Non-PFOS/non-PFAS Photoacid Generators: Environmentally Friendly Candidates for Next Generation Lithography

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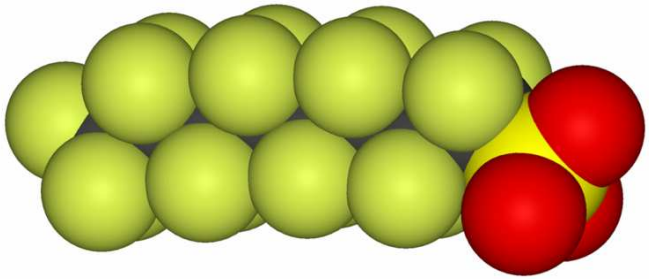
Project Objectives

- To develop novel PFOS-free PAGs that meet the stringent performance demands required by semiconductor manufacturing and do not pose a risk to public health or the environment.

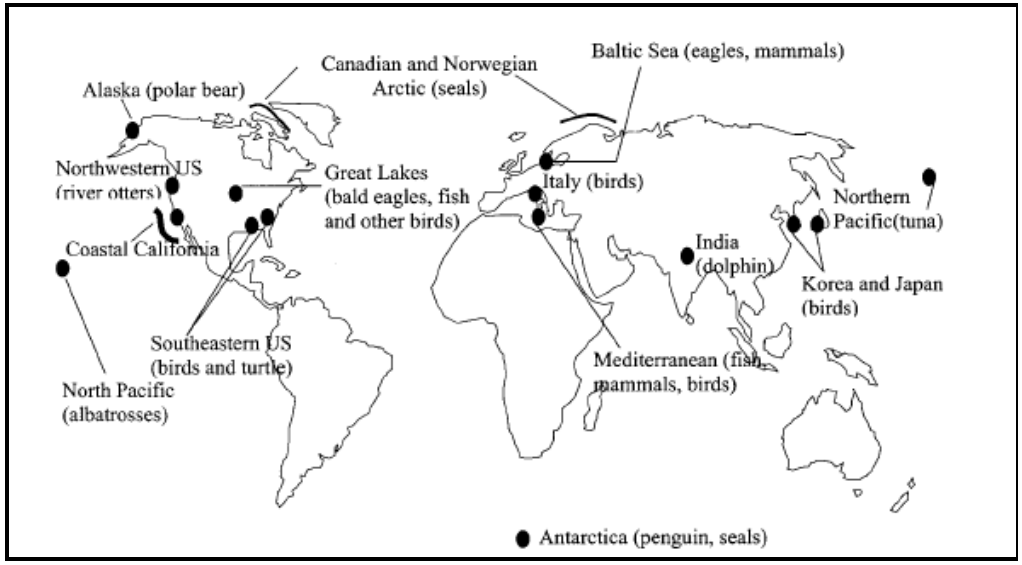
Why the development of new PAGs is necessary?

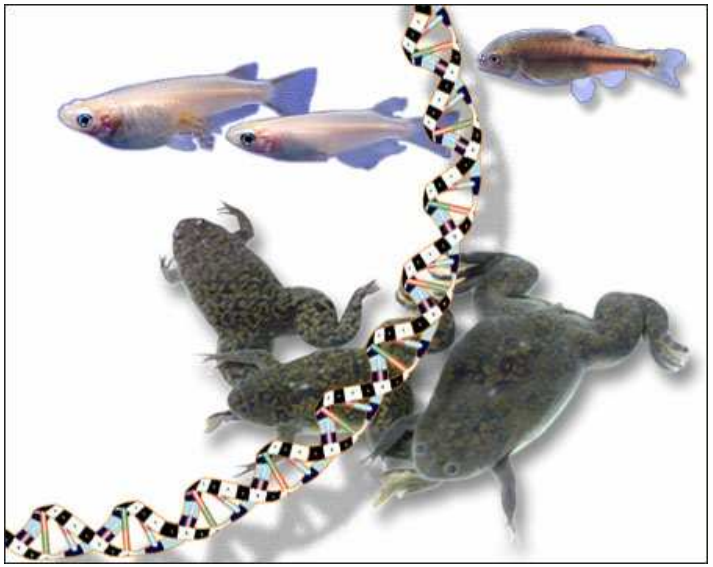
- PFOS, the most common PAG in the lithography process is known to bioaccumulate.
- It is recalcitrant.
- Not known to undergo further degradation by any biological means.



Why the development of new PAGs is necessary?

- Relatively high concentrations of PFOS have been reported in mammals, birds, and fish from locations throughout the world.





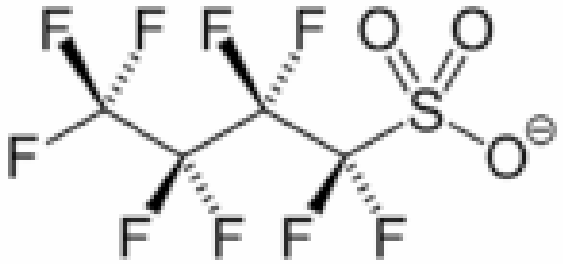
Giesy et al. (2001) Environ. Sci. Tech. 35:1339

Why the development of new PAGs is necessary?

- PFOS use is being regulated and forbidden for many industries by the EPA:
  - 2002: Proposed Toxic Substances Control Act (TSCA) and Significant New User Rule (SNUR) forbidding the use of PFOS with exemptions for semiconductor industry.
  - 2006: Reduction of PFOA emissions by 95% by 2010 and 100% by 2015.
  - 2006: SNUR issued to limit the use of 183 PFOAS.

