Barriers associated with trace organics and discoveries on how to reuse semiconductor Fab wastewater for ultrapure make-up water

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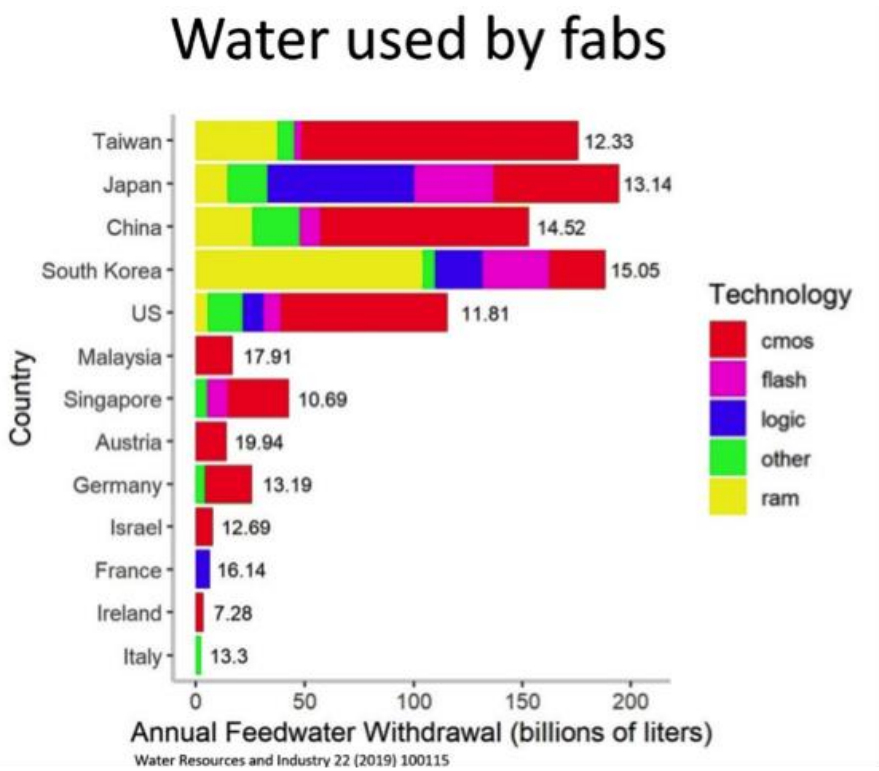


Fabs use a LOT of water (~1000 L per 12” wafer)

A typical Fab uses as much water as 50,000 to 100,000 homes per year

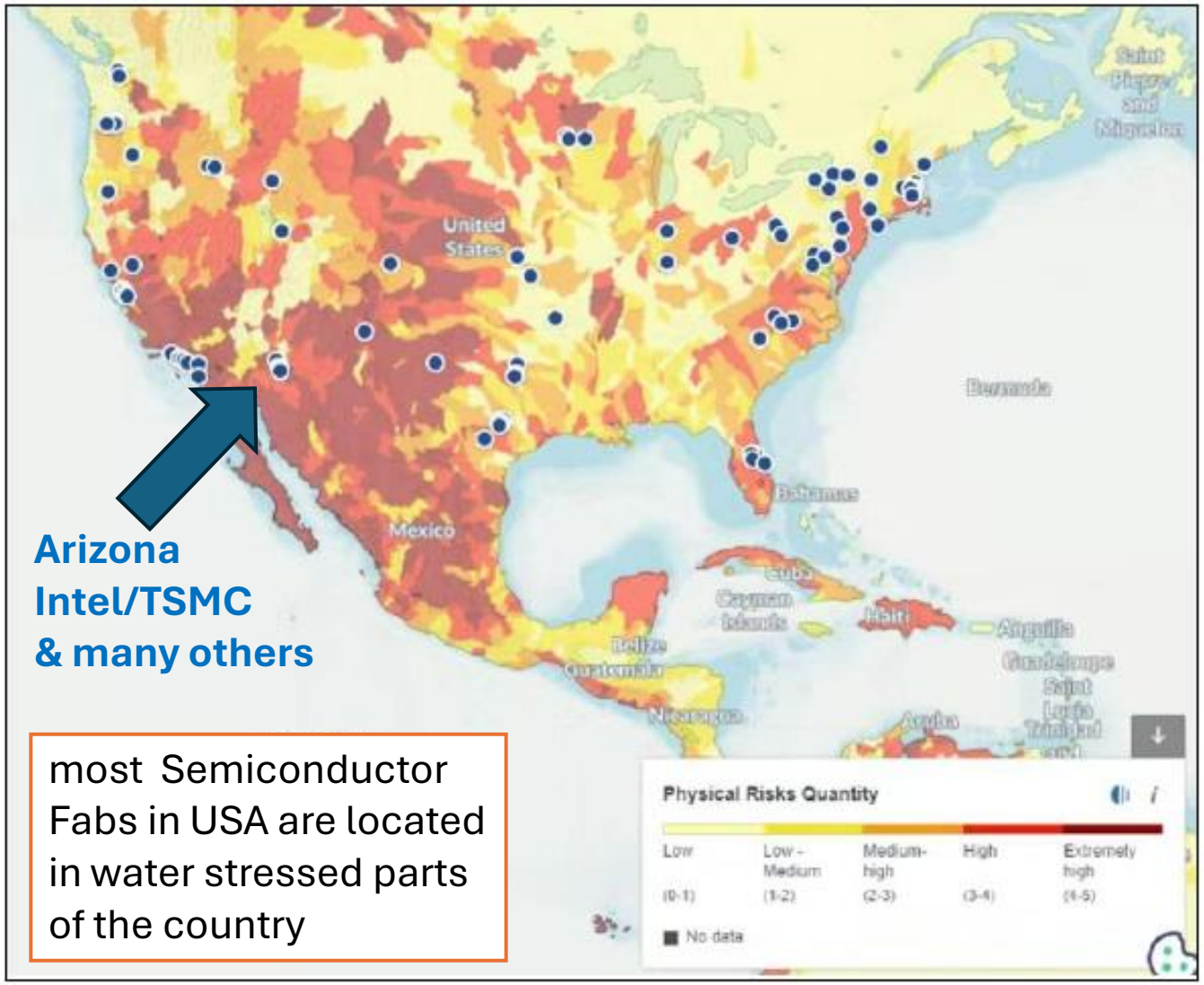


Figure 1: Overlay of U.S.-based chip fab locations (SIA, 2023) on the physical water risks quantity map maintained by the World Resources Institute (www.wri.org/aqueduct).

John H. Rydzewski (WEFTEC, 2024)

Typical Fab Wastewater Treatment Train
with Zero Liquid Discharge (ZLD)

