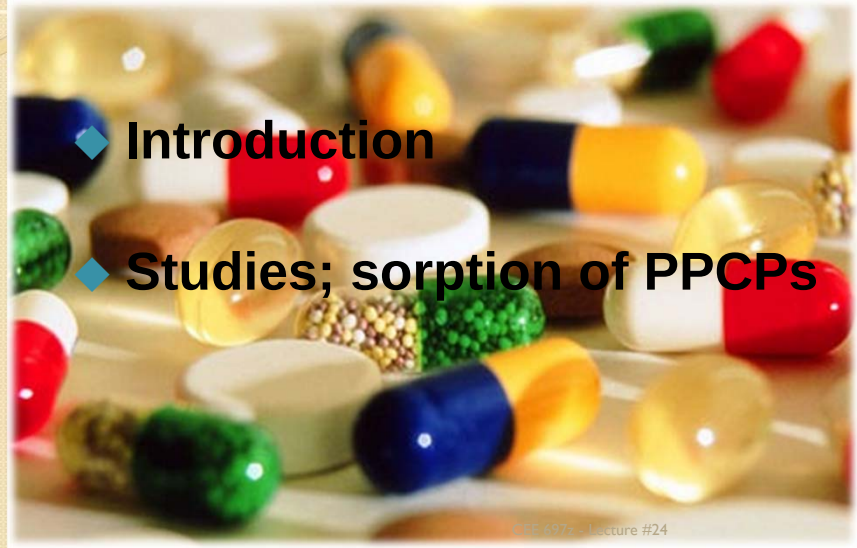
Print version

Sorption of PPCPs

Organic compounds in water and wastewater

Soonmi Kim

Outline



- Introduction
- Studies; sorption of PPCPs

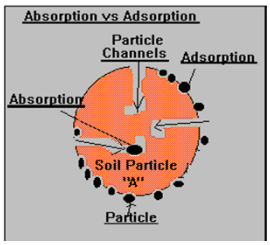
Introduction

Sorption?

Sorption is a physical and chemical process by which one substance becomes attached to another

Adsorption

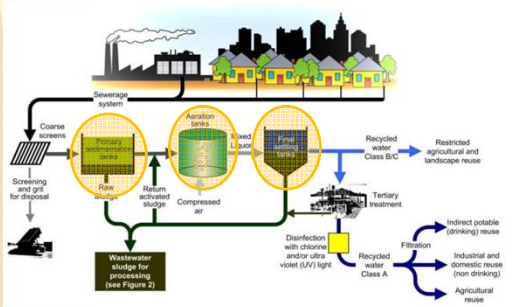
Accumulation of the molecular species at the surface rather than in the bulk of the solid or liquid

