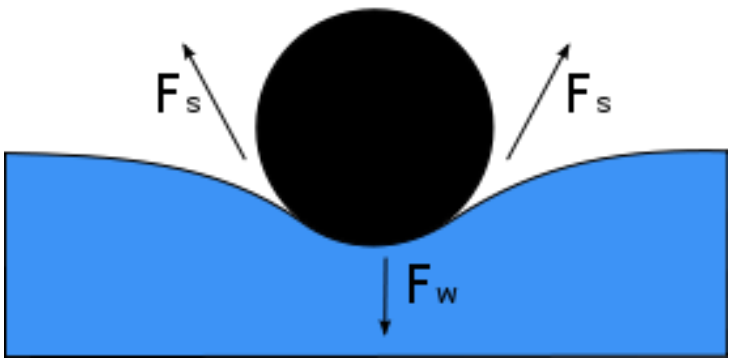
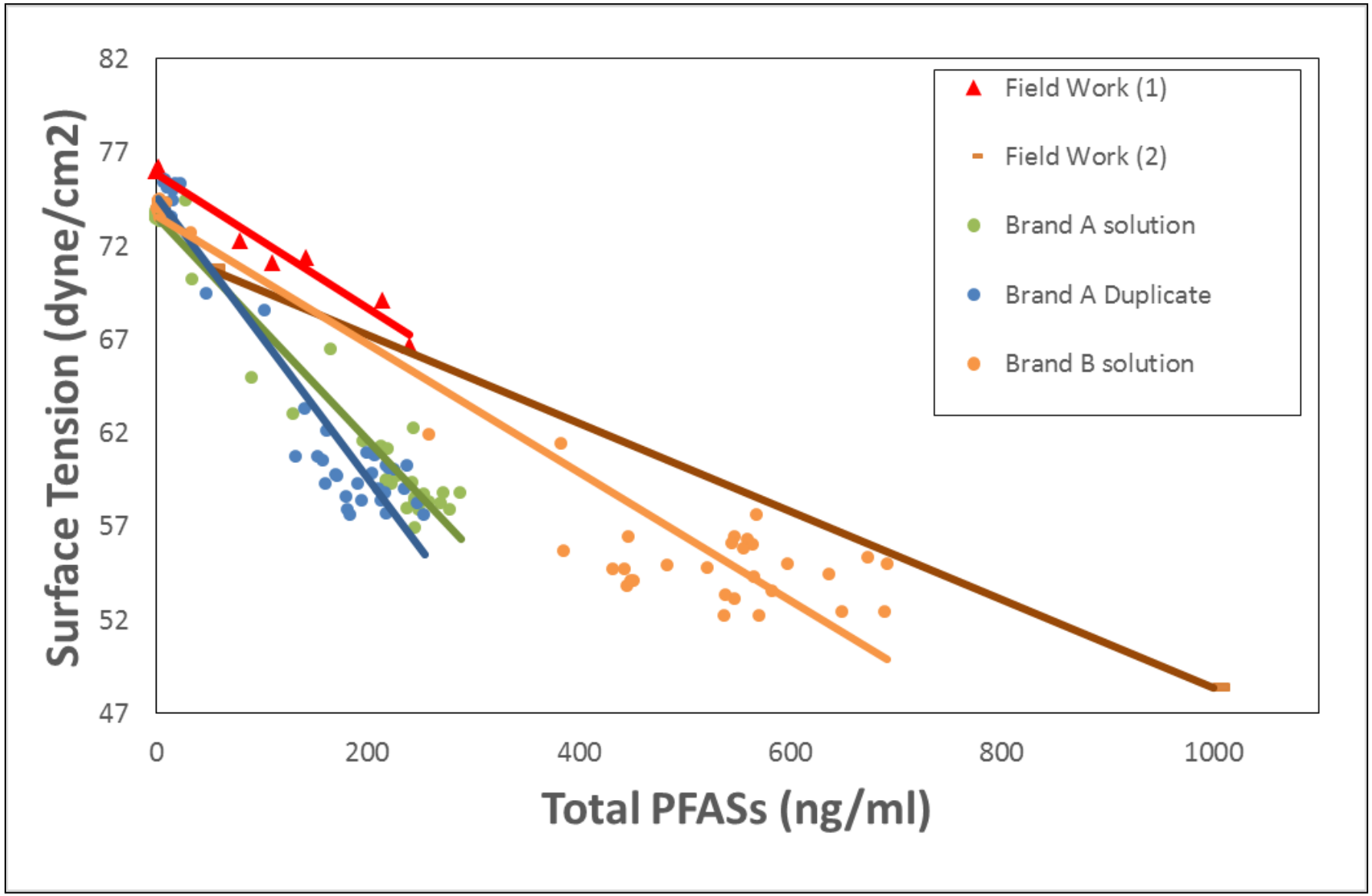
» A simple and economical parameter to estimate the concentrations of surfactants in water.

