Treatment of Emerging Contaminants by UV/H_2O_2 in Water Reuse Applications

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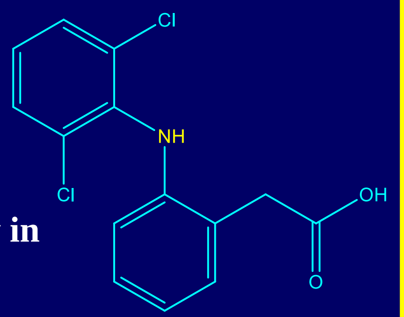
Background (contaminants of emerging concern)

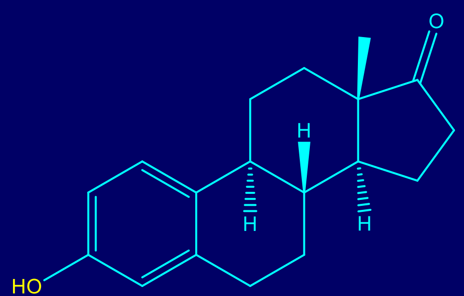
Diclofenac

- A non-steroidal anti-inflammatory drug (NSAID).
- LD_{50}=390mg/kg (orally in mice).



Estrone

- An estrogenic hormone.
- Carcinogenic for human females, and endocrine-disrupting for human males.

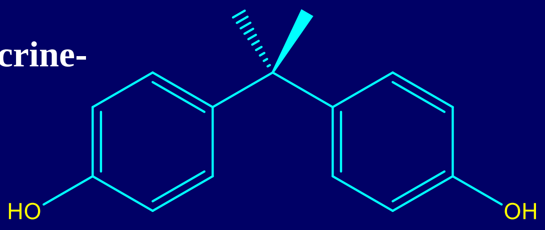


Triclosan

- An antimicrobial agent.
- Potential hazard of endocrine-disrupting chemical.

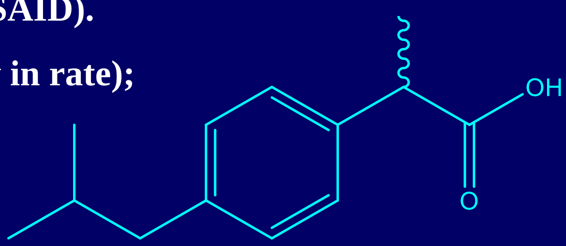
Bisphenol A

- Used in plastic.
- Potential hazard of endocrine-disrupting chemical.



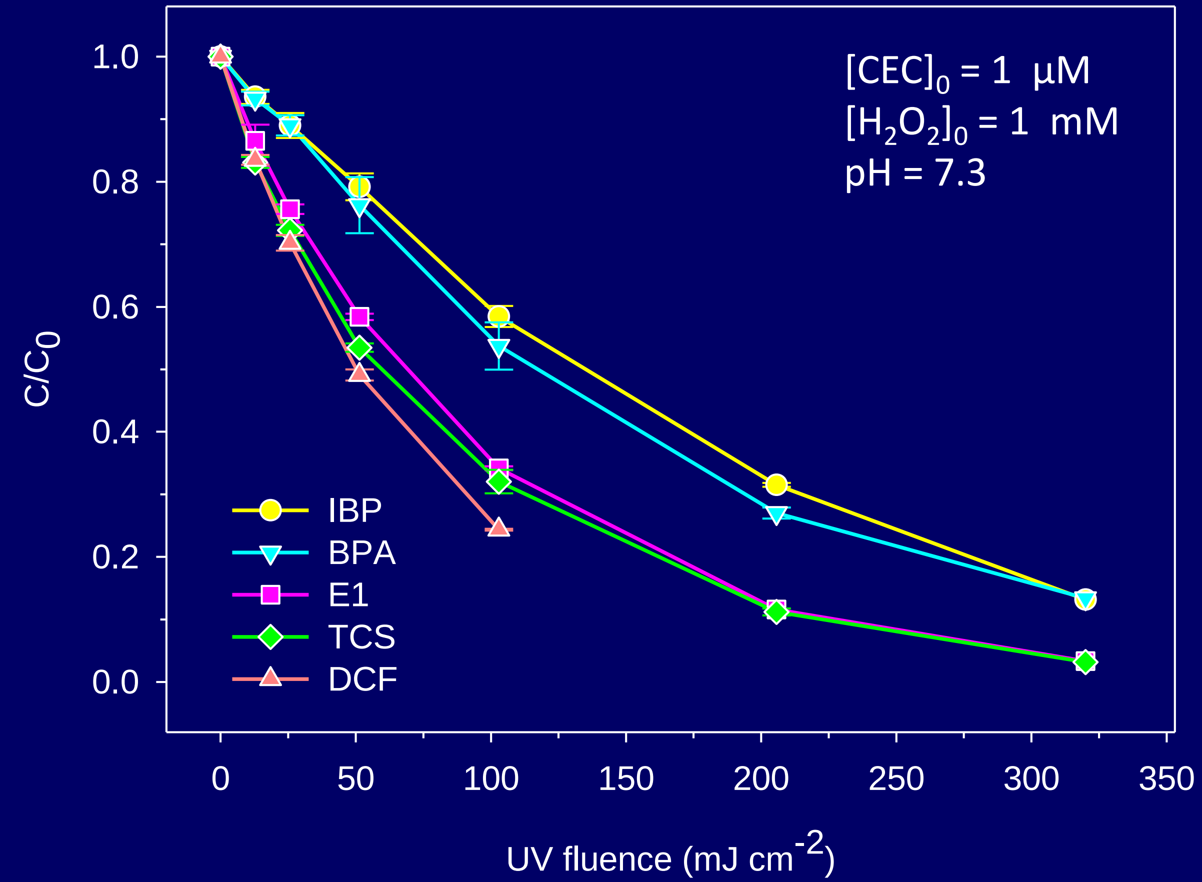
Ibuprofen

- A non-steroidal anti-inflammatory drug (NSAID).
- LD_{50}=636mg/kg (orally in rate); 740 (orally in mouse).

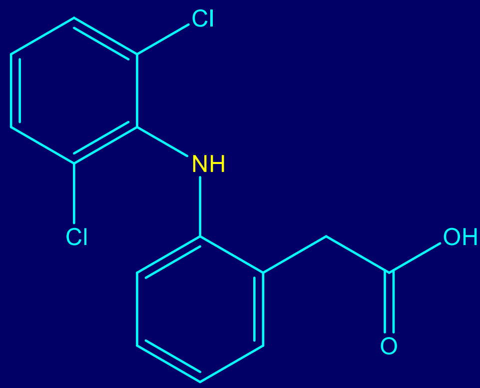


❑ **A limited number of studies have appeared on the success of removing these compounds with conventional treatments.**

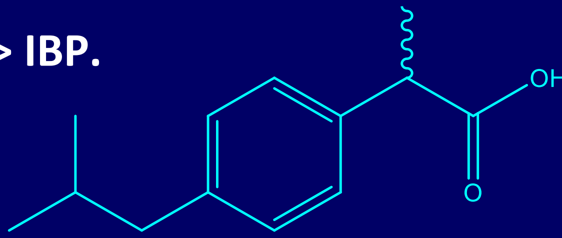
Decomposition of a mixture of 5 CECs by UV/H_2O_2