Why the development of new PAGs is necessary?

- Replacements for PFOS based on shorter alkyl perfluoronated chains (i.e. PFBS) challenge the same problems that their predecessor:
  - Recalcitrance



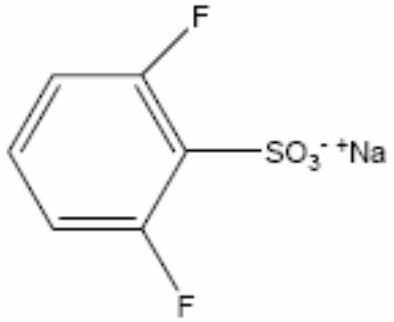
Why the development of new PAGs is necessary?

- Any replacement PAG will need to have:
  - Comparable acidity, sensitivity, miscibility, and superior line edge roughness characteristics in a photoresist formulation.
  - Will also need to demonstrate improved **environmental compatibility.**

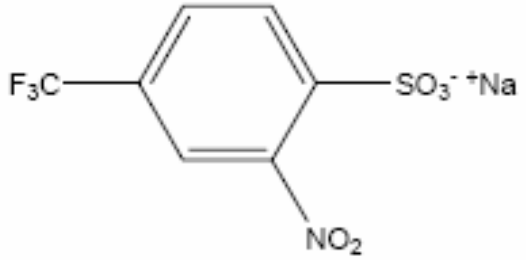
New PAGs

- We therefore propose to develop new PFOS-free (and PFAS-free) PAGs (Cornell University) and investigate **the environmental behavior of these PFOS-free alternatives** (Univ. of Arizona).

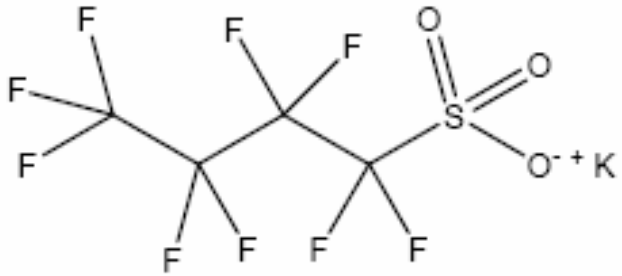
PAGs and Counterions Tested



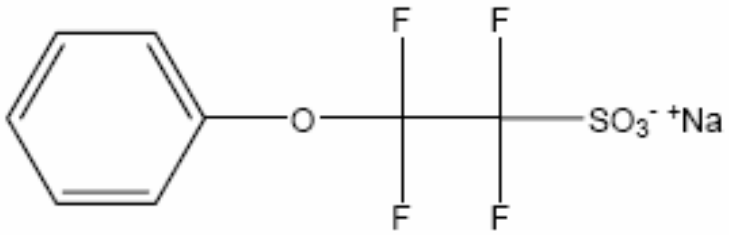
SF Sulfonate 1



SF Sulfonate 2



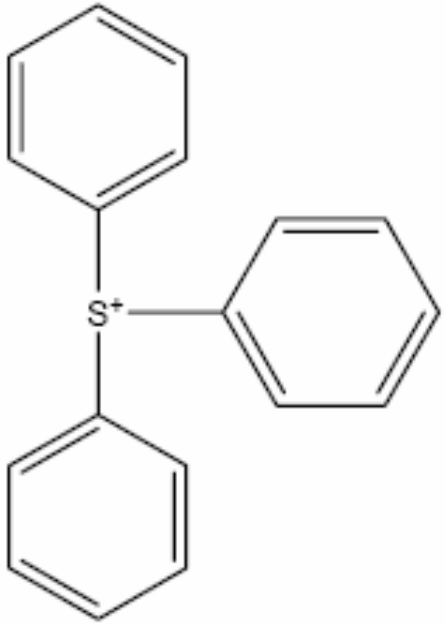
Potassium Perfluoro-1-butanesulfonate



PF Sulfonate 1

PAGs and Counterions Tested

Diphenyliodonium



Triphenylsulfonium

Environmental Toxicity

MICROTOX

MTT ASSAY

METHANOGENIC INHIBITION TEST

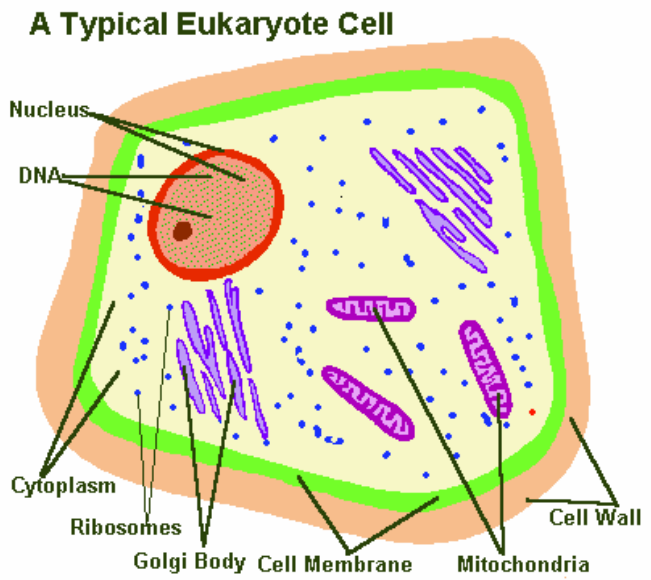
Material and Methods

- The inhibitory potential of three non-PFOS PAGs (SF1, SF2 and PF1) and their counter ions, diphenyl iodonium (DPI) and triphenyl sulfonium (TPS), (Fig. 1) was evaluated using three different bioassays:
  - the Mitochondrial Toxicity Test (MTT);
  - Microtox® (a widely-used, commercial assay utilizing a marine bacterium that emits fluorescence),
  - and the methanogenic inhibition test.

