Fluorescence Spectroscopy to Quantify Treatment of Wastewater by Ozonation and Advanced Oxidation Processes:

On Line Measurement of Trace Organics Removal

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Outline

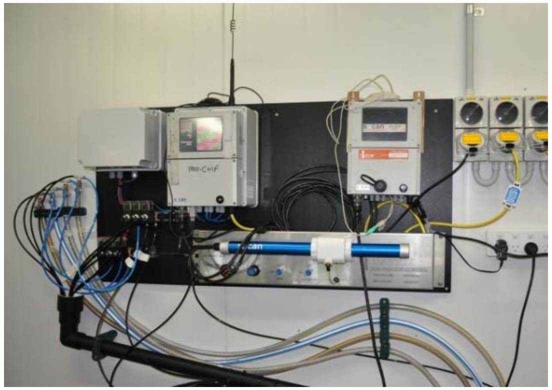
- *Fluorescence of wastewater* and its changes caused by advanced oxidation processes
- Correlations between *pharmaceuticals/personal care products* (PPCP) degradation and fluorescence changes
- Fundamental aspects of such correlations
- Modeling and potential applications

Personal background

- Born in the city of Kazan, Russia
- Kazan State University
  - M.S. In physics, spectroscopy
- Kazan State Technological University
  - PhD in physical chemistry; electrochemistry

Research interests

- Characterization of dissolved organic matter
  - NOM and EfOM
- Disinfection by-products
  - I-DBP and N-DBP
- Emerging contaminants
- Advanced oxidation processes
- Heavy metals
- Corrosion and electrochemistry
- Nuclear remediation



Growing scarcity of water and alternative water supplies

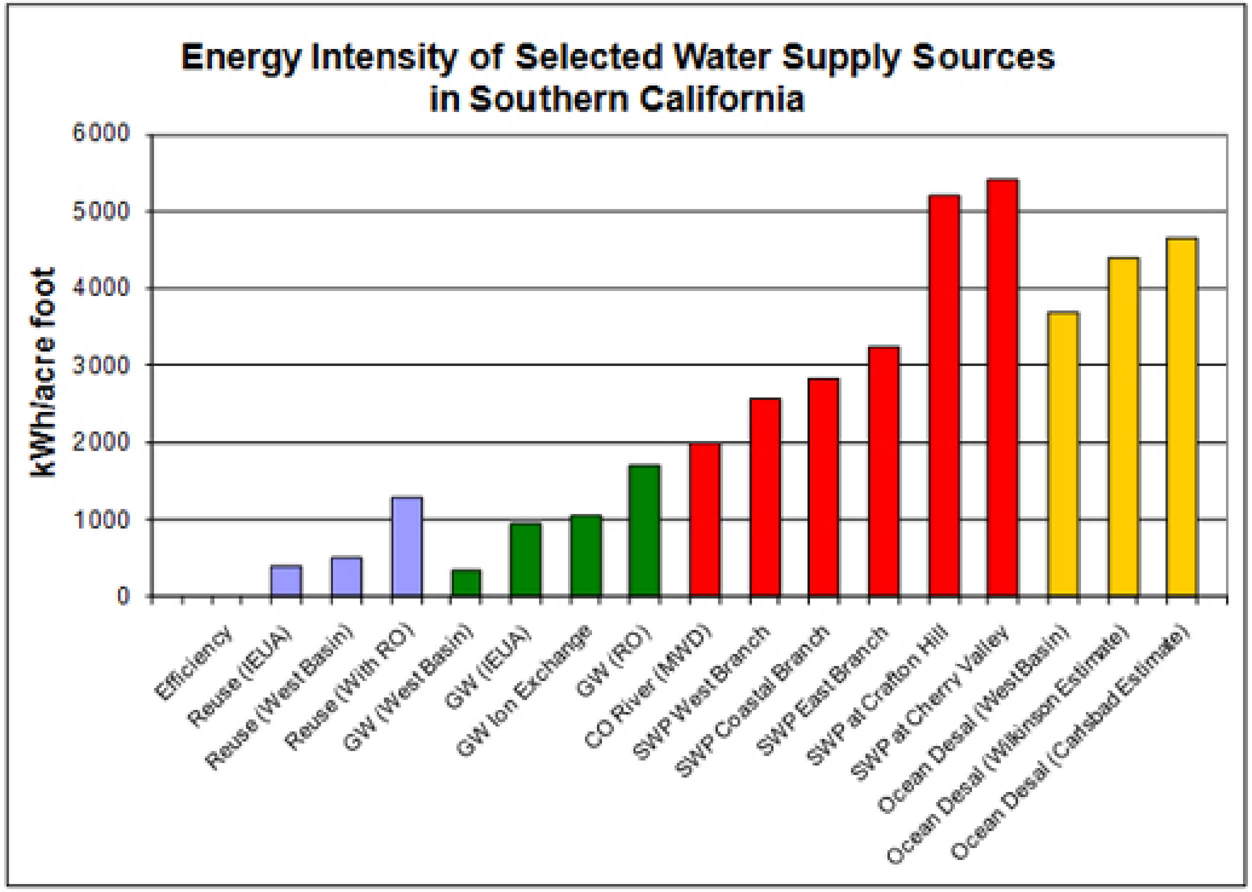
Some general facts concerning recycled water

- In the ***United States***, 0.1% of municipal wastewater was recycled in 2010.
  - The largest site in the U.S. is in ***Orange County, Calif***., where a system replenishes groundwater with 70 mgd of treated effluent.
- ***Israel*** reuses almost 70% of its wastewater each year for agriculture.
  - Much of the leftover sewage water is reused for other purposes.
- The second most efficient recycled water user, ***Spain***, recycles 12% of its wastewater for agriculture.
- In ***Singapore***, 15% of water originates from treated effluent. Most is used for irrigation or manufacturing; some for drinking.

Some general facts concerning recycled water

- The bigger hurdle to public acceptance may be psychological.
  - The notion of treated sewage “hooks into the intuitive concept of contagion” and contamination.
- In 1998 in San Diego the water department’s initiative was derided as “toilet to tap”. Council members refused to discuss it.
  - A 2004 poll commissioned by the San Diego County Water Authority found that 63 % of respondents opposed reuse.
  - a 2011 poll showed that local opposition to reuse had dropped to 25 %.

Comparison of energy intensity (per acre-feet, or 1233 m^3)

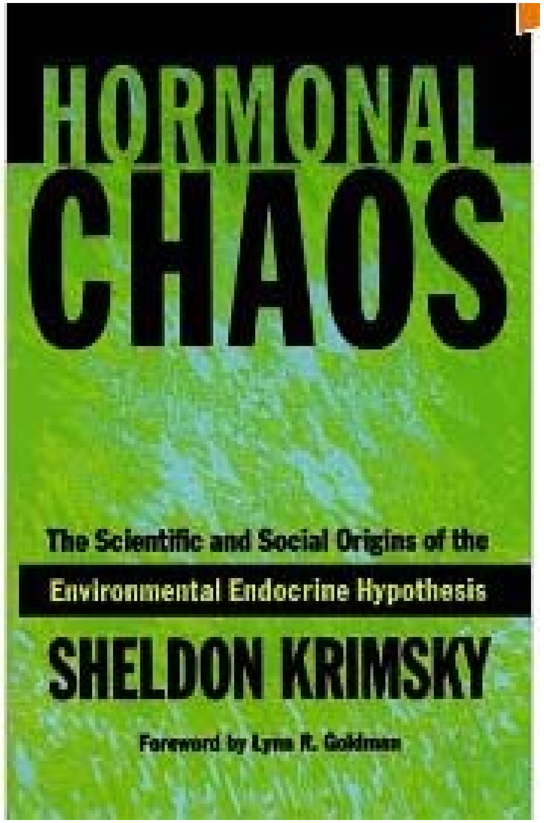


Trace-level organic contaminants

- **Thousands of trace-level organic contaminants exist everywhere in the environment**
  - Effects in wildlife have been documented
  - Long-term effects on human populations are unknown
- **Urban runoff, municipal wastewater and recreational activities are their major sources**
- **Control of these contaminants requires that several steps be taken**
  - Further quantitate their occurrence and *effects*
  - Develop and implement voluntary and mandatory standards and regulations
  - Apply advanced treatment methods to point sources. other measures for non-point sources

Why the concern?

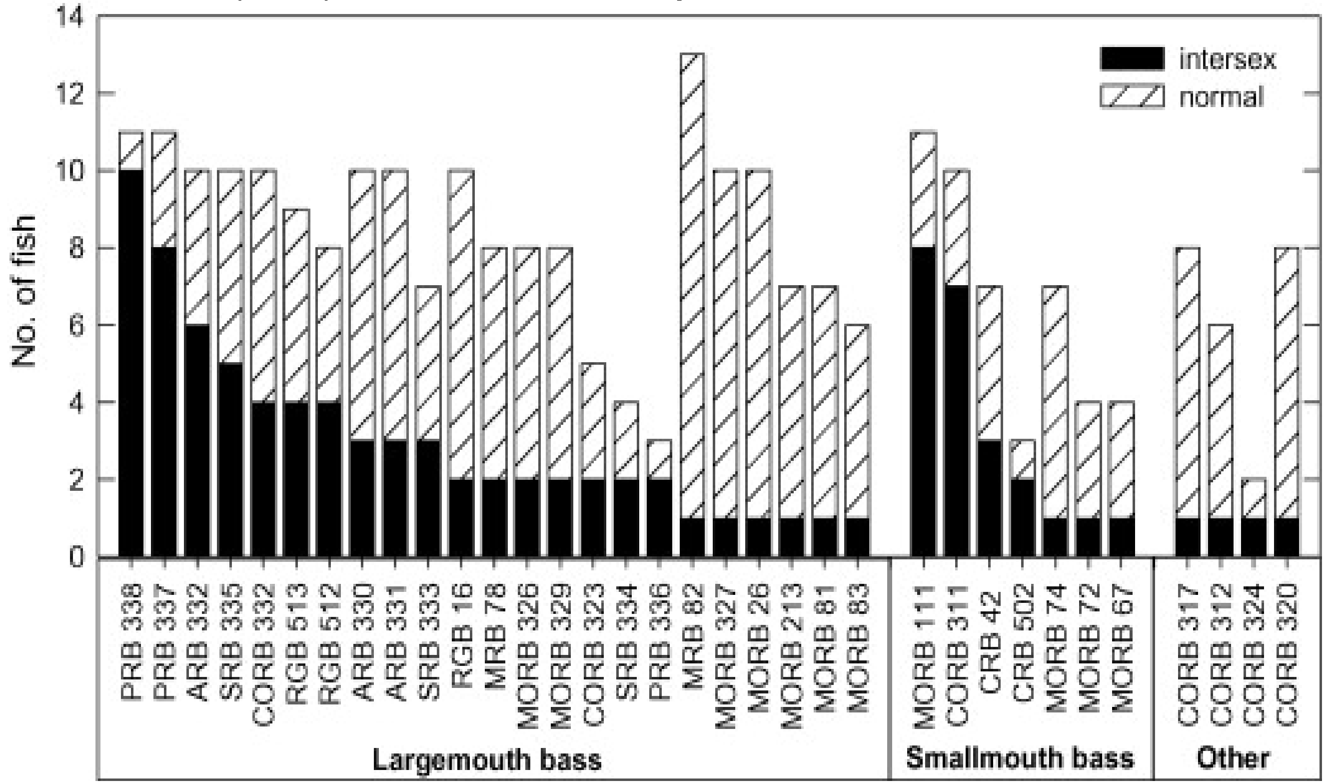
- Thousands of chemicals are getting into the environment with both known and unknown concentrations and effects
  - >62,000 species that in principle can exert endocrine disruption
- Possibilities to detect these chemicals increase dramatically as analytical methods become more sensitive.
- Reports of intersex fish and other species have triggered public interest and anxiety