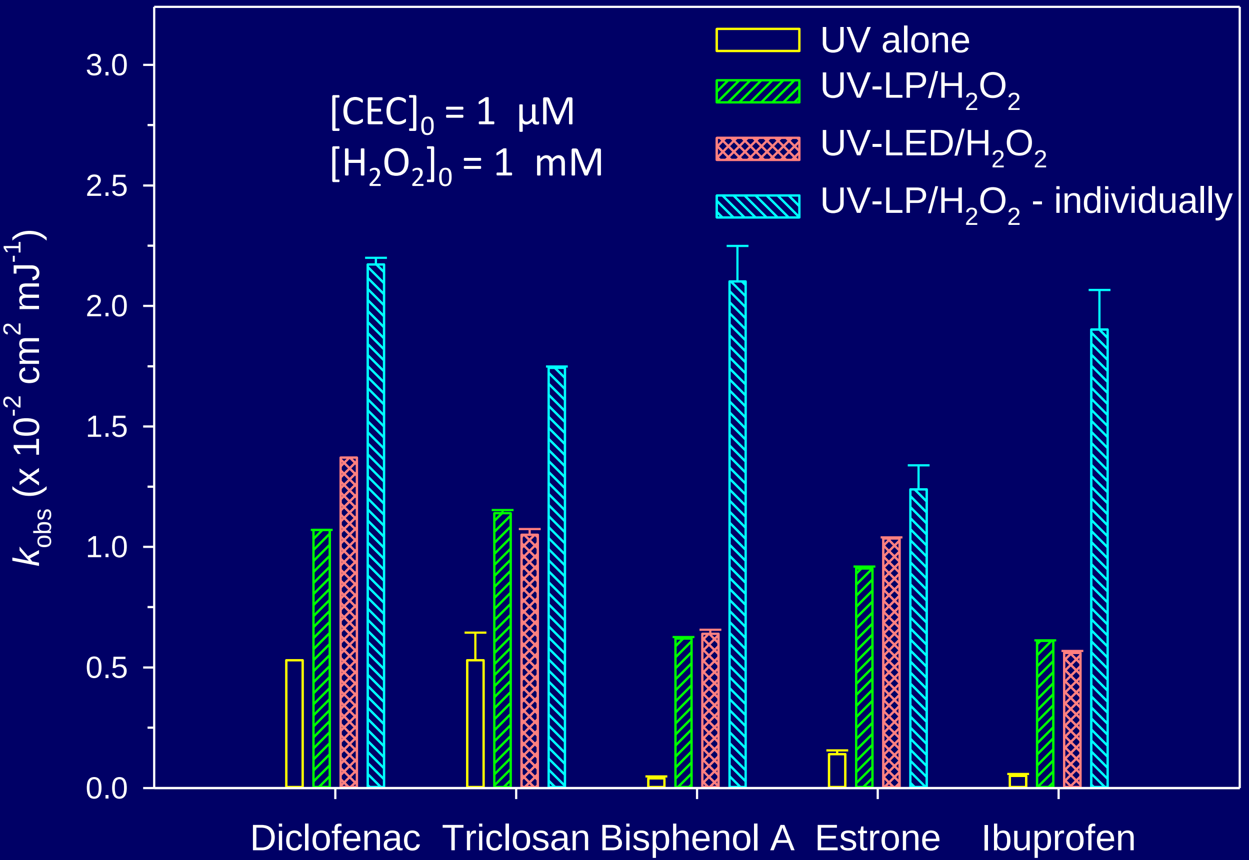
- **DCF: Diclofenac**
- **TCS: Triclosan**
- **E1: Estrone**
- **BPA: Bisphenol A**
- **IBP: Ibuprofen**



- **UV/H_2O_2 can efficiently remove 5 CECs, especially for diclofenac.**
- **The degradation rate follows the order: DCF > TCS > E1 > BPA > IBP.**
- **$^{\bullet}$OH is non-selective oxidant. The different degradation rates might relate to the different structure.**



Decomposition of 5 mixed CECs by UV alone & UV/H_2O_2

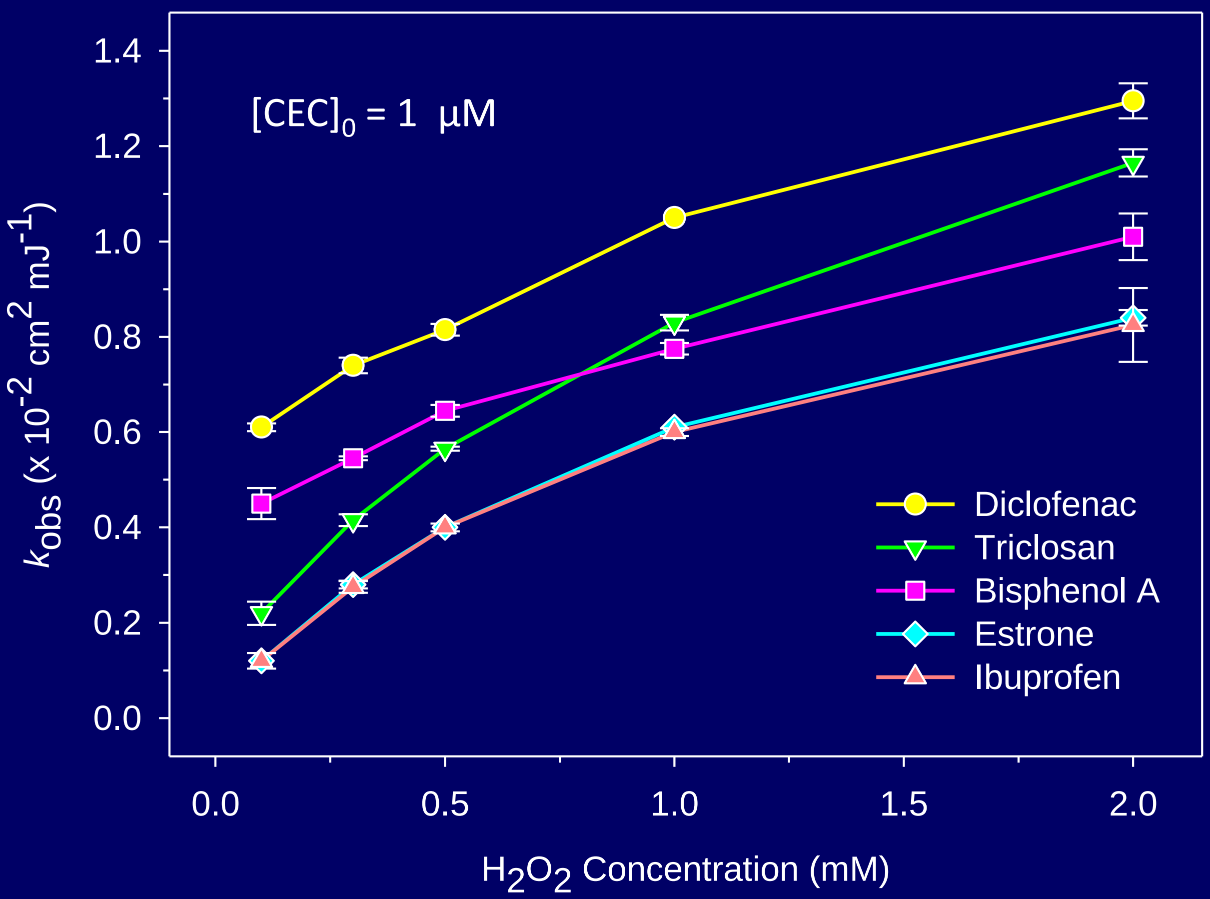


- **UV/H_2O_2 can remove 5 CECs much faster than UV alone due to the formed $^{\bullet}OH$.**
- **The feasibility and effectiveness of LED-UV in the activation of H_2O_2.**

$$k_{obs} = -\ln\left(\frac{C}{C_0}\right)$$ **: observed pseudo−first order rate**