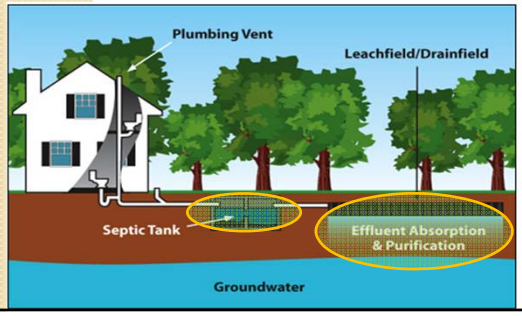


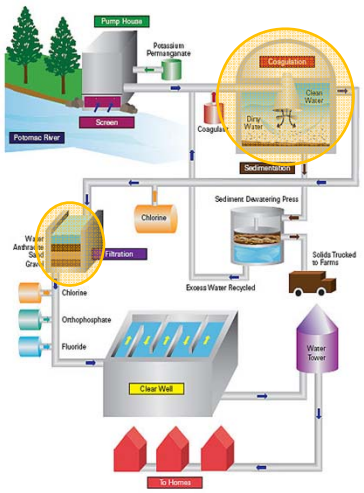
Absorption

Assimilation of molecular species throughout the bulk of the solid or liquid

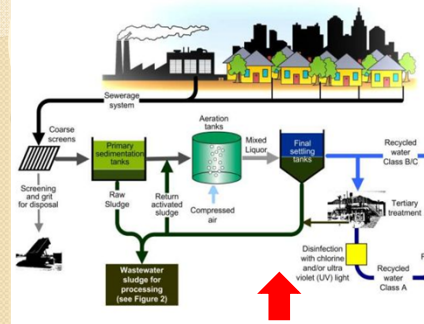
Introduction



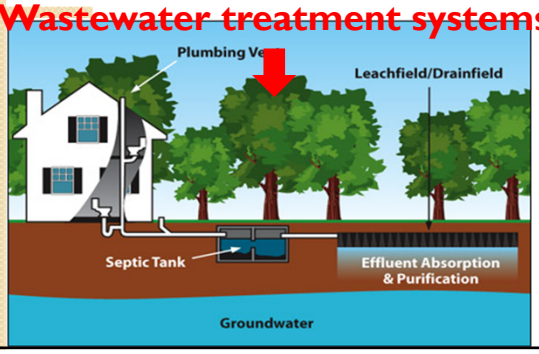


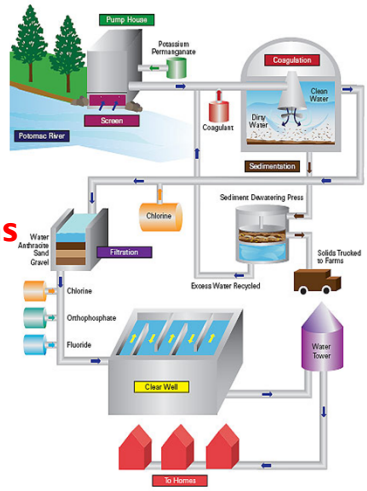


Introduction



Wastewater treatment systems

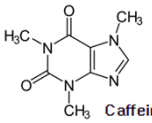


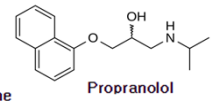


Factors affecting Sorption

1) Sorbent properties

2) Sorbate properties



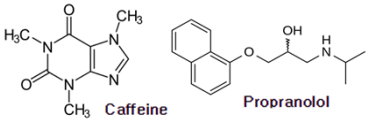


3) Solution properties

Factors affecting Sorption

1) Sorbents properties

2) Sorbate properties



3) Solution properties

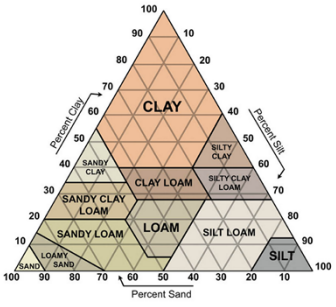
Sorbents

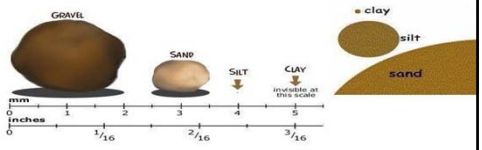
1. Types of sorbent

1) Biosolids (Sludge)
- Primary sludge
- Secondary sludge

2) Soils
- Sand
- Silt
- Clay

3) Coagulants
- Al, Fe, or Mn complex



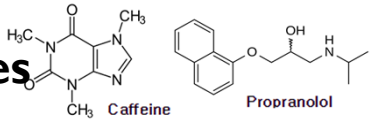


2. Surface area of sorbents

Factors affecting Sorption

1) Sorbent properties

2) Sorbate properties



3) Solution properties

Sorbate properties

Molecular Weight (MW)

- in general, as increase MW, solubility decreases, adsorption increases
- as increase MW, diffusivity decreases, so rate of transport decreases
- at very high MW, may exclude some compounds from small pores

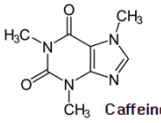
Polarity

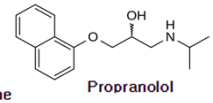
- in general, if more polar, more hydrophilic, less absorption (stronger interaction with polar H_2O)
- as more non-polar, more hydrophobic, more absorption (i.e. increase in aliphatic carbon chain length for carboxylic acids results in increased absorption)
- number and type of substituent atoms or groups on organic carbon structure affects extent of absorption

Factors affecting Sorption

1) Sorbents properties

2) Sorbate properties





3) Solution properties

Solution properties (cont.)