Occurrence of intersex animals

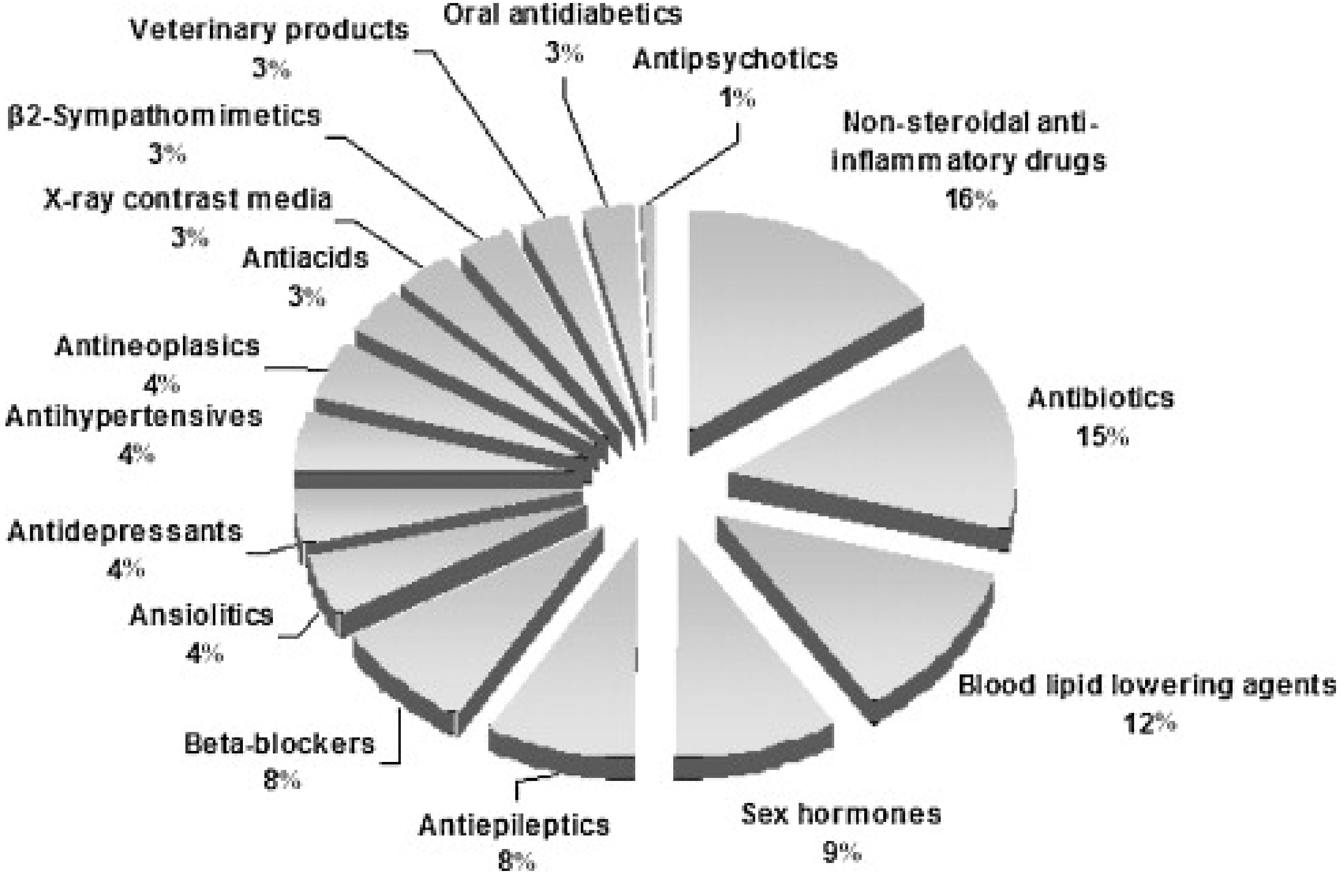
Intersex condition in male fish by site

(ARB, Apalachicola River Basin; CORB, Colorado River Basin; CRB, Columbia River Basin; MORB; Mobile River Basin; MRB, Mississippi River Basin; PRB, Pee Dee River Basin; RGB, Rio Grande Basin; SRB, Savannah River Basin)



Therapeutic classes detected in the environment, expressed in relative percentages

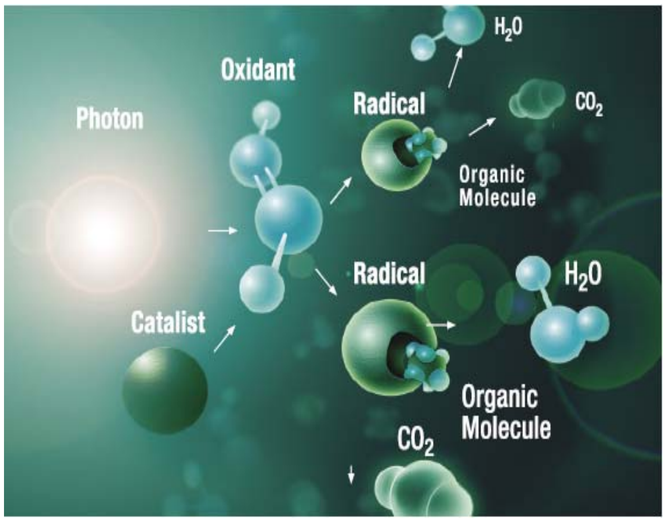
(Santos et al. J. Haz. Materials, 175 (1–3), 45–95)



Problems with the removal of compounds of emerging concern

- Wastewater treatment processes are not designed to remove trace-level CECs
- Many of CECs are hydrophilic and resistant to biodegradation
  - In many cases by design
- Some of these compounds are designed to have very high toxicity
  - Antineoplastic agents
  - Amounts may be small but effects may be substantial

Advanced oxidation processes



- Advanced oxidation processes (AOP) techniques that produce hydroxyl radicals by a variety of methods
  - Ozonation
  - Ozone/ hydrogen peroxide combinations
  - Ozone/UV and H_2O_2/UV
  - Fenton and photo-Fenton
  - Other
- The hydroxyl radical (OH▪) is one of the strongest and environmentally friendly oxidants
  - Also present in our bodies but that not a good news!

Advantages of AOPs

- Rapid degradation of most organic contaminants
  - But not all!
  - NDMA, TCEP, synthetic musks etc.
- Little selectivity and simultaneous removal of many CECs
- Disinfection takes place in parallel with degradation of chemical contaminants
- Removal of COD and color.
- Increase of effluent biodegradability.
- Little or now unwanted by-products
  - Some by-products do exist

AOP treatment of Wastewater: Major Questions Concerning Online Monitoring

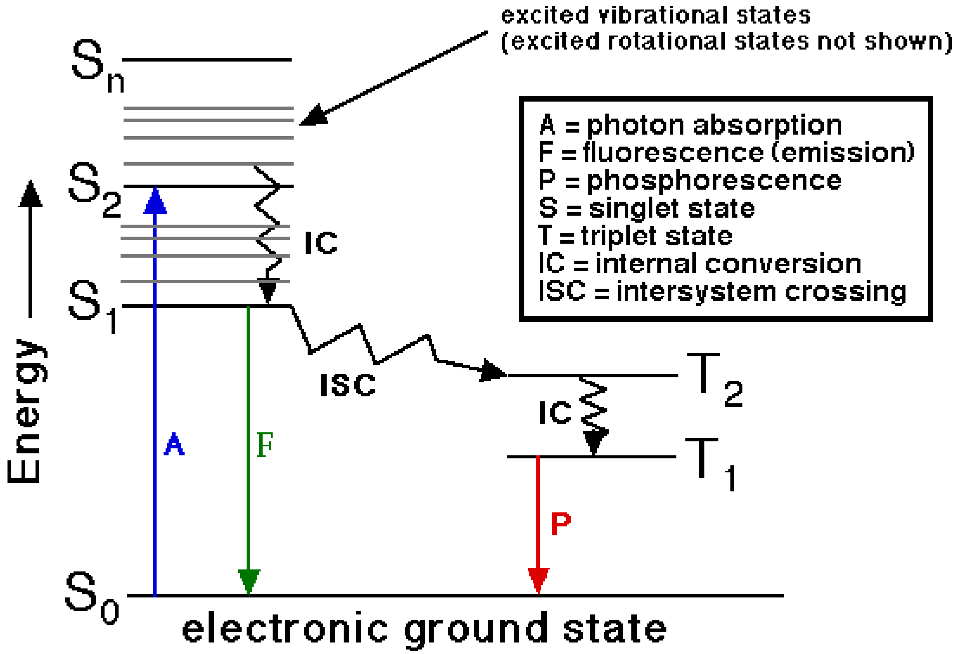
- Impact of treatment (notably, advanced oxidation processes) on effluent organic matter (EfOM) and trace organic compounds?
- Can the changes in EfOM be correlated to destruction of trace organic compounds?
- Are the correlations consistent in a continuous pilot-scale operation and in different wastewaters ?