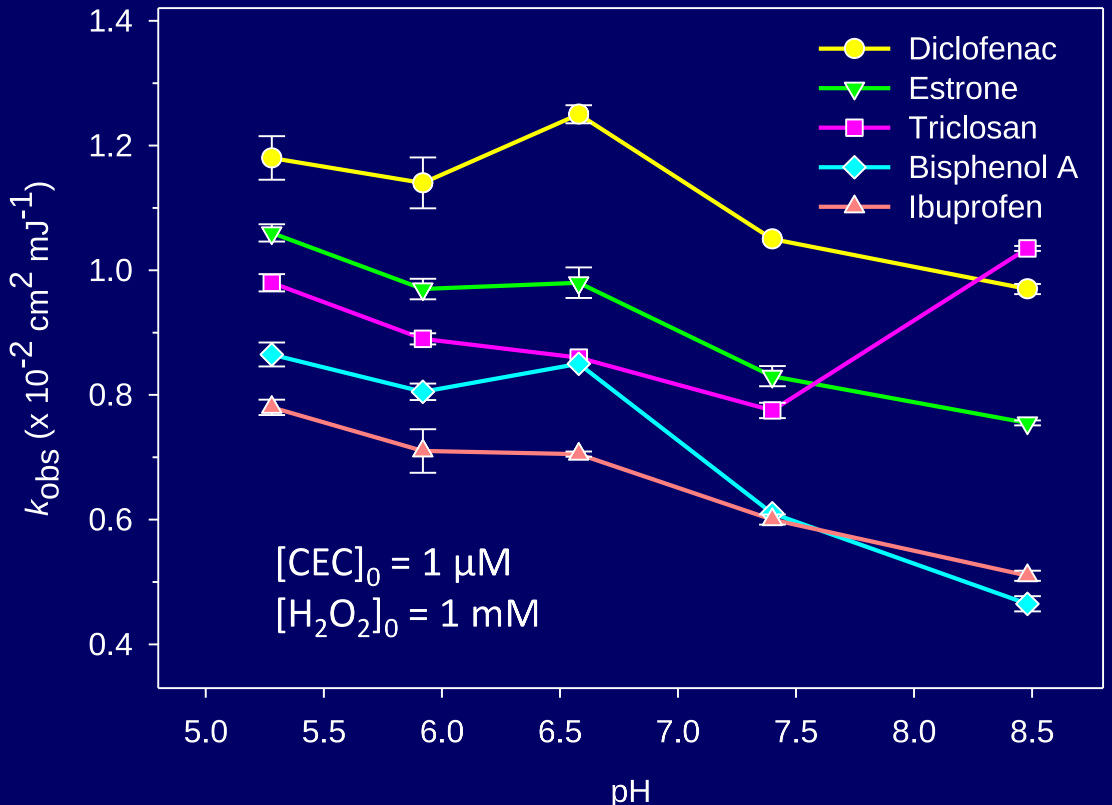
- **Degradation efficiency of 5 CECs in the mixture is lower than that of individual degradation of 5 CECs, due to the competition for $^{\bullet}OH$ among them.**

Effects of H_2O_2 dose on UV/H_2O_2 process

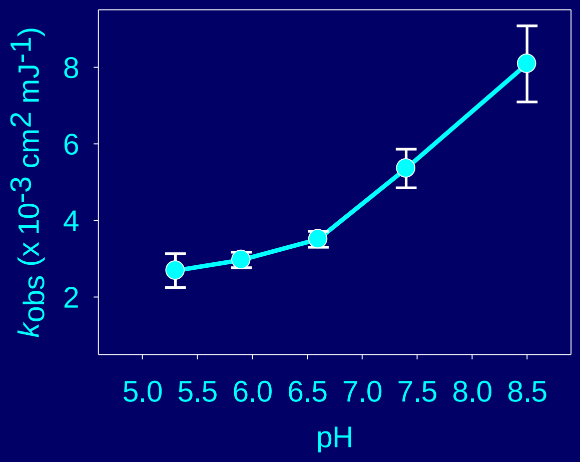


- As the initial concentration of H_2O_2 increased continually from 0.1 mM to 2 mM, k_{obs} increased non-linearly, due to the competition of excess H_2O_2 for $^{\bullet}OH$ with target contaminants.

Effects of pH on UV/H_2O_2 process

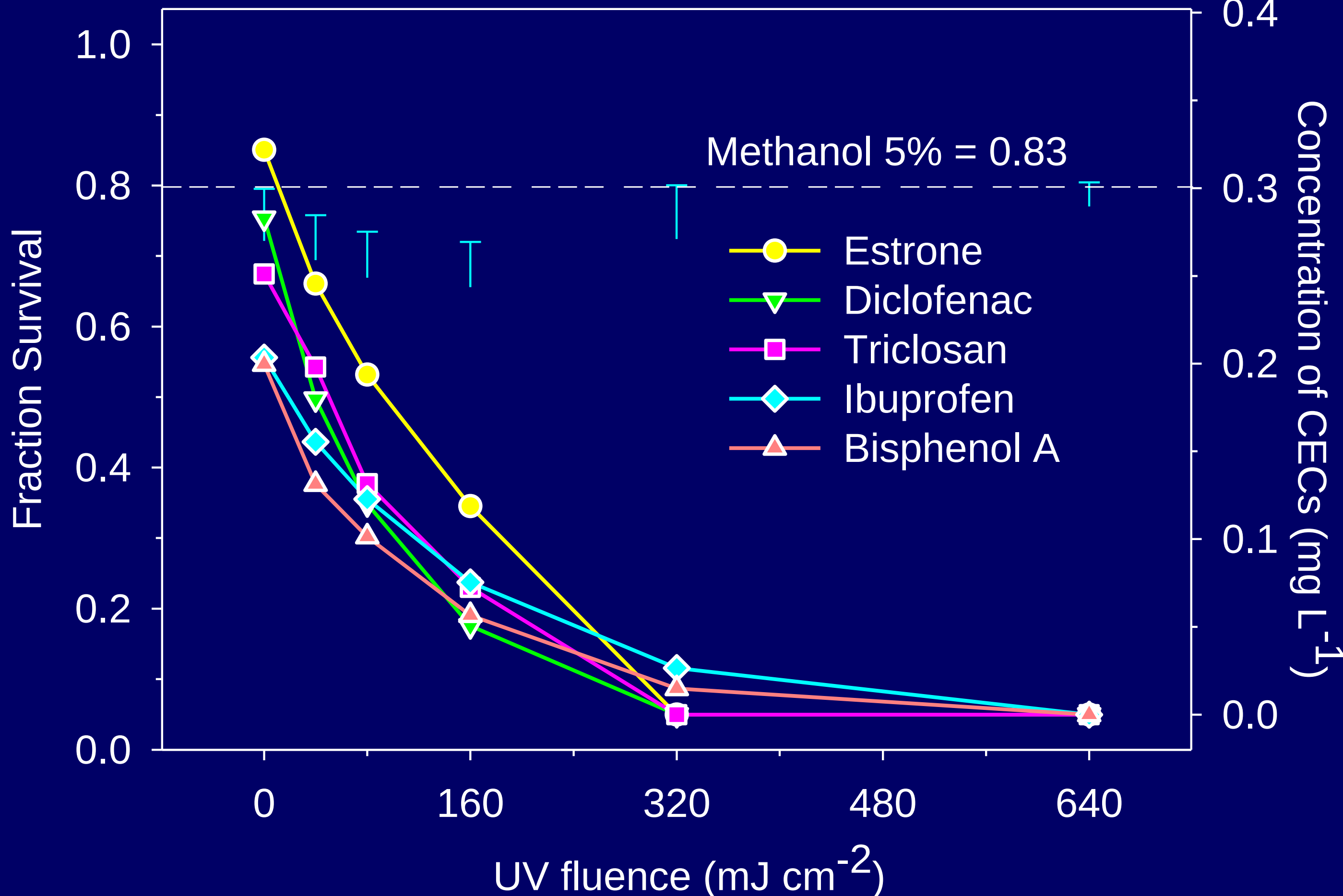


Direct photolysis of triclosan →



- The optimum pH for most CECs is 6.5 except for triclosan (optimum pH = 8.5).
- Lower degradation rate constant at pH > 6.5 for diclofenac, estrone, bisphenol A, and ibuprofen is because of scavenging of $^{\bullet}OH$ by the increased OH^-:
  - $^{\bullet}OH + OH^- \rightarrow O^{\bullet -} + H_2O$ ($k = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$)
- Higher rate at pH 8.5 for triclosan may be due to the increased photolysis of triclosan.