» Molecular binding force on the surface of a liquid (in dyne/cm or mN/m).



Surface tension



Surface tension

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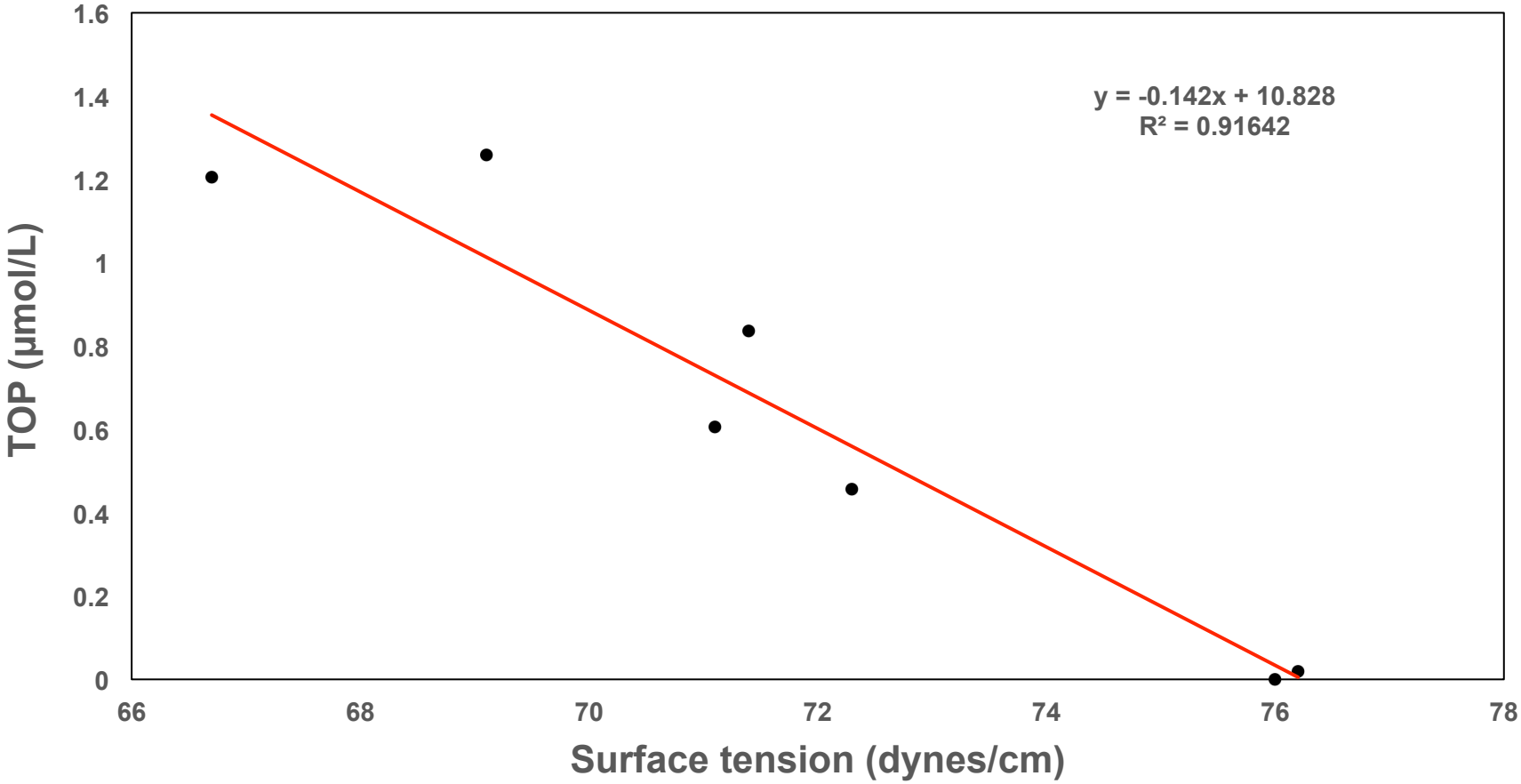
Surface tension allows to assess aproximately the concentration of surfactants and to monitor the removal of these compounds in a treatment process.