MTT Assay

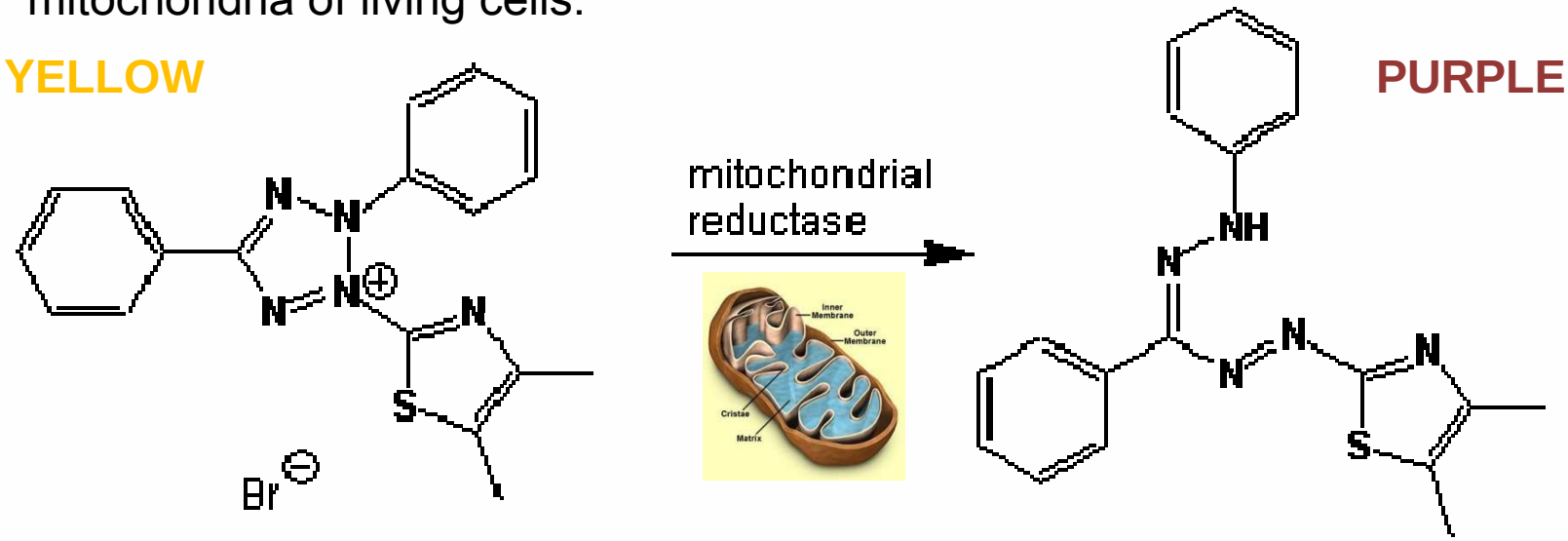
- **WHAT?** MTT assay is a laboratory test and a standard colorimetric assay for measuring cellular proliferation (cell growth).

- **WHY?** It is used to determine cytotoxicity of potential toxic materials.
  - The main reaction happens in the mitochondria of living cells. Mitochondria is a component of all Eukaryotic cells (Humans cells are Eukaryotes). Thus this test can be correlated with Human toxicity.



MTT Assay

- **HOW?** Yellow MTT (3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) is reduced to purple formazan in the mitochondria of living cells.



- This reduction takes place only when mitochondrial reductase enzymes are active, and therefore conversion is directly related to the number of viable (living) cells.

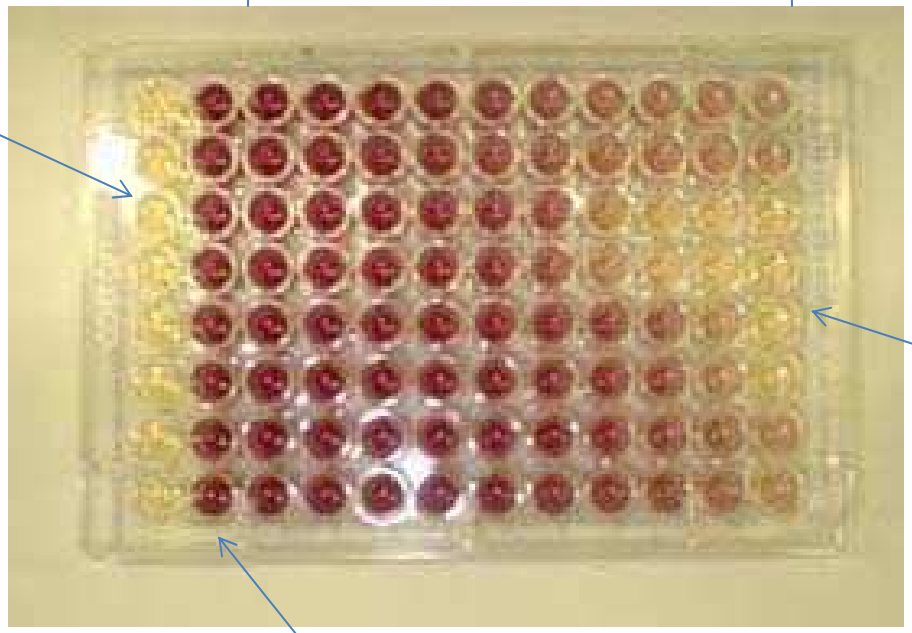
MTT Assay

- A solubilization solution (usually either dimethyl sulfoxide) is added to dissolve the insoluble purple formazan product into a colored solution.
- The absorbance of this colored solution can be quantified by measuring at a certain wavelength (usually between 500 and 600 nm) by a spectrophotometer.
- When compared to untreated control cells, the effectiveness of the agent in causing death of cells can be deduced, through the production of a dose-response curve.