Cytotoxicity of treated CECs by UV/H_2O_2



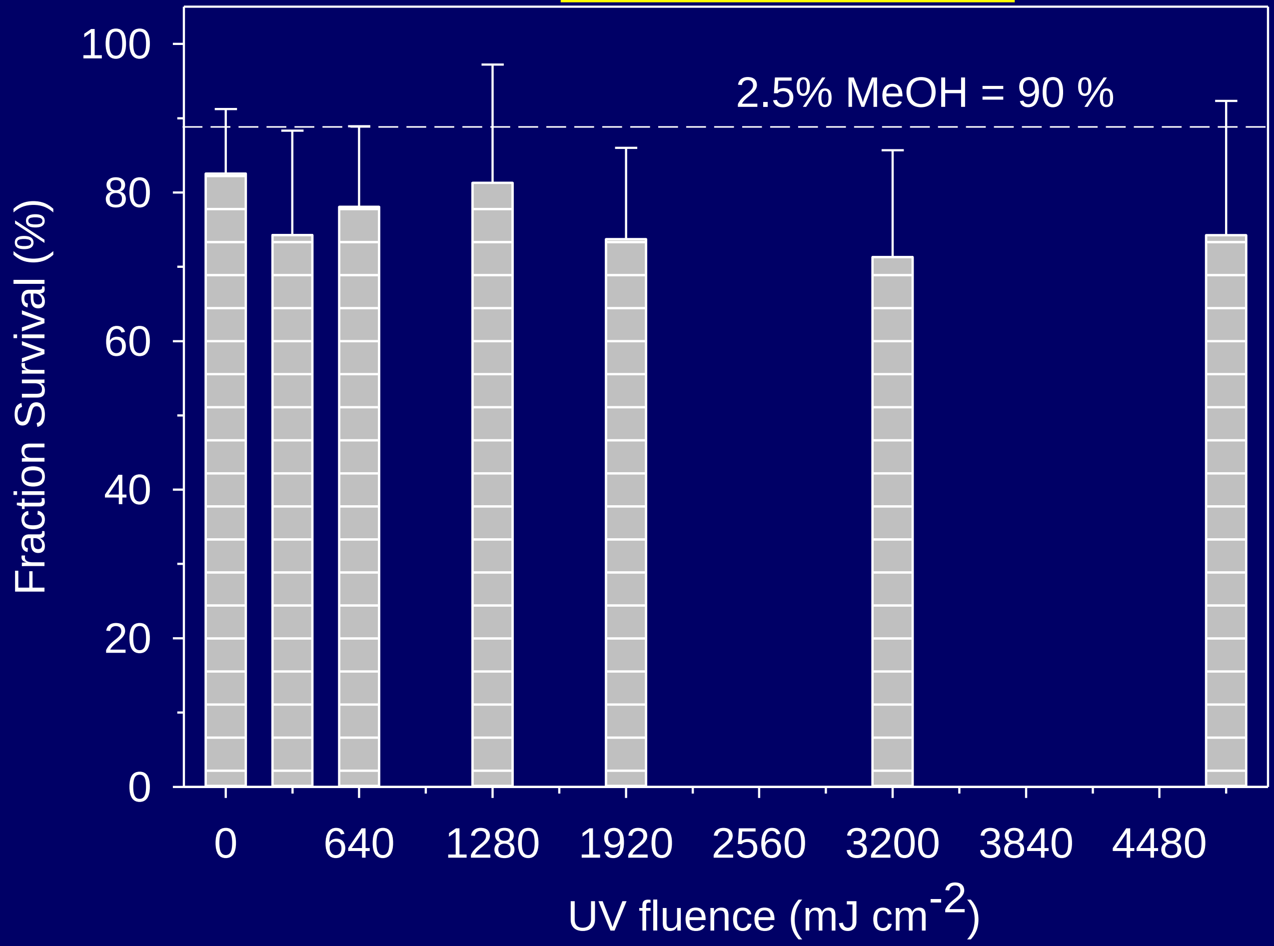
- **ER cell line**
- **MTT assay.**

[CEC]$_0$ = 1 μM
[H_2O_2]$_0$ = 1 mM

- **The higher the bar, the lower the toxicity.**

❖ **Although 5 mixed CECs were totally removed after 640 mJ cm^{-2} UV fluence, cytotoxicity of 5 mixed CECs did not change after the treatment by UV/H_2O_2, which might be due to the formation of transformation products of these CECs.**

Cytotoxicity of treated CECs by UV/H_2O_2 with <u>long UV irradiation</u>



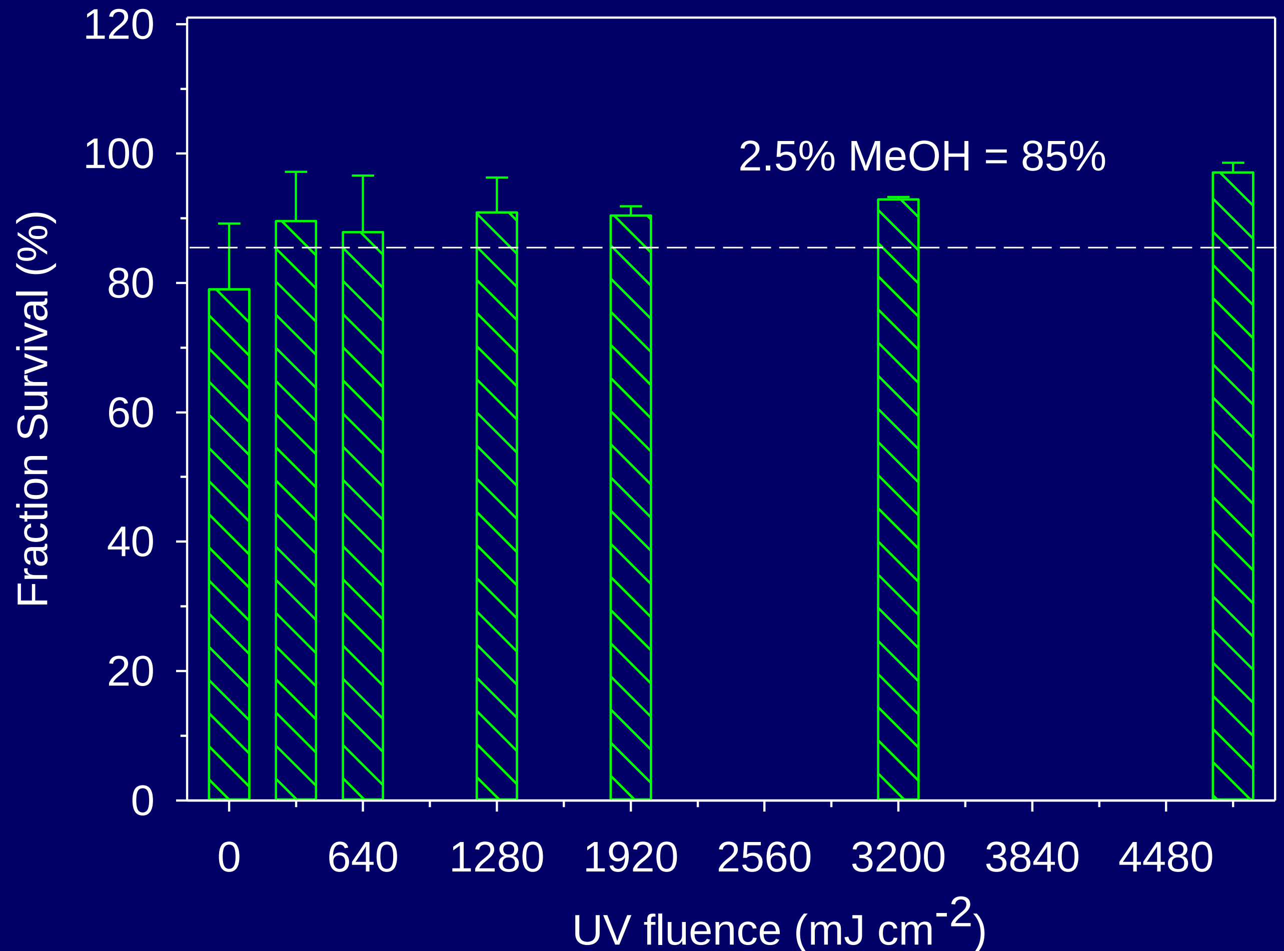
- **CYP1A-bla LS-180 cell line**
- **MTT assay.**

$[CEC]_0$ = 1 μM
$[H_2O_2]_0$ = 1 mM

- **The higher the bar, the lower the toxicity.**

- **Even the treatment time prolonged to 4800 mJ cm^{-2} UV fluence, cytotoxicity of 5 mixed CECs did not change after the treatment by UV/H_2O_2.**