Basic facts about effluent organic matter (EfOM) and its fluorescence

- Several operationally defined components classes
  - Humic-like species
  - Proteins
  - Other biopolymers
  - "Building blocks"
- Potentially multiple groups of fluorophores
    - PARAFAC can be used to discern their contributions
    - Up to 15 or even 20 fluorophore groups have been reported

In situ methods: absorbance and fluorescence spectroscopy

- Optical spectroscopy
  - Absorbing a photon results in promotion of electron to higher energy level
    - π bonds (double bonds, aromatic rings)
    - non-bonding valence electrons (N, O)
  - Return of electron to ground state = release of energy
    - Fluorescence: release excess energy as photon of light
    - Most likely to occur in molecules with little vibrational flexibility (rigid rings)

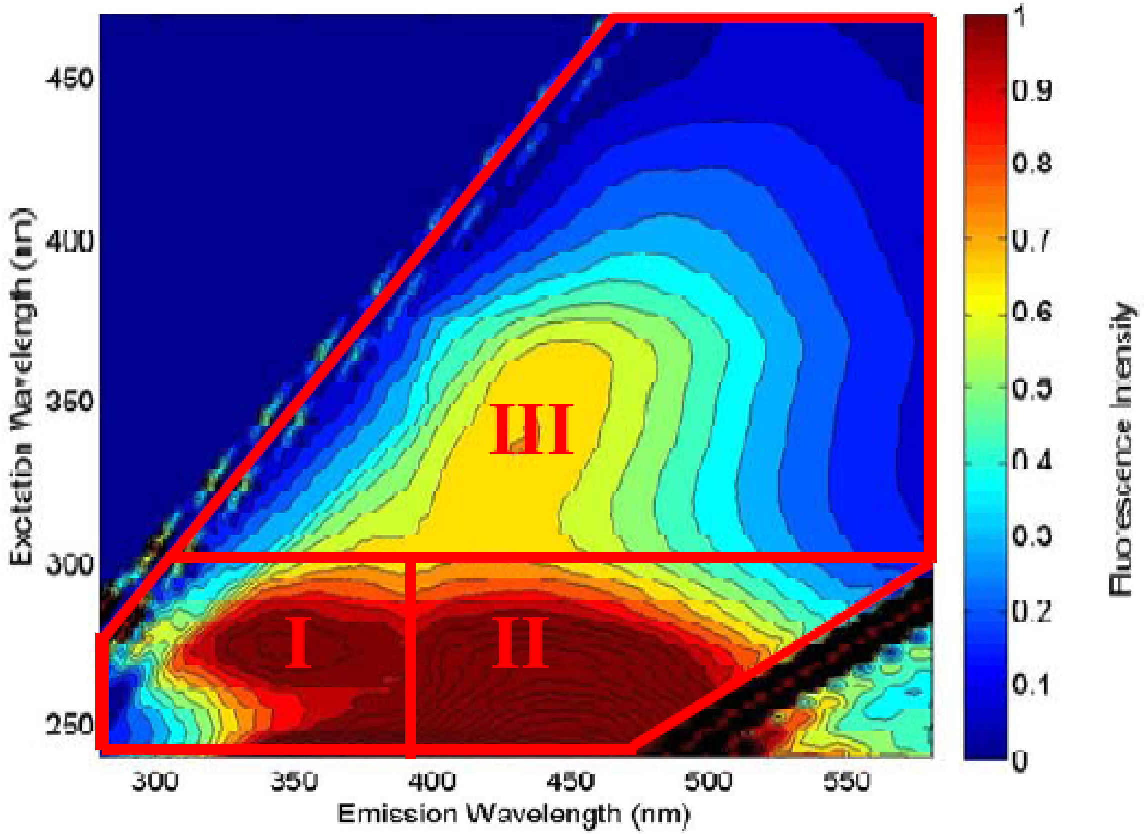


Basic facts about EfOM fluorescence

- Several modes of data acquisition and analysis
- Continuous mode
  - <u>2D emission spectra (fixed excitation λ)</u>
  - 2D excitation spectra (fixed emission λ)
  - Synchronous spectra (fixed λ_{em}-λ_{ex} difference)
  - <u>3D excitation-emission spectra</u>
- Time-resolved fluorescence spectroscopy
- Fluorescence quenching

Typical features of 3D EEM of EfOM

Humic-like substances



Proteins, soluble microbial products

Fulvic-like substances

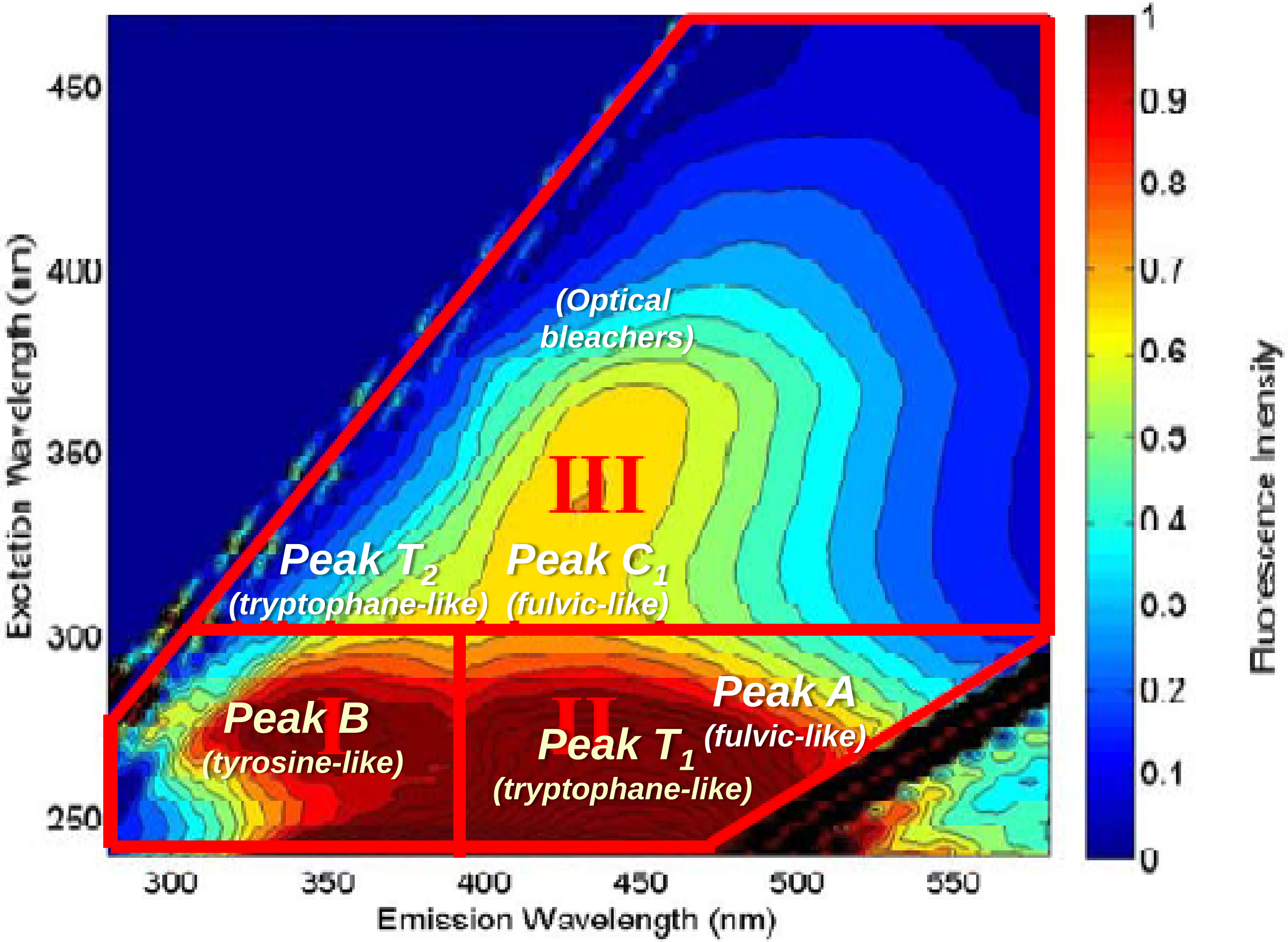
More specific assignments of EEM peaks

(Henderson et al. Water Research, 2009, 43, 863)

Table 2 – Summary of correlations found between fluorescence peak intensities of sewage impacted water and common water monitoring p

System	Instrument	Peaks reported	Parameters measured	Correlations reported (peak/parameter/Pearson's r [unless marked])		
River water	Perkin–Elmer LS-50B	A	PO_4^{3-}	T_1	PO_4^{3-}	0.8
(62 sites within catchment)	luminescence	C_1	NO_3^-		NO_3^-	0.87
	spectrophotometer	T_1	BOD			
		T_2	DO	T_2	BOD	0.85
		B	NH_3		NH_3	0.7
			$UV_{254,\ 340,\ 410}$		DO	−0.65
River water	Perkin–Elmer LS-50B	T_1	Conductivity	C_1	TOC	0.68
(12 sites within catchment)	luminescence	C_1	TOC			
	spectrophotometer	C_2	$UV_{254,\ 340,\ 410}$			
Effluent (sewage and trade including	Varian Cary	T_1	BOD_5	For the entire		
pollution incidents –223 samples)	Eclipse fluorescence			data set:		
and surface water (246 samples)	spectrophotometer	T_2	TOC	T_1	BOD_5	0.906[a]
		C_2			TOC	0.876[a]
		A				
				T_2	BOD_5	0.848[a]
					TOC	0.802[a]
				C_2	BOD_5	0.771[a]
					TOC	0.87[a]
				A	BOD_5	0.72[a]
					TOC	0.808[a]