Fab Processes

Peroxide Quenching

Solid Waste

Biological treatment for solvents & ammonia

Reverse osmosis

Brine

Chem Softer & Ic Excha

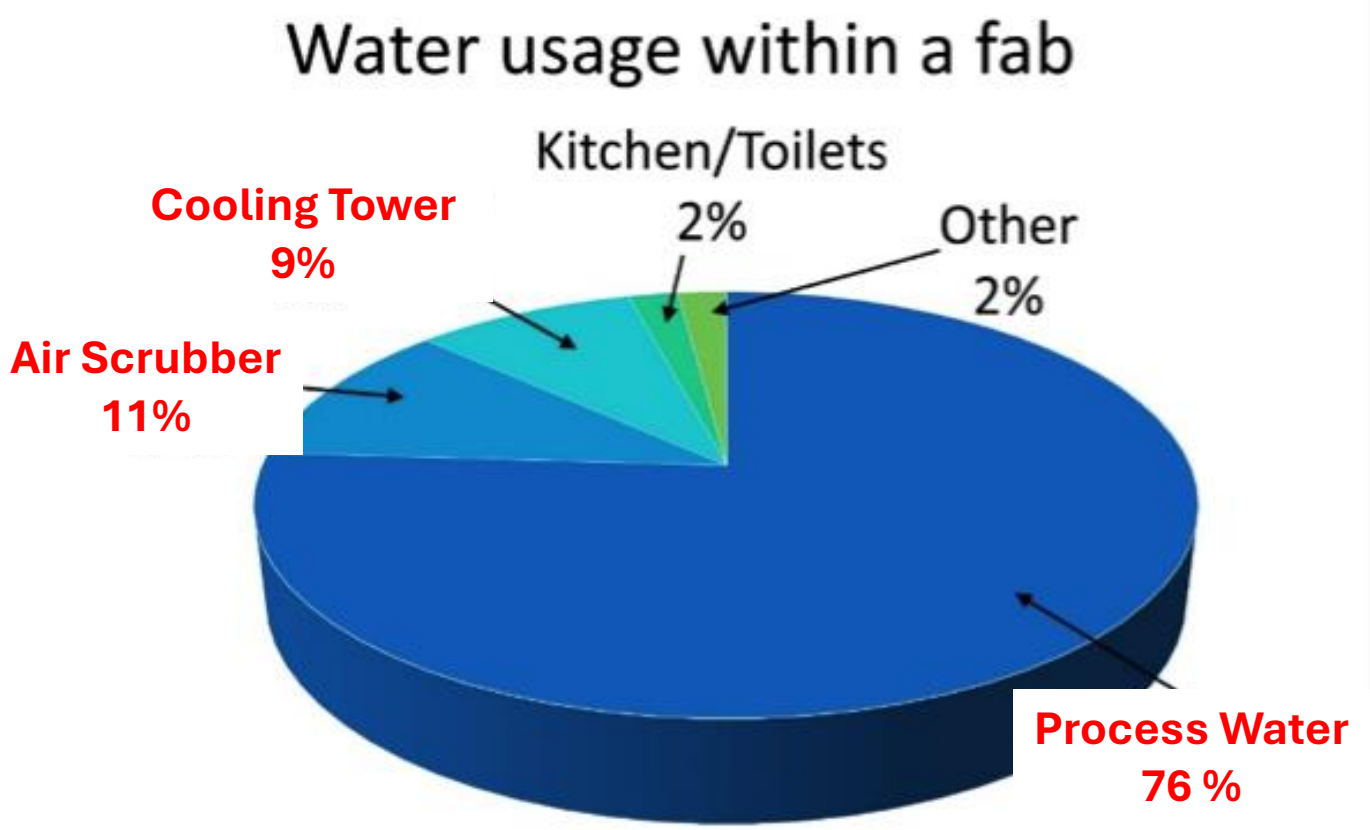
Solid Waste

Distillation & Crystalliz-ation

Clean water

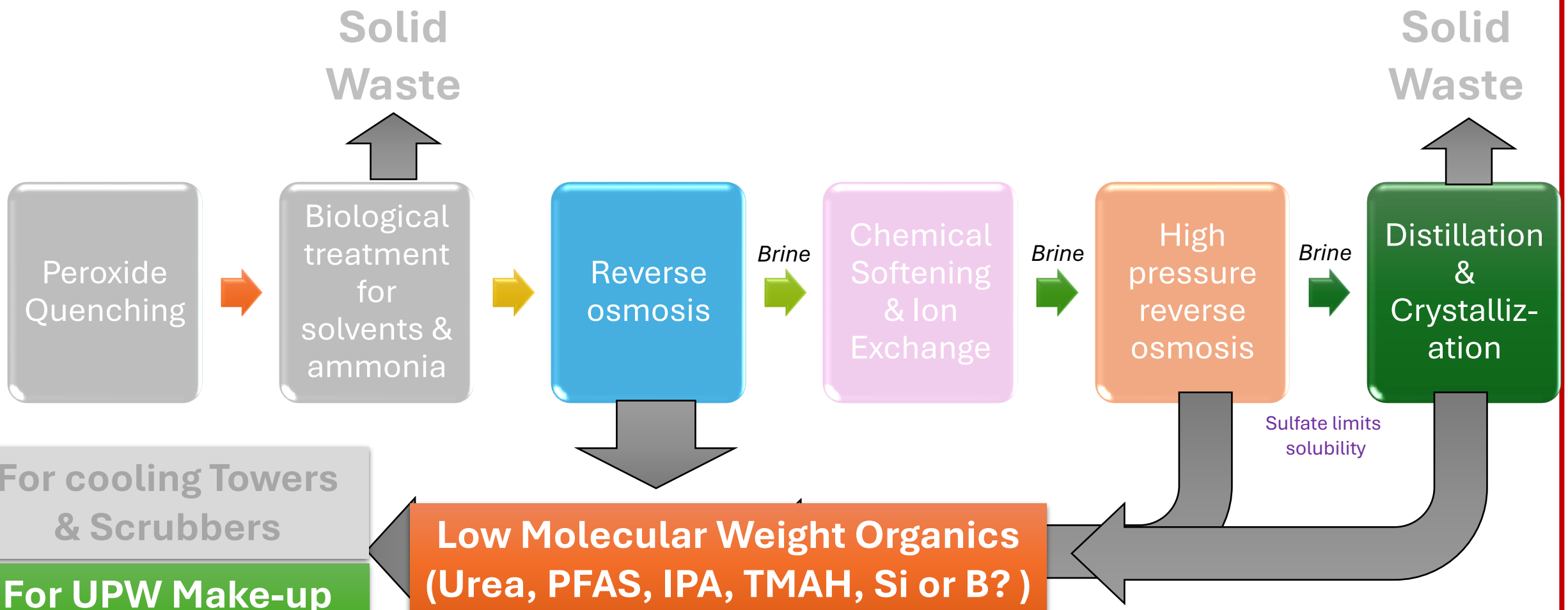
For cooling Towers & Scrubbers

Simply **not enough "reuse" water demand** without reusing water in Fab for process make-up water



Usually ultrapure Water (UPW) quality

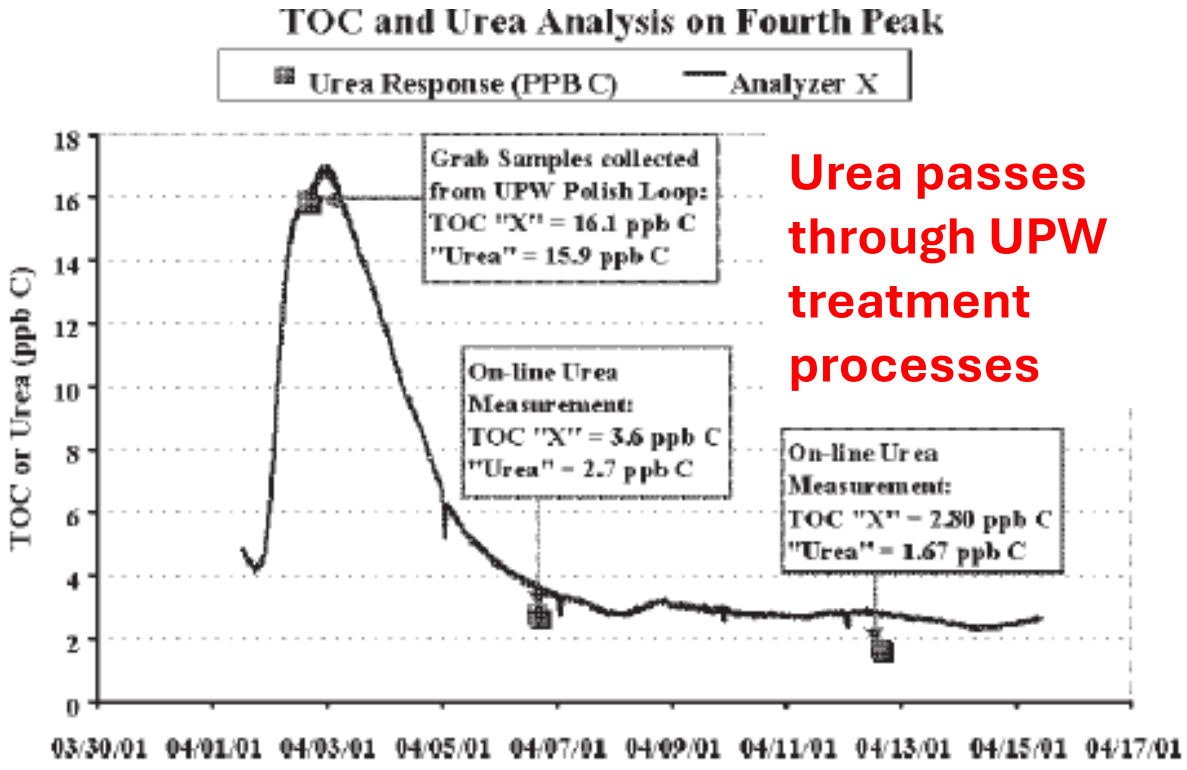
Challenges to Reusing Industrial Wastewater



Research Need

- Develop treatment processes to effectively **destroy urea and other compounds present in RO permeate** from Fab wastewater

- Use this treated water as UPW make-up water



Urea passes through UPW treatment processes

Figure 5. Plot showing correlation between the measured urea concentration and the TOC concentration measured by Analyzer X during the fourth excursion.

