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CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #13

Prediction Methods: Going beyond Hammett I

Brezonik, pp.553-578

David A. Reckhow

Introduction

Ozonation

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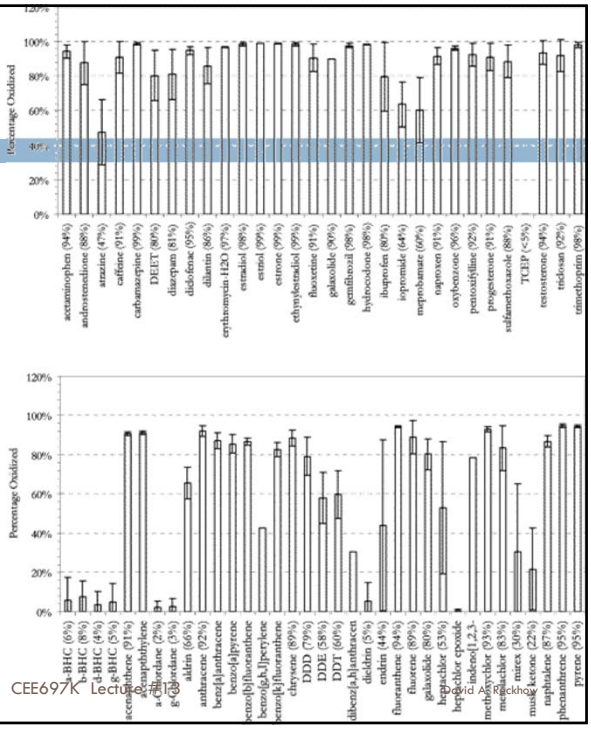
- Removal by ozone



Westerhoff et al., 2005 [EST 39:17:6649]

QPAR: GAC adsorption of PPCPs

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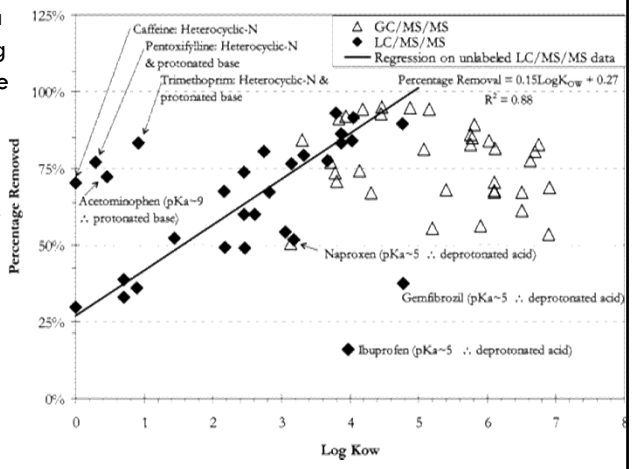
- EDC/PPCP removal as a function of predicted log K_{ow} based upon average removal data from all four source water experiments (5 mg/L WPM; 4-h contact time). Selected LC/MS/MS compounds are identified



Westerhoff et al., 2005 [ES&T, 39:6649]

QAAR – Oxidation of PPCPs

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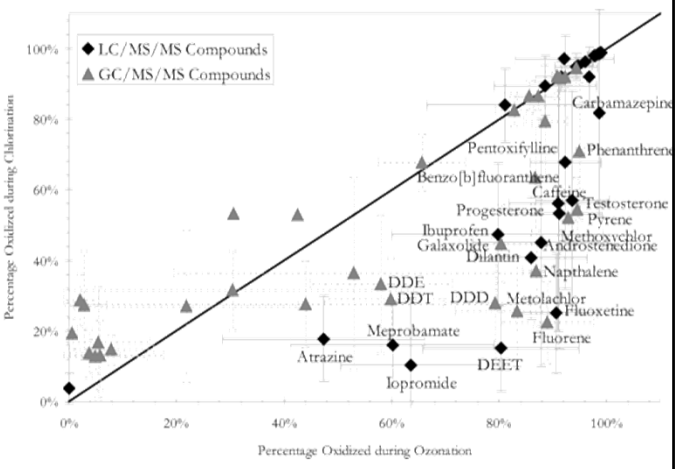
- Average percentage removal of LC/MS/MS and GC/MS/MS compounds by ozone and chlorine across four waters spiked with EDC/PPCPs (PVW, ORW, SRW, CRW).
  - Solid line represents 1:1 removal between ozonation and chlorination experiments. Error bars represent one standard deviation in percentage removal based on experiments in the four waters.



Westerhoff et al., 2005 [ES&T, 39:6649]

Other approaches

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- Extending estimations to more robust & empirical approximations

Table 12.1
Overview of predictive methods for fate and transport properties

Fate and Transport Property	Chemical Information	Approach	Data Input
Biodegradation rate (or tendency)	Substructure fragments	Howard-Boethling group contribution	Functional group correlation parameters
Hydrolysis rate constant at basic pH Electronic and steric model (Taft equation)	Steric (*Es*) and electronic (σ^*) parameters of tabulated chemicals	Multi-variable linear Regression (MLR) analysis of tabulated data	Correlation parameters (group contribution) optimized
Percent removal by: Ozone, chlorine, UF	Adsorption, distribution and metabolism data	Monte Carlo (MC) statistical mechanics simulations and MLR analysis	2D molecular structures
Air-water partitioning (Henry's law constant)	Structure fragments	Activity coefficient model (ie., UNIFAC) with thermodynamic relationships, or Hine-Mookerjee as 2nd option	Vapor pressure and BIP
Adsorption onto activated carbon	Substructure fragments	Liquid-phase Polanyi isotherm model	Aqueous solubility limit, molar volume at Tb, liquid density