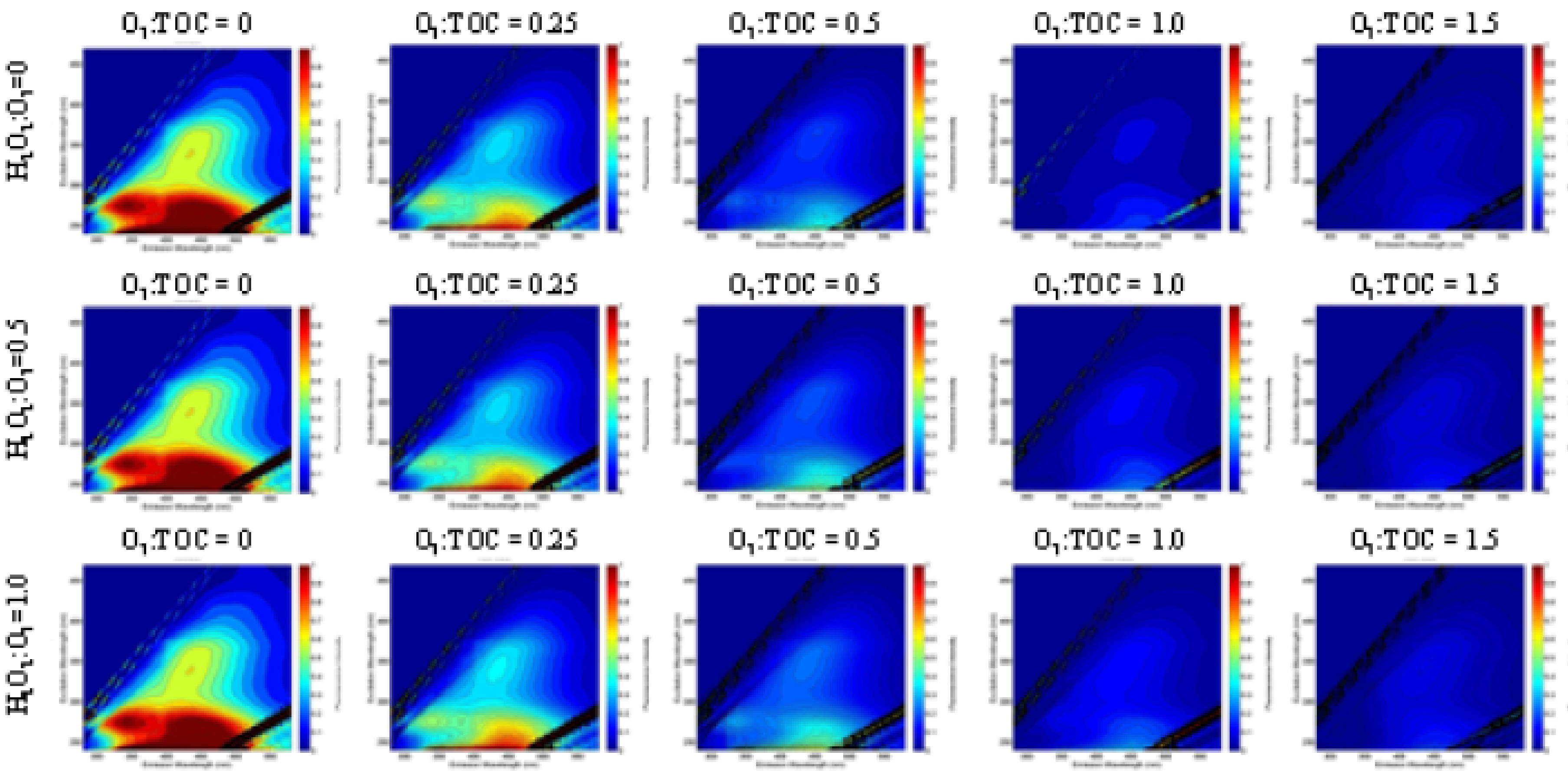
More specific assignments of EEM peaks



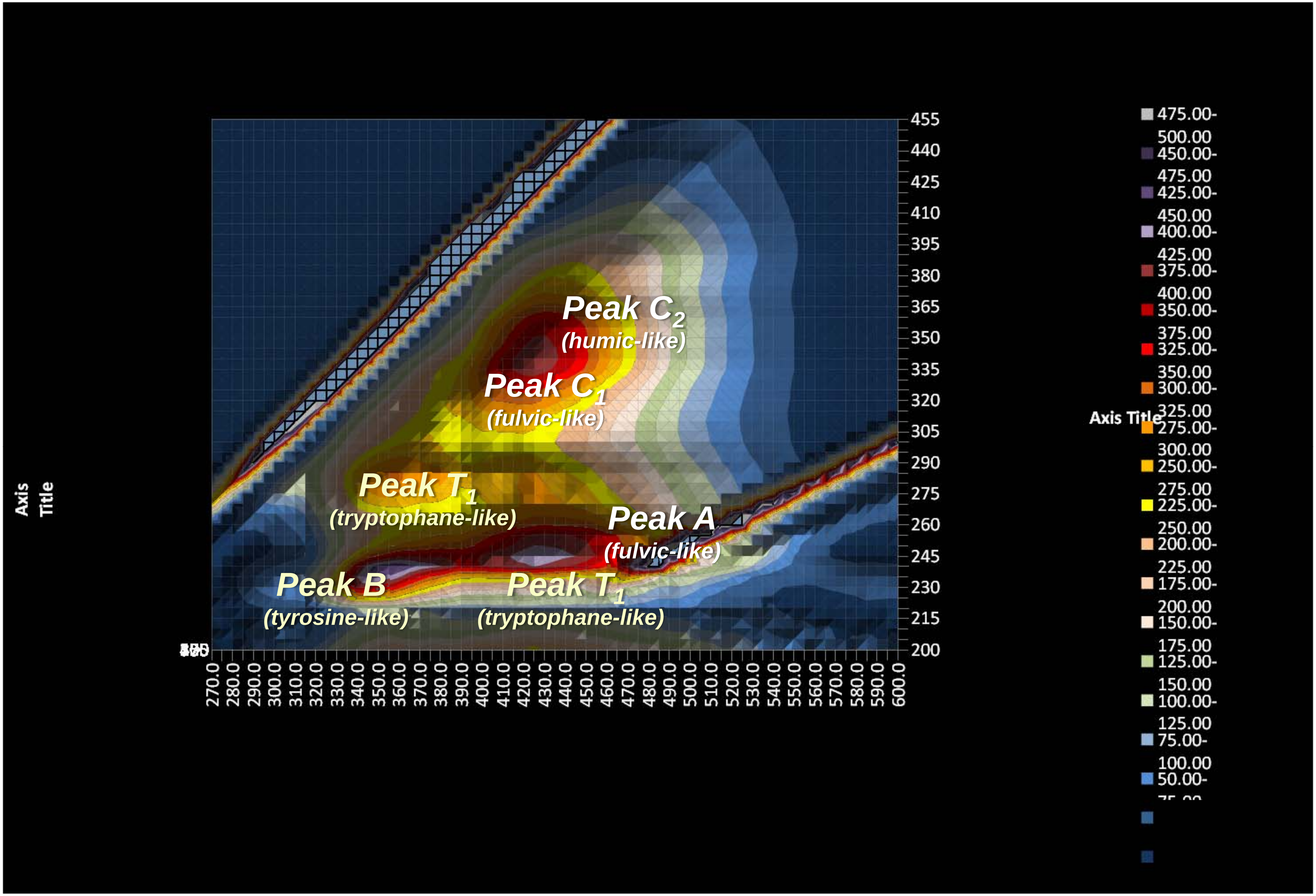
In situ methods and information about intrinsic effluent organic matter (EfOM)

- Can *in situ* methods, notably ***fluorescence*** give us information about the nature of EfOM and its reactivity?
- Can ***fluorescence*** help evaluate the extent of degradation of trace-level contaminants by advanced oxidation processes?
- Can such methods be used practically for online monitoring of wastewater effluents?

Typical changes of fluorescence spectra in AOP conditions

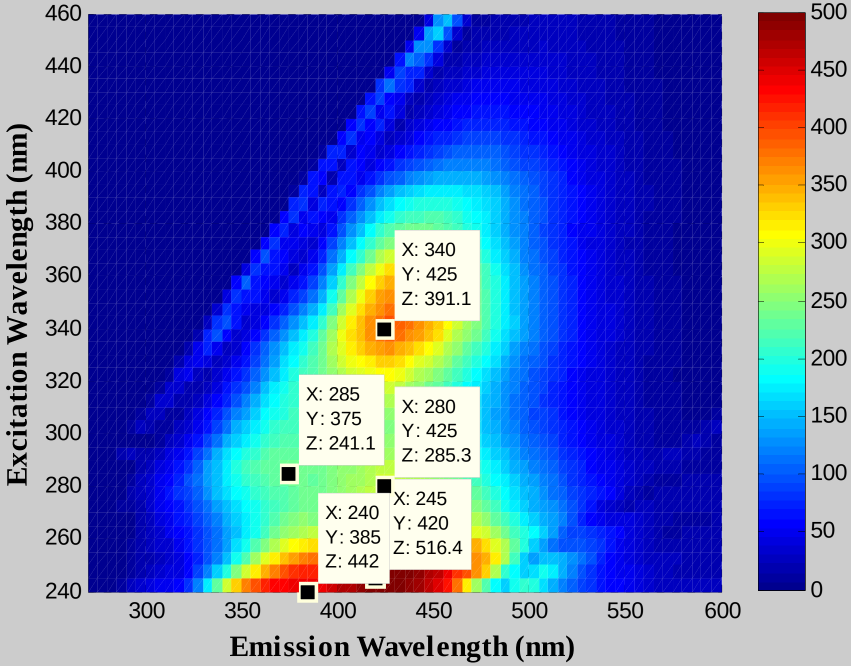


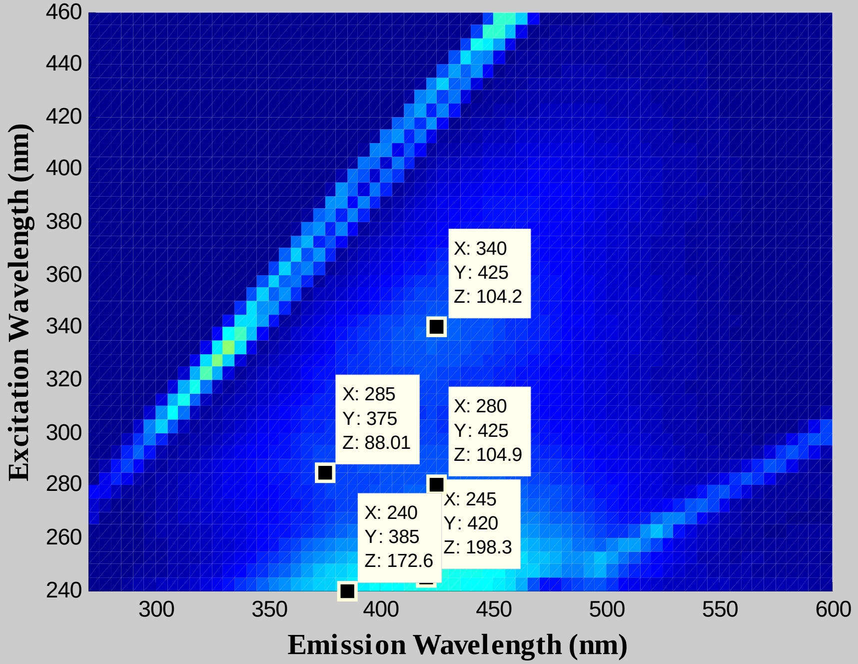
EEM of unfiltered CCWRD wastewater



Typical EEM data for MWRDGC (unfiltered wastewater)

