Università degli Studi di Padova

Department of Chemical Sciences (UNIPD) &
Department of Environmental Engineering
(NEDUET)

Plasma-based approaches for removing micropollutants/emerging contaminants from water; Case study of PFAS

Presenter: Mubbshir Saleem

Technical Meeting on Emerging Applications of Plasma Science and Technology

Sep 19 – 22, 2023

IAEA Headquarters

Expertise and roles

Prof. Ester Marotta
Associate professor
in Organic Chemistry

- Group and activities coordination
- Problem solving

Dr. Eng. Mubbshir Saleem
Researcher
Environmental Engineering

- Design of plasma source and power supplies
- Design, execution and management of the experiments

Giulia Tomei
PhD student in
Chemical Sciences

- Chemical analyses
- Mass spectrometry analyses
- Experimentation

Dr. Goran Sretenović
Collaborator, plasma physics
University of Belgrade

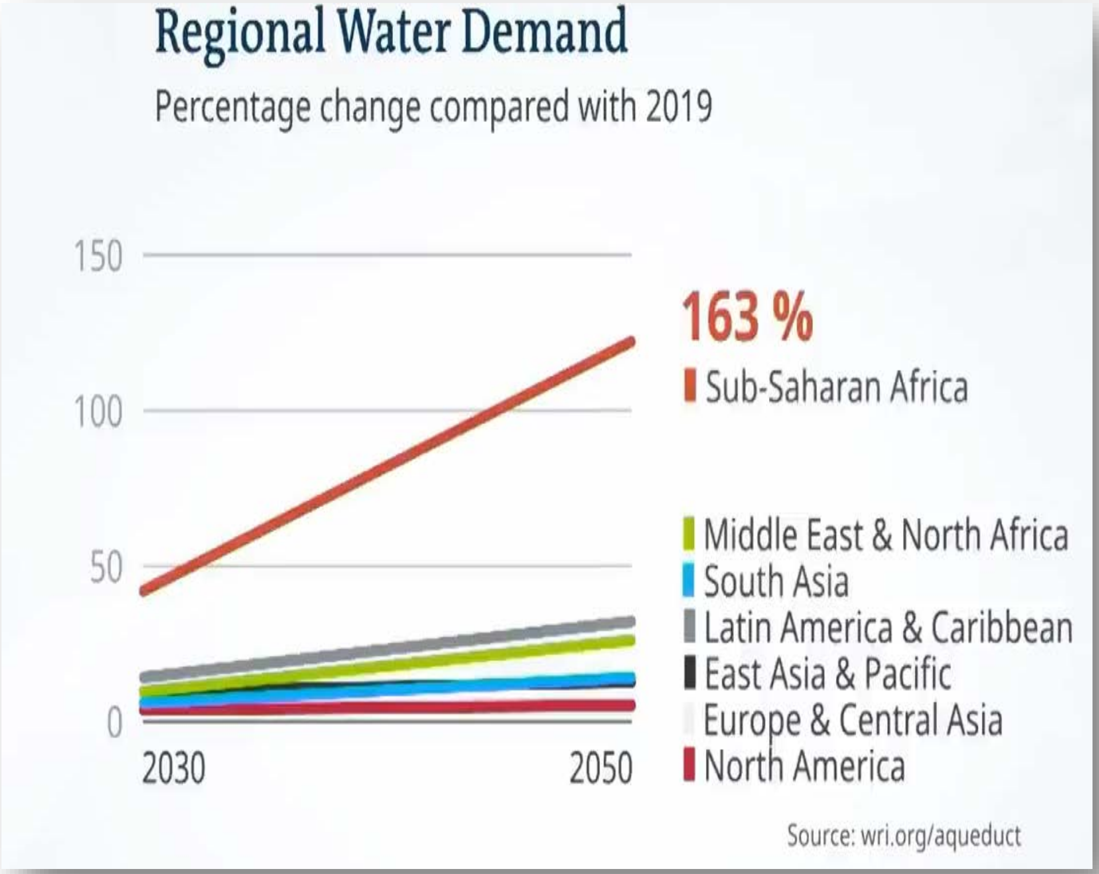
- Mass spectrometry analyses
- Plasma diagnostics

Thirsting for Solutions: Confronting Water Scarcity Amid Rising Demand

1 in 4 person does not have enough water to meet the demand for drinking, agriculture and industry.

And that number is set to rise

(World Resources Institute)



The way Forward

- Water Conservation and Efficient use
- Wastewater Management and Reuse

Unveiling the Unseen?

Micropollutants

- Micropollutants are biological or chemica… present in … trace quanti… the micro/na… level) as a … activities.

…merging

… often used for

…ecause of lower

2. Health impact is expected but not quantified.
3. unmonitored or unregulated

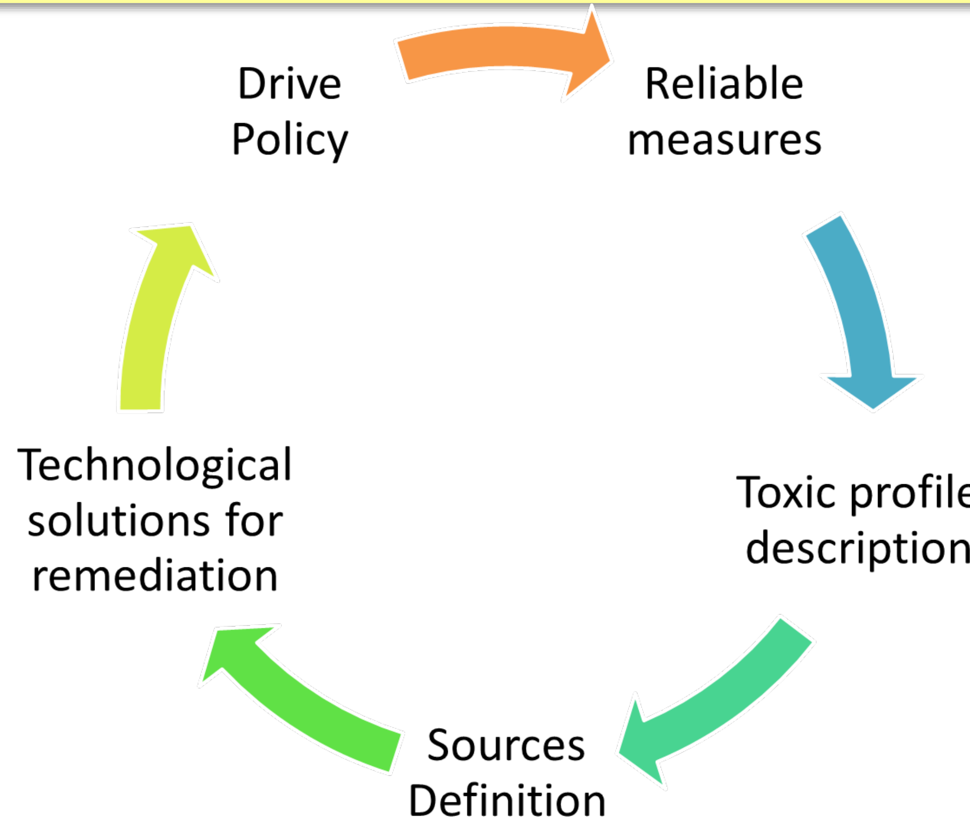
Università degli Studi di Padova

Department of Chemical Sciences (UNIPD) &
Department of Environmental Engineering
(NEDUET)

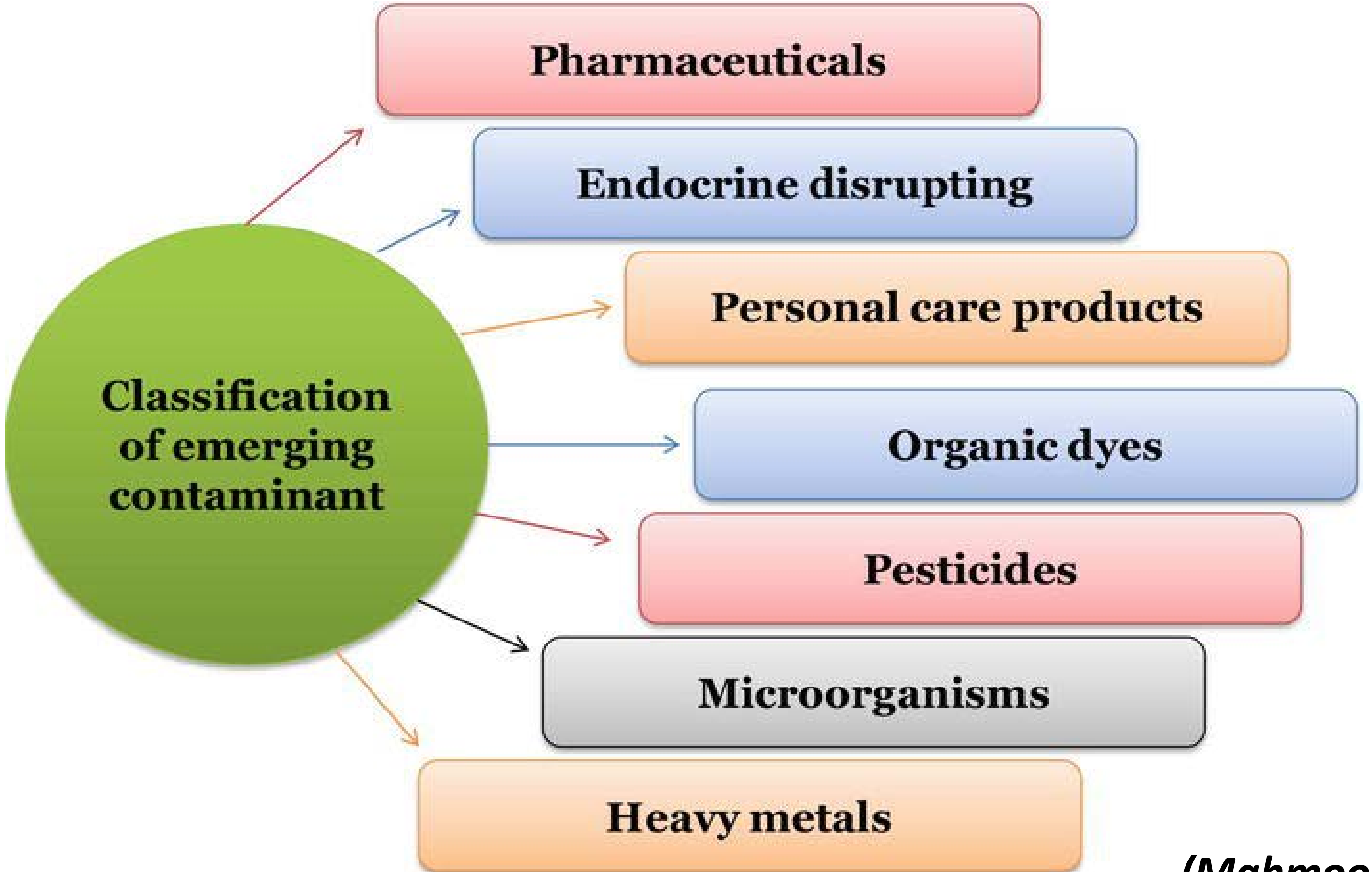
Advance analytical techniques in micropollutant detection and their perspective for environment

WHO has evaluated the health risks about ECs and concluded that these are generally very low. So, we have time to act appropriately

PREVENTIVE MEASURES – NOT A CRISIS



Chromatograpy-high Resolution Mass Spectrometery can re-style risk management in environment by using **non-target analysis** and the **omic approach**

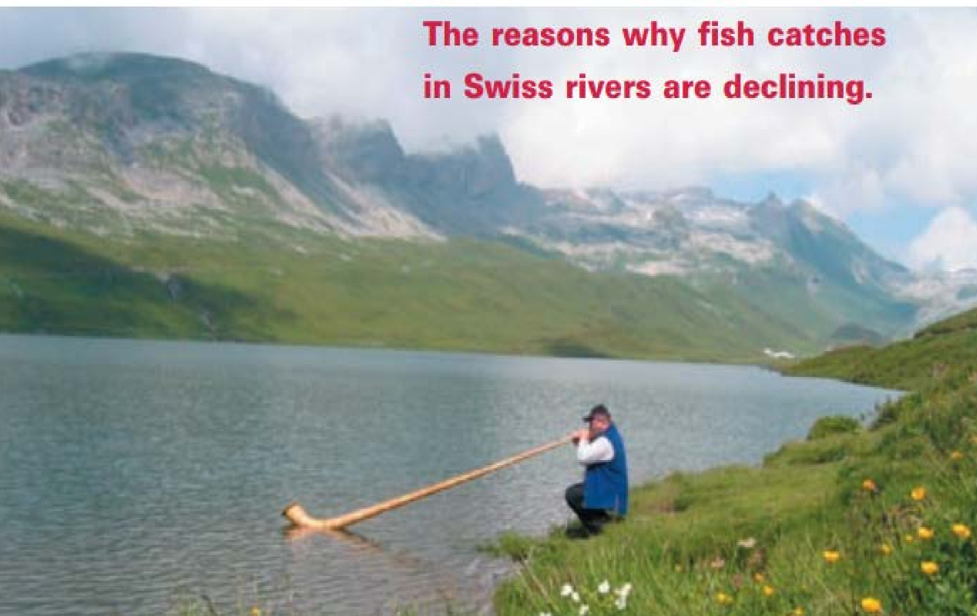


(Mahmood et al 2022)