Cytotoxicity of treated Diclofenac by UV/H_2O_2



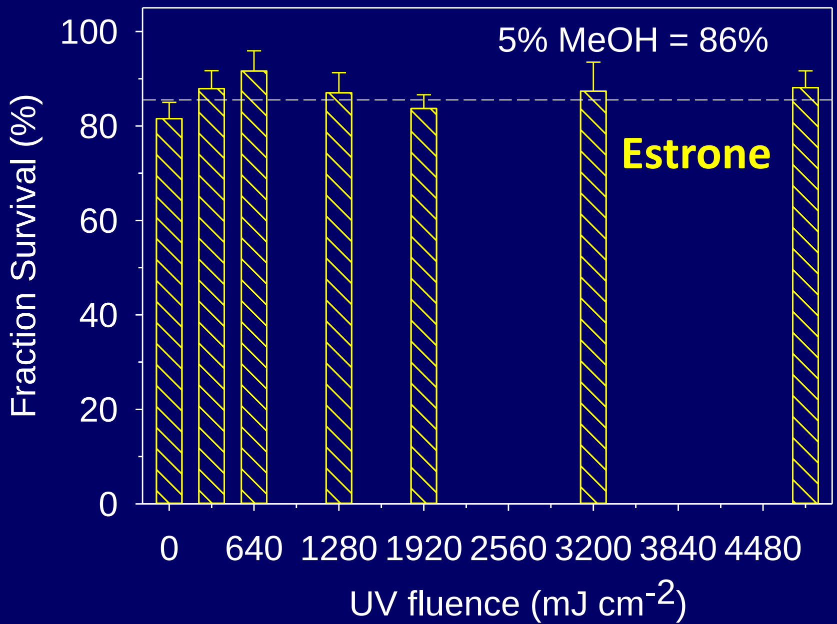
- CYP1A-bla
  LS-180 cell line
- MTT assay.

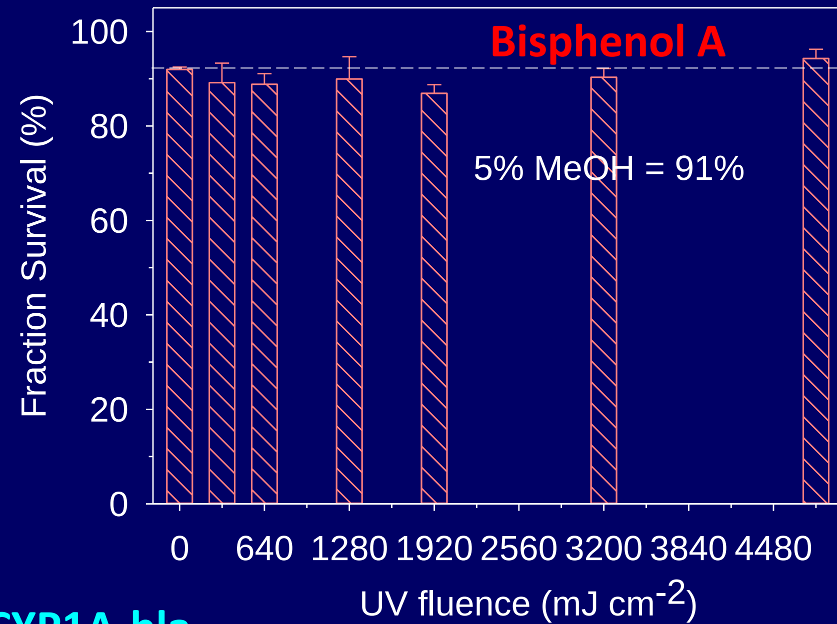
[Diclofenac]$_0$ = 1 μM [H_2O_2]$_0$ = 1 mM

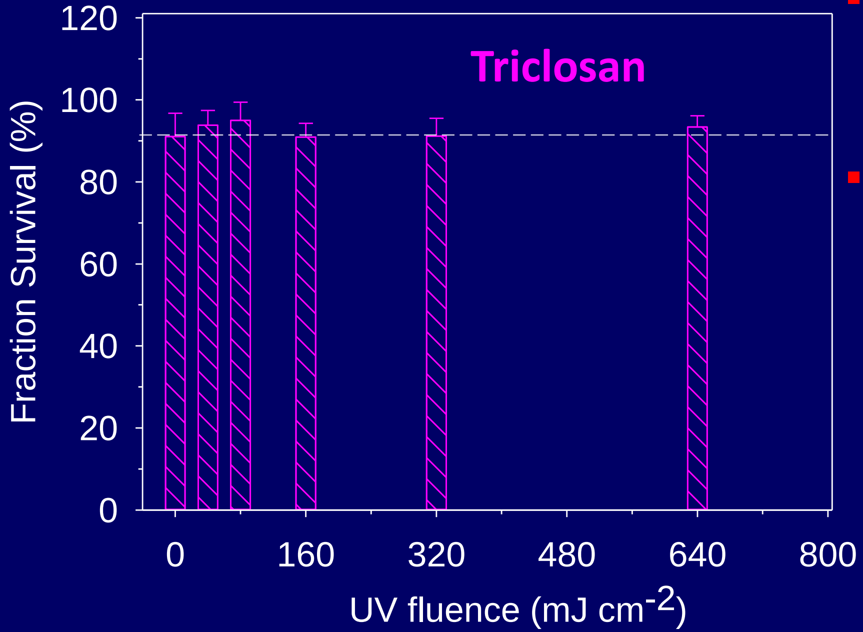
- The higher the bar, the lower the toxicity. Measured by LS180 and MCF-7 assay.

- **The cytotoxicity of treated diclofenac decreased after the complete degradation by UV/H_2O_2, which might be due to the formation of less toxic transformation products.**