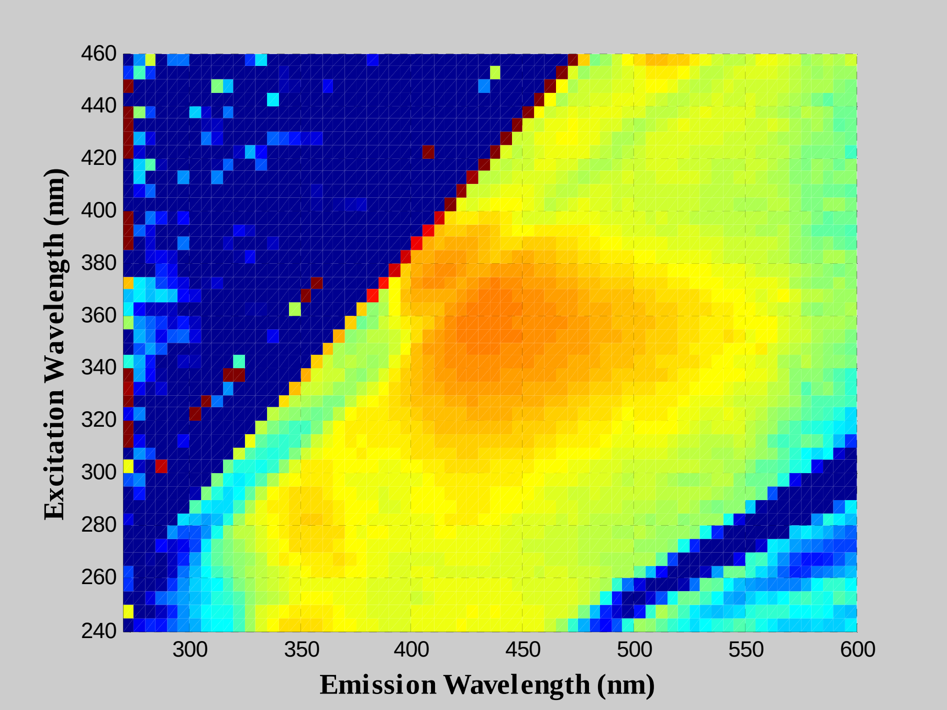
Raw unfiltered water **O_3/TOC=0.25**



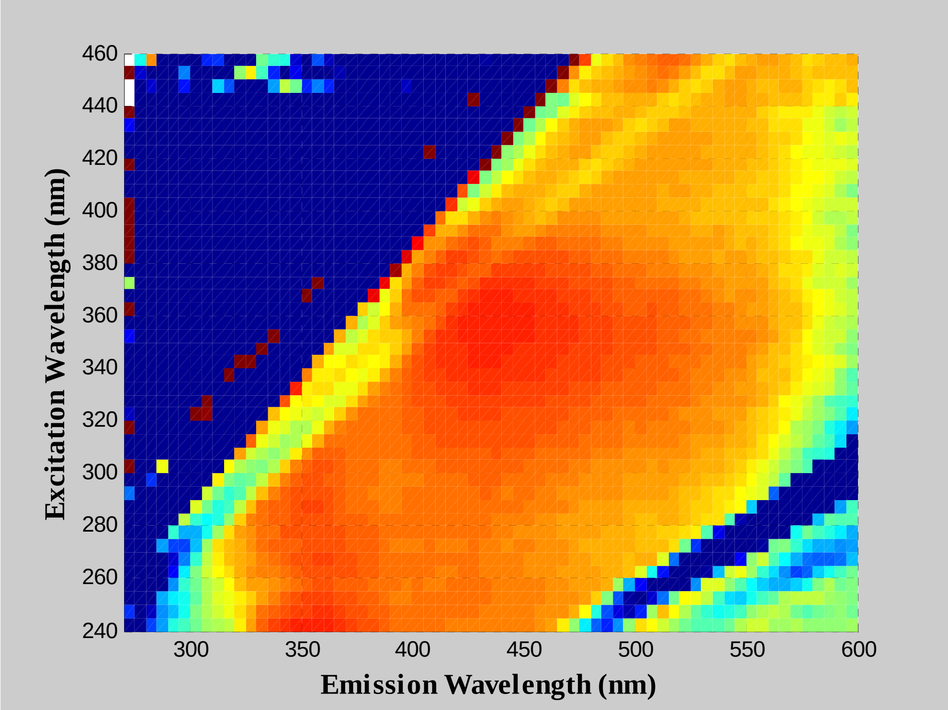


Typical EEM data for MWRDGC (unfiltered water)