MTT Assay

Treatment wells

Positive control (a known toxicant is added)



Less color change indicates more toxicity at that concentration.

Negative control (no toxicant)

MTT Assay

- The PAG counter ions, DPI and TPS, showed the highest toxic effects in the MTT assay (Fig. 2). PF1 was the only PAG displaying toxicity in this bioassay.

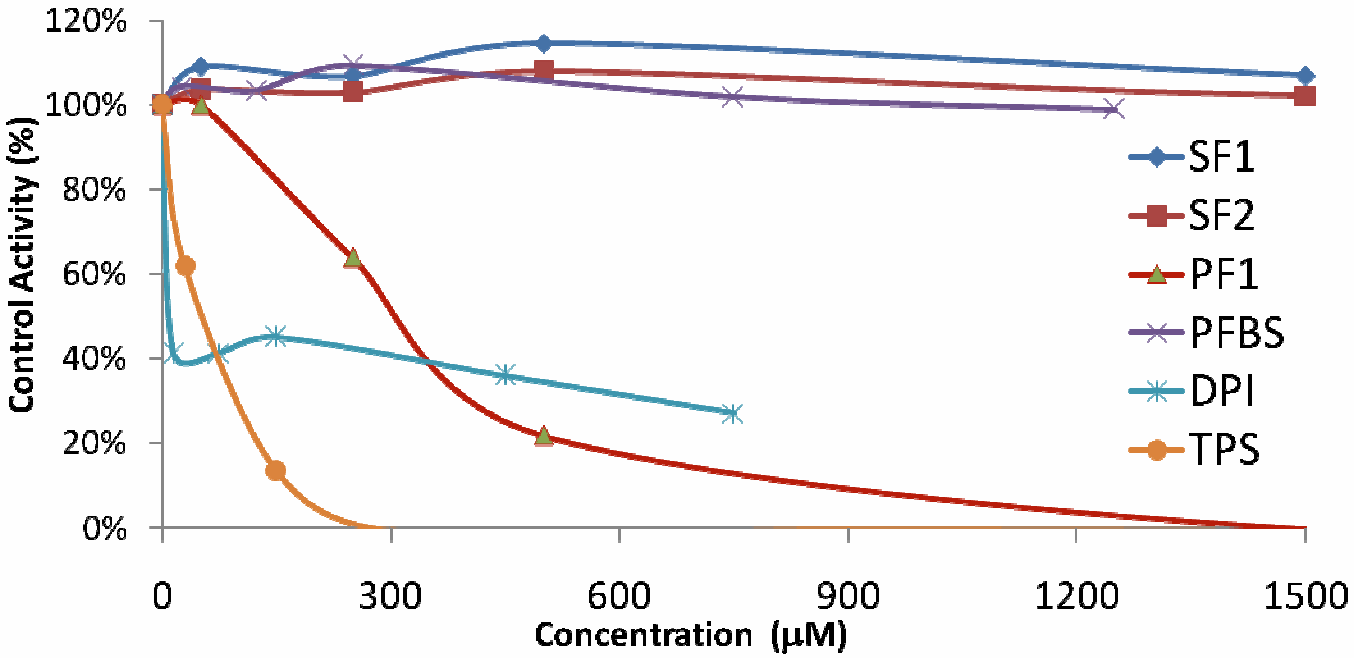


Fig. 2- Inhibitory effect of the new non-PFOS PAGs and the PAG counter ions in the MTT bioassay.

Microtox Assay

- **WHAT?** Microtox is a standardized toxicity test system which is rapid and sensitive. It has a high reproducibility is ecologically relevant and cost effective.

- **WHY?** There exists numerous studies and a large body of published data comparing the Microtox® system with toxicity values for fish, crustaceans and algae for a wide range of organic and inorganic chemicals.
  - Microtox® assays can be completed within an hour and a report available within 24 hours, making them a very rapid form of testing.

Microtox Assay

Table 1: Partial list of toxic compounds detected by Microtox Systems

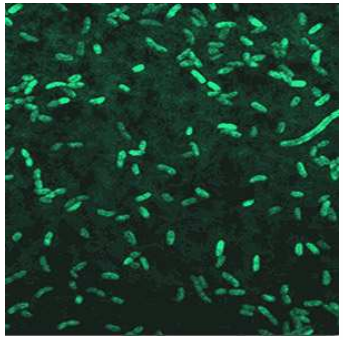
Arsenic *	**Mercury** *
Sodium Cyanide *	Selenium
Potassium Cyanide *	Chromium
PR-Toxin	Copper
Aflatoxin *	Ochratoxin
Rubratoxin	Chloroform
Ammonia	Sodium Lauryl Sulfate
Benzoyl Cyanide	**Lindane** *
DDT	Cresol
Formaldehyde	**Malathion** *
Carbaryl	**Flouroacetate** *
Trinitrotoluene (TNT)	**Parathion** *
4-phenyl Toluene	Carbofuran
Pentachlorophenol	Patulin
Paraquat	Diazinon
Cyclohexamide	**Cadmium** *
Quinine	Dieldrin
Lead	