Cytotoxicity of treated estrone, triclosan, and bisphenol A by UV/H_2O_2







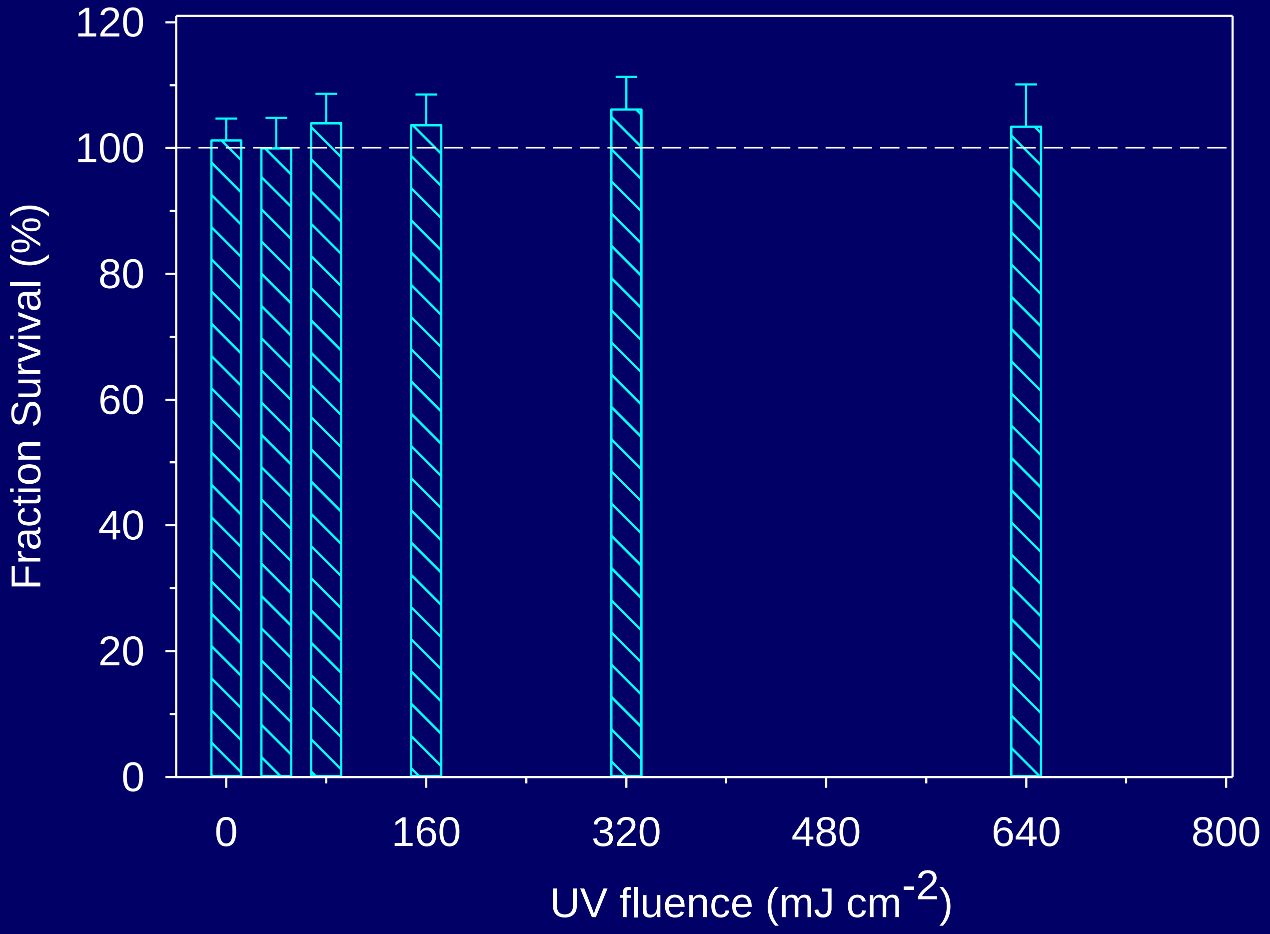
- **CYP1A-bla**

  LS-180 cell line
- **MTT assay.**

$[\mathbf{CEC}]_0 = 1\ \mu M$
$[H_2O_2]_0 = 1\ mM$

❖ **The cytotoxicity of treated estrone, triclosan, and bisphenol A decreased a little bit after the complete degradation by UV/H_2O_2, which might be due to the formation of less toxic transformation products.**

Cytotoxicity of treated Ibuprofen by UV/H_2O_2



- **CYP1A-bla**
  LS-180 cell line
- **MTT assay.**

[**Ibuprofen**]$_0$ = 1 µM
[H_2O_2]$_0$ = 1 mM

- **The higher the bar, the lower the toxicity.**

❖ **The untreated Ibuprofen and its transformation products showed very low cytotoxicity in UV/H_2O_2 system.**

UV-based AOPs for water reuse applications: UV/H_2O_2

Example: Wastewater Reuse in Orange County, California, USA

- **Groundwater Replenishment System (GWRS)**

Secondary Effluent →

Microfiltration (MF)

Reverse Osmosis (RO)

Ultraviolet Light

→ **Seawater Intrusion Barrier**

Recharge Basins

Between MF and RO:

5.7 mM Cl^-
1.0 mM NO_3^-
7.31 mg L^{-1} TOC
Bicarbonate alkalinity as 192 mg $CaCO_3$ L^{-1}
Carbonate alkalinity as 13.33 mg $CaCO_3$ L^{-1}

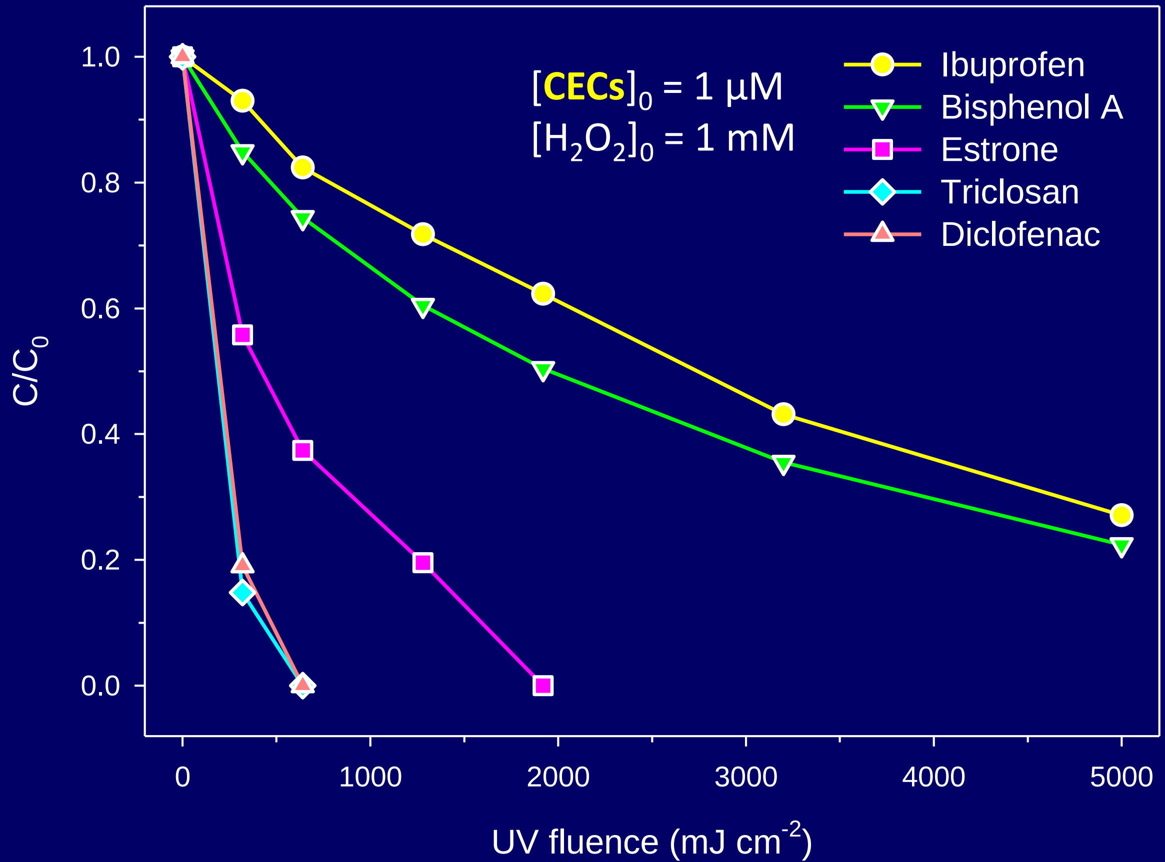
Between RO and UV:

0.1 mM Cl^-
0.63 mM NO_3^-
0.75 mg L^{-1} TOC
Bicarbonate alkalinity as 226.7 mg $CaCO_3$ L^{-1}

Benedict, K. B.; McFall, A. S.; Anastasio, C., Quantum Yield of Nitrite from the Photolysis of Aqueous Nitrate above 300 nm. *Environmental Science & Technology* **2017,** *51* (8), 4387-4395.

Mazellier, P.; Leroy, E.; De Laat, J.; Legube, B., Transformation of carbendazim induced by the H2O2/UV system in the presence of hydrogenocarbonate ions: involvement of the carbonate radical. *New Journal of Chemistry* **2002,** *26* (12), 1784-1790.