pH
- affects ionization of sorbate and surface of sorbent
- in general, as pH decreases, sorption increases
- uncharged sorbates adsorb more than charged (ionized) sorbates

Ionic Strengh
- in general, more sorption as ionic strength increases
- better adsorption of DOC as increase Ca^{+2}, Na^{+}

Temperature
- extent of sorption increases as temperature decreases
- rate of sorption decreases as temperature decreases

Solution properties

Competing sorbates

- sorbate with stronger affinity (binding) for surface can displace sorbate with weaker affinity
- most real waters involve mixtures of sorbates
- changes in mixture can affect sorption
- for a heterogeneous sorbate measured by a composite parameter such as TOC (or COD), extent of sorption can depend on initial concentration used in batch experiment

Presence/absence of dissolved oxygen

- sorption capacity increased in presence of $O_2(aq)$

Possible interactions

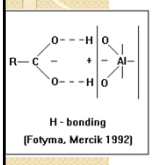
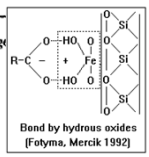
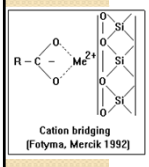


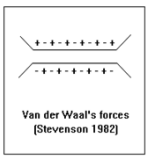
Table 1. Characteristic interactions associated with categories of adsorption

Category and Characteristic Interaction	Representation of Interaction	Interaction Range
CHEMICAL		
Covalent	H_2 H_2O	Short Range
Hydrogen Bond		Short Range
ELECTROSTATIC		
Ion-Ion		$1/r$
Ion-Dipole		$1/r^2$
PHYSICAL		
Dipole-Dipole (Coulombic)		$1/r^3$
(Keesom energy)		$1/r^6$
Dipole-Induced Dipole (Debye energy)		$1/r^6$
Instantaneous Dipole-Induced Dipole (London dispersion energy)		$1/r^6$

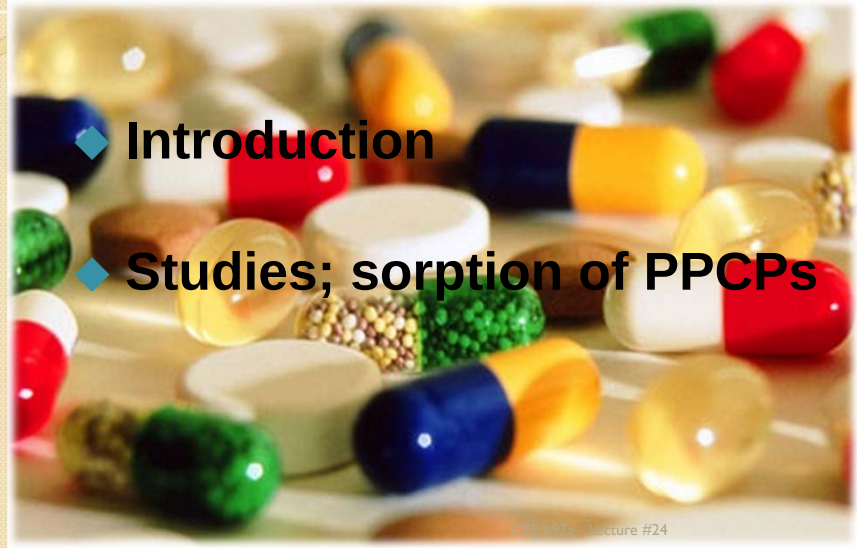
*Adapted from Israelachvili, 1985.







Outline



- Introduction
- Studies; sorption of PPCPs

Sorption coefficient (K_d)

- The ratio of the concentrations of a compound in the sorbent phase and in the solution phase at equilibrium; Linear isotherm

$K_d = C_{sorbed}/C_{dissolved}$

C_{sorbed} : concentration of solbate in sorbent (μg/kg)