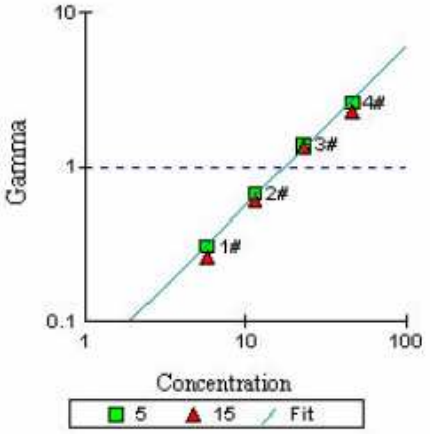
* Indicates specific chemical and biological threats specifically identified by name by the US Air Force in the study *"Chemical and Biological Warfare Threat: USAF Water Systems at Risk"* Major Donald Hickman, US Air Force Counterproliferation Center, September 1999.

Microtox Assay

- **HOW?** The Procedure employs the bioluminescent marine bacterium *Vibrio fischeri* as the test organism. The bacteria are exposed to a range of concentrations of the material being tested.

- The reduction in intensity of light emitted from the bacteria is measured along with standard solutions and control samples. The change in light output and concentration of the toxicant produce a dose / response relationship.





Microtox Assay

- In agreement with the findings of the MTT assay, the PAG counter ions were also the most inhibitory compounds in the Microtox assay (Table 1). PF1 also displayed microbial inhibition, albeit at relatively high concentrations (50% inhibitory concn. (IC_{50})= 1.6-2.2 mM).

Table 2. Inhibitory effect of the new PAGs and their counter ions in the Microtox bioassay. IC50 and IC80 are the concentrations of the compounds causing 50 and 80% inhibition in the assay.

	IC50 (µM)			IC80 (µM)		
Compound	**5 min**	**15 min**	**30 min**	**5 min**	**15 min**	**30 min**
SF1	NT*	NT	NT	NT	NT	NT
SF2	NT	NT	NT	NT	NT	NT
PF1	2195	1705	1614	9698	5467	4371
PFBS	NT	NT	NT	NT	NT	NT
DPI	40	10	5	179	48	22
TPS	40	29	38	145	78	76

*NT= Not toxic at the highest concn. tested: SF1 (11250 µM); SF2 (11250 µM), PFBS (11250 µM)