Around 100000 chemicals are used in this world today
Over 800 chemicals are suspected and known Endocrine disrupting (EDCs)

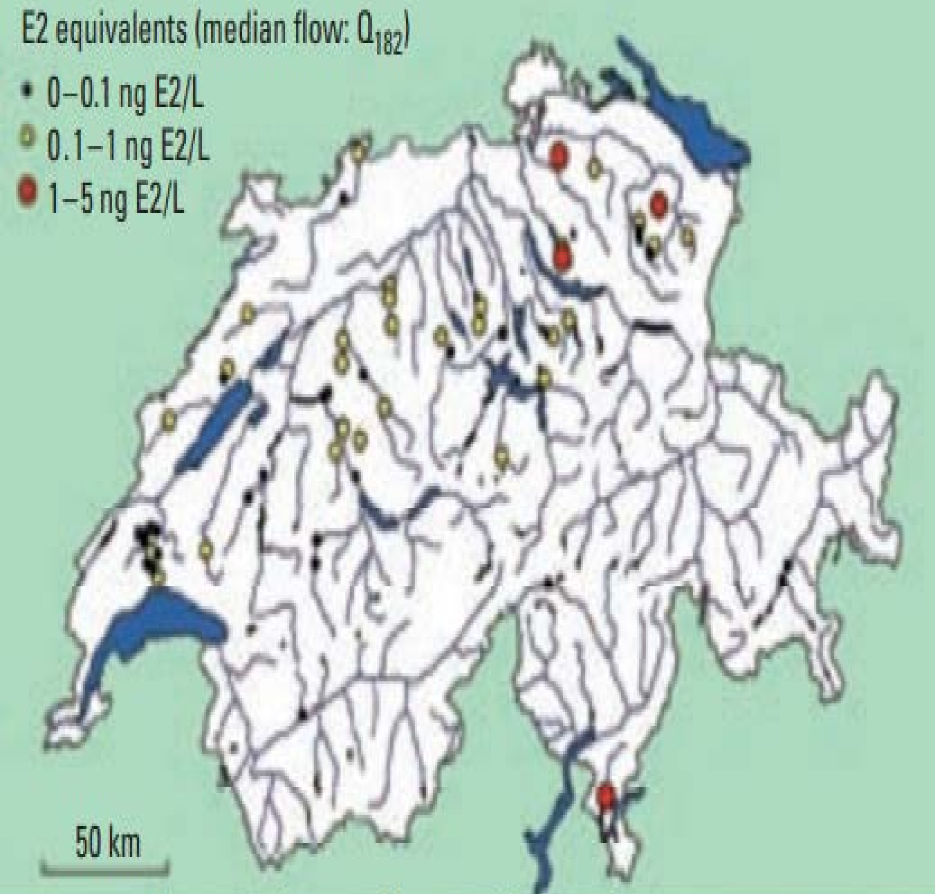
1. Adult fish are failing to reproduce,
2. Health and fitness of the fish are impaired.
3. **Chemical pollution (both nutrients and micropollutants),**
4. The poor morphological quality and longitudinal connectivity of rivers,
5. Insufficient food quality,

Where Have All *the* FISH Gone?

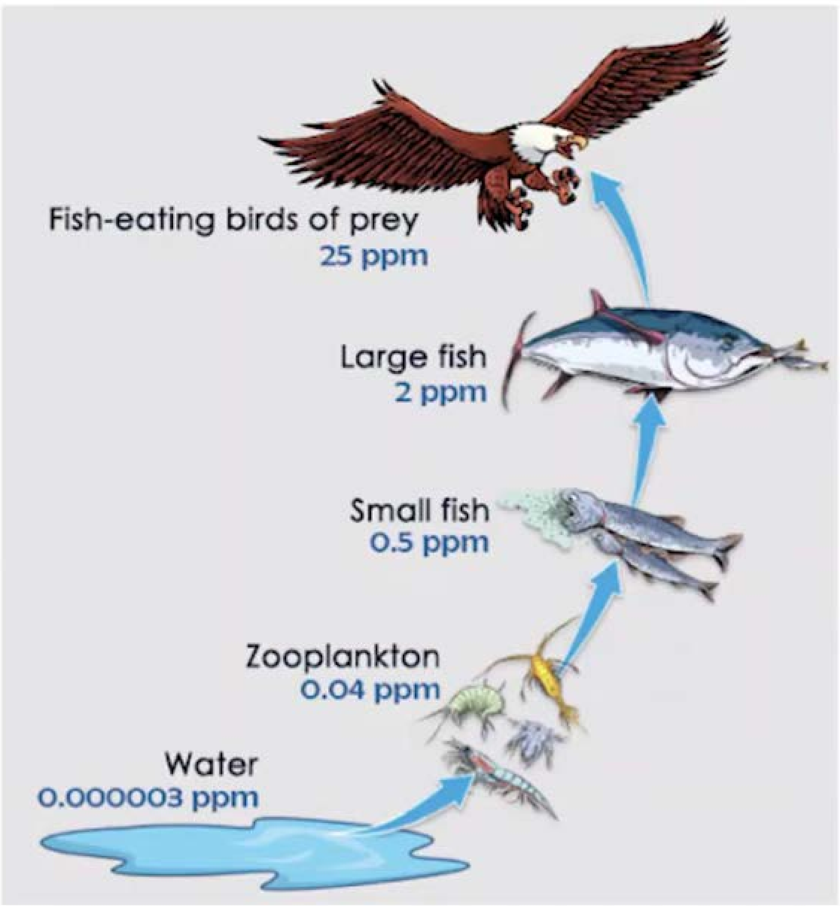


Estrogen disrupters escape from wastewater treatment plants

The levels of estrogenicity downstream of municipal wastewater treatment plants were calculated on the basis of the number of inhabitants in the catchment, elimination rates of estrogen in WWTPs, and median flows in the receiving waters. Q_{182} is the flow rate for at least 182 days/yr; E2 is 17-β-estradiol.



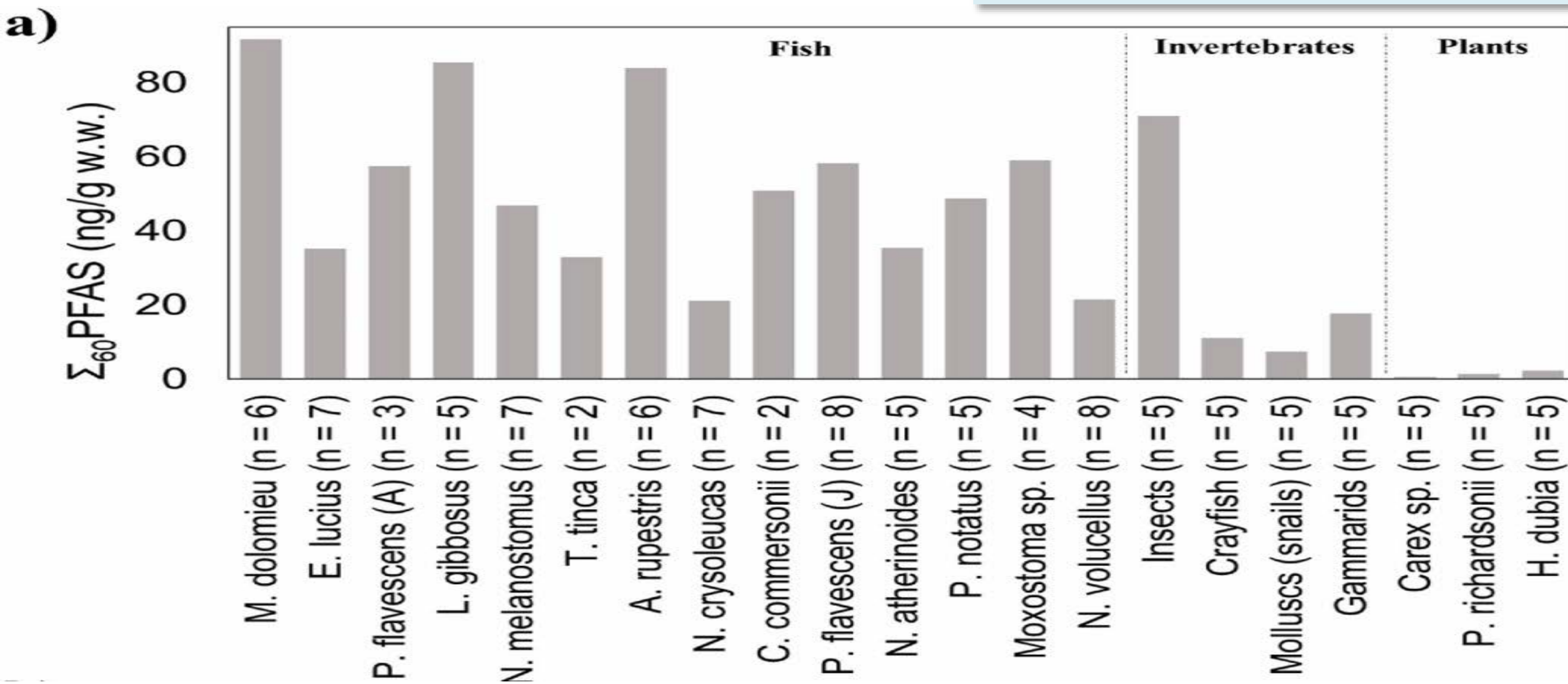
CECs can bioaccumulate and biomagnify



Bioaccumulation and trophic magnification of emerging and legacy per- and polyfluoroalkyl substances (PFAS) in a St. Lawrence River food web

Gabriel Munoz [a], Laurie Mercier [b], Sung Vo Duy [a], Jinxia Liu [c], Sébastien Sauvé [a], Magali Houde [b]

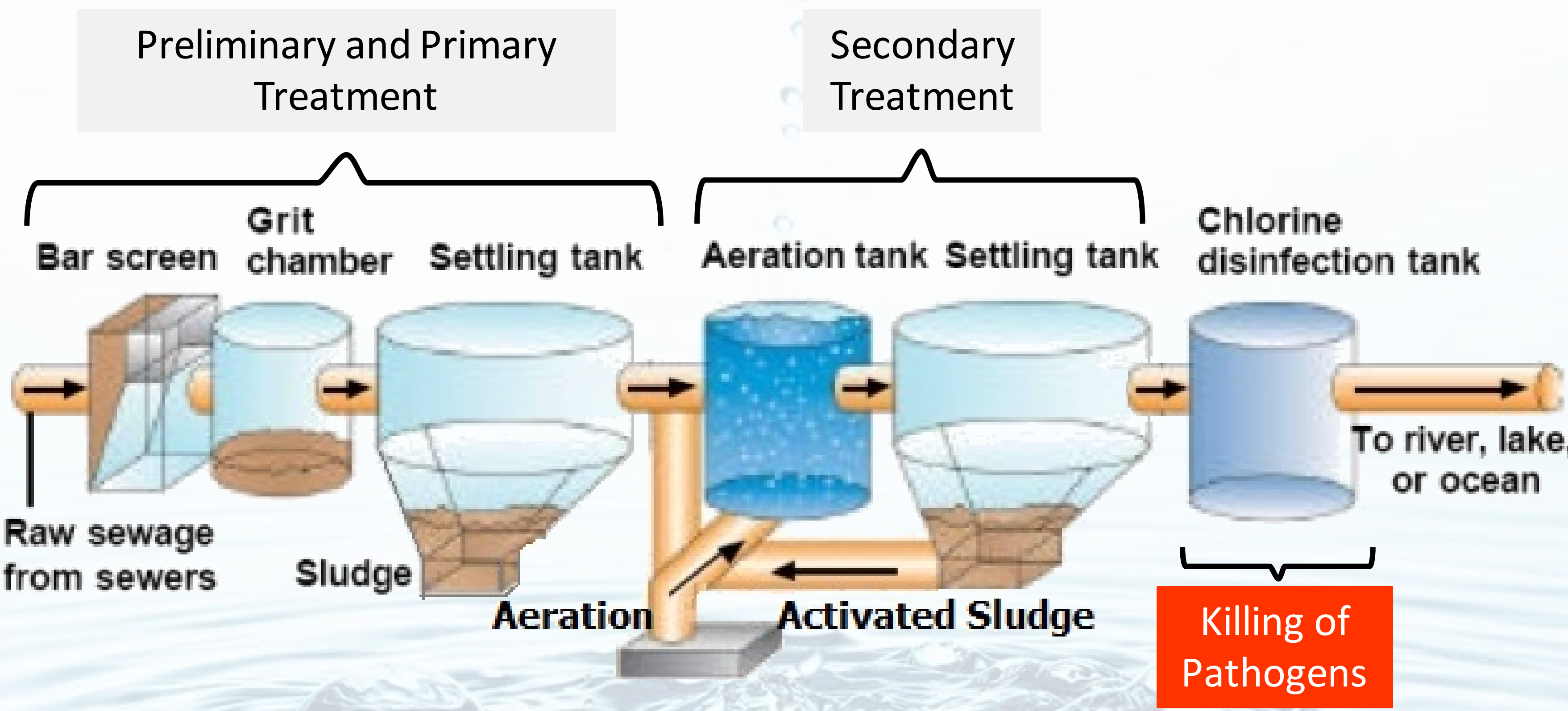
Show more



Conclusions

- PFAS found at high frequency and relative abundance in predators.
- Federal guidelines were frequently exceeded, indicating that PFOS may represent ecotoxicological risks to mammalian and avian consumers