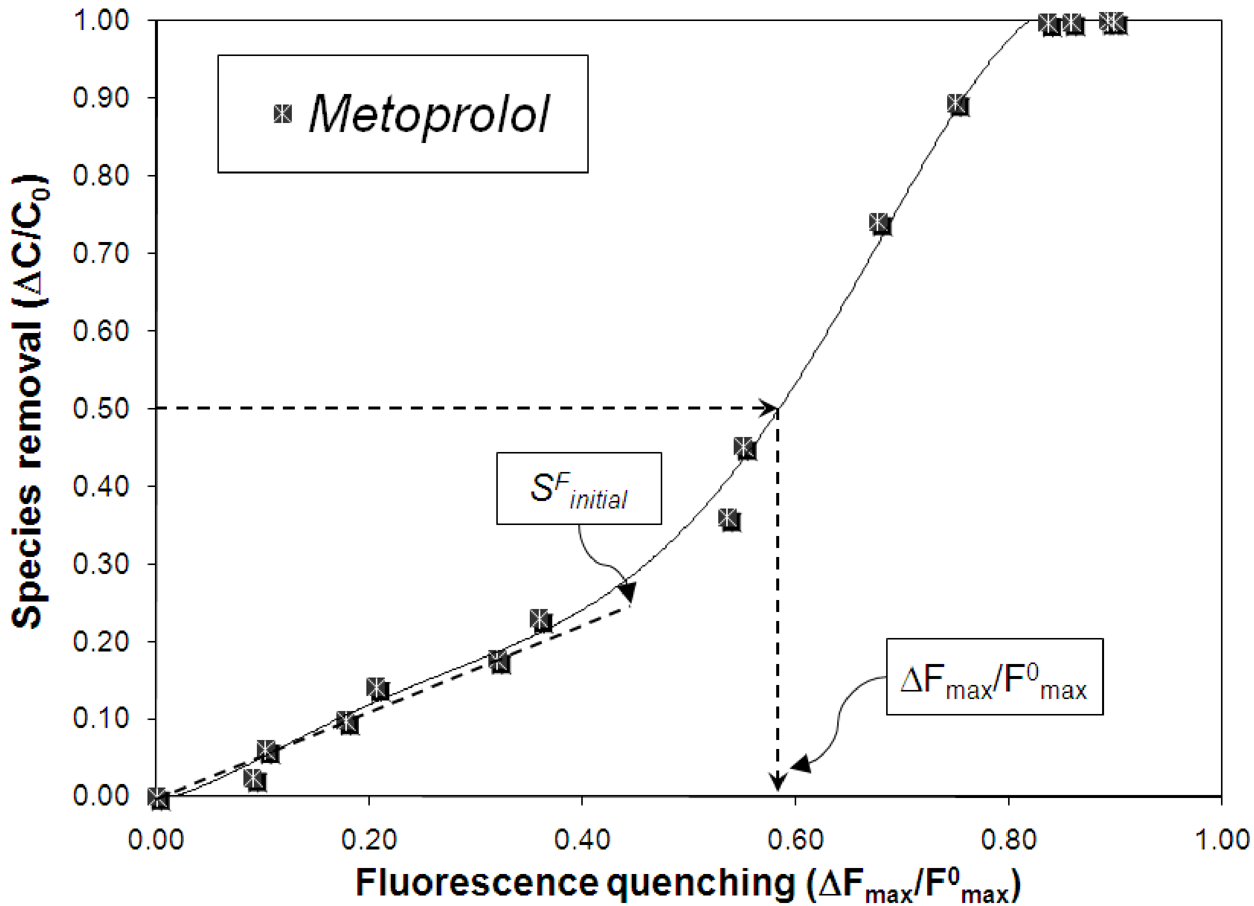
O_3/TOC=0.25



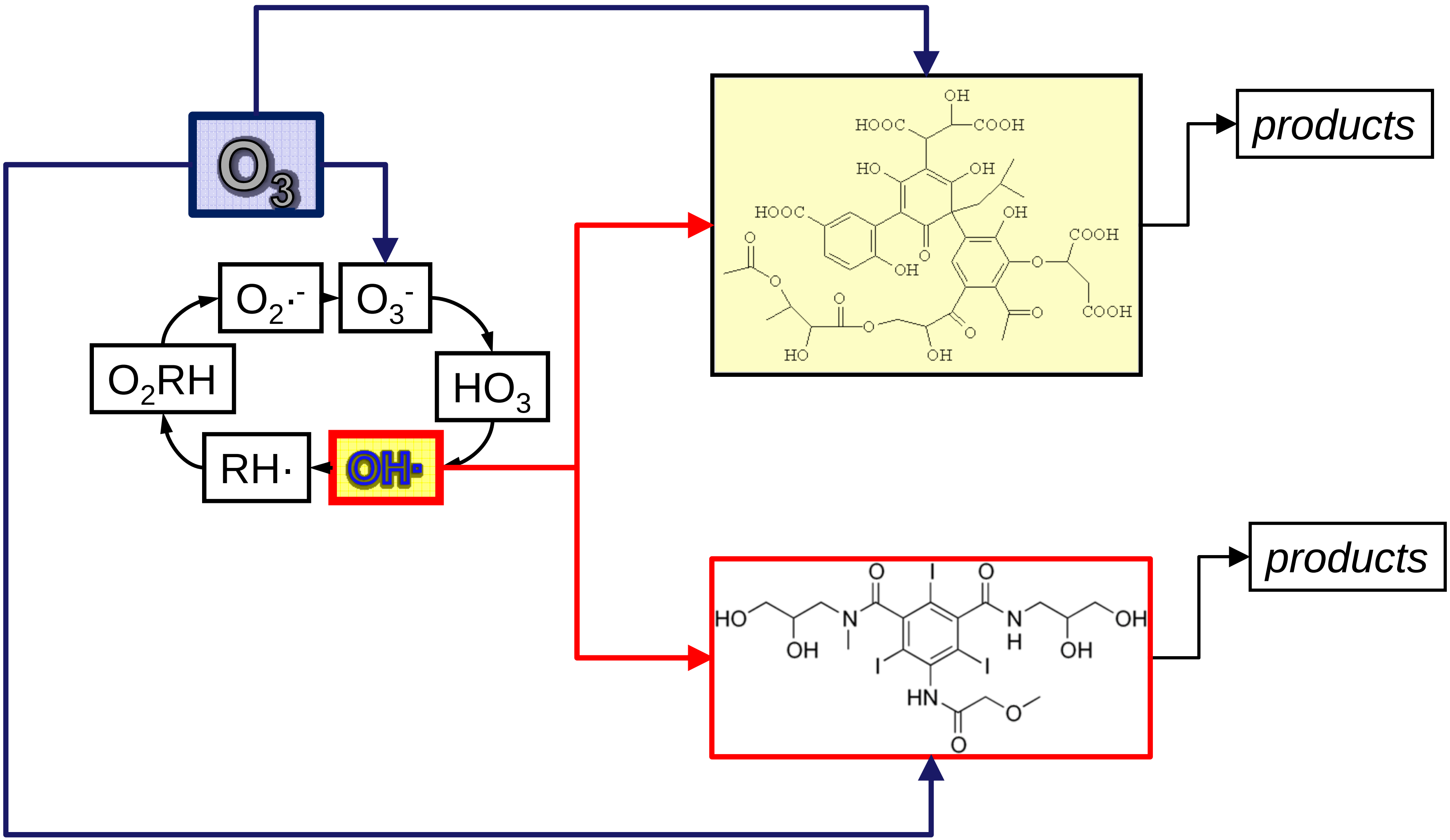
O_3/TOC=0.50



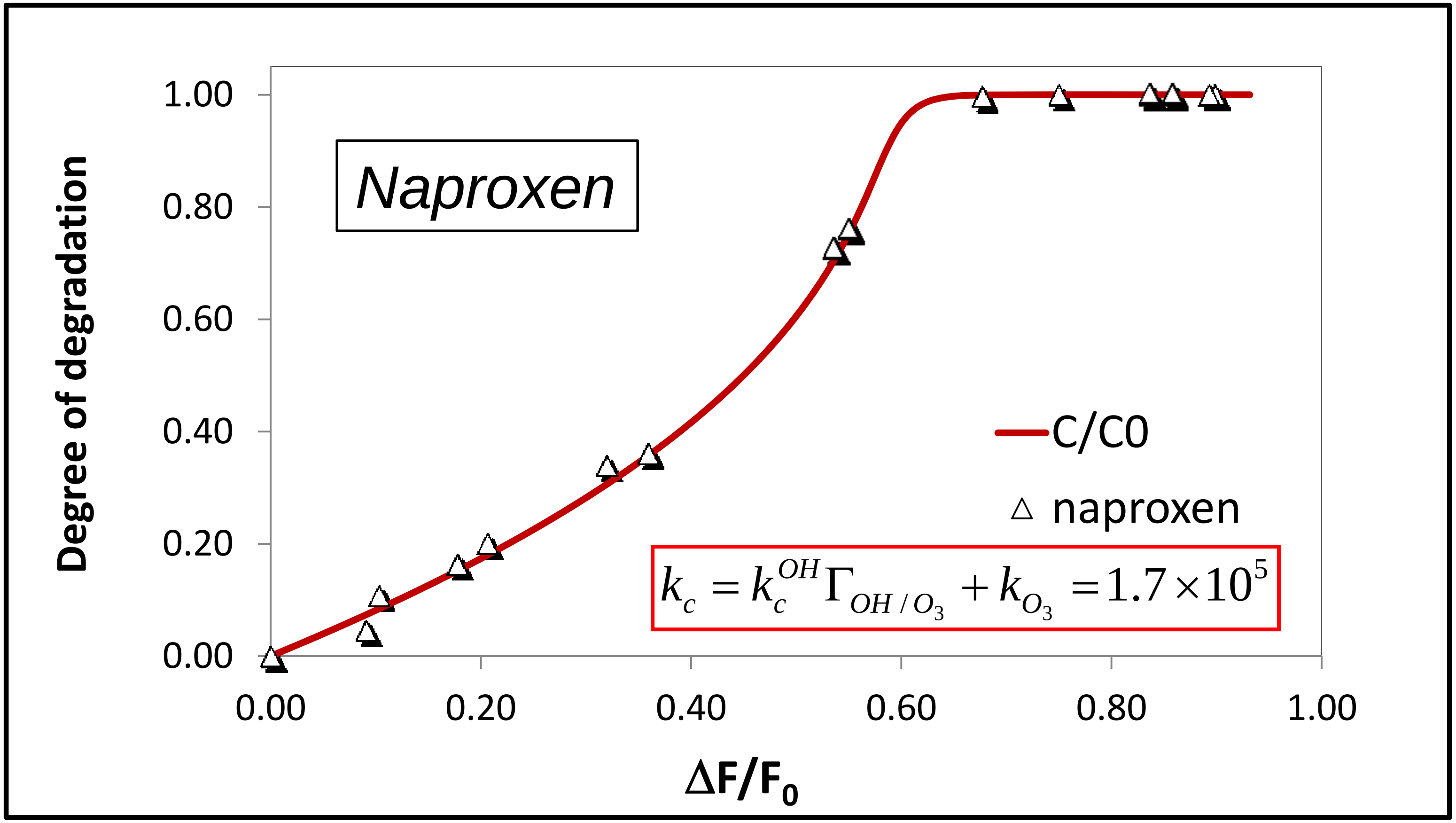
$\Delta C/C_0$ vs. $\Delta F/F_0$ changes for metoprolol



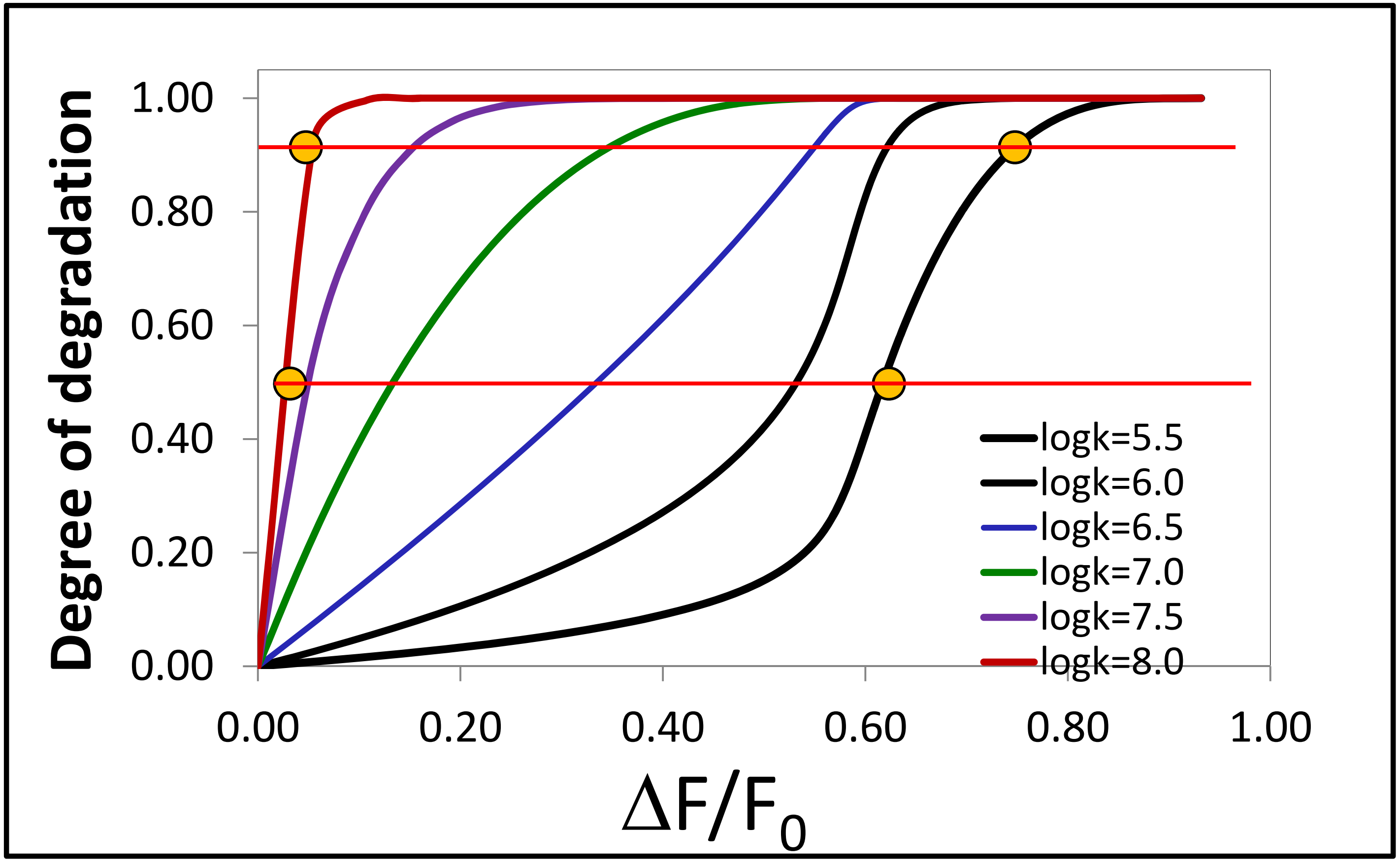
General scheme of parallel EfOM and EDC/PPCP oxidation



$\Delta C/C_0$ vs. $\Delta F/F_0$ changes for naproxen



Model predictions of typical shapes of $\Delta C/C_0$ vs. $\Delta F/F_0$ relationships



AOP treatment of Wastewater: Major Questions Concerning Online Monitoring

- Are AOP-induced changes of wastewater optical properties correlated with the destruction of all CECs?
- Are they applicable to both chemical and microbiological contaminants?
- Are the correlations consistent in different wastewaters?
- Are data generated in lab-scale conditions applicable for continuous operations?