Rydzewski, *ULTRAPURE WATER® -UP190220 (2002)*

Approach

X* can be produced by UV Light, Ozone or other processes

But which X* should we produce ?

Urea
or other
Low molecular
Weight organic
Compounds

+

Reactive Radical Species (X*)

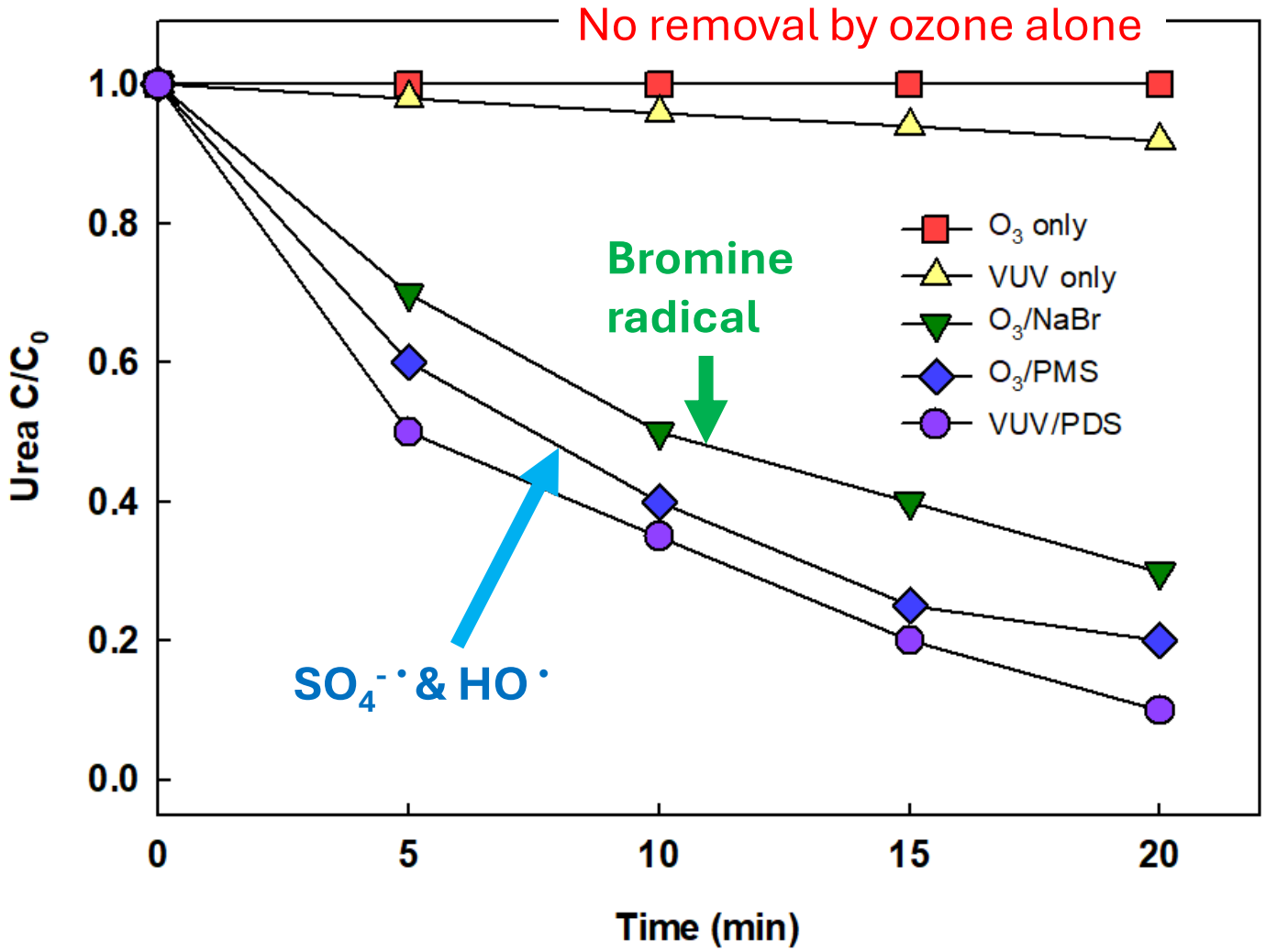
→

CO_2 & ions
easily removed by UPW processes

	O_3	•OH	$SO_4^{\bullet-}$	$e^-_{(aq)}$	H•	$O^{\bullet-}$	Br•	$Br_2^{\bullet-}$	HBrO	$Cl_2^{\bullet-}$	$CO_3^{\bullet-}$
Urea	5×10^{-2}	**7.9×10^{5}**	-	3×10^{5}	$< 3\times10^{4}$	-	-	-	-	-	1×10^{3}
Tetramethylammonium hydroxide (TMAH)	-	7.5×10^{7}	9×10^{4}	-	-	1.2×10^{8}	-	-	-	$< 1\times10^{3}$	-
Acetone	3.2×10^{-2}	1.1×10^{8}	-	6.5×10^{9}	2.6×10^{6}	-	-	-	-	1.4×10^{3}	1.6×10^{2}
Isopropanol (IPA)	1.9	7.5×10^{9}	5.3×10^{7}	-	7.4×10^{7}	1.2×10^{9}	-	-	-	1.5×10^{5}	4.3×10^{4}
Dimethyl sulfoxide (DMSO)	8.1	6.6×10^{9}	-	2.4×10^{6}	6.2×10^{6}	-	-	-	-	-	-