Conventional Wastewater Treatment Stages

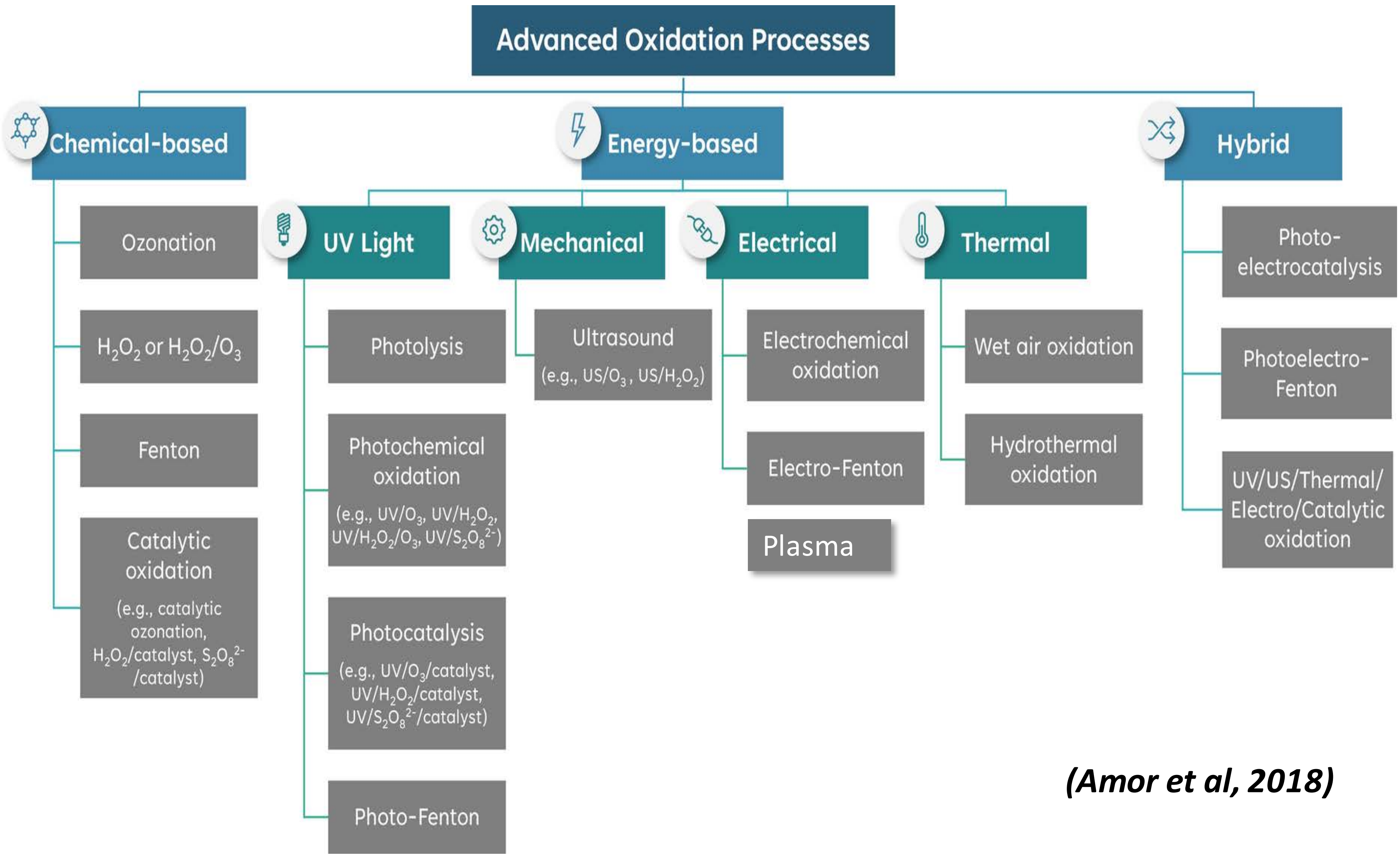


Wastewater and sewage: Many emerging contaminants, including pharmaceuticals and personal care products, can enter the environment through treated wastewater that is discharged into rivers and lakes.

Fate of Some common NSAIDs (nonsteroidal anti-inflammatory drugs) in conventional wastewater treatment systems

Drugs	Unit operations	Removal (%)	Region
Ibuprofen	AcS/phosphate removal	78-100	Aura, Tampere, Harjavalta (Finland)
	AcS/N/DeN/phosphate removal	92-99	Helsinki, Seinajoki, Turku (Finland)
	1^{O} settling, AcS, 2^{O}	60-70	Galicia (Spain)
	1^{O} Settling, AcS/N/DeN, 2^{O} settling	86	S. England
	1^{O} Settling, AcS	75	Rio de Janeiro (Brazil)
	AcS, ppt with $FeCl_3$	62-79	on Lake Geneva (W. Switzerland)
Diclofenac	Conventional WWTP	17	Berlin (Germany)
	AcS, P removal	23-60	Aura, Tampere, Harjavalta (Finland)
	AcS/N/DeN/phosphate removal	9-25	Helsinki, Seinajoki, Turku (Finland)
	1^{O} Settling, AcS	75	Rio de Janeiro (Brazil)
	AcS, disinfection	18	Baltimore (USA)
Naproxen	AcS/phosphate removal	55-98	Aura, Tampere, Harjavalta (Finland)
	AcS/N/DeN/phosphate removal	69-94	Helsinki, Seinajoki, Turku (Finland)
	1^{O} Settling, AcS	78	Rio de Janeiro (Brazil)
	AcS/N/DeN, sand filtration	50-80	Kloten/Opfikon (Switzerland)
Ketoprofen	AcS/phosphate removal	51-100	Aura, Tampere, Harjavalta (Finland)
	AcS/N/DeN/phosphate removal	63-98	Helsinki, Seinajoki, Turku (Finland)
	AcS, ppt with $FeCl_3$	15-72	on Lake Geneva (W. Switzerland)
	1^{O} Settling, AcS	69	Rio de Janeiro (Brazil)
Mefenamic acid	1^{O} Settling, AcS/N/DeN, 2^{O} settling	91	S. England
	1^{O} Settling, AcS, ppt with FeCl3, 2^{O} settling	28-74	on Lake Geneva (W. Switzerland)
	AcS, ppt with $FeCl_3$	19-69	on Lake Geneva (W. Switzerland)

Chronic exposure to ibuprofen at 0.1 - 1 µg/L affects several endpoints related to the reproduction of the fish *(Han et al, 2010)*.



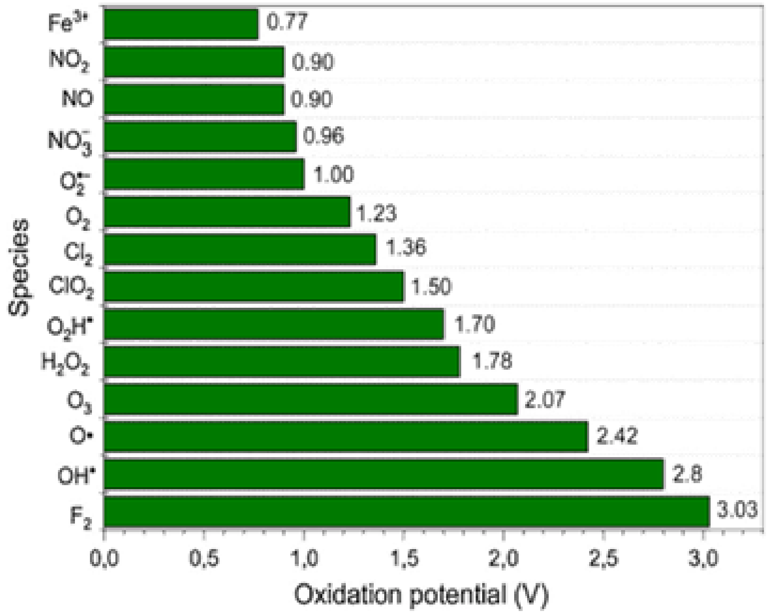
(Amor et al, 2018)

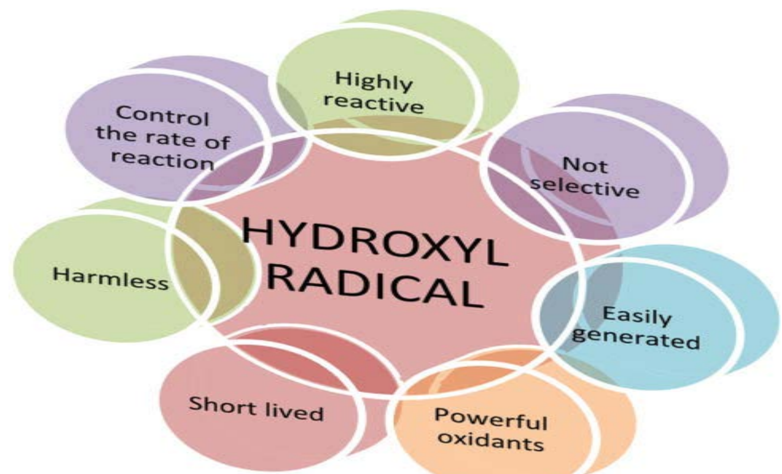
The Hyroxyl Radical (˙OH)

- ˙OH can indiscriminately degrade numerous organic pollutants.

- ˙OH have a very short lifetime, they are only in situ produced during application through different methods, including:

  1. Peroxone (H_2O_2 and O_3),
  2. irradiation (such as ultraviolet light or ultrasound)
  3. catalysts (such as Fenton reaction with Fe^{2+})
  4. Atmospheric plasma





(Ahmed et al, 2021) **Some features of hydroxyl radical**

Atmospheric non-thermal plasma

*When plasma interacts with water at the **plasma-liquid interface**, it generates various highly reactive species which interact with contaminants and ultimately mineralize it.*

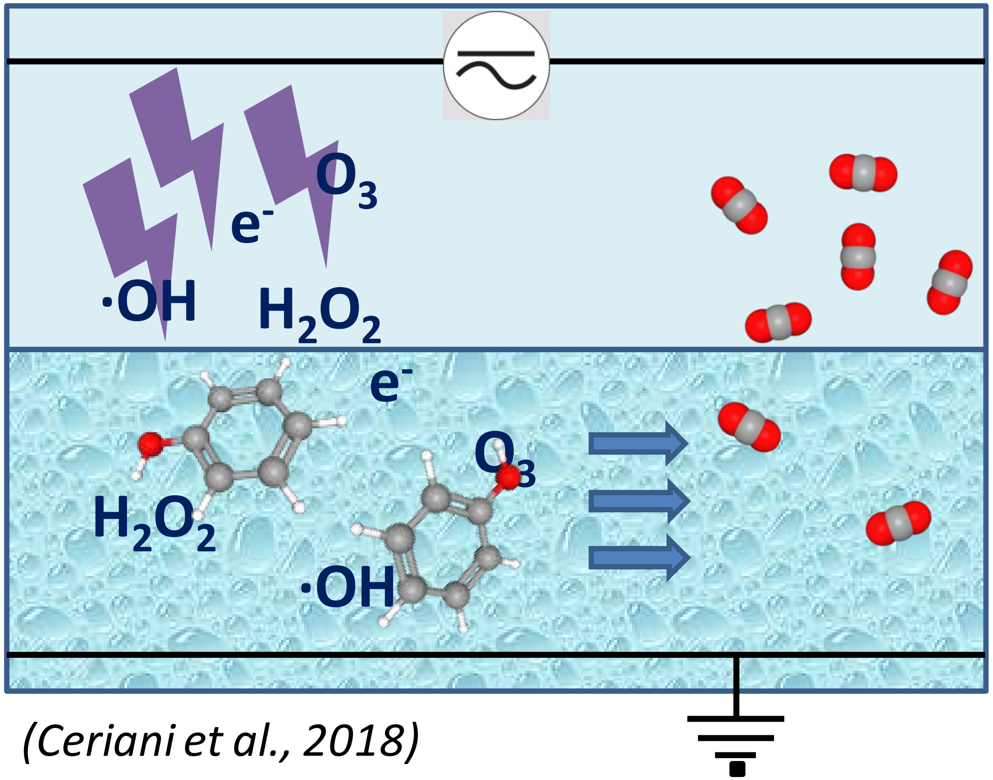
REACTIVE SPECIES

$$O_2 + e^- \rightarrow 2O^{\cdot} + e^-$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$H_2O + e^- \rightarrow \cdot H + \cdot OH + e^-$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2$$



(Ceriani et al., 2018)

AP: advantages and challenges

- ✓ No need for heat, vacuum or pressure
- ✓ In situ generation of reactive species (e^-, ions, $^{\bullet}OH$, $^{\bullet}H$, H_2O_2, ..) without addition of chemicals
- ✓ No need for added chemicals, catalysts or special materials
- ✓ Only consumable is energy: it can be powered by renewable energy sources

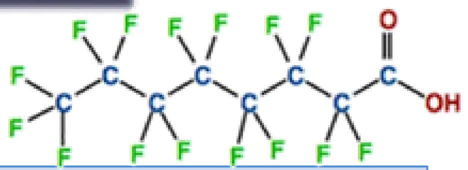
GREEN TECHNOLOGY

- ✓ Simple and robust apparatus, with fast switch on/off procedures
- ✓ High versatility of application
- ✓ High efficacy and efficiency, also with most refractory pollutants like PFAS, with > 99% degradation

- ✓ Energy costs
- ✓ Scaling-up

The Contaminant(s)

PFOA

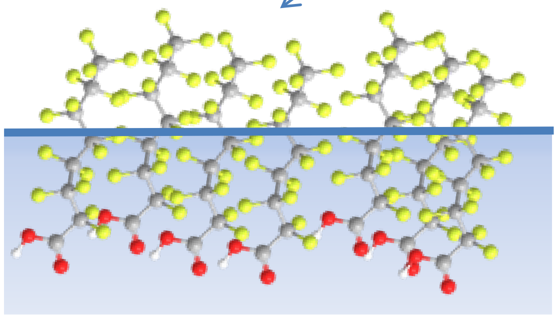


Persistent organic pollutant

PFOA= Perfluorooctanoic acid

- **Xenobiotic compound** with wide industrial application
- highly soluble in water
- non-volatile
- Chemically inert
- surfactant properties

5-6 Carbon protruding from Liquid surface



Why to Treat PFOA ?