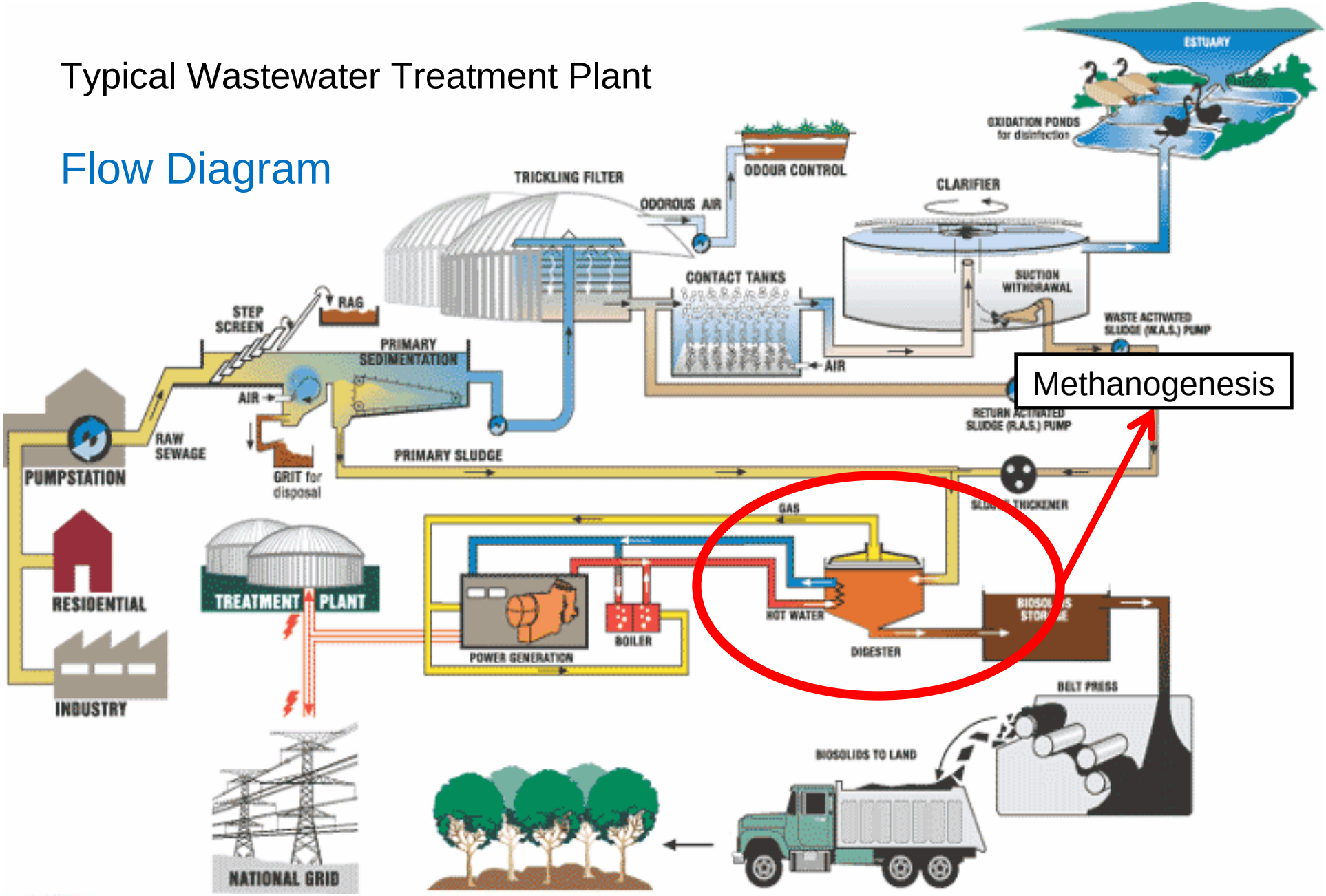
Methanogenic Inhibition

- **WHAT?** The Methanogenic Inhibition test consist on the measurement of the rate of methane production under anaerobic conditions of a mixed methanogenic inoculate. Usually this inoculate is obtained from Municipal or Industrial Wastewater treatment plants, or sediments.

- **WHY?** Methanogenic-toxicity data are important, since methanogenesis is the final step in the degradation of organic matter in many anaerobic environments, including sediments, wetlands, and wastewater treatment systems.

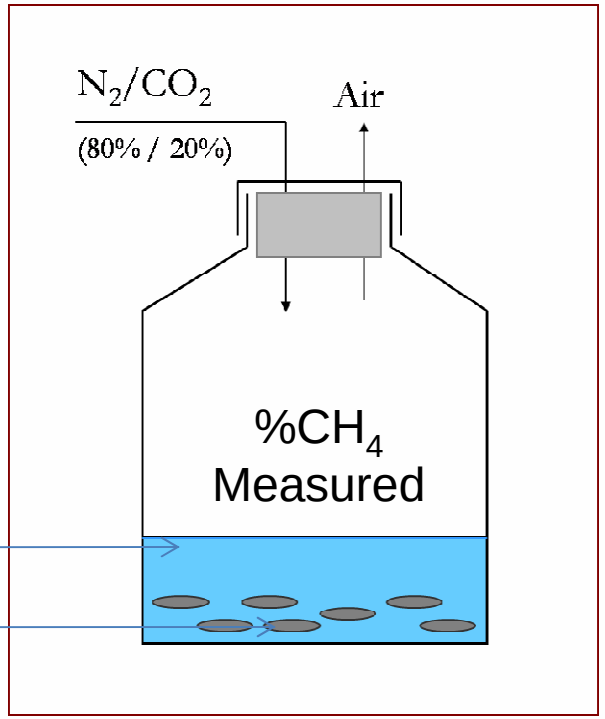
Typical Wastewater Treatment Plant

Flow Diagram



Methanogenic Inhibition

- **HOW?** The test consists of dosing a methanogenic mixed culture with the desired toxicant, then analyze the production rate of methane and compare the results to a control non-dosed set.
  - Two classes of methanogens were evaluated: hydrogen-utilizing and acetatoclastic methanogens.

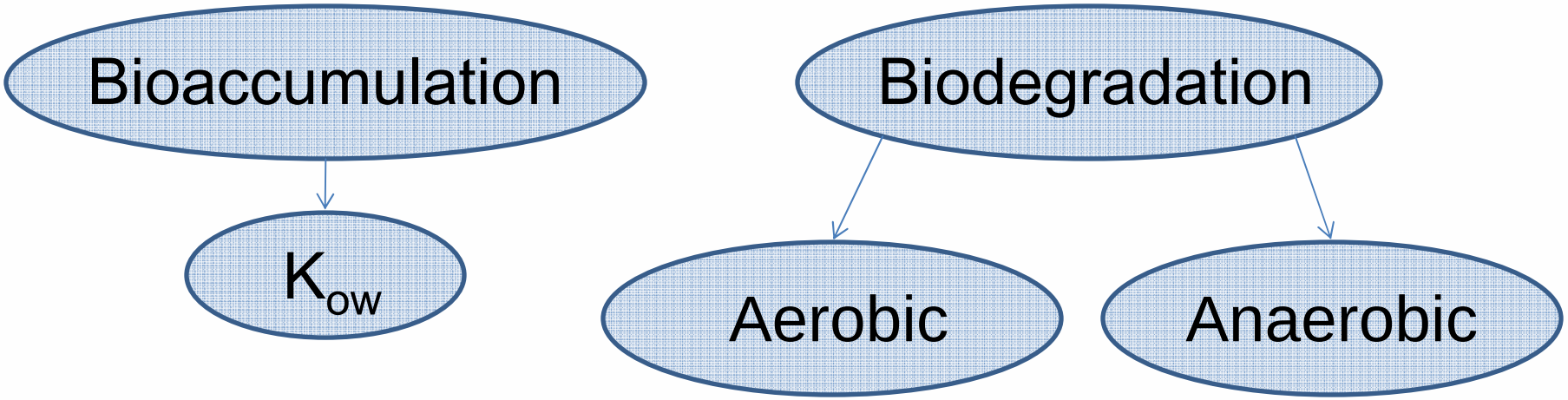


Methanogenic Inhibition

- The counter ions displayed inhibition towards H_2 and acetate-utilizing methanogenic microorganisms (Table. 3). In contrast, the PAGs were generally not toxic. SF2 was an exception, with an IC_{50} value of 1470 µM. Methanogens constitute an important microbial population in anaerobic sludge digestors. Severe methanogenic inhibition can result in process failure.