Participating utilities in the United States

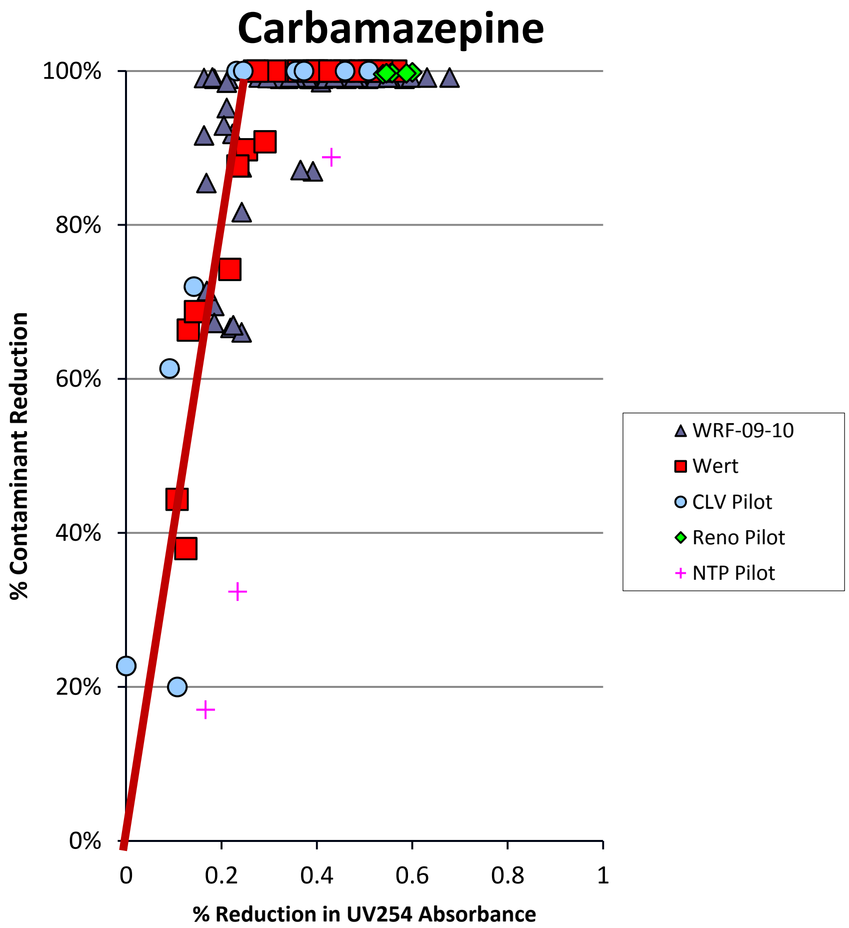
Summary of target compounds and rate constants

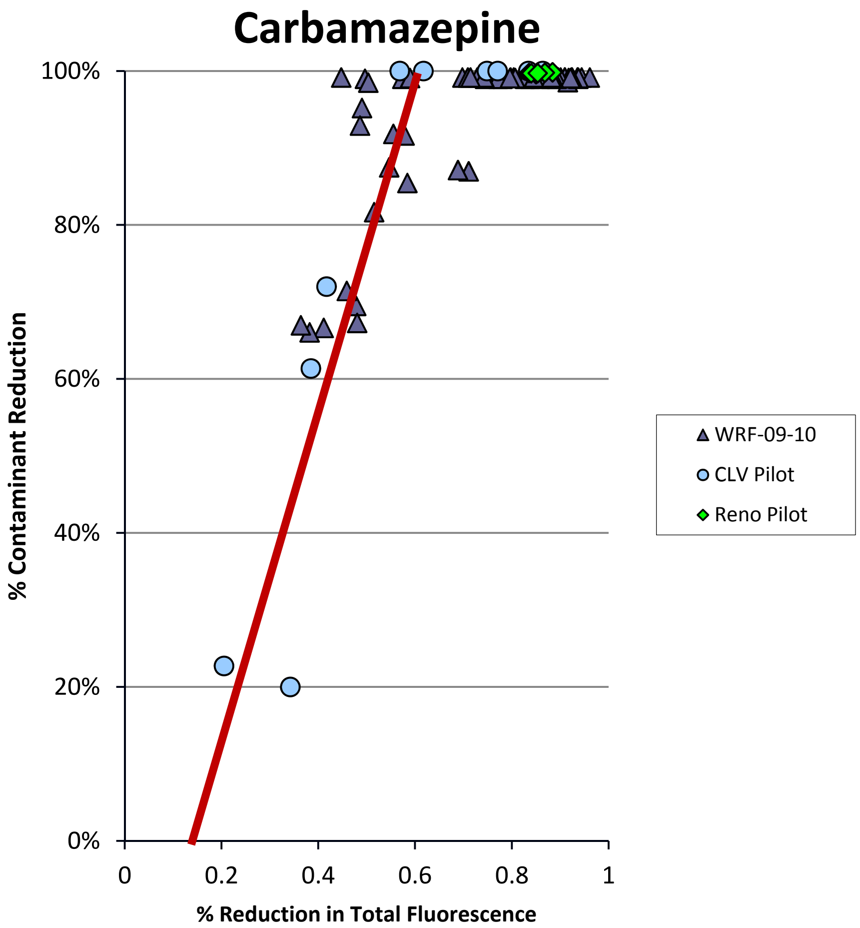
Compound	MRL (ng/L)	k_{O_3}[1] ($M^{-1}s^{-1}$)	$k_{\cdot OH}$[1] ($M^{-1}s^{-1}$)	CDPH Classification[2]
Group 1 – High reactivity with both ozone and ·OH				
Bisphenol A	50	$7x10^5$	$1x10^{10}$	A. Hydroxy Aromatic
Carbamazepine	10	$3x10^5$	$9x10^9$	C. Nonaromatic with carbon double bonds
Diclofenac	25	$1x10^6$	$8x10^9$	D. Deprotonated amine
Naproxen	25	$2x10^5$	$1x10^{10}$	E. Alkoxy polyaromatic
Sulfamethoxazole	25	$3x10^6$	$6x10^9$	B. Amino/acylamino aromatic
Triclosan	25	$4x10^7$	$1x10^{10}$	A. Hydroxy aromatic
Trimethoprim	10	$3x10^5$	$7x10^9$	D. Deprotonated amine
Group 2 – Moderate reactivity with ozone and high reactivity with ·OH				
Atenolol	25	$2x10^3$	$8x10^9$	D. Deprotonated amine
Gemfibrozil	10	$2x10^4$	$1x10^{10}$	F. Alkoxy aromatic
Group 3 – Moderate reactivity with both ozone and ·OH				
DEET	25	<10	$5x10^9$	G. Alkyl aromatic
Ibuprofen	25	10	$7x10^9$	G. Alkyl aromatic
pCBA	10,000	<10	$5x10^9$	G. Alkyl aromatic
Phenytoin	10	<10	$6x10^9$	G. Alkyl aromatic
Primidone	10	<10	$7x10^9$	G. Alkyl aromatic
Group 4 – Low reactivity with ozone and moderate reactivity with ·OH				
1,4-Dioxane	500	<1	$3x10^9$	Alternative criterion (0.5-log removal)
Atrazine	10	6	$3x10^9$	D. Deprotonated amine
Meprobamate	10	<1	$4x10^9$	H. Saturated aliphatic
Group 5 – Low reactivity with both ozone and ·OH				
Musk Ketone	100	<1	$1x10^9$	I. Nitro aromatic
TCEP	200	<1	$7x10^8$	H. Saturated aliphatic

AOP wastewater treatment conditions

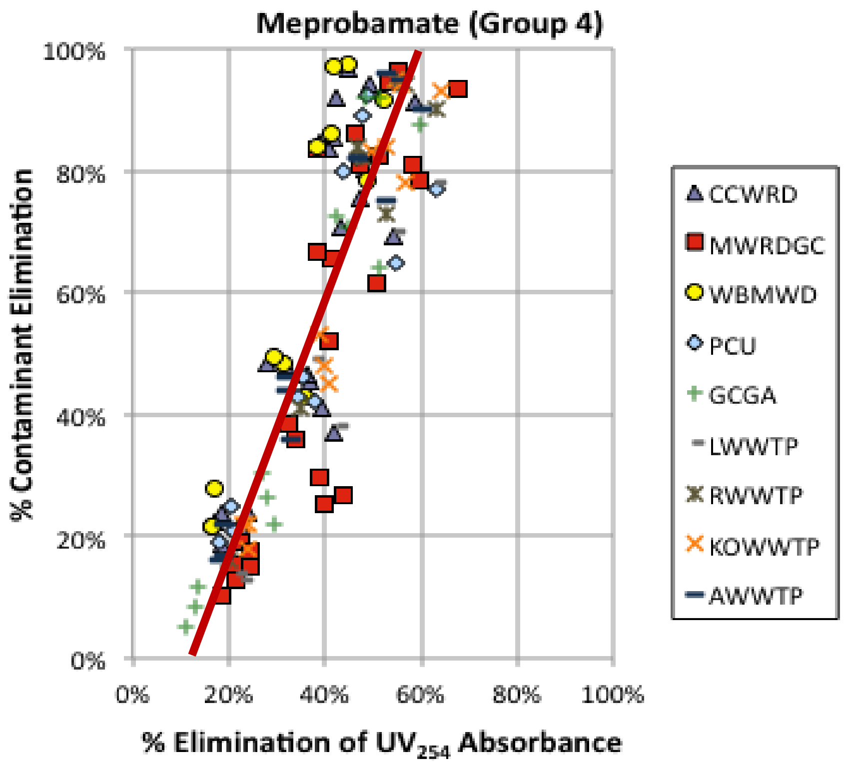
- *Ozonation per se*
  - O_3/DOC mass ratios 0 to 1.5
- H_2O_2/O_3 treatment
  - Molar H_2O_2/O_3 ratios 0. 0.5, 1.0
- UV/H_2O_2 treatment
  - UV dose up to 750 mJ/cm^2
  - H_2O_2 concentrations up to 10 mg/L

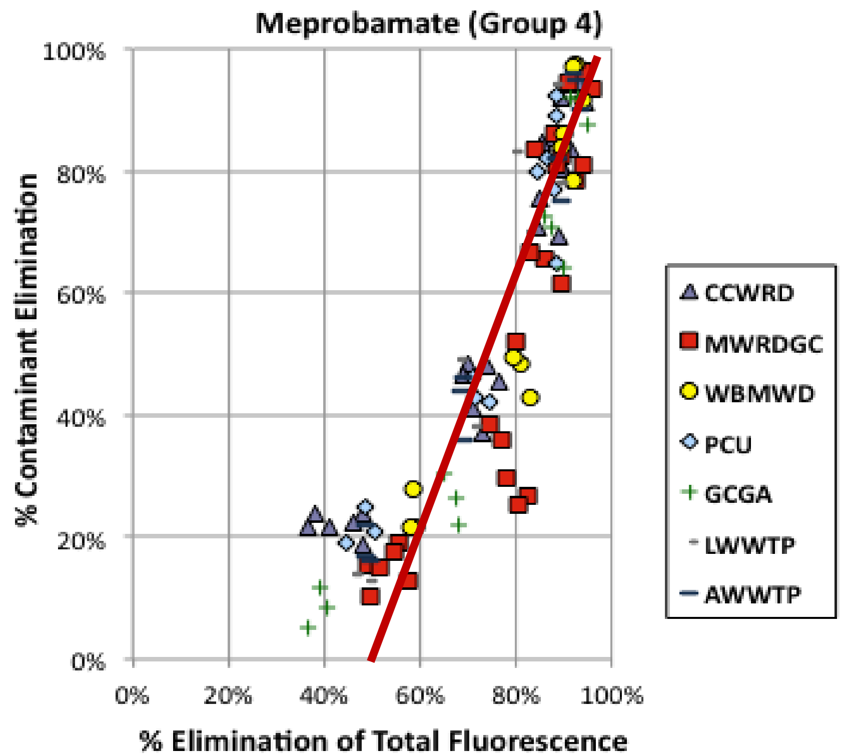
Diff. absorbance and fluorescence vs. $\Delta C/C_0$ correlations for carbamazepine