Health effects

- Known endocrine disruptor and expected carcinogen
- Mean half life in human body between 2 to 6 years.
- 20% increase in average mortality in PFOA contaminated area in Veneto Region

Pathologies In PFOA	% Increase due to PFOA exposure
Diabetes	21% men and 48% women
Cerebrovascular diseases	34% men and 29% women
Infarction	22% men and 24% women
Alzheimer's disease	33% men and 35% women
Mortality due to breast Cancer	11%

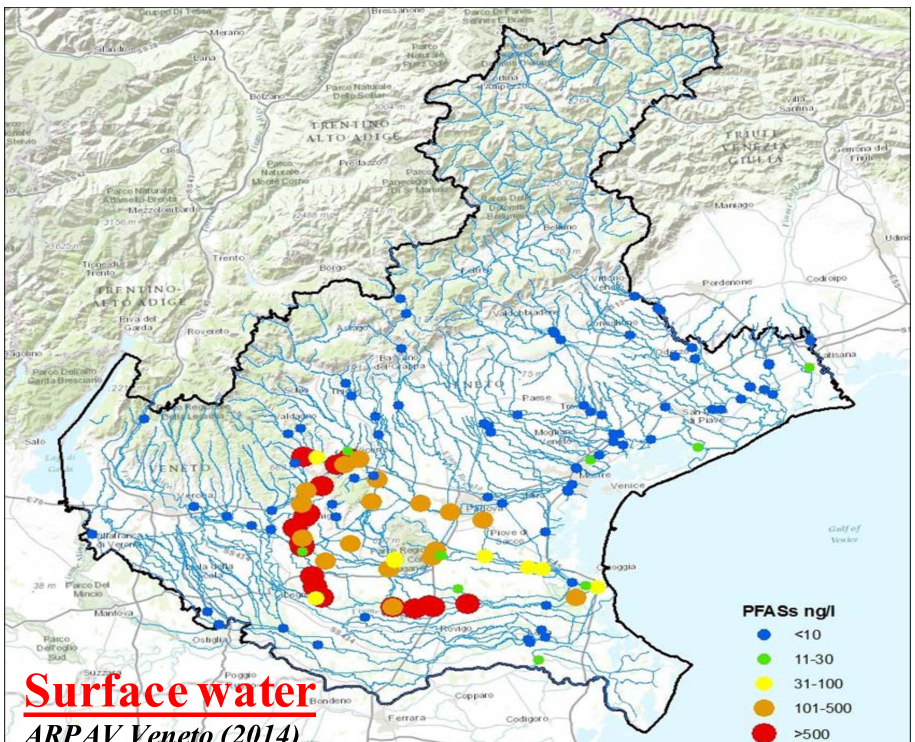
(Mastrantonio et al., 2017)

Contamination of PFASs in Veneto - Italy

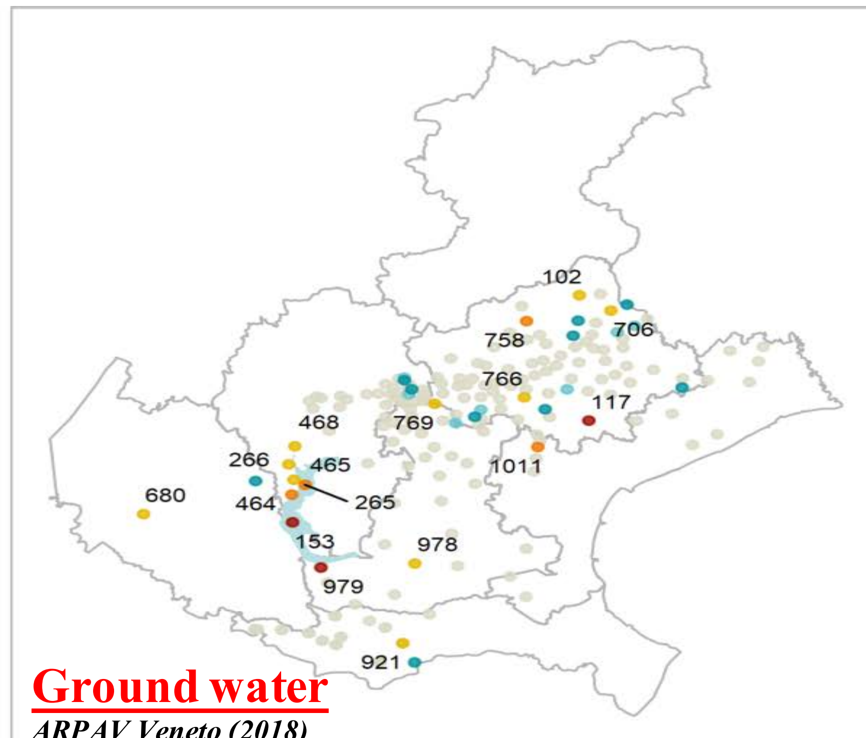
Two main ways of propagation:

- **Surface waters > 500 ng/L**
- **Groundwater > 1000 ng/L**

New EPA's PFOA limit 4 ppt



Surface water
ARPAV Veneto (2014)

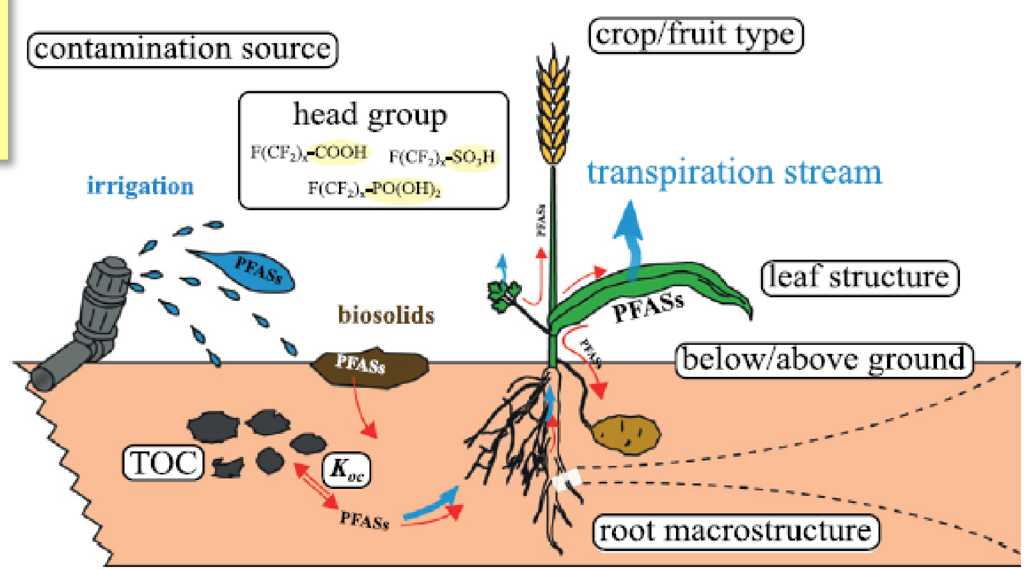


Ground water
ARPAV Veneto (2018)

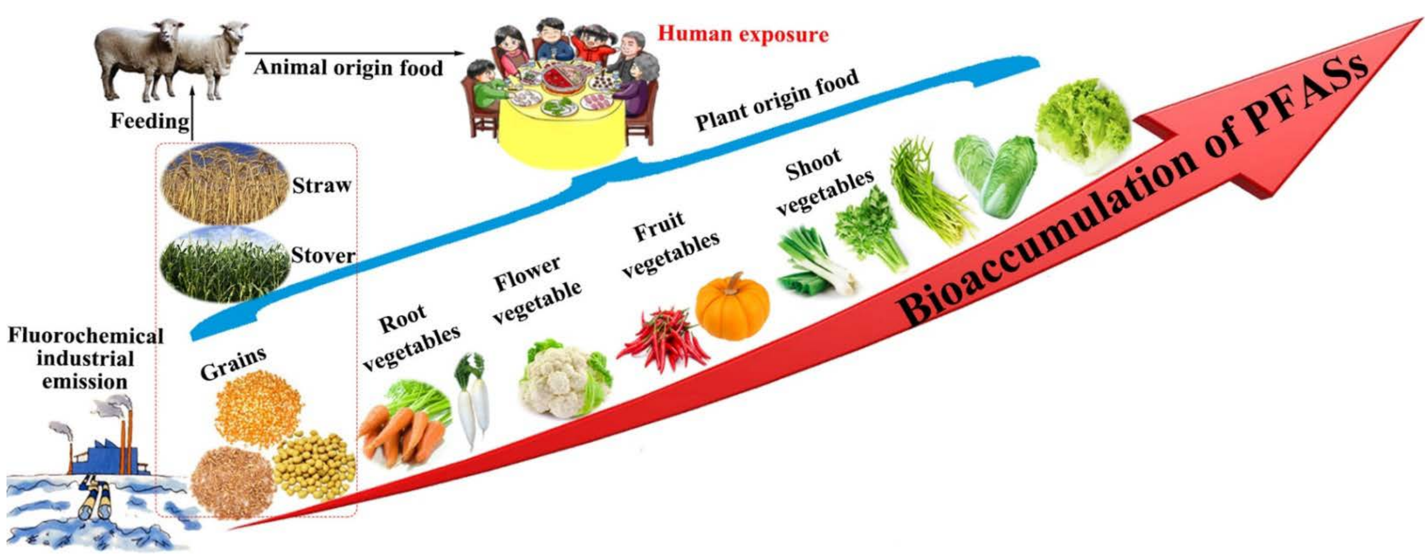
PFAS accumulation in the Food Chain

The main factors affecting the translocation of PFAS

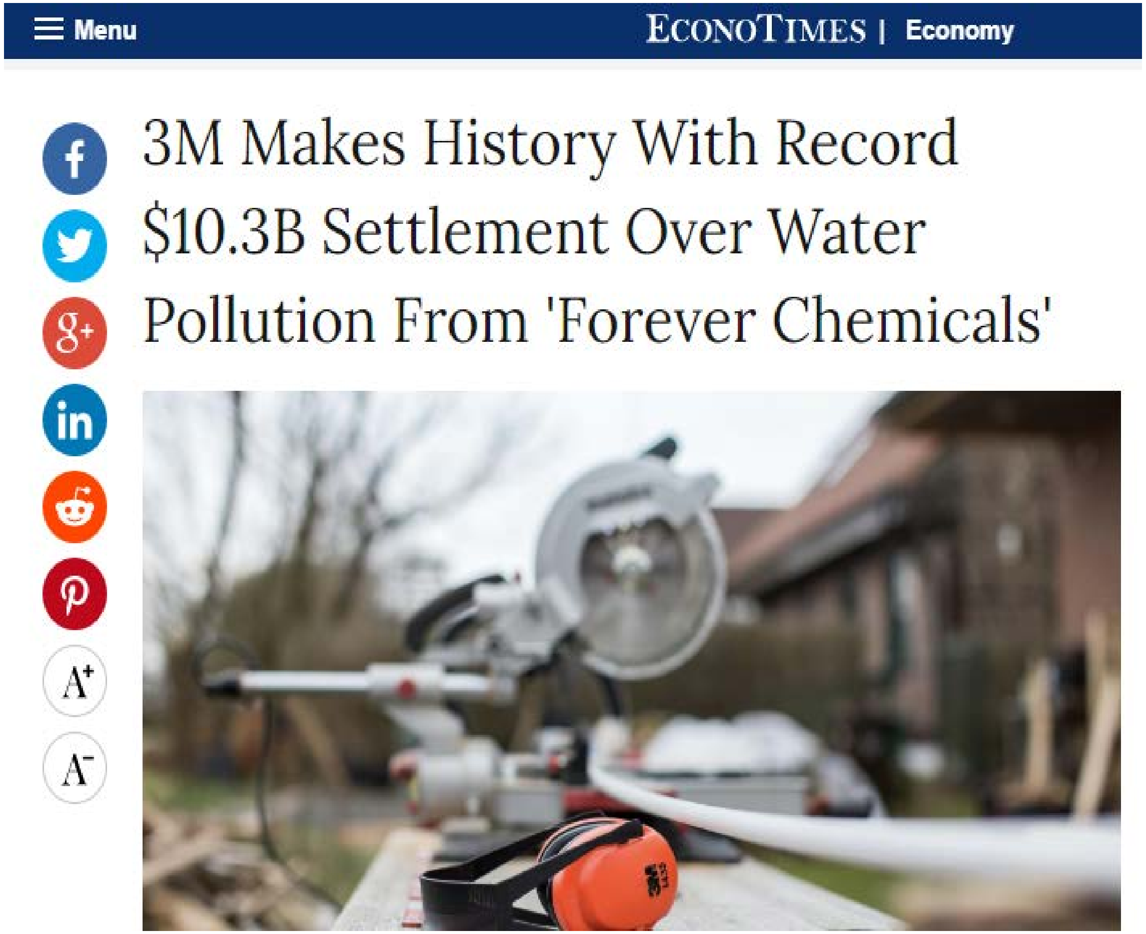
1. Protein content of the plant (positively correlated with accumulation) Wen et al. (2016)
2. Length of the chain of PFASs (the longer-chained compounds has lower accumulation rates)