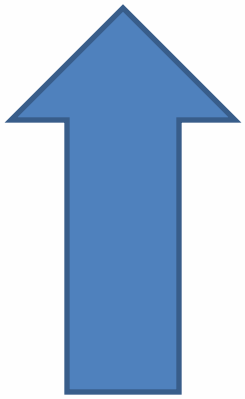
	Acetatoclastic		Hydrogen-utilizing	
NAME	Concentration (µM)	Inhibition	Concentration (µM)	Inhibition
SF Sulfonate 1	2589	6.98% ± 0.95%	2589	3.03% ± 3.06%
SF Sulfonate 2	1850	62.60% ± 2.83%	1850	4.45% ± 5.04%
PF Sulfonate 1	1830	42.71% ± 3.63%	1830	-1.68% ± 0.61%
Perfluorobutane sulfonate	1672	15.08% ± 1.46%	1672	7.41% ± 2.21%
Triphenylsulfonium	1519	31.28% ± 2.52%	1519	51.01% ± 20.61%
Diphenyliodonium	1779	55.90% ± 0.72%	711	27.74% ± 4.58%

Environmental Behavior

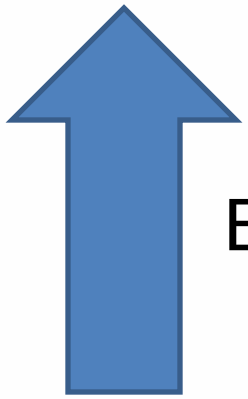


Bioaccumulation

- The octanol-water partition coefficient (Kow) is a parameter that measures the ability of a compound to dissolve in an organic matrix.
- This definition is what allows us to correlate Kow values with bioaccumulation potential.



K_{ow}



Bioaccumulation

Bioaccumulation

- Log K_{ow} coefficients were estimated and calculated using three different methods:
  - Fragment addition: based on structural properties.
  - Software: KOWWIN program to estimate Log K_{ow}.
  - Chromatography: Linear regression using well-known compounds and comparing retention times.

Bioaccumulation

- Due to their intrinsic low acidification constant (strong acidity), the ionic form of the PAGs will be the dominant under normal environmental conditions (neutral PH). Therefore the Log Kow of the ionic form was calculated.

Table 4. Estimates of Log Kow for the ionic PAGs

Estimation Method	SF1	SF2	PF1	PFBS	PFOS
Fragment Addition Software KOWWIN	-2.35	-2.01	-0.02	NE	NE
Chromatography	-2.55	-2.17	0.18	0.26	4.13
	-2.52	-2.06	0.10	0.13	4.20

NE = Not Estimated

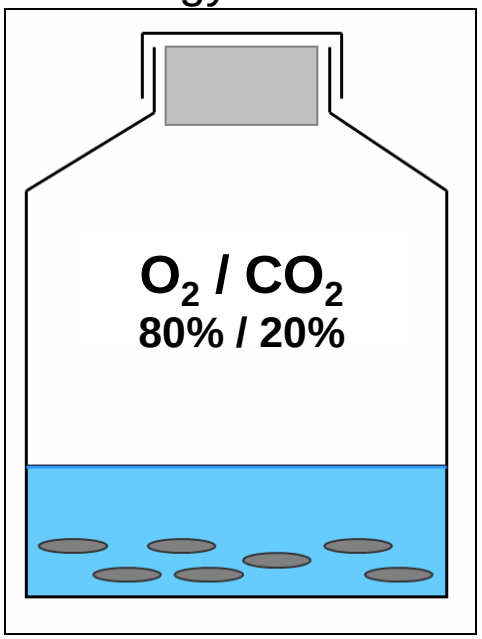
Biodegradation

- The biodegradation study consisted of three different treatments:
  - **Aerobic Degradation:**
    - Compounds as solely carbon and energy source.
    - Methane cooxidation.
  - **Anaerobic Degradation:**
    - Hydrogen as electron donor.