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Treatment to remove PFAS and petroleum hydrocarbons

» Emergency response at a heliport and following the train derailment at Lac Mégantic.

» Laboratory tests performed thereafter to better understand and validate treatment approaches.

» Study of co-contamination involving fluorosurfactants and petroleum hydrocarbons with contamination present in suspended, colloidal and dissolved forms.

Case study 1 – Loss of product at a heliport

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- Accidental loss of the content of an underground tank, a solution designed to produce fire fighting foam.
- Work performed on the basis of an emergency response with a fixed monetary amount.
- Hydraulic confinement using an upgradient well to slow down the dispersion of the plume.
- Pumping and treatment of the groundwater using a foaming column and a sequence of filters, sand Ultrasorption and GAC.
- *In situ* washing of the vadose zone.

Case study 1 – Loss of product at a heliport

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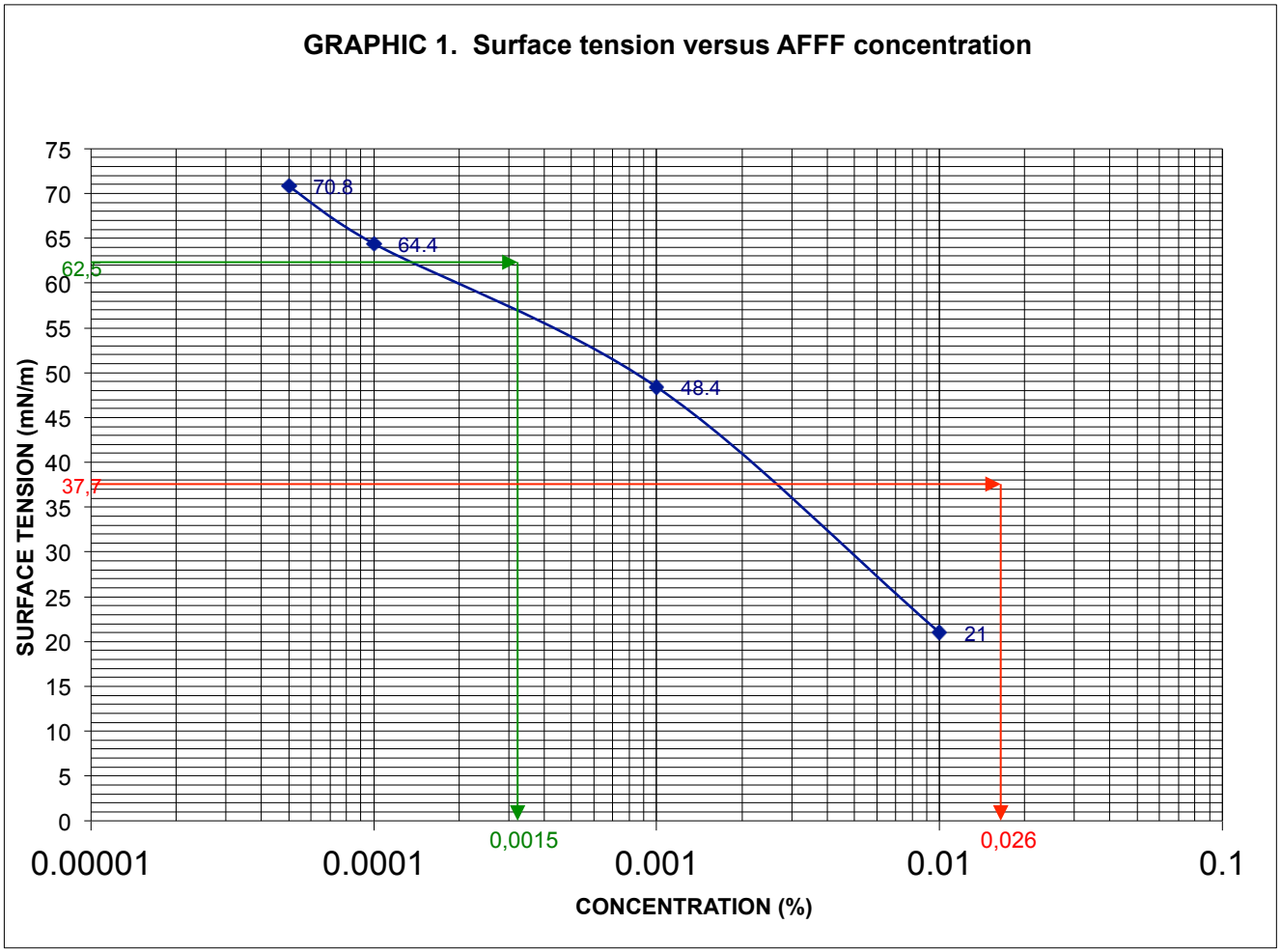
Split spoon sample showing the native sandy soil

Mobile unit used to eliminate contaminants from groundwater and soils

Verification of the water quality using a standard

Waste disposal (recovered concentrate and filtration media)

Case study 1 – Loss of product at a heliport



» The analyses of fluorosurfactans being long, complex and costly, Sanexen also used surface tension to estimate the concentration of AFFFs.