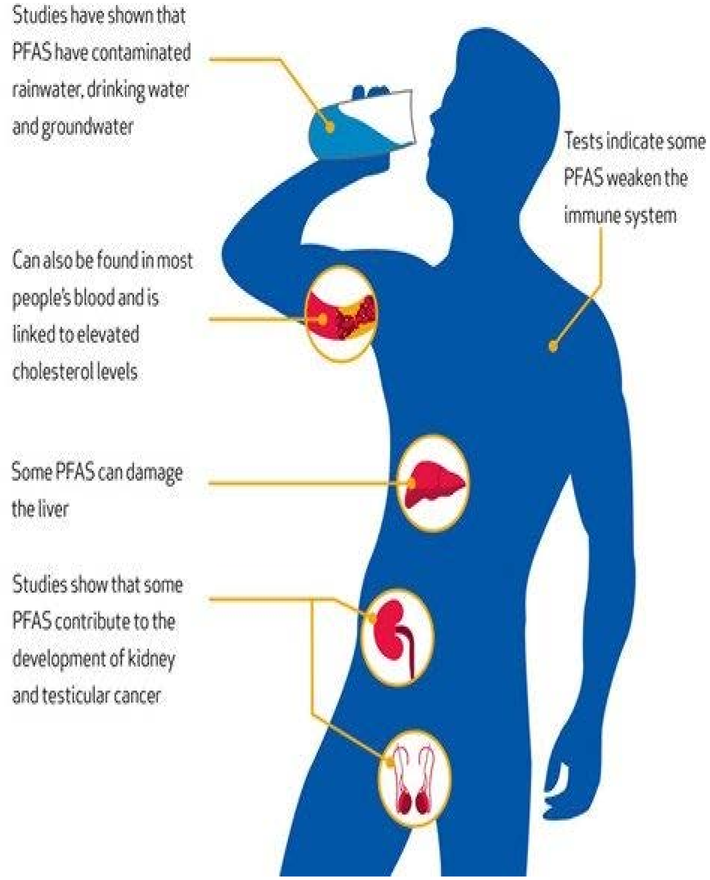
Lesmeister et al. (2021)



Liu et al. (2019)


Menu
EconoTimes | Economy

3M Makes History With Record $10.3B Settlement Over Water Pollution From 'Forever Chemicals'



Why Use Plasma?

1. **Most** common treatment technologies for PFOA removal:
   - ✓ Activated carbon
   - ✓ Ion-exchange

However,
- short breakthrough times in case of Ion-exchange
- Disposal of waste saturated adsorbent and concentrated brine solution (from ion-exchange resin regeneration),

2. **More energy efficient** in comparison to other advanced oxidation processes (AOPs) in PFOA removal (Stratton et al., 2017)
   1. **8 times** more efficient than **activated persulfate,**
   2. **4 times** more efficient than **electrochemical treatment,**
   3. **over 57 times** more efficient than **sonolysis.**

3. **Insitu generation** of reactive species without chemicals (OH, H, e-, H_2O_2, etc.), Especially
   - ✓ **aqueous electrons and free electrons**
   - ✓ **major contributor of PFOA degradation**

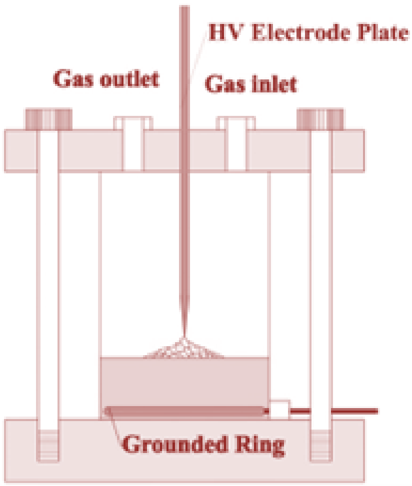
Comparison of scaled-up PFAS destruction technologies

	Electrochemical Oxidation	Plasma Treatment	Sonolysis
Technology Readiness Level (0-9)	6–8	**7–9**	5–7
Pre-treatment requirement	no, but advantageous	no	no
Requirement for chemical	no	no	no
Energy per order of magnitude (EEO)	93 kWh/m3	11 kWh/m3	230-1300 kWh/m3
Ability to reach ng/L PFAS limits	yes	yes	yes
Effective for waters with high or low salinity	more efficient at higher salinities ~ tens of g/L	More efficient at lower salinities	More efficient at moderately high salinities
Effective for waters with high organic load or pH	yes	yes	yes

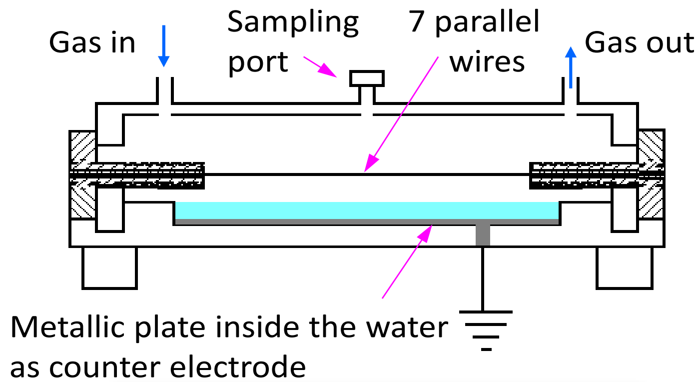
(Blotevogel et al, 2023)

UNIVERSITÀ DEGLI STUDI DI PADOVA

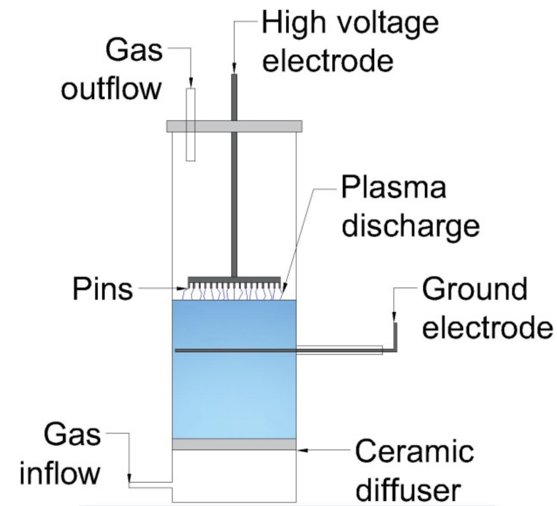
Department of Chemical Sciences (UNIPD) & Department of Environmental Engineering (NEDUET)



Liquid-contact discharge

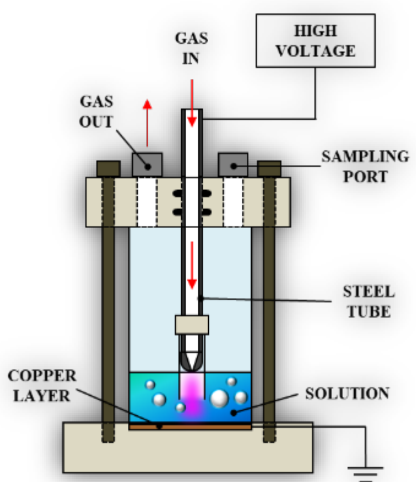


7-wires corona discharge

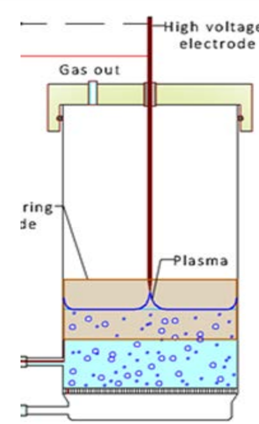


Multipin liquid-contact discharge

Plasma Reactors and Important Results



Plasma in gas bubbles

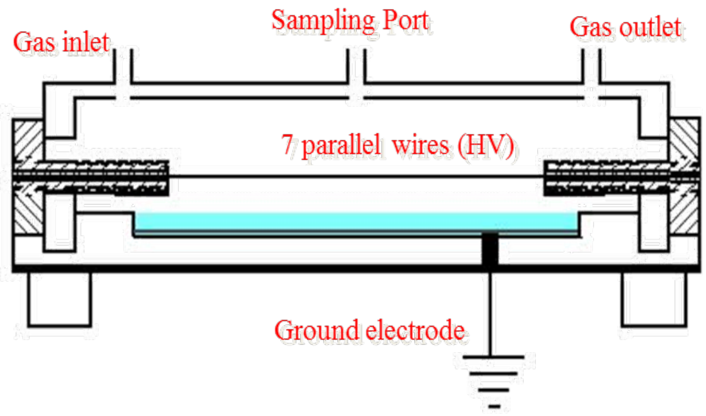


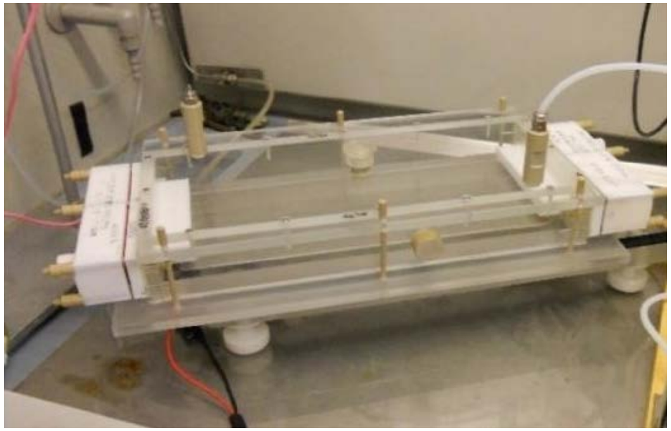
Radial Plasma discharge

Università degli Studi di Padova

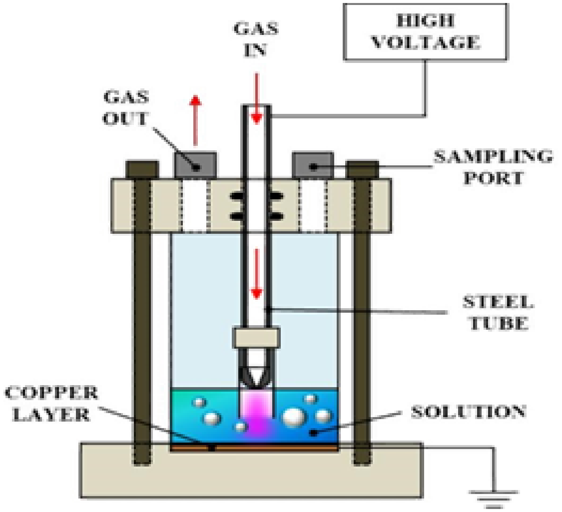
Department of Chemical Sciences (UNIPD) & Department of Environmental Engineering (NEDUET)

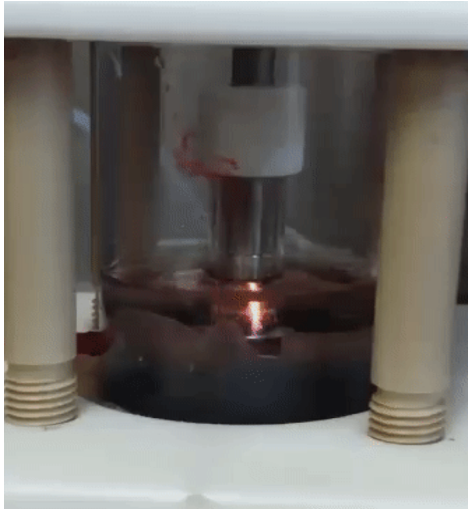
Wire to plate corona Discharge



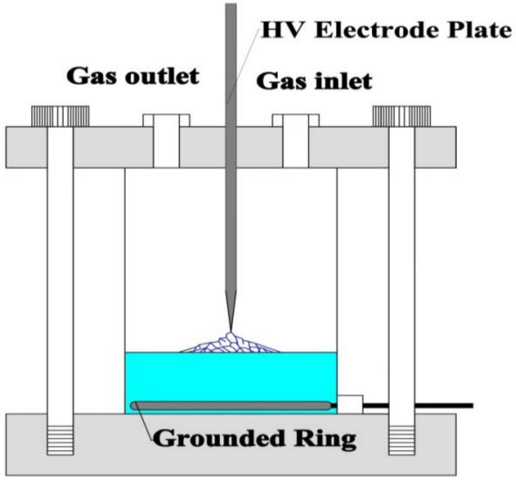


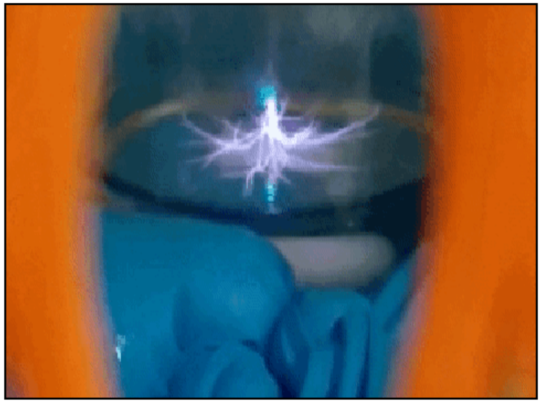
Plasma discharge in a gas bubble inside the solution