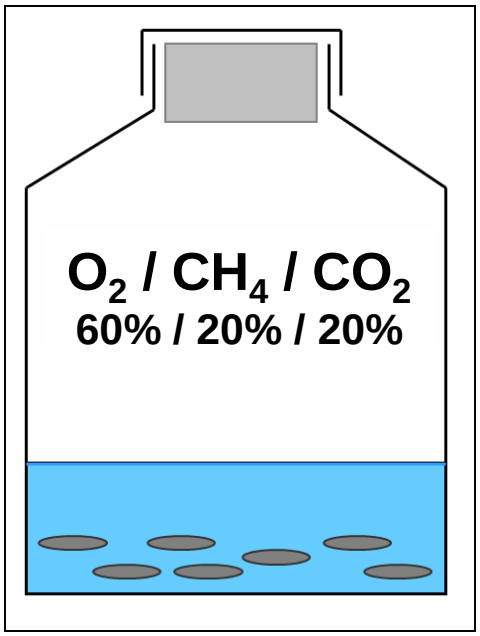
Biodegradation

AEROBIC

Carbon and Energy Source

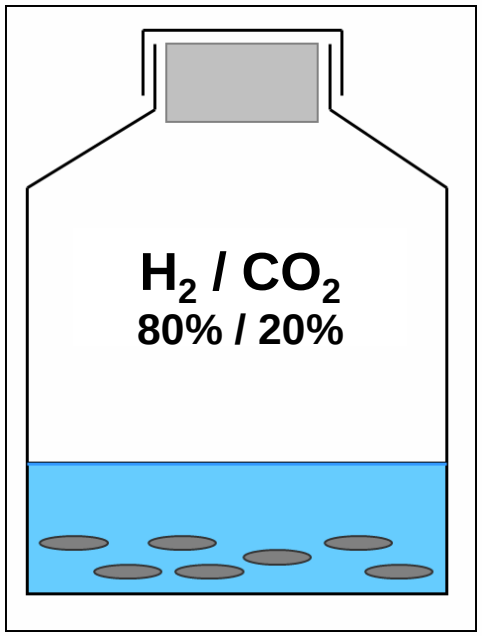


Methane Cooxidation



ANAEROBIC

Hydrogen as Electron Donor

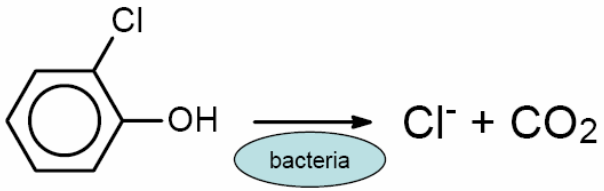


ACTIVATED SLUDGE

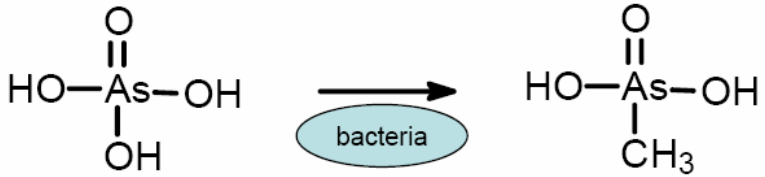
DIGESTER SLUDGE

Biodegradation

- Biodegradation is a biologically catalyzed transformation of a chemical resulting in simpler forms
  - **Mineralization:** Conversion of organic compounds to mineral products.



  - **Biotransformation:** transformation of pollutant by a biological process



Biodegradation

- In this study we measured both mineralization and biotransformation.
  - Mineralization was estimated by measuring the fluoride released in solution with a fluoride electrode.
  - Biotransformation was estimated by liquid chromatography with shifting of retention times.

Biodegradation: Mineralization

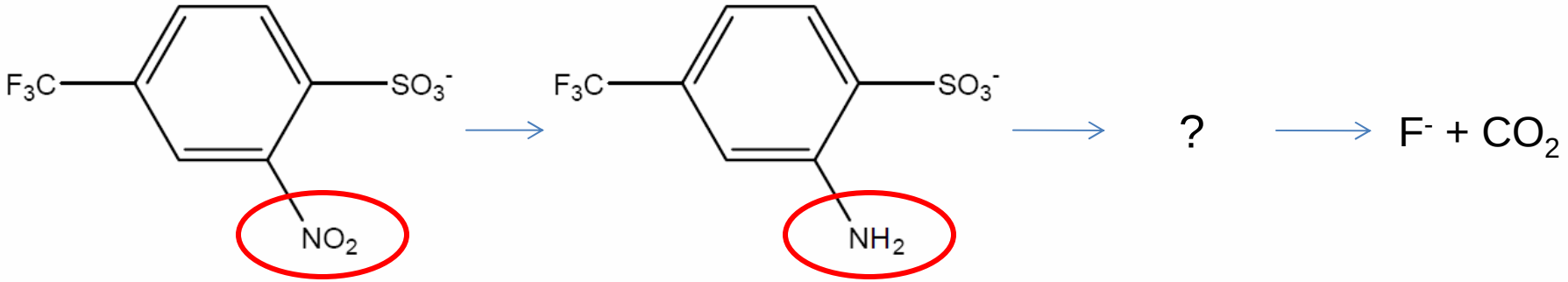
Table 5. Fluoride Released as a % of total fluoride content of PAG

	Aerobic Treatment		Anaerobic Treatment
PAG	Solely Carbon and Energy Source (After 26 days)	Methane Cooxidation (After 75 days)	Hydrogen as Electron Donor (after 158 days)
SF1	0.63 ± 0.04	1.58 ± 0.09	0.53 ± 0.30
SF2	1.57 ± 0.25	1.28 ± 0.05	9.23 ± 0.46
PF1	0.42 ± 0.00	1.29 ± 0.07	0.39 ± 0.13
PFBS	ND	ND	ND

ND= Not Detected (Detection Limit 0.1 ppm Fluoride)

Biodegradation: Biotransformation

- Of the three new PAGs treated, only SF2 showed complete biotransformation, with 100 % of the PAG being biotransformed under anaerobic conditions.
  - Even though the actual structure of the new compound has not been characterized, based on previous knowledge the most probably path followed is:



Conclusions : Toxicity

- The counterions, diphenyl iodonium (DPI) and triphenyl sulfonium (TPS), showed the highest toxic effects in all three tests.
- The new PAGs, SF1 and SF2, were not inhibitory, or only at very high concentrations.
- PF1 displayed inhibition in the MTT and Microtox assays but the toxicity levels were 1-2 orders of magnitude lower compared to those determined for the counter ions.

Conclusions : Biodegradation

- SF2 was the more biodegradable PAG. Being mineralized to up to 10% under anaerobic conditions.

- The addition of a nitro group proved to be favorable for biotransformation, allowing 100% biotransformation for PAG SF2.

Summary

- Counterions were much more toxic than the PAGs studied.
- Addition of different functional groups (aromatic rings, nitro groups), allow the PAGs to be more favorable to biodegradation.

Future Work

- Complete ongoing studies of the toxicity of PAGs and counter ions under aerobic and nitrifying conditions.
- Further investigate the susceptibility of the novel PAGs to biodegradation by microorganisms commonly found in wastewater treatment systems.

Acknowledgements

- SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing.
- Dr. Ober's Group at Cornell University.
- Dr. Reyes Sierra and Dr. Jim Field at University of Arizona.