Case study 1 – Loss of product at a heliport

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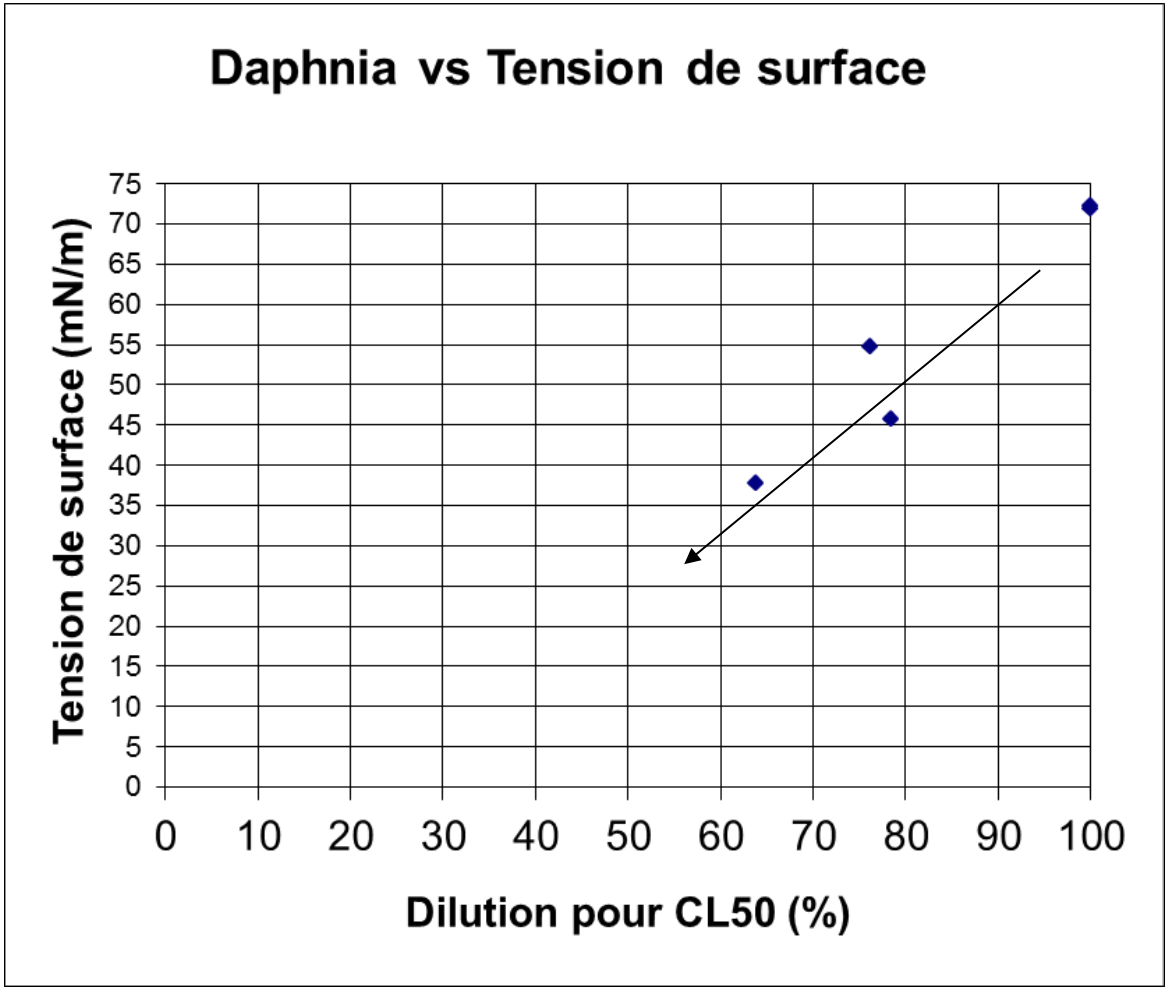
» Acute toxicity vs concentration of surfactant with Daphnia Magna



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SUMMARY

» Product lost: 15 000 L at 10%;

» About 180 m^3 of contaminated;

» Treatment at 50 L/min; injection of part of the water;

» 4,5 millions liters of water treated over 3 months;

» Removal efficiency (in water): 95 %;

» 377 kg of product recovered;

» 30 m^3 waste material disposed of;

» Acute toxicity criteria met for Daphnia Magna and trout.

Laboratory studies

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- » Impact of co-contaminants (petroleum hydrocarbons, ashes, etc.) on fluorosurfactants removal;
- » Applicability and compatibility of different quantification methods depending on the type of foam used;
- » The work plan calls for the use of water and soils from sites that would require environmental remediation;

CITY CENTER OF LAC-MÉGANTIC
JULY 6TH, 2013
Derailment of a 72 wagons train convoy carrying 8 million liters of crude oil Photos from *La Presse*

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» Equipment mobilization to the municipal wastewater treatment plant

» Treatment of the water accumulated in the municipal wastewater plant basins (about 5000 m^3) followed by the cleaning of the basins and the rebooting of the plant.

» Treatment of the raw water from the red zone and from other points of collection around the accident zone

- Water originating from the fire in the red zone;
- Underground and sewer water;
- Runoff (rain water);
- Water collected by skimming from the piers and pier like structures around the lake and river

- Operation of the municipal wastewater treatment plant was interrupted to prevent the release of crude oil directly to the river.
- A thick foam due to the use of AFFFs on the response site covered the plant basins.