Self-pulsing discharge in contact with liquid



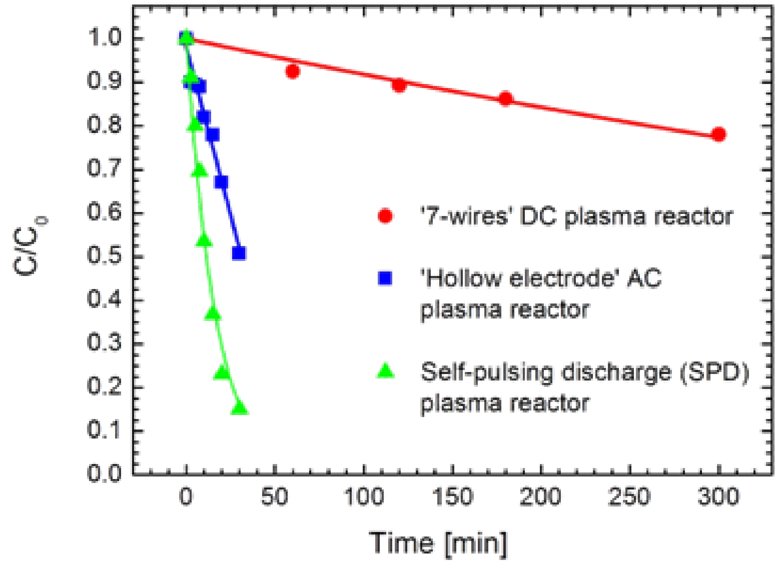


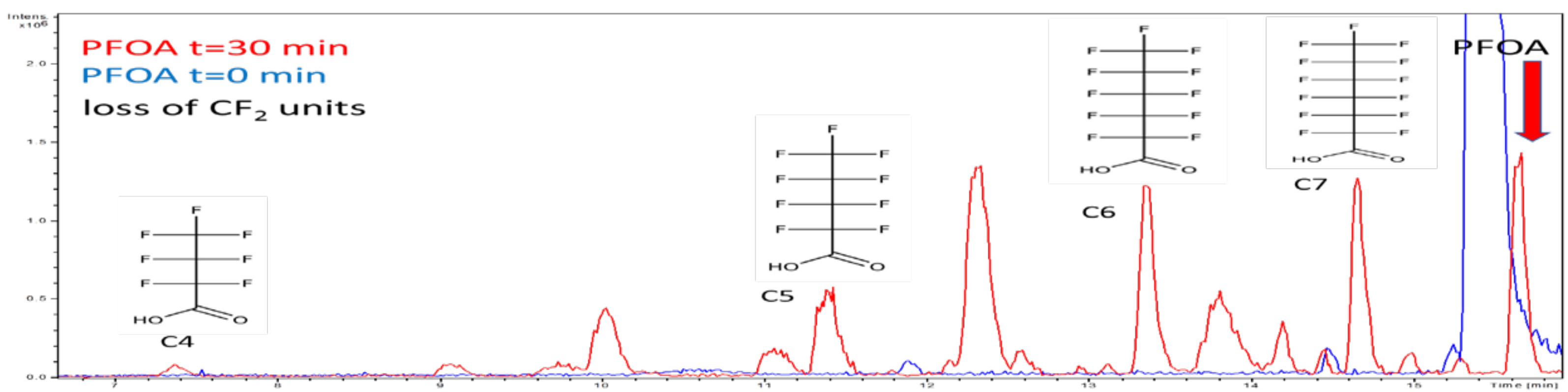
Università degli Studi di Padova

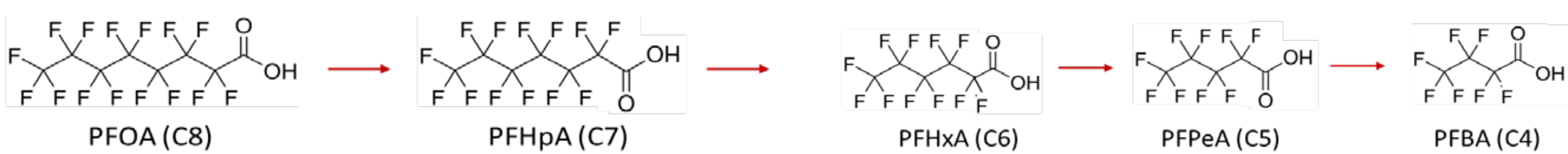
Department of Chemical Sciences (UNIPD) & Department of Environmental Engineering (NEDUET)

Performance Comparison

1. Self-pulsing discharge was more efficient than the other two discharge types.
2. corona discharge and plasma in gas bubbles were efficient in degrading other organic compounds like phenol they showed limited performance in degrading PFOA.
3. PFOA degradation produce short chain homologues through chain reduction

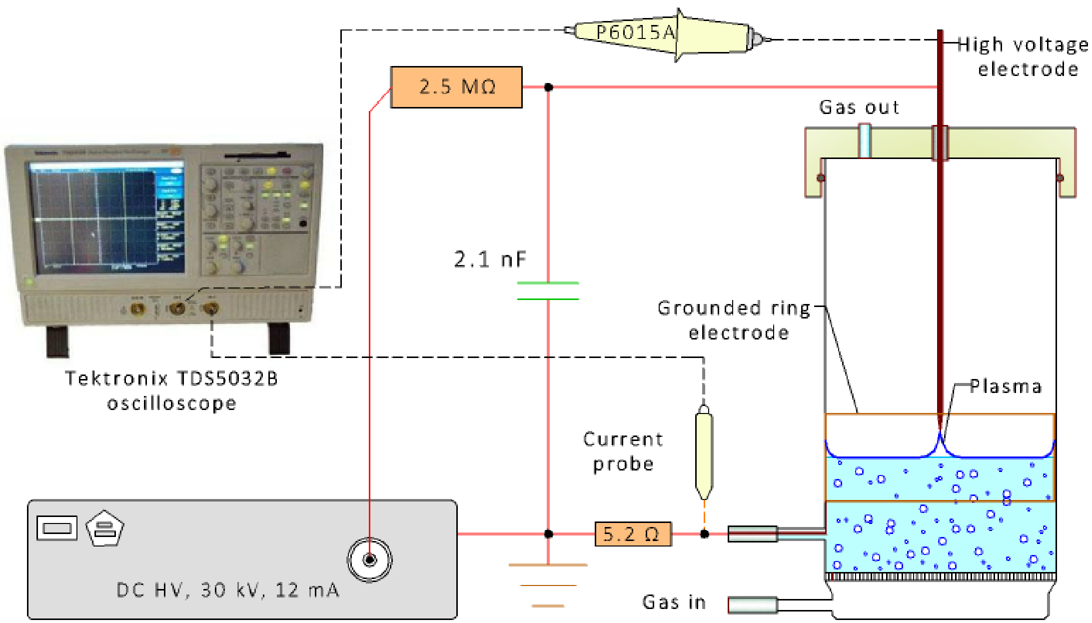






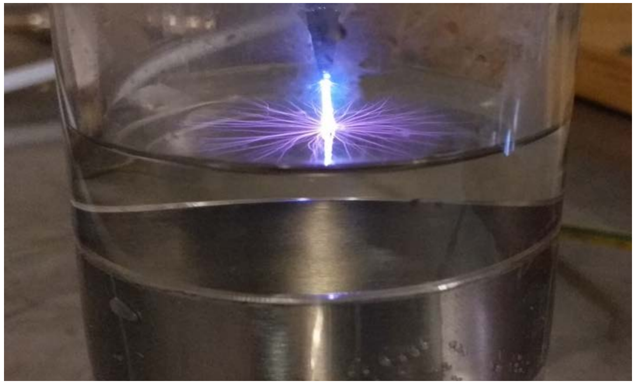
RAdial Plasma discharge (RAP)

- HV stainless steel electrode 6 mm above solution
- Grounded ring electrode at the **gas-liquid interface**
- Argon bubbling = **100 mL/min**
- Treated Volume = **30 mL**
- Input Power = **4 W**



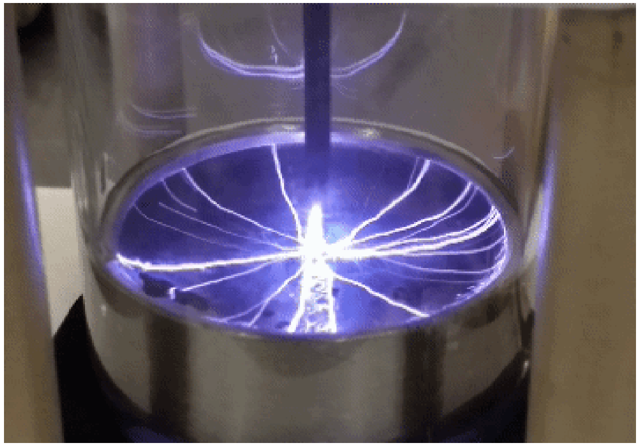
SPD Discharge

Submerged ground electrode



RAP Discharge

Ground electrode at the gas-liquid interface



Saleem et al. (2022)

UNIVERSITÀ DEGLI STUDI DI PADOVA

Department of Chemical Sciences (UNIPD) & Department of Environmental Engineering (NEDUET)

Important Results

- First order decay constant was inversely related to the initial PFOA concentration.
- For 41.4 µg/L, kinetics was even faster and by-products were < LC-ESI/MS detection threshold (0.41 µg/L, 10^{-9} M) in < 2.5 min
- Upto 76% mineralization
- 45% and 85% TOC removal after 30 and 60 min for 4.14 mg/L PFOA solution.

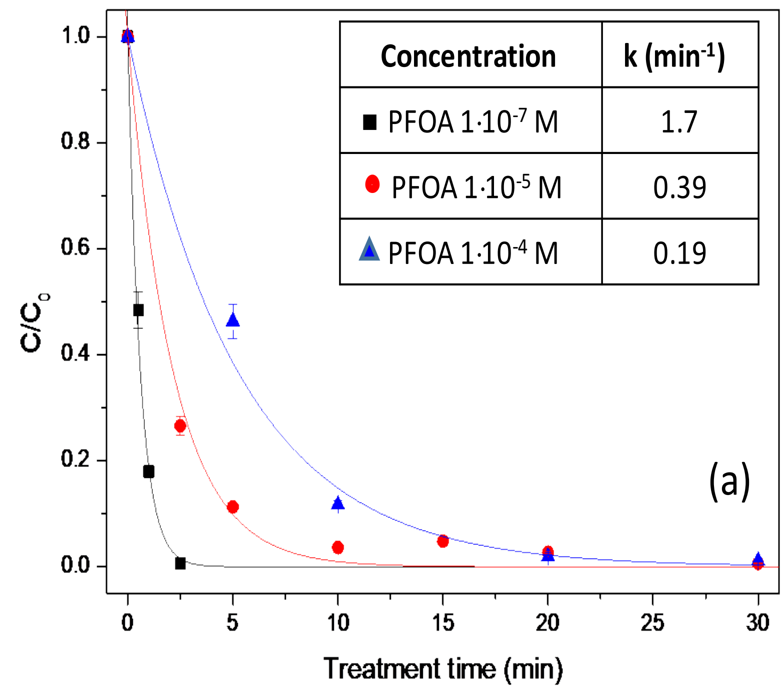


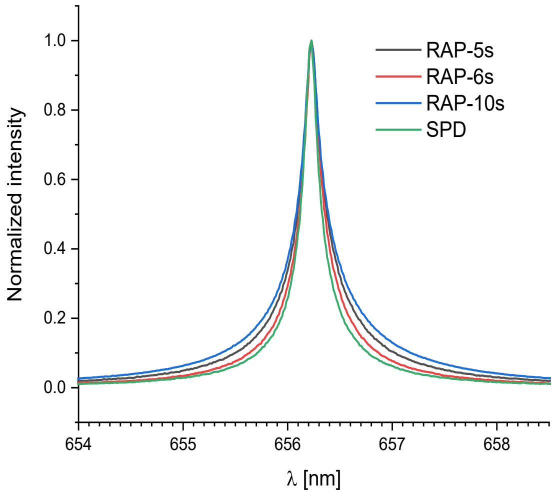
Table 1 RAP's observed k, G_{50} and EE/O values at various PFOA concentrations at 4 W