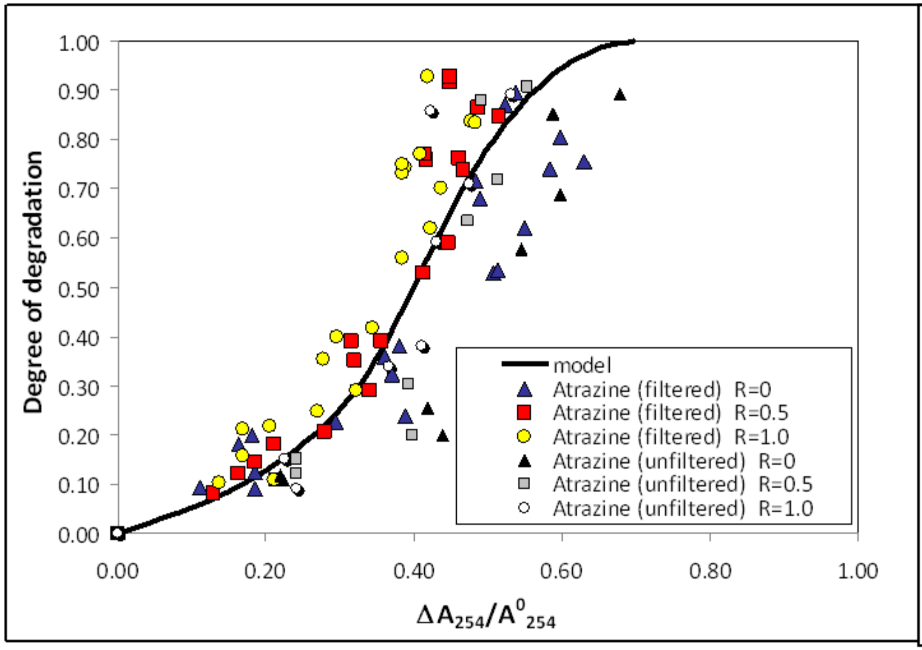


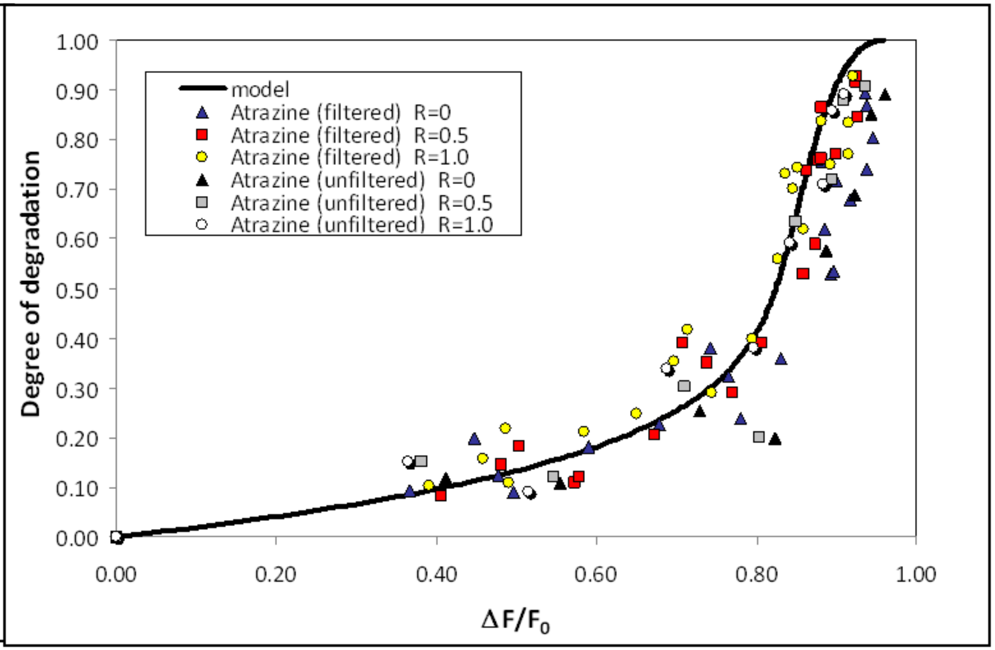
Correlations between the elimination of absorbance and fluorescence for meprobamate



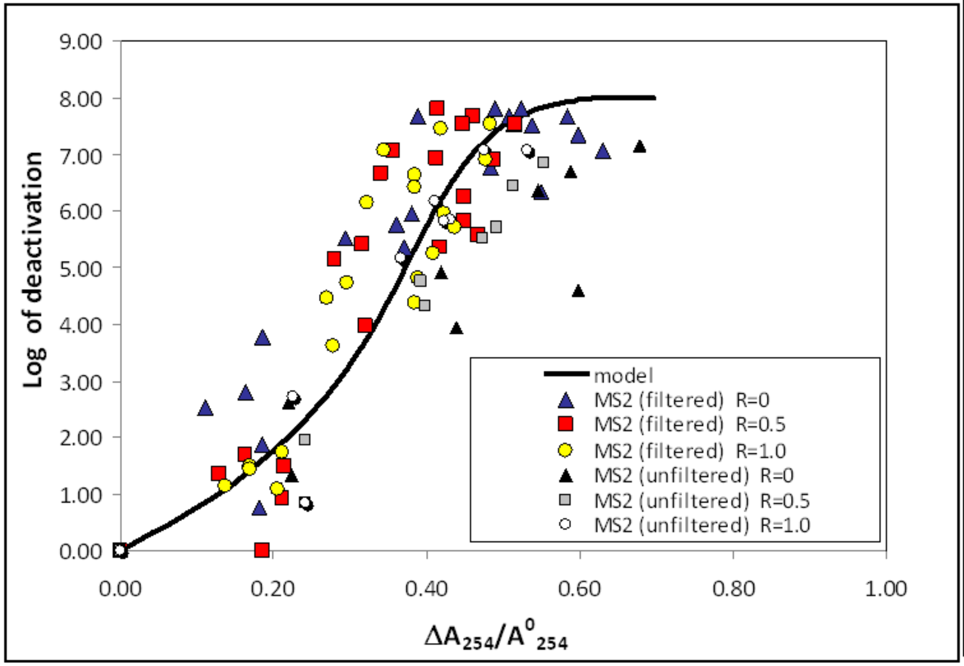


Data for atrazine

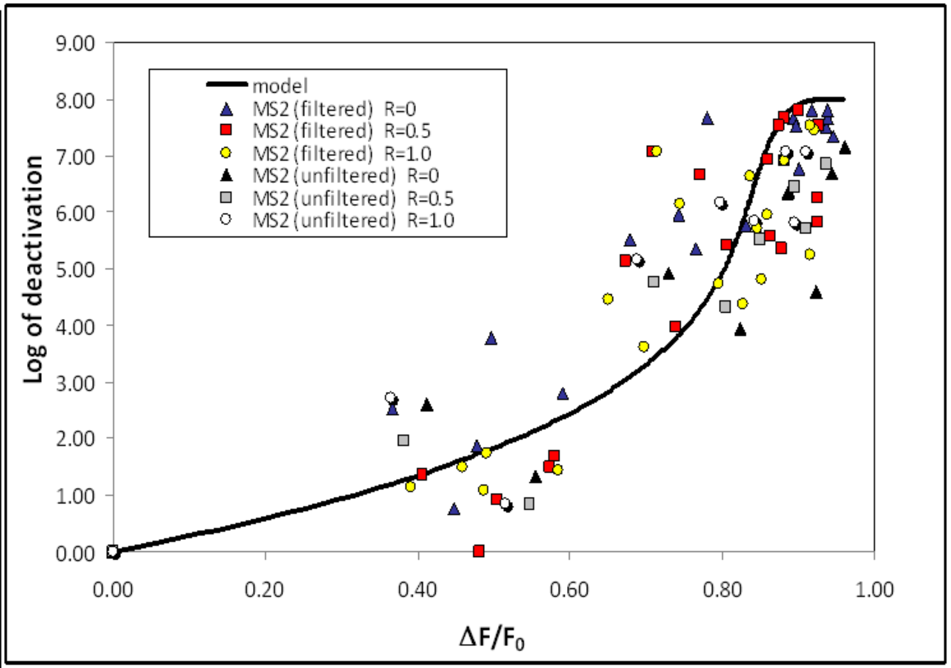




Data for MS2



Log of deactivation
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0.00
0.20
0.40
0.60
0.80
1.00
$\Delta A_{254}/A^0_{254}$
model
MS2 (filtered) R=0
MS2 (filtered) R=0.5
MS2 (filtered) R=1.0
MS2 (unfiltered) R=0
MS2 (unfiltered) R=0.5
MS2 (unfiltered) R=1.0



Log of deactivation
9.00
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0.00
0.20
0.40
0.60
0.80
1.00
$\Delta F/F_0$
model
MS2 (filtered) R=0
MS2 (filtered) R=0.5
MS2 (filtered) R=1.0
MS2 (unfiltered) R=0
MS2 (unfiltered) R=0.5
MS2 (unfiltered) R=1.0

Conclusions

- **AOP and the evolution of EfOM fluorescence**
  – 3D EEM and HP SEC data indicate largely non-specific oxidation of all fluorophore groups
- **Fluorescence and and EDC/PPCP degradation**
  – Removal of all EDC/PPCP species is correlated with fluorescence changes
  – Same applies to pathogens
  – Correlations are robust, interpretable but not necessarily linear
- **Practical and theoretical significance**
  – EfOM fluorescence is a good option for on-line monitoring
  – Further experimentation and implementation are needed.

Acknowledgements

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Questions?