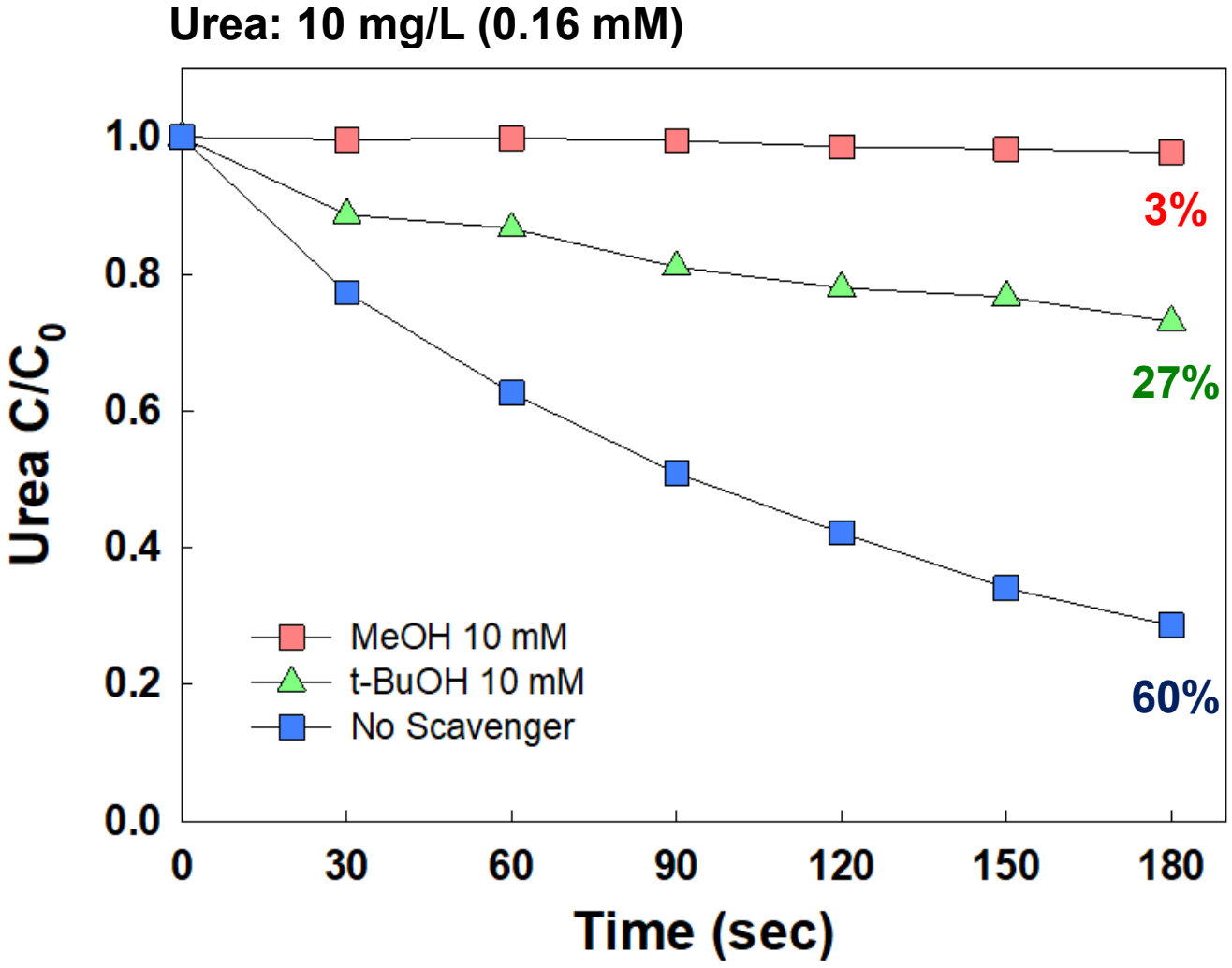
Approach #1 – Ozone + Bromide *or* Peroxymonosulfate (PMS)

Produces bromine radical ($Br^{\bullet}$), sulfate radical ($SO_4^{-\bullet}$) or hydroxyl radical ($HO^{\bullet}$)



Approach #1 – Ozone + Peroxymonosulfate (PMS)

Differentiating mechanisms



MeOH: Quench HO• and $SO_4^{\bullet-}$

t-BuOH: Quench only HO•

$k_{HO\bullet}$ **7.9×10^{5}** M^{-1} s^{-1}

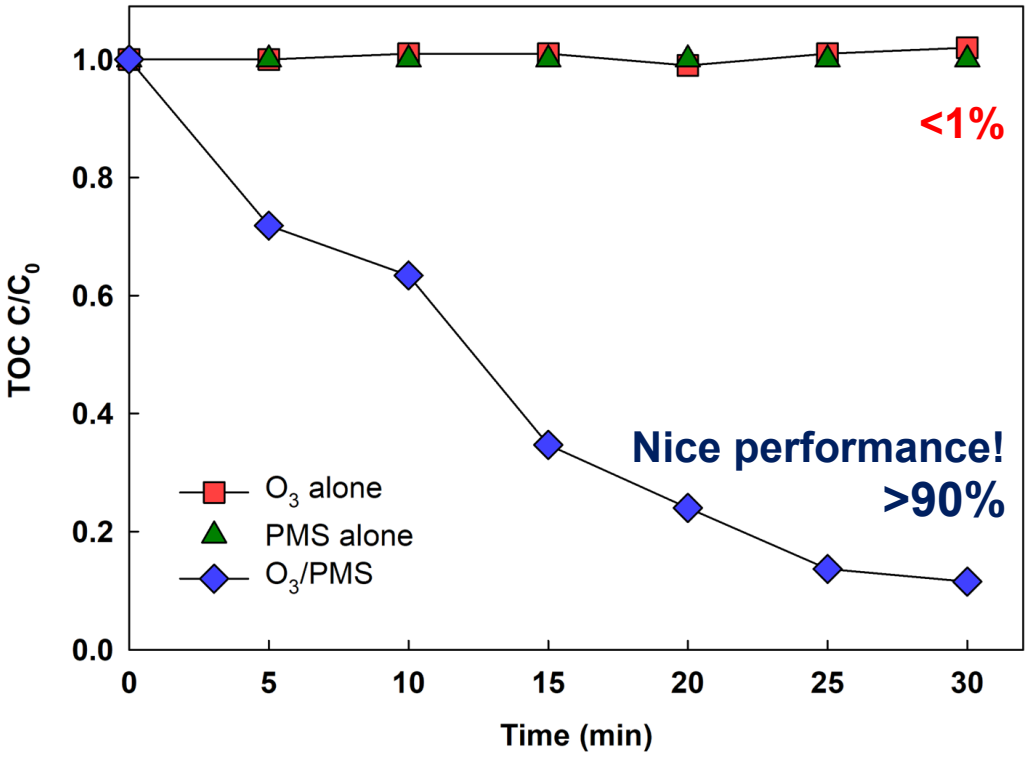
(from literature)

$k_{SO4\bullet-,urea}$: **4.01×10^{7}** M^{-1} s^{-1}

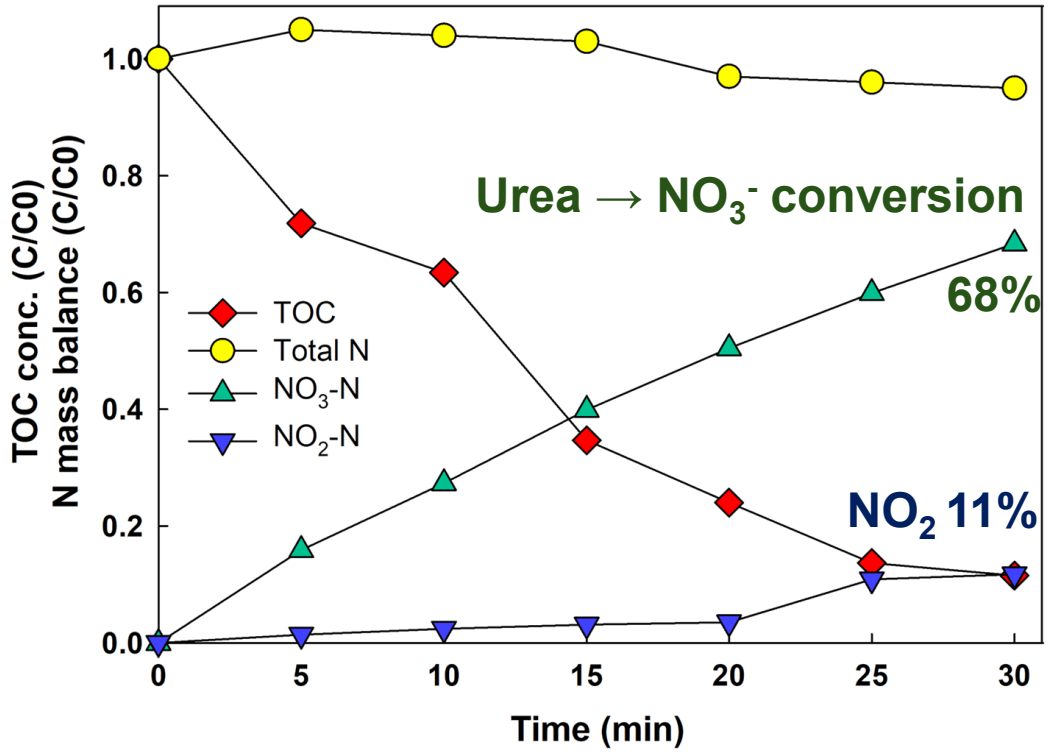
from Xin Yang Group (Sun Yat-Sen University)