Raw water containing unburnt crude oil, pyrolysis oil, soot, ashes, fire fighting foam, debris, soil particles, ect.

Emergency Response Water Treatment

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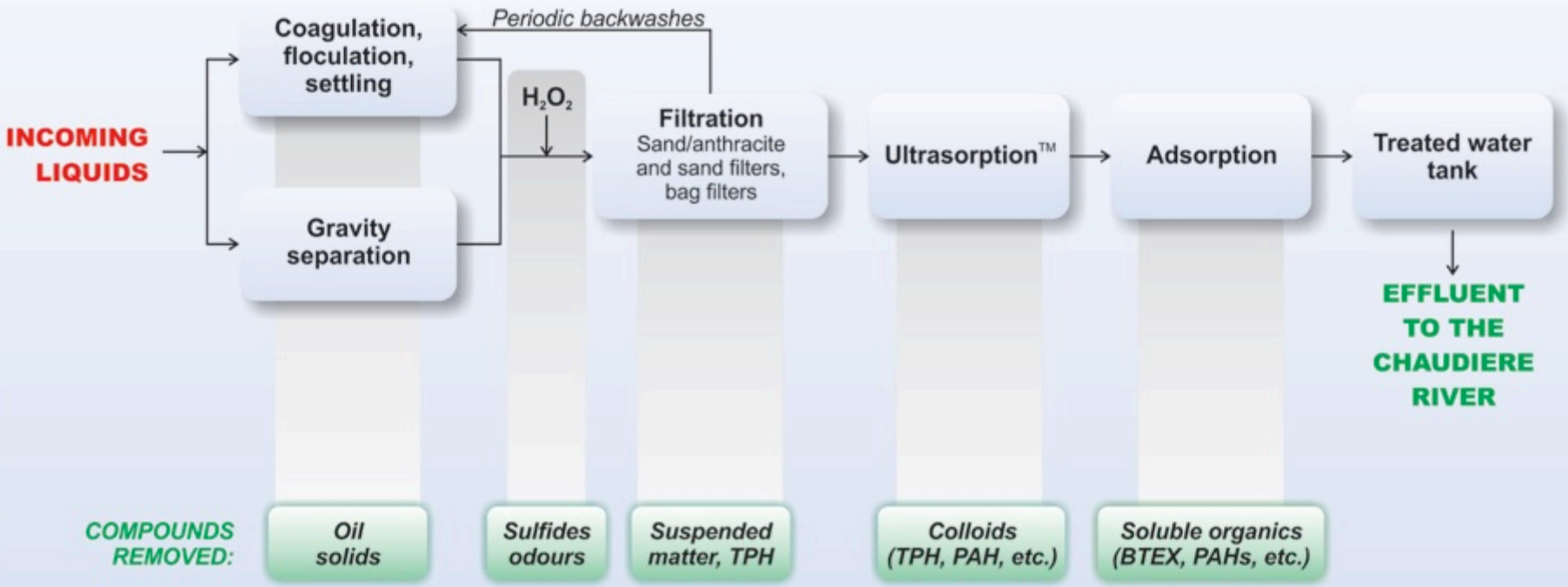
TREATMENT SCHEMATIC - Processes used



Notes: Three treatment trains operating in parallel
Operation 24/7
Filter media replaced as necessary