Volume (mL)	Concentrations	% Degradation	k (min^{-1})	G_{50} (mg/kWh)	EE/O (kWh/m^3)
30	41.4 mg/L, ($1 \cdot 10^{-4}$ M)	98.9% in 30 min	0.19	2364.6	13.8
	4.14 mg/L, ($1 \cdot 10^{-5}$ M)	99.3% in 30 min	0.39	527	6.0
	41.4 µg/L, ($1 \cdot 10^{-7}$ M)	>99% in 2.5 min	1.7	22.5	3.9
100	4.14 mg/L, ($1 \cdot 10^{-5}$ M)	>99% in 15 min	0.46	2070.4	1.02

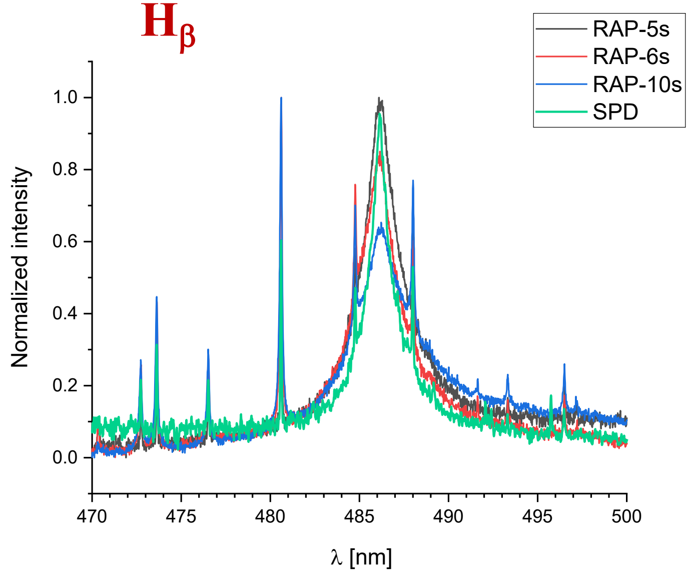
Saleem et al. (2022)

OES measurments and electron densities

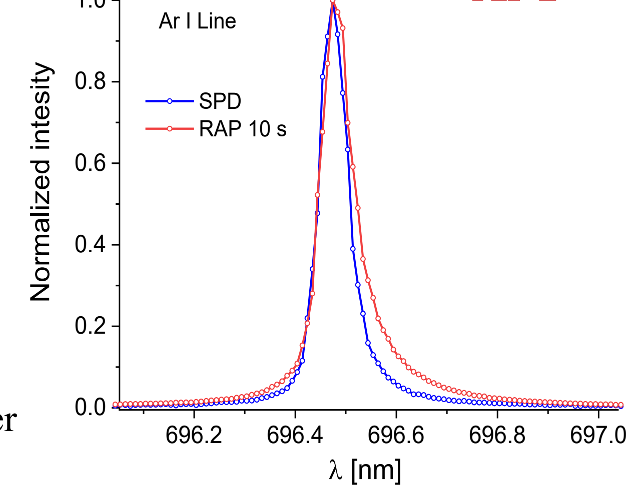
H_α



H_β



Ar I



Normalized H_α and H_β emission for SPD and RAP reactors.

- The line profiles are wider for all three RAP recordings which indicates higher electron density in RAP discharge compared to SPD.
- Higher Ar ion emissions for RAP compared to SPD.

	RAP	SPD
n_e [cm^{-3}] Low density component	$8.6 \cdot 10^{16}$	$5.5 \cdot 10^{16}$
n_e [cm^{-3}] High density component	$6.9 \cdot 10^{15}$	$4.7 \cdot 10^{15}$

Comparison of the Ar I 696 nm line profiles for RAP and SPD reactors.

The recorded line is wider for the RAP reactor, which also confirms higher electron density.

Mass Balance

In terms of:

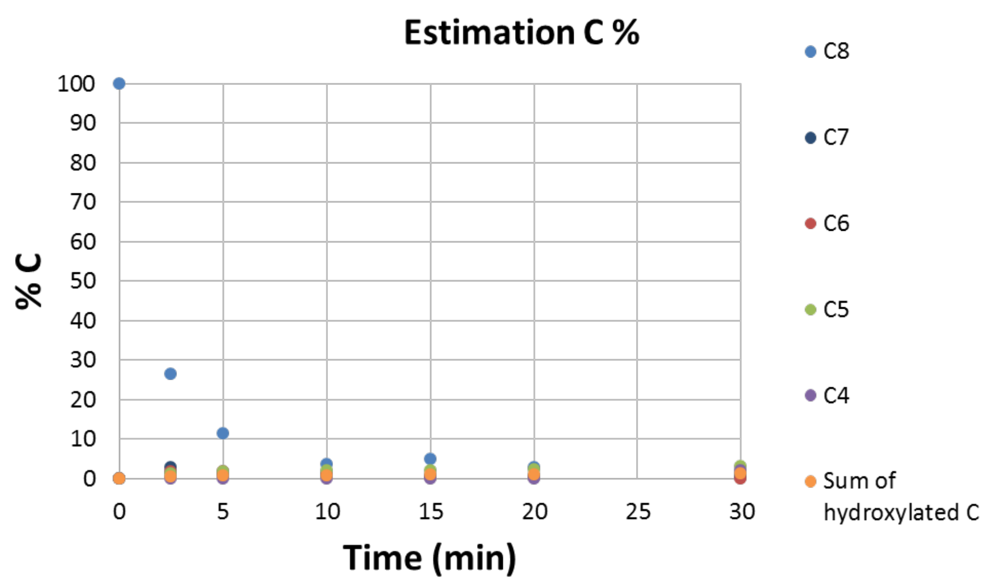
1. **Residual PFOA and byproducts:** accounts for less than 10% of the carbon initially present as PFOA.

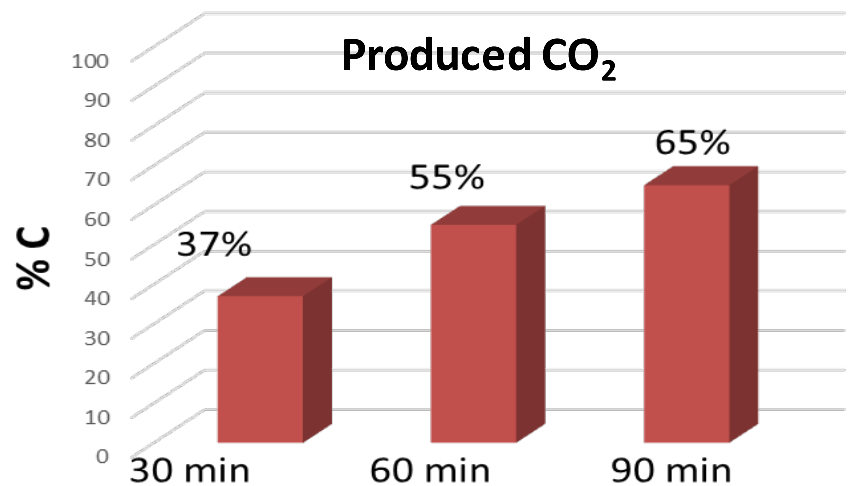
2. **Dissolved Fluoride:** 58.5 % with respect to the initial total fluoro contained in PFOA

3. **Produced CO_2:** was measured by GC-TCD recirculating Ar gas in a sampling bag during the treatment

4. **Volatile by products ?**

1. **Undetected byproducts?**

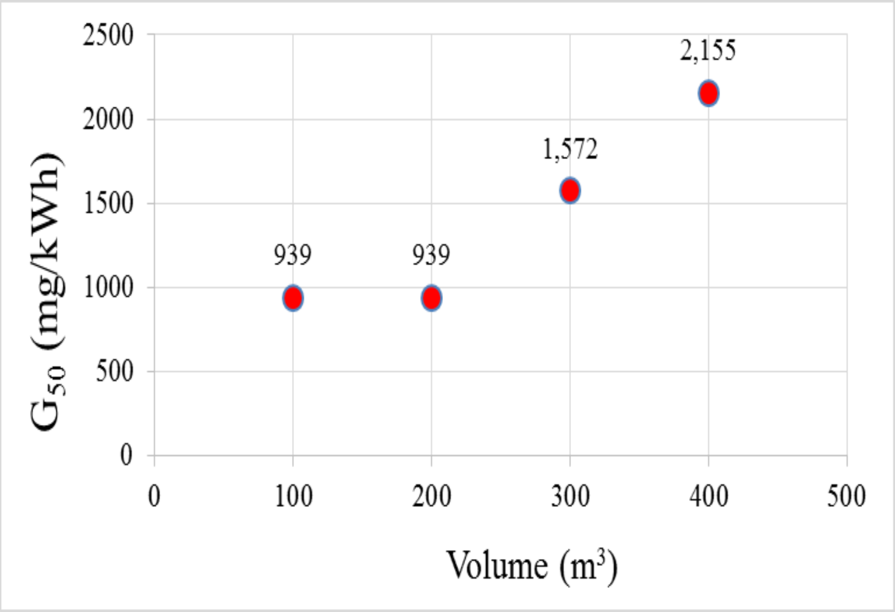




Effect of treated volume on energy efficiency

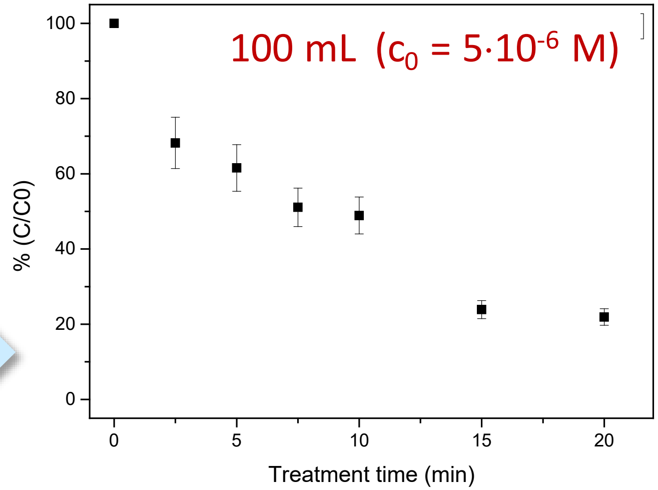
- For 400 mL solution volume
  - Highest G_{50} = **2155 mg/kWh**
- Energy efficiencies can further be improved for higher treated volumes

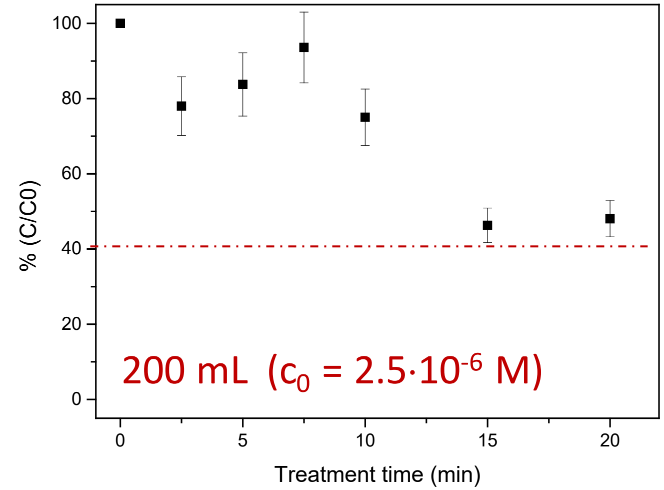
- PFOA = **4.14 mg/L (10^{-5} M)**
- Argon = **200 mL/min**
- Volume = **100-400 mL**
- Power = **4 W**

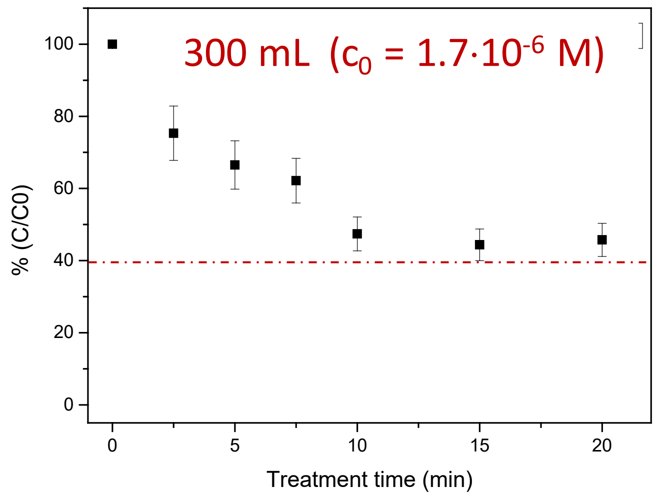


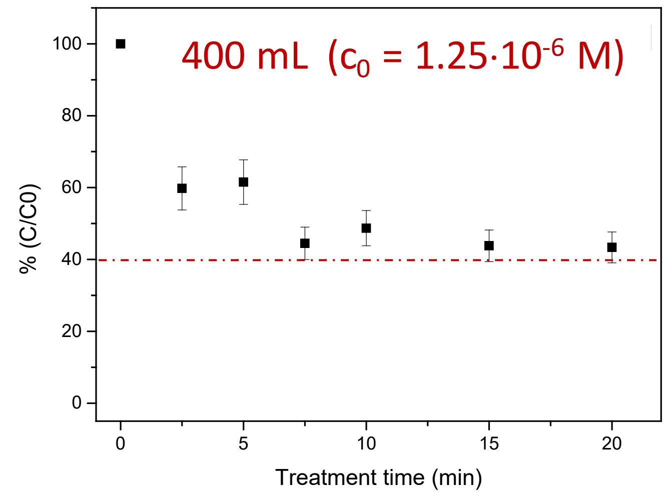
Effect of bubbling- treating same mass of PFOA with different volumes