By-Products of Urea oxidation
TOC = Total organic carbon

TOC removal (Co = urea 10 ppm)



Nitrogen mass balance



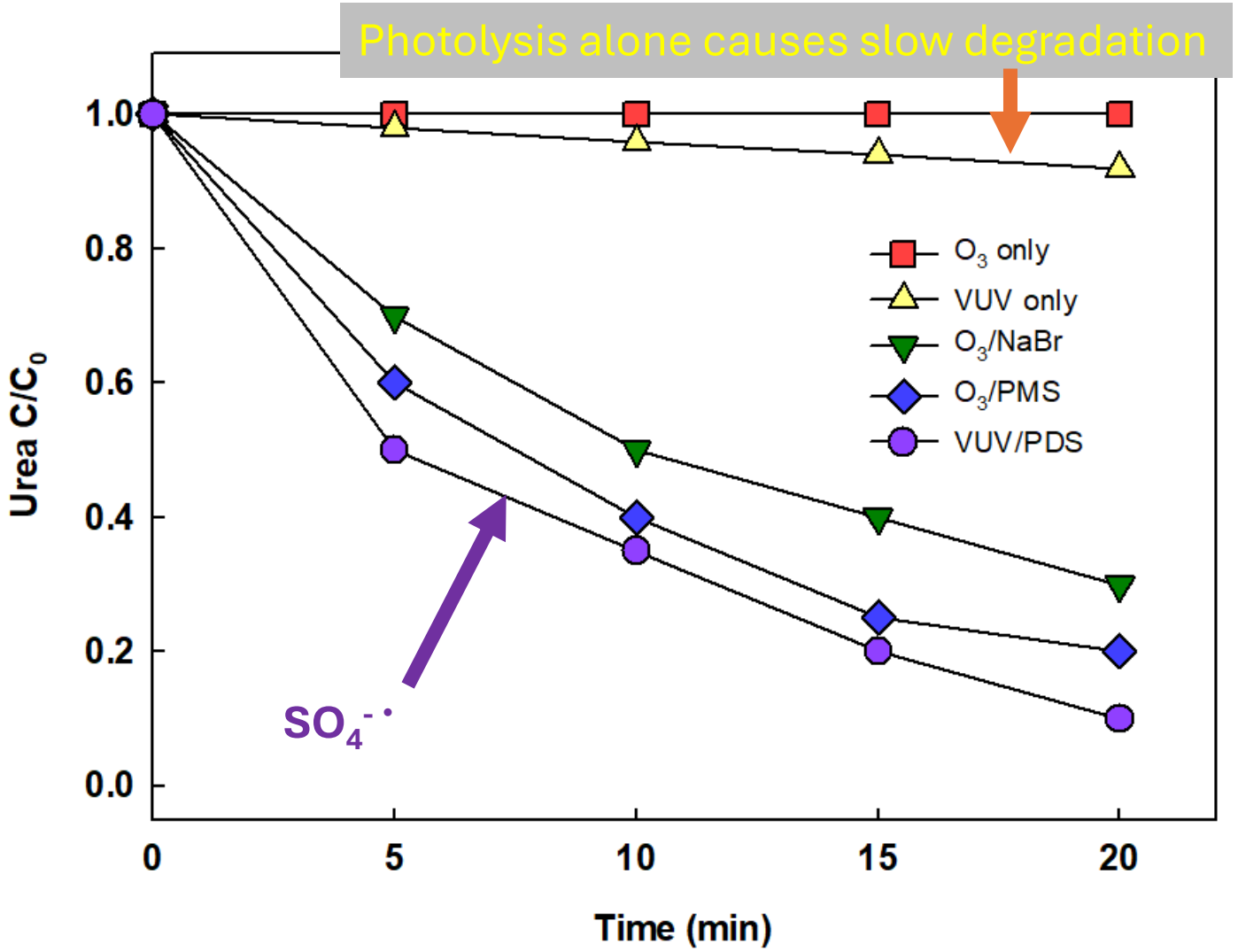
Approach #2 – Vacuum Ultraviolete Light + Peroxydisulfate (PDS)

Produces sulfate radical ($SO_4^{-\bullet}$) + 185nm/254 nm light

Low pressure
mercury lamp
46 W

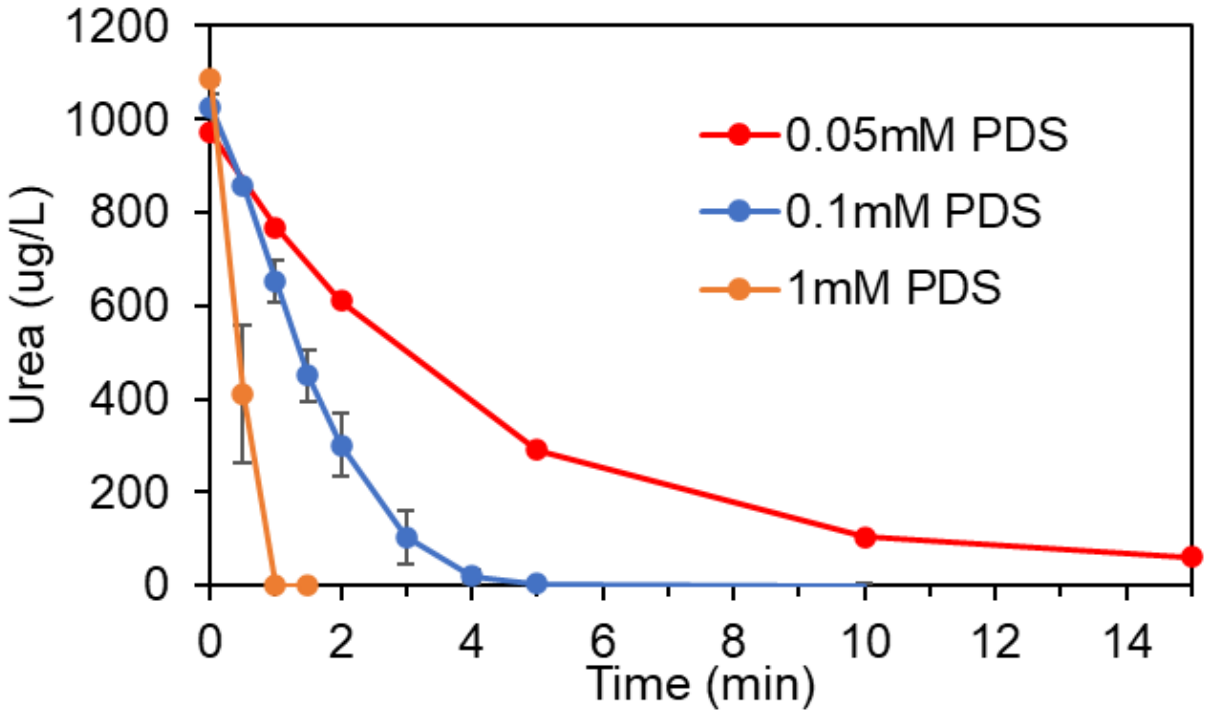
$$S_2O_8^{2-} + h\nu \rightarrow SO_4^{-}$$