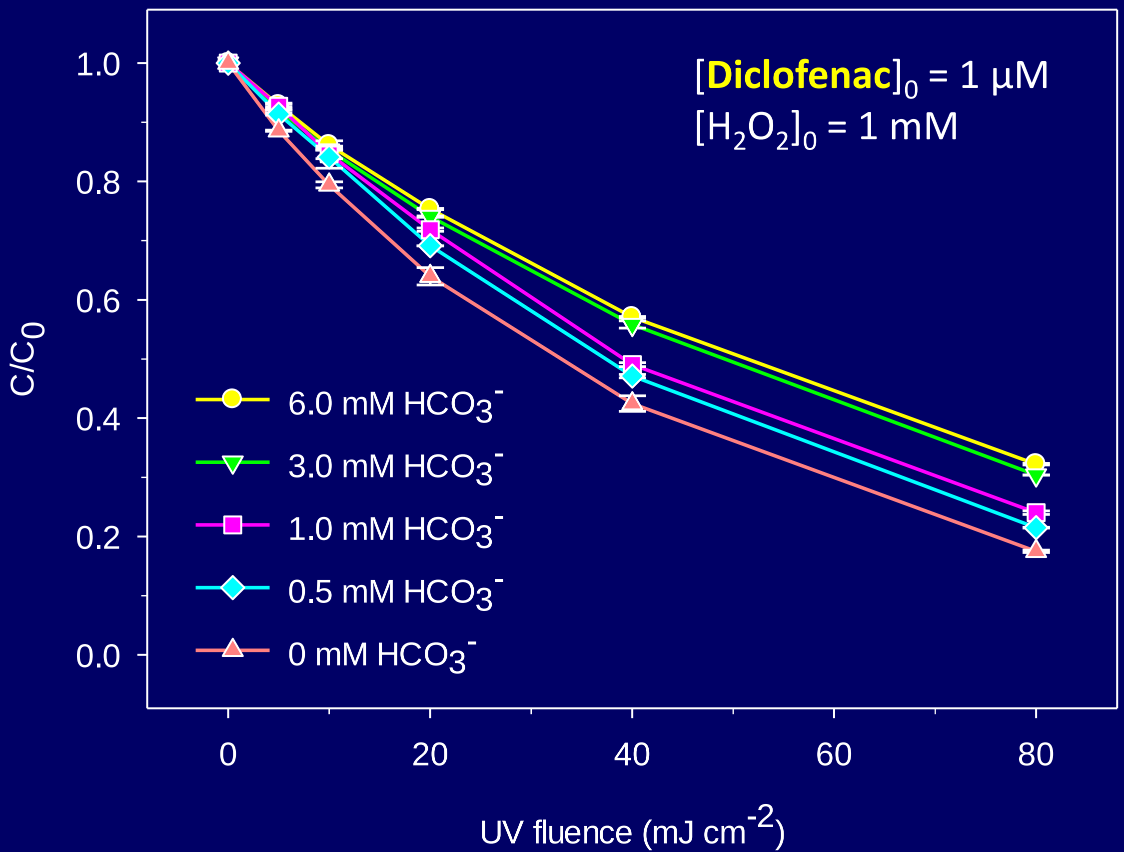
Application of UV/H_2O_2 to remove 5 mixed CECs in RO permeate



- **Degradation of 5 mixed CECs by UV/H_2O_2 in RO permeate that was collected from Orange County Water District.**
- **Quenching compounds in RO permeate significantly impressed the degradation of CECs by UV/H_2O_2.**

- **Triclosan and diclofenac were able to be efficiently removed from RO permeate by UV/H_2O_2 after 960 mJ cm^{-2} UV fluence.**
- **Estrone needed more time to be totally removed from RO permeate by UV/H_2O_2.**
- **Ibuprofen and bisphenol A could not be efficiently removed from RO permeate by UV/H_2O_2 after 5000 mJ cm^{-2} UV fluence.**

Effects of HCO_3^- on UV/H_2O_2 process



$$k_{\cdot OH,DCF} = 7.5 \times 10^{9}\ M^{-1}s^{-1}$$ [1]

$$k_{CO_3^{\bullet -},DCF} = 4.8 \times 10^{7}\ M^{-1}s^{-1}$$

（$k_{CO3\bullet-,diclofenac}$ **determined in our lab**）

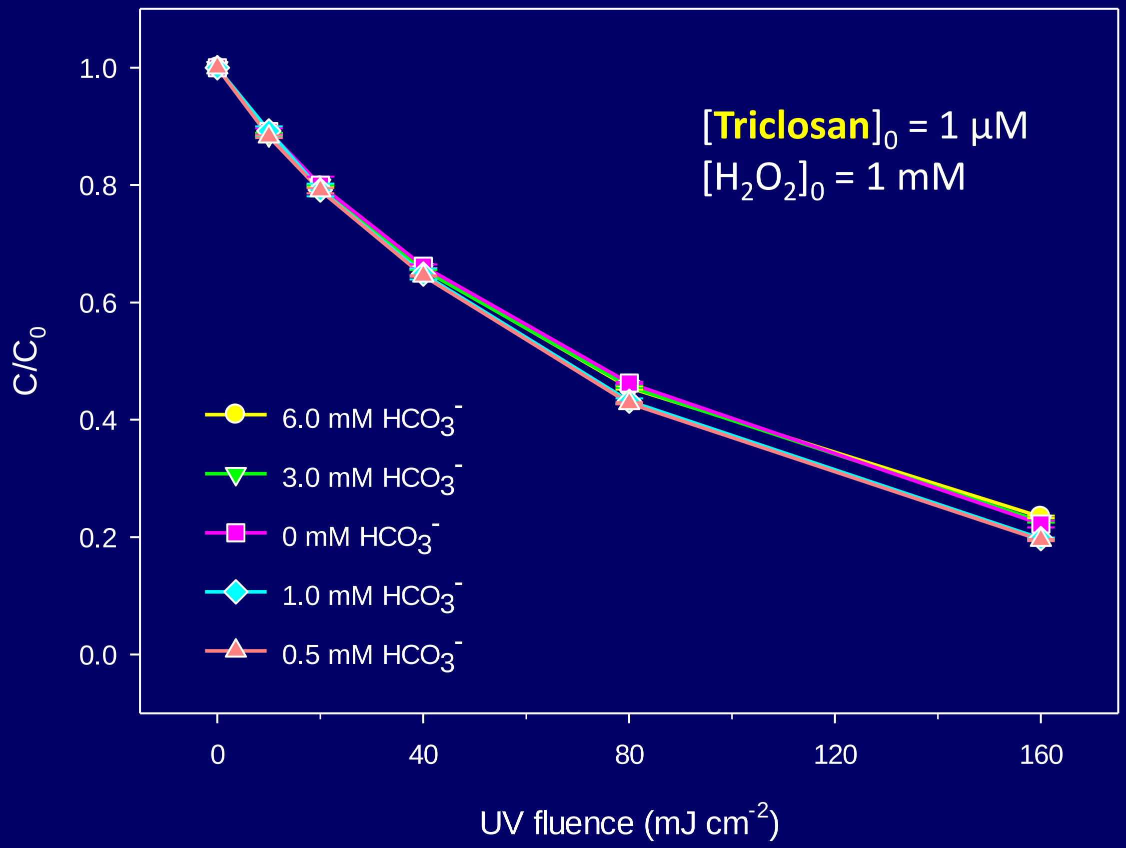
❖ **Degradation rates of diclofenac decreased with the increasing HCO_3^- :**

➢ $$^{\bullet}OH + HCO_3^{2-} \rightarrow CO_3^{\bullet -} + H_2O \qquad k_{\cdot OH,HCO_3^-} = 8.5 \times 10^{6}\ M^{-1}s^{-1}$$ [2]

[1] Huber, M. M.; Canonica, S.; Park, G.-Y.; von Gunten, U., Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. *Environmental Science & Technology* **2003,** *37* (5), 1016-1024.

[2] Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B., Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O−) in Aqueous Solution. *Journal of Physical and Chemical Reference Data* **1988,** *17* (2), 513-886.

Effects of HCO_3^- on UV/H_2O_2 process



$k_{\cdot OH,TCS} = 1.1\times\ 10^9\ M^{-1}s^{-1}$ [1]