RA13-310-1-04.cdr

Ultrasorption® Filter treating 400 m^3/day

Adsorption Modules treating 400 m^3/day

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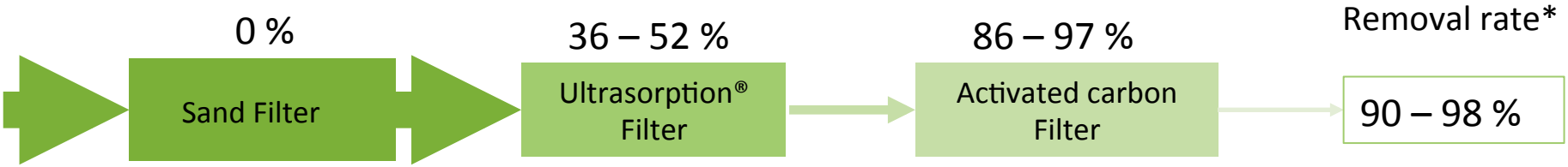
Removal Efficiency

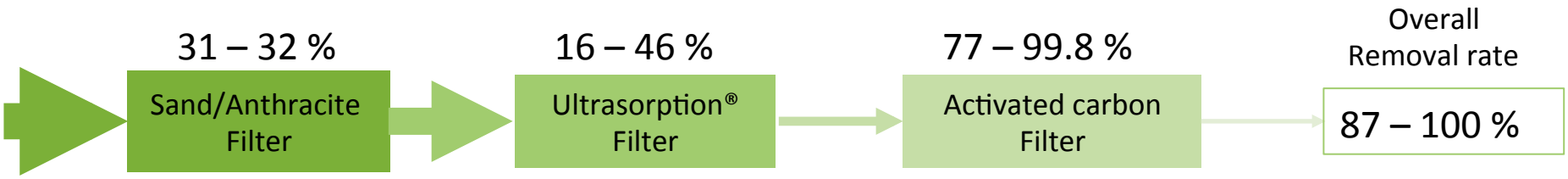
» Global efficiency of 87 to 90 % for the 21 directly measurable PFAS compounds (raw water of 17 µg/L);

» Removal efficiency of 98 to nearly 100 % for all the compounds directly quantifiable using the TOP method (raw water charge of 500 µg/L)

Small system: **Water treatment unit of 150 L/min**



Large system: **Water treatment unit of 550 L/min**



* Rates are respectively for the removal of directly quantified PFAS and of total PFAS

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Treatment efficiency for all detectable PFAS

(data in µg/L)

Parameters	Raw water	Treated water	Chaudiere River (volumetric flow ratio of 3200:1)	Drinking water Guidance Values (Health Canada)
PFOS	< 0.1	< 0.1	< 0.00003	0.3
PFOA	0.5	0.1	0.00003	0.7
∑ 21 PFAS	16.8	1.2	0.0004	-
∑ PFAS	500	2	0.0006	-

» There was little PFOA and PFOS in the water;

» There was a lot of other fluorosurfactants present;

» The treatment system removed these compounds successfully.

Management practices and measures

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» Knowledge of products used (in the past, on inventory, and for present/future use)

» Confining measures for water and foam

- During firefighting exercises or simulations
- During actual fire fighting events or incidents

» Disposal (waste management) or treatment of water

» Using less toxic products for fire fighting operations

» Characterization and rehabilitation of impacted sites

Management practices and measures

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- Using impotent/non-toxic fighter fighting foam during fire fighting training exercises or simulations
- Storing concentrate products with more than one layer of preventive confinement (double-walled)
- Put in place methods and tools for the dry adsorption of products in case of an accidental spill
- Recuperation and reuse of solutions or product preparations
- A very pertinent guide developed in Australia: http://www.defence.gov.au/environment/docs/afff_may08.pdf

THANKS

NSERC CRSNG

Natural Sciences and Engineering Research Council of Canada

Conseil de recherches en sciences naturelles et en génie du Canada

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Fonds de recherche sur la nature et les technologies Québec

Contacts:

Jean Paquin: jpaquin@sanexen.com

Prof. Jinxia Liu: jinxia.liu@mcgill.ca

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Environmental Fate, Toxicity & Treatment

QUESTIONS?

Montreal, Avril 14-16, 2016

National Workshop on Federal Contaminated Sites

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