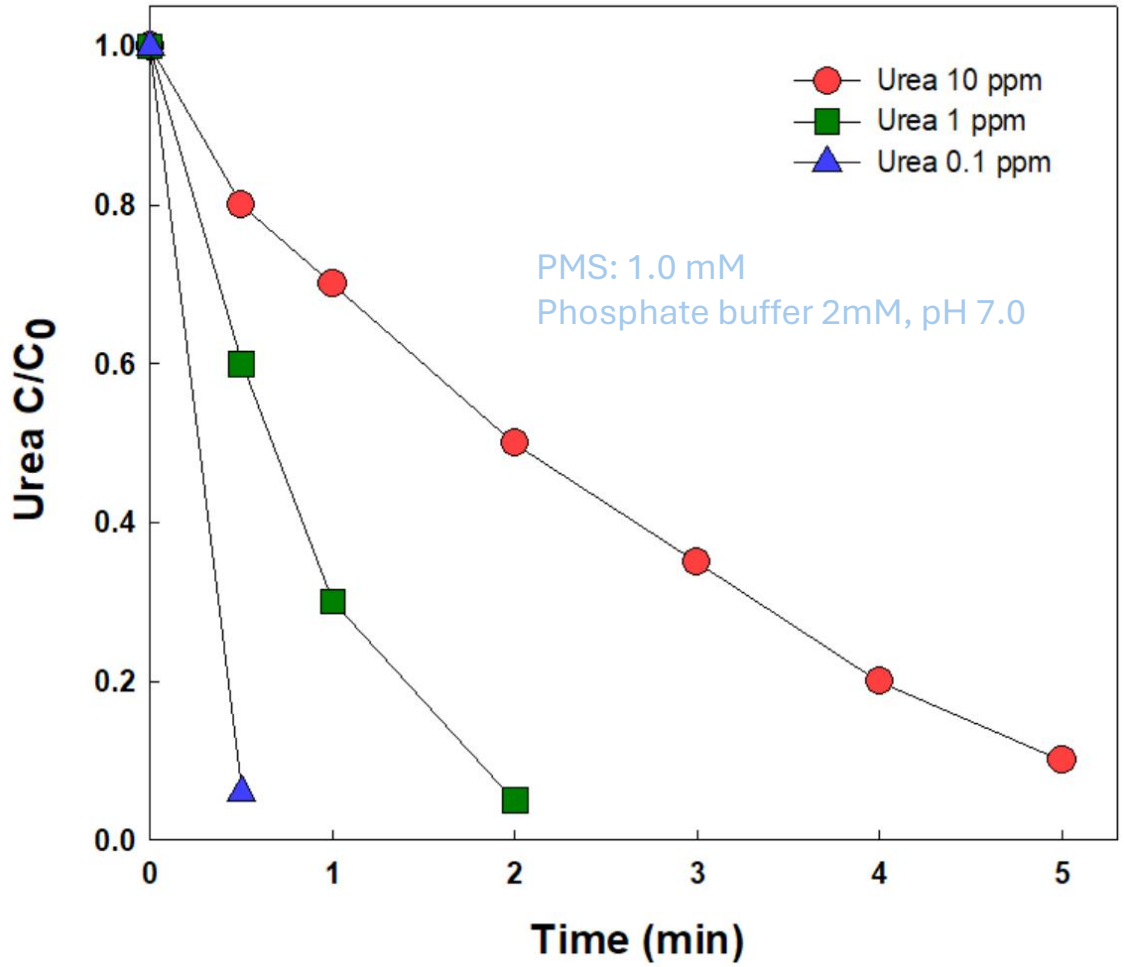
VUV/UV/PDS technology:
Volume = 2.65 L
46 W lamp:185/254nm
Spike PDS, 23.8-238 mg/L $Na_2S_2O_8$
Urea:1-60 mg/L



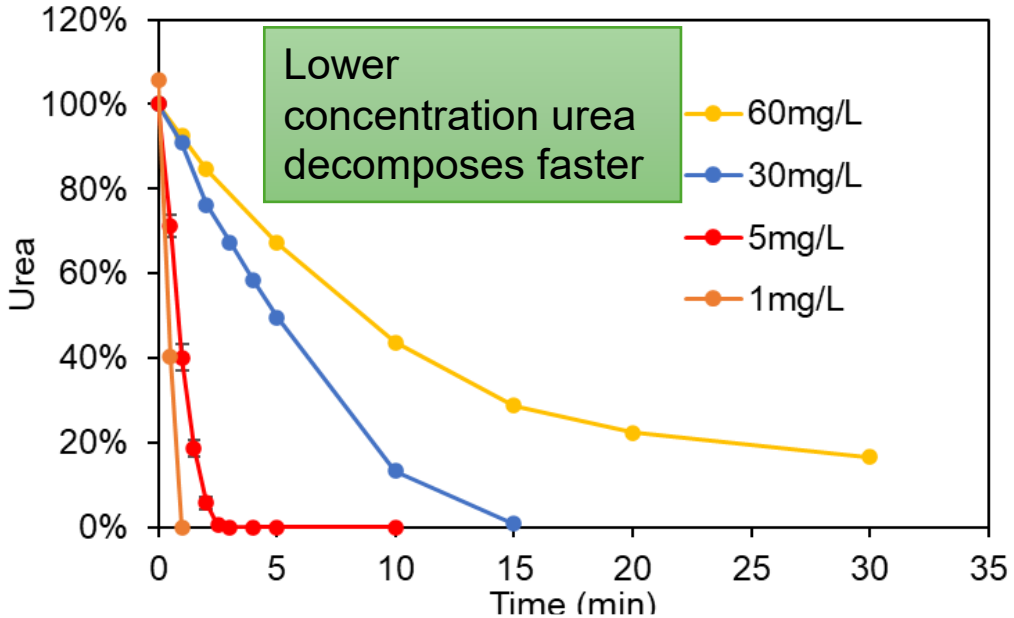
Effects of initial PDS or Urea Concentrations

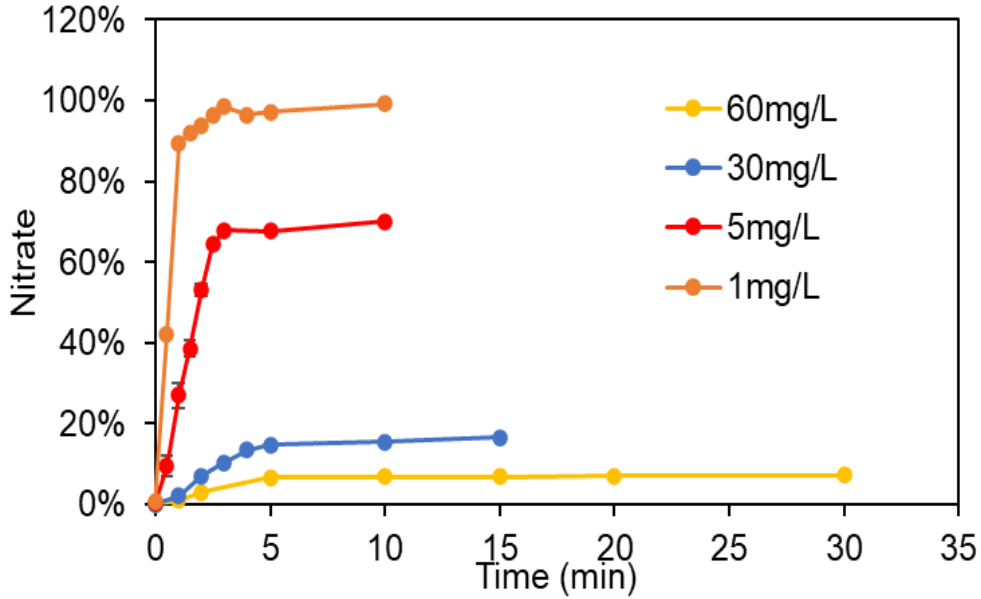
Each influences steady state $SO_4^{-}\bullet$ concentrations