$k_{CO_3^{\bullet -},TCS} = 1.4\times\ 10^8\ M^{-1}s^{-1}$

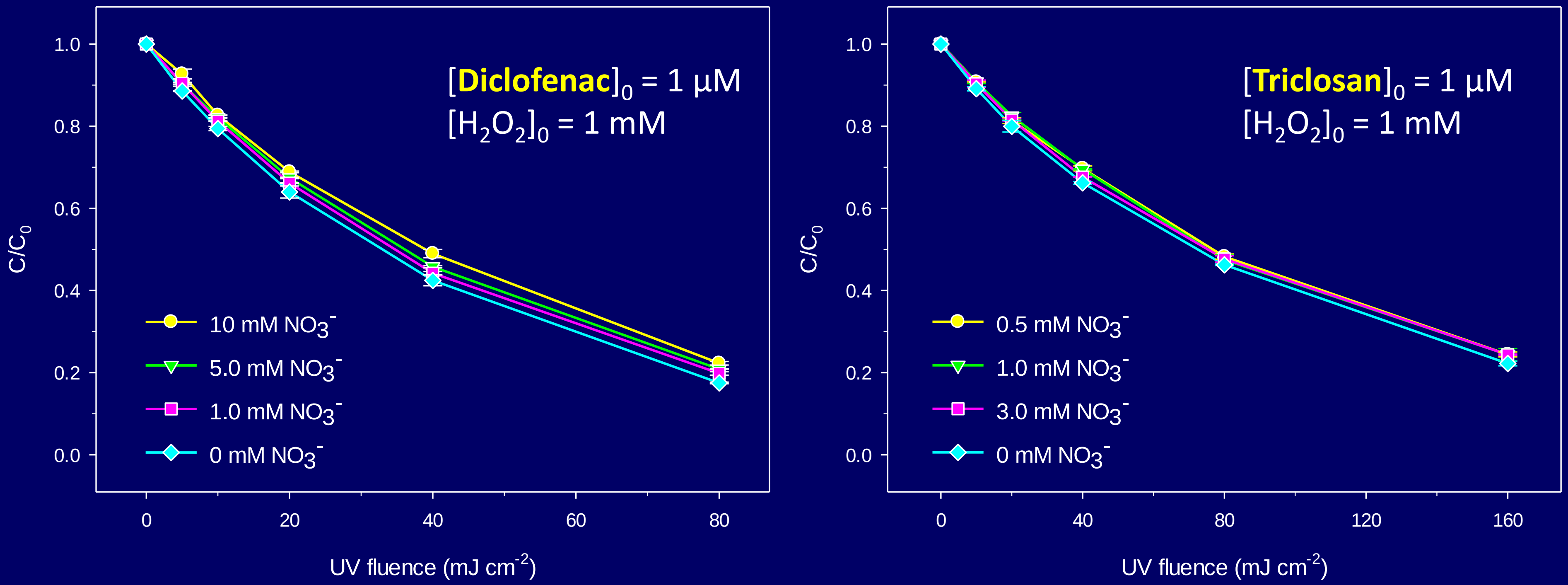
（$k_{CO3\bullet-,triclosan}$ **determined in our lab**）

- **Degradation rates of triclosan did not change obviously with the increasing HCO_3^- :**
  - $^{\bullet}OH + CO_3^{2-} \rightarrow CO_3^{\bullet -} + H_2O$ $\quad k_{\cdot OH,HCO_3^-} = 8.5\times\ 10^6\ M^{-1}s^{-1}$ [2]

[1] Huber, M. M.; Canonica, S.; Park, G.-Y.; von Gunten, U., Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. *Environmental Science & Technology* **2003,** *37* (5), 1016-1024.

[2] Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B., Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O−) in Aqueous Solution. *Journal of Physical and Chemical Reference Data* **1988,** *17* (2), 513-886.

Effects of NO_3^- on UV/H_2O_2 process



- **Degradation rates of diclofenac and triclosan did not change significantly with the increasing NO_3^- .**
- **NO_3^- can also be activated by UV photolysis to produce $^{\bullet}OH$.**

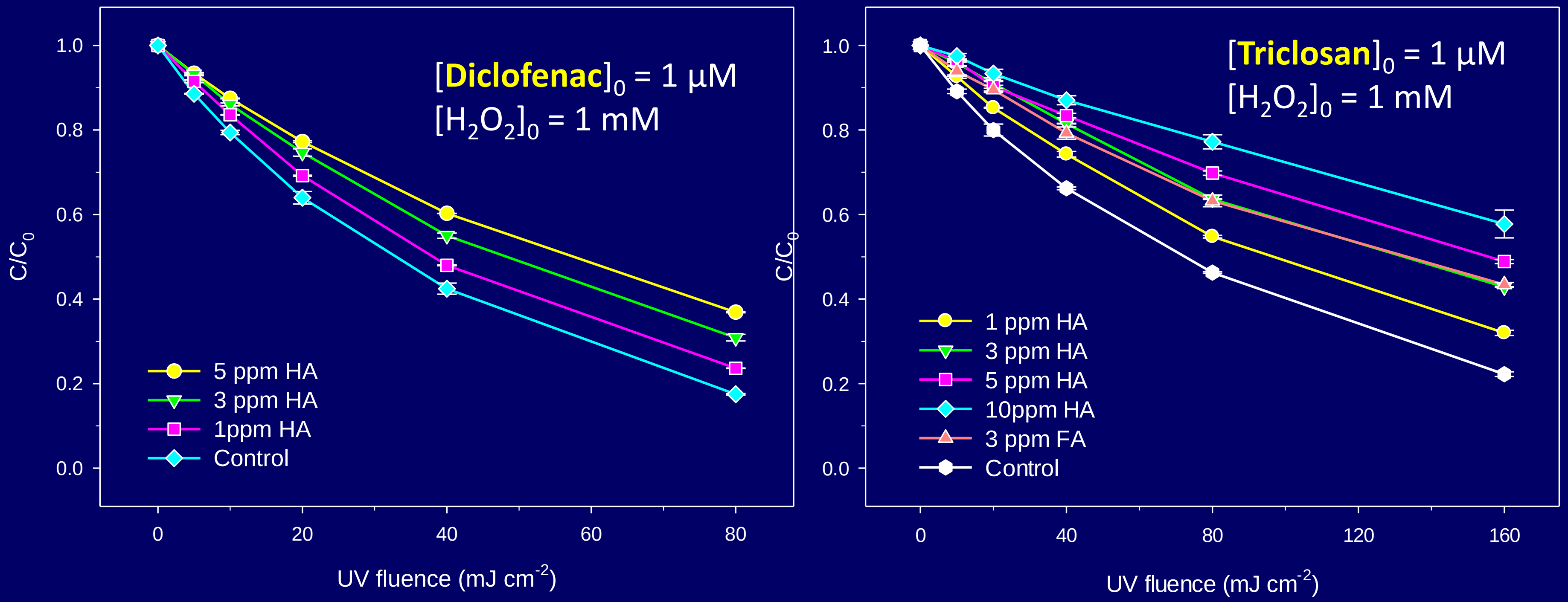
➢ $NO_3^- + hv \rightarrow NO_3^{-*}$

➢ $NO_3^{-*} \rightarrow NO_2 + {}^{\bullet}O^-$

➢ ${}^{\bullet}O^- + H_2O \rightarrow {}^{\bullet}OH + OH^-$

Benedict, K. B.; McFall, A. S.; Anastasio, C., Quantum Yield of Nitrite from the Photolysis of Aqueous Nitrate above 300 nm. *Environmental Science & Technology* **2017,** *51* (8), 4387-4395.

Effects of NOM on UV/H_2O_2 process



- **Degradation rates of diclofenac and triclosan markedly decreased with the increasing amount of NOM.**

  - $^{\bullet}\mathrm{OH} + \mathrm{NOM} \rightarrow \mathrm{Products} \quad = 2.23 \times 10^{8}\ L\ (mol\ C)^{-1}\ s^{-1}$

- **Compared to HCO_3^-, NO_3^-, and Cl^-, NOM will be the primary quenching compounds in field water matrix.**

Westerhoff, P.; Mezyk, S. P.; Cooper, W. J.; Minakata, D., Electron pulse radiolysis determination of hydroxyl radical rate constants with Suwannee river fulvic acid and other dissolved organic matter isolates. *Environmental Science & Technology* **2007,** *41* (13), 4640-4646.

Conclusions

- UV/H_2O_2 can remove 5 CECs much faster than UV alone due to the formed $^{\bullet}OH$.
- Although the 5 mixed CECs were totally removed, cytotoxicity of them did not decrease after the treatment of UV/H_2O_2 at pH = 7, even with longer UV irradiation time. Transformation products would be analyzed to further study the impacts on human and ecological health.
- UV/H_2O_2 treatment shows to be more effective for diclofenac, triclosan, and estrone than for ibuprofen and bisphenol in RO permeate.
- The HCO_3^- slightly inhibited the degradation of diclofenac while it did not affect the degradation of triclosan by UV/H_2O_2; NO_3^- did affect the decomposation of diclofenac nor triclosan; NOM could significantly impress the removal efficiency of both diclofenac and triclosan.

Acknowledgements

- Financial support from the USGS-WRRI (2015SC101G).
- Help from Orange County Water District

QUESTIONS?