NO bubbling



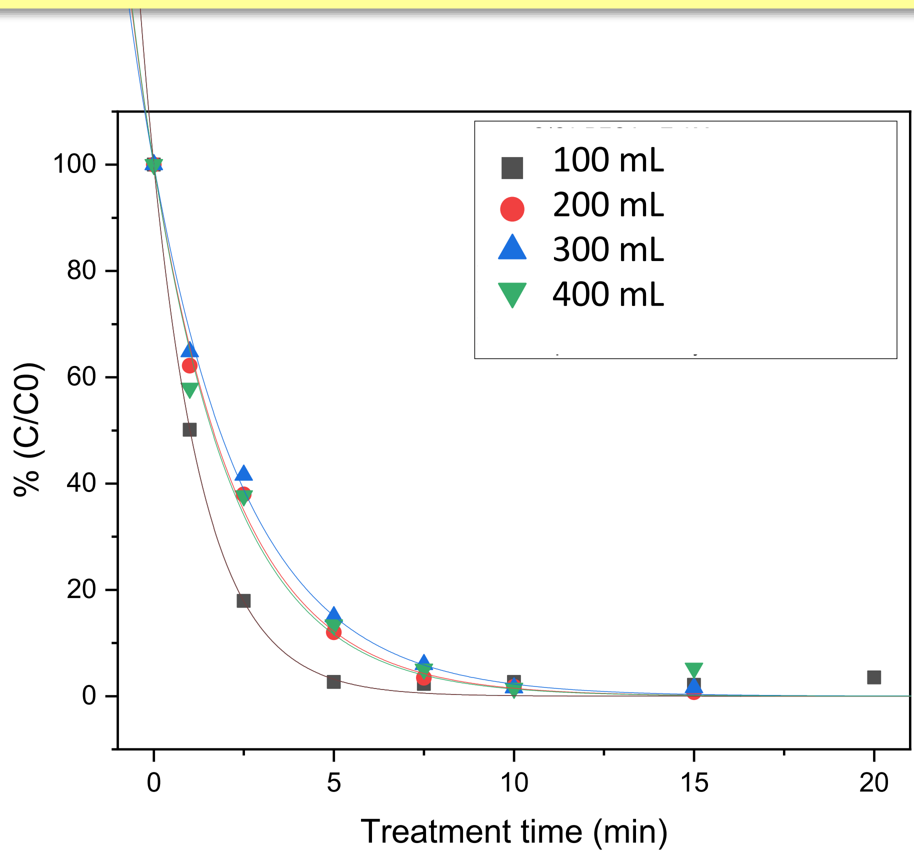






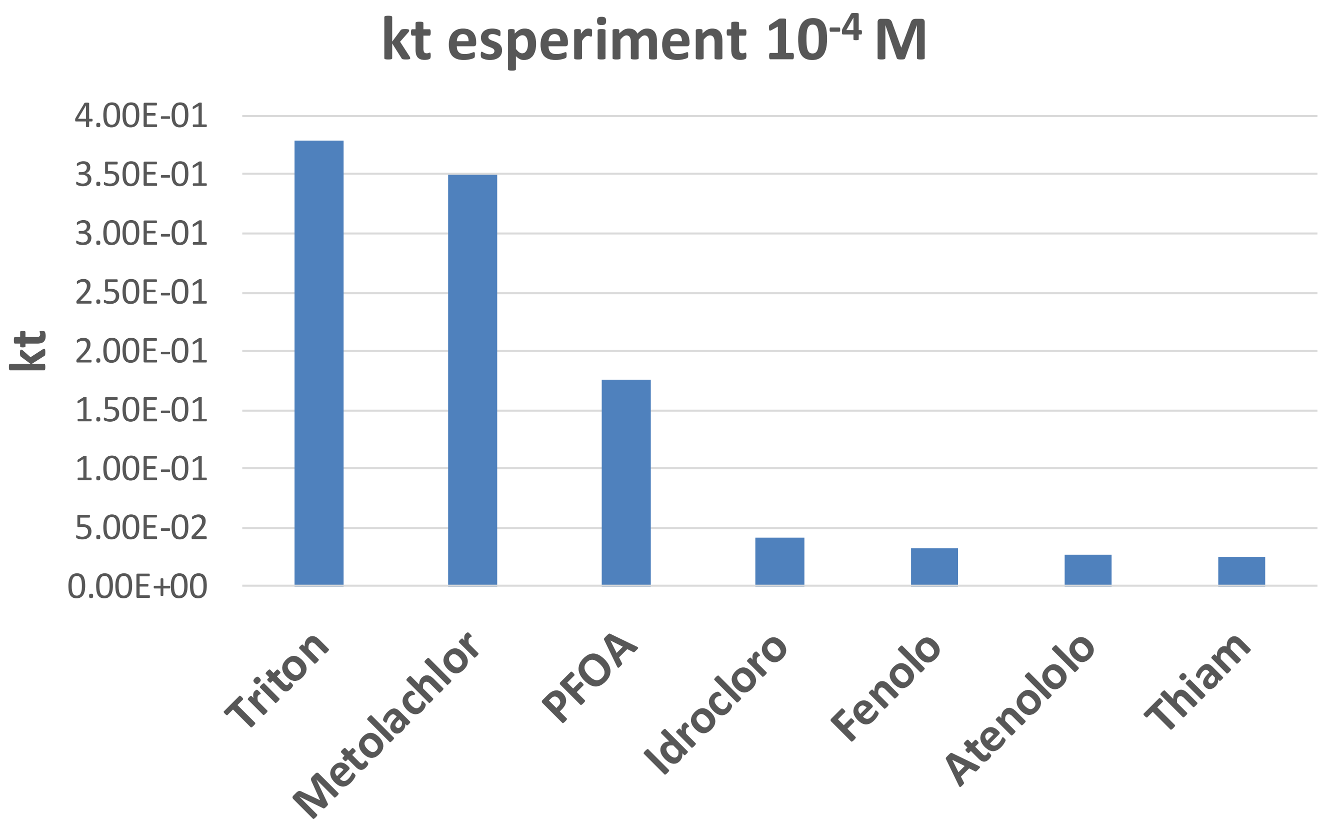
Effect of bubbling- treating same mass of PFOA with different volumes

bubbling



Bubbling is very effective in moving PFOA towards the plasma-liquid interface

Performance of RAP with different compounds

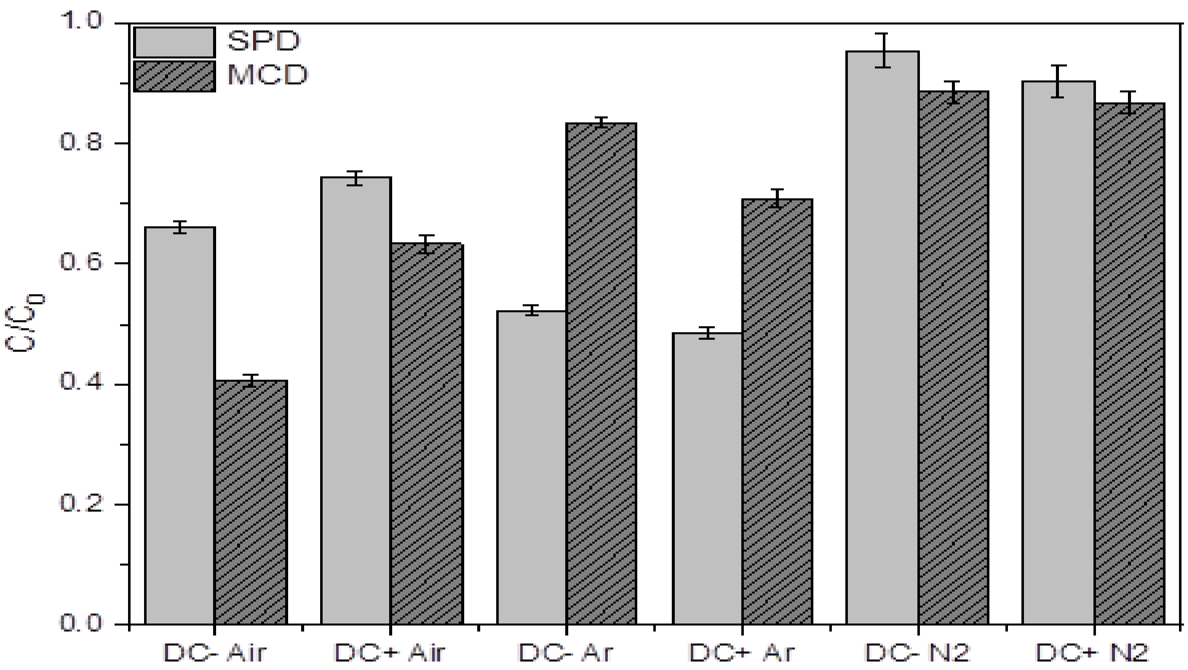


Triton > Metolachlor > PFOA >> hydroclorotiazide > Phenol > Atenolol > Thiamethoxam

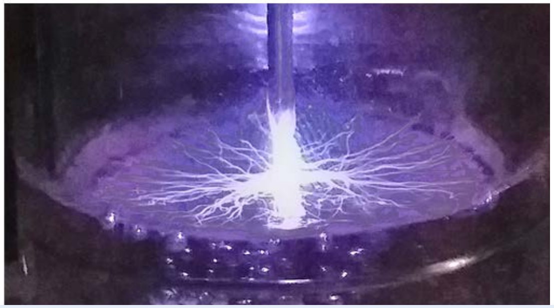
Università degli Studi di Padova

Department of Chemical Sciences (UNIPD) &
Department of Environmental Engineering
(NEDUET)

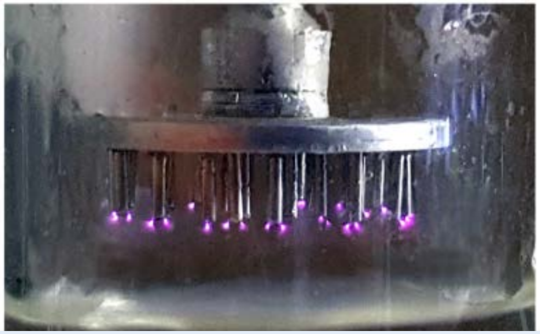
Dimethyl phthalate (DMP) removal in SPD and MCD reactors



Effect of:
type of plasma discharge (SPD or MCD)
voltage polarity (-ve or +ve)
Plasma feed gas (Air, Argon and Nitrogen)
(input power = 1.5 W, treatment time = 15 min)



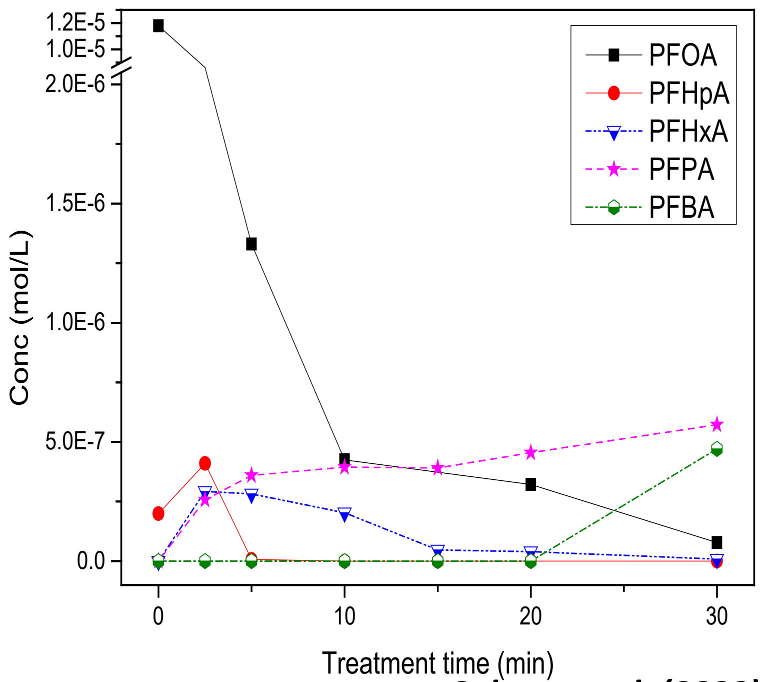
Self-pulsing Discharge (SPD)



Multipin Corona Discharge (SPD)

Current Challenges

- Tailoring Plasma Solutions to Contaminant Challenges
- Meeting Regulations: Standalone or Treatment Train Approach?
- Surface Behavior of Lower Chain PFAS: Reduced Activity and Kinetics
- Long-Term Performance of plasma systems?



Saleem et al. (2022)

Thank you for your attention