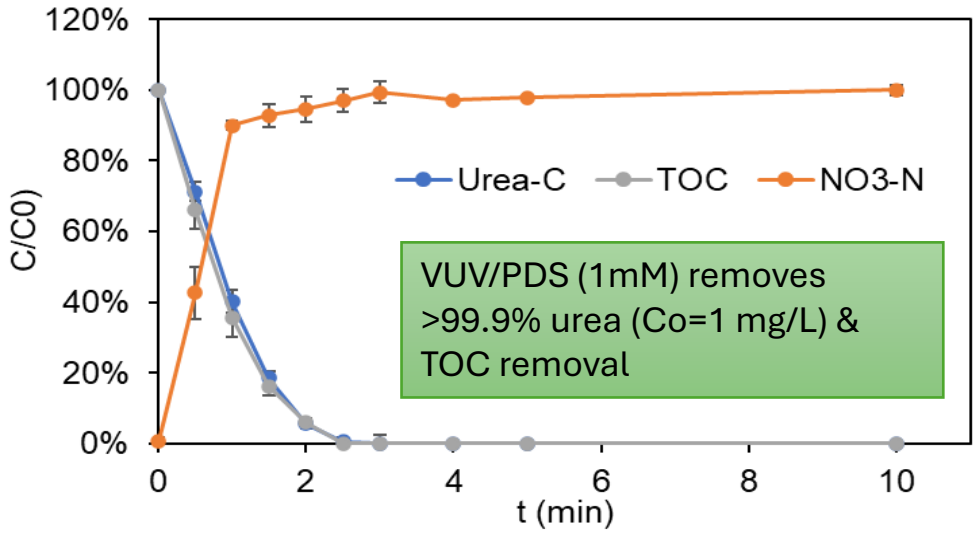


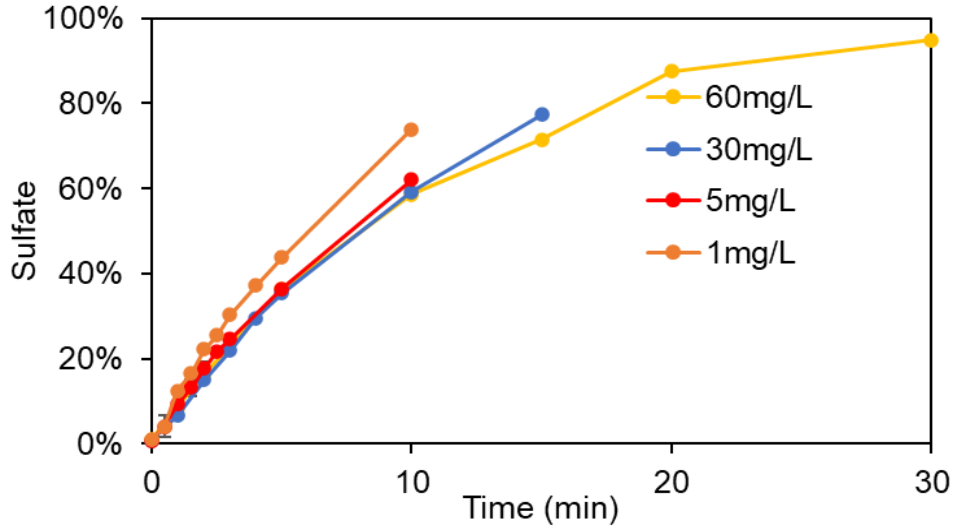
By-products of urea reactions with VUV/PDS (1 mM)





Nitrate formation: Mechanisms change at higher initial Urea concentrations

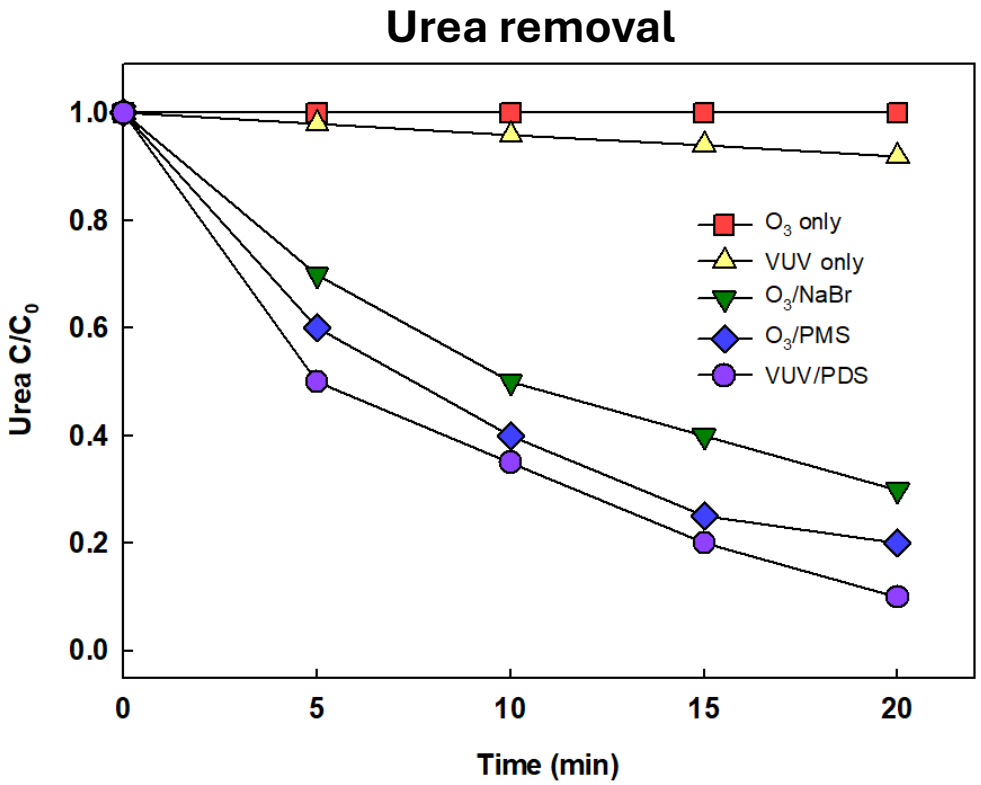


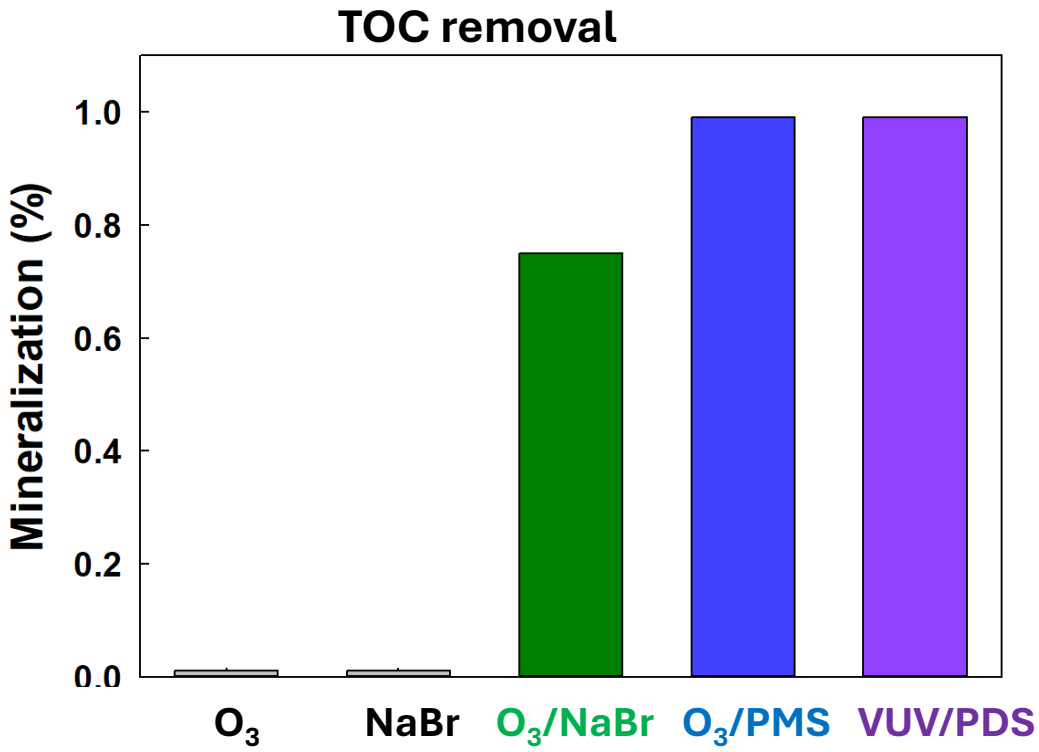


Not all PDS are converted into sulfate. There are PDS left in the solution.