Snyder et al., 2007 *"Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes"* [AWWARF final report]

Volatilization

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- Henry's law constants by UNIFAC

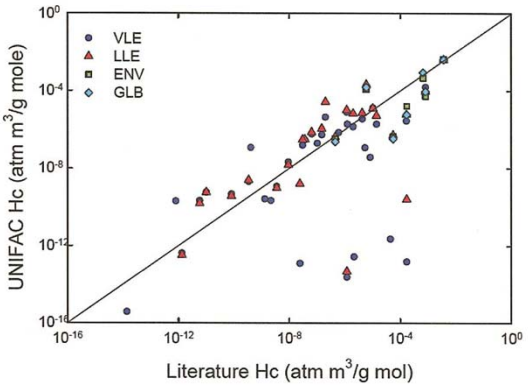

Figure 12.3 Comparison of predicted and experimental Henry's constants

Snyder et al., 2007 *"Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes"* [AWWARF final report]

Hydrolysis I

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- Returning to more fundamental LFERs

Table 12.8
Chemical range of literature hydrolysis LFER correlations

Estimate	Basis	Chemical Classes Covered
k_0	Hammett Correlation	Benzyl halides; dimethyl benzyl halides; benzyl tosylates (all in mixed organic/aqueous solvents.)
k_{OH}	Hammett Correlation	Benzene ring-substituted compounds based on $ArCOOCH_3$, $ArCOOCH_2CH_3$, $ArCH_2COOCH_2CH_3$, $ArCH{=}CHCOOCH_2CH_3$, $ArCONH_2$, $AroCOCH_3$, $ArCH_2OCOCH_3$, $ArCON(CH_3)_2$, $ArCONHCH_3$, $ArCH_2Cl$, and $ArOSi(CH_2CH_3)_3$ (all in mixed organic/aqueous solvents).
k_{OH}	Taft Correlation	Dialkyl phthalate esters
k_{OH}	Correlation with pKa of leaving group	Aryl esters of methylphosphonic acid ($(CH_3)_2CHOP(O)(CH_3)OAr$); carbamates of the form: (1) $(C_6H_5)NHCOOAr$; (2) $CH_3N(C_6H_5)COOAr$; (3) $CH_3NHCOOAr$; (4) $(CH_3)_2NCOOAr$.

Snyder et al., 2007 *"Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes"* [AWWARF final report]

Hydrolysis II

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- Applied to PPCPs

Table 12.9
Hydrolysis rate constant estimation method recommendation

Category	Chemical Name	CAS#	Estimation Method	Parameter availability
I	DCPA solution	1861321	Hammett	NO
	Acetylsalicylic Acid	50782	Hammett	NO
	DDT	50293	Hammett	NO
	Fluoxetine	54910893	Hammett	NO
	Methoxychlor	72435	Hammett	NO
	Mirex	2385855	Hammett	NO
II	Acetophenone	98862	N/A	Not needed
	Androst-4-ene-3,17-dione	63058	N/A	Not needed
	Anthracene	120127	N/A	Not needed
	Benzo[a]pyrene	50328	N/A	Not needed
	Bisphenol A	80057	N/A	Not needed
	Cholesterol	57885	N/A	Not needed
	Estriol	50271	N/A	Not needed
	Guaiacol	90051	N/A	Not needed
	Ibuprofen	15687271	N/A	Not needed
	Nabumetone	42924538	N/A	Not needed
	Naproxen	22204531	N/A	Not needed
	Nonylphenol	25154523	N/A	Not needed
	Para-Dodecylphenol	104438	N/A	Not needed
	Pentachloronitrobenzene	87865	N/A	Not needed
	Phenol, 4-tert-Butyl	98544	N/A	Not needed
	Progesterone	57830	N/A	Not needed
	Resorcinol	108463	N/A	Not needed
	Testosterone	58220	N/A	Not needed
	Vanillin	121335	N/A	Not needed
	Coprostanol	360689	N/A	Not needed
	Diethylstilbestrol	56531	N/A	Not needed
	Aniline	62533	N/A	Not needed
	Benzenehexachloride (BHC)	118741	N/A	Not needed
	Musk Ketone	81141	N/A	Not needed
III	Toxaphene	8001352	No published corr.	–
	Nonachlor, trans-	39765805	No published corr.	–
	Heptachlor	76448	No published corr.	–
	Nadolol	42200339	No published corr.	–
	Propranol	525666	No published corr.	–
	Aldrin	309002	No published corr.	–
	Allethrin, d-trans	584792	No published corr.	–
	Bromacetic acid	79083	No published corr.	–
	1,2-dibromoethane	106934	No published corr.	–
	Chloroacetic acid	79118	No published corr.	–
	o-Chloroaniline	95512	No published corr.	–
	Chlorpheniramine	132229	No published corr.	–
	Chloroform	67663	No published corr.	–
	Pentachloronitrobenzene	82688	No published corr.	–
IV	Diethyl Phthalate (DEP)	84662	Taft	YES
	Butyl benzyl phthalate (BBP)	85687	Taft	NO

Class I Hammett correlation applies (limited parameters)
Class II No hydrolyzable groups (negligible hydrolysis)
Class III No correlation for chemical class and/or difficult to classify (e.g. polyfunctional)
Class IV Taft correlation applies (limited parameters)

Snyder et al., 2007 *"Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes"* [AWWARF final report]

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- To next lecture