Comparing Degradation & ByProducts

VUV/PDS emerges as better potential candidate to destroy Urea



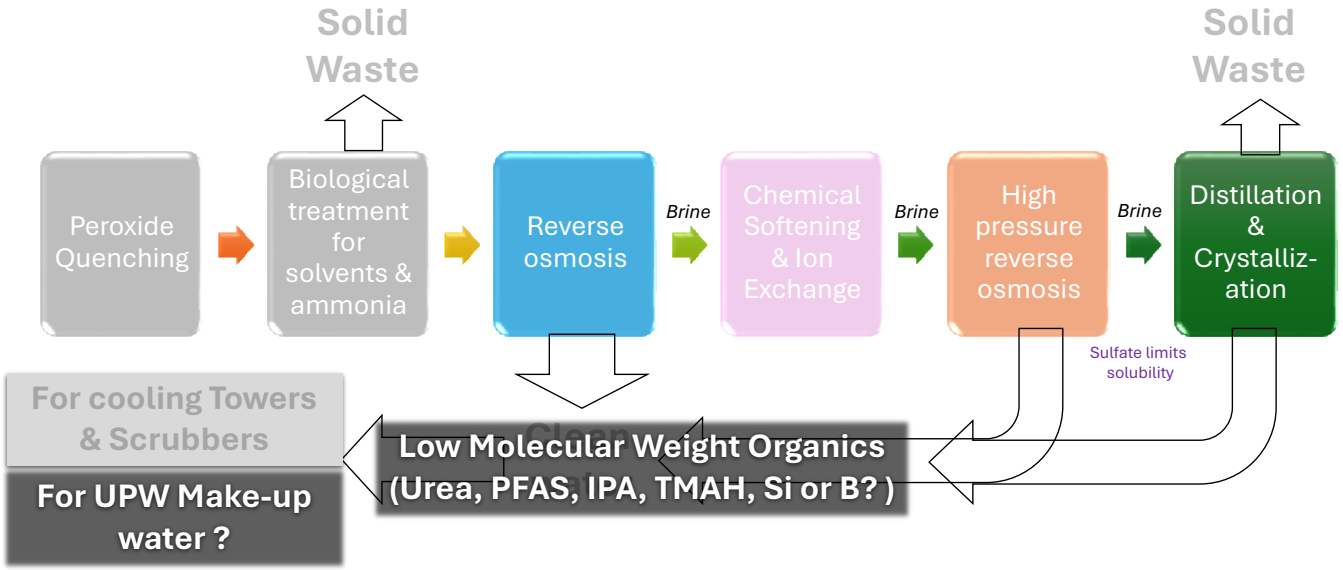


Broader perspective around capabilities of Radical Species to oxidize target LMW Organics

	O_3	•OH	$SO_4^{\bullet-}$	$e^-_{(aq)}$	H•	$O^{\bullet-}$	Br•	$Br_2^{\bullet-}$	$Cl^{\bullet}$	$Cl_2^{\bullet-}$	$CO_3^{\bullet-}$
Urea	5×10^{-2}	7.9×10^{5}	4.0×10^{7}	3×10^{5}	$<3\times10^{4}$	-	1.3×10^{7}	BDL	-	-	1×10^{3}
Tetramethylammonium hydroxide (TMAH)	-	7.5×10^{7}	9×10^{4}	-	-	1.2×10^{8}	6.6×10^{6}	BDL	-	$<1\times10^{3}$	-
Acetone	3.2×10^{-2}	1.1×10^{8}	$<10^{6}$	6.5×10^{9}	2.6×10^{6}	-	5.2×10^{7}	BDL	1.1×10^{8}	1.4×10^{3}	1.6×10^{2}
Isopropanol (IPA)	1.9	7.5×10^{9}	5.3×10^{7} 7.1×10^{7}	-	7.4×10^{7}	1.2×10^{9}	2.6×10^{7}	BDL	1.1×10^{9}	1.5×10^{5}	4.3×10^{4}
Dimethyl sulfoxide (DMSO)	8.1	6.6×10^{9}	2.0×10^{9}	2.4×10^{6}	6.2×10^{6}	-	5.8×10^{7}	BDL	1.8×10^{9}	3.1×10^{6}	-

Red values provided by collaborator: *Xin Yang Group (Sun Yat-Sen University)*

Conclusions



- **Sulfate radical** generated by **VUV/PDS** (faster) or **O_3/PMS** can mineralize urea and other low molecular weight organics present in reverse osmosis permeates of Fab wastewaters
- **Byproducts of this process** (nitrate, sulfate) are at lower concentrations than present in municipal tap water - and therefore **readily removed by existing UPW treatment systems**
- **Pilot testing** of process + UPW system will start late 2025

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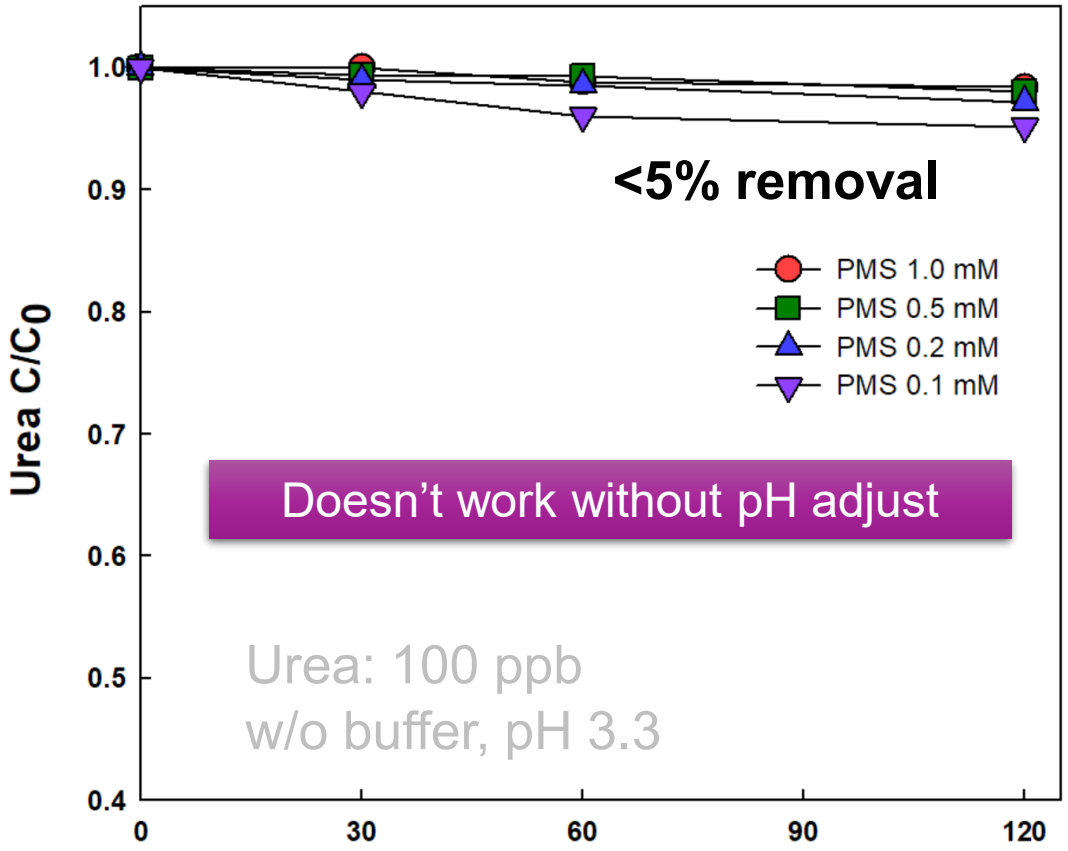
Effect of solution pH

PMS is acidic when added to RO permeate water



Works between 5 < pH < 9