$C_{dissolved}$: concentration of solbate in solution (μg/L)

$$q = k_{lin} c$$

q =Mass adsorbed / Mass of adsorbent

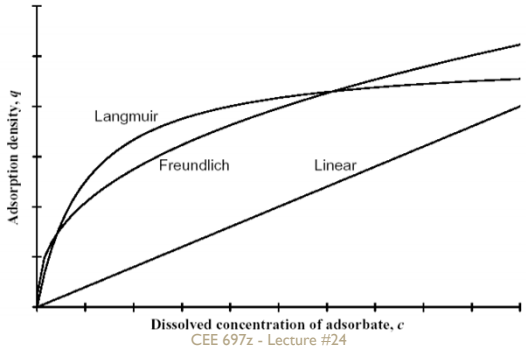
Other isotherms

Freundlich

$$q = k_f c^n$$

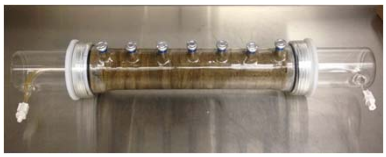
Langmuir

$$q = q_{max} \frac{K_L c}{1 + K_L c}$$

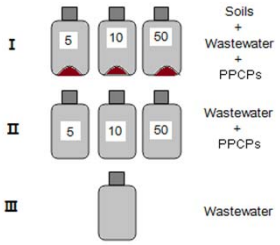


Standard methods for K_d and K_F determination

1) Column displacement studies



2) Batch sorption expreriments



Factors affecting determination of sorption coefficient

1. Phases associated sorption

- Solid phase
- PPCPs in aqueous phase
- DOM (Dissolved organic Matter) in aqueous phase

2. PPCPs properties

- Hydrophobic PPCPs
- Non-hydrophobic ionisable PPCPs

K_d in soils

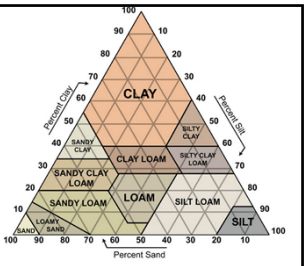


Table 4. Sorption coefficients for gemfibrozil to sand, a sandy loam, and a silt loam soil

	Freundlich equation			Linear equation		
Sorbent	K_f	$1/n$	r^2	K_d	r^2	Log K_{oc}
Sand	0.24	0.68	0.96	0.12	0.94	2.08
Sandy loam	1.31	0.83	1.00	1.06	1.00	1.91
Silt loam	12.38	1.37	0.97	9.2	0.99	2.57

Yu Fang (2011)

Table 1 A summary table of PPCP sorption on soils or sediments

Solute chemical names	pK_a	S_w (mg/L)	logK_{ow}	MW	Sorbent description	pH	TOC (%)	K_d (mL/g)	Reference
Bisphenol A (BPA)	9.59–10.2	120–300	3.4	228.3	Sediment	7.15–7.71	2.06–6.29	3.7–11.5[a]	Zeng et al. 2006
					Soil	8.9	1.9	2.75[a]	Ying et al. 2003
					Soil	6.9–8.13	0.92–2.11	4.94–8.62[a]	Fent et al. 2003
					Minerals	4–10		12.3–212.8[a]	Shareef et al. 2006
					Zeolite			11.2[a]	Tsai et al. 2006a
17β-Estradiol (E2)	N/A	3.6	3.1 to 4.0	272.3	Soil	7.2–7.6	0.8–1.4	16.0–29.6[a]	Stumpe and Marschner 2007
					Soil		3.3–9.2	80.2–455.5[a]	Casey et al. 2003
					Soil	7.9	9.2	84.41	Casey et al. 2005
					Soil			3.6–83.2	Lee et al. 2003
					Minerals			4.9–177.2	Van Emmerik et al. 2003
					Minerals		0	11.3–40[a]	Casey et al. 2003
17α-Ethinyl Estradiol (EE2)	10.4	11–44	4.15	296.4	Sludge	7.1	27.7	584	Andersen et al. 2005
					Soil		0.95–1.88	53.7–97.7[a]	Yu and Huang 2005
					Soil	8.9	1.9	6.98[a]	Ying et al. 2003
					Soil	6.4–7.3	0.22–2.91	2.33–23.4	Lee et al. 2003
					Minerals	4–10		41.4–744.9[a]	Shareef et al. 2006
Carbadox (CBX)	N/A	N/A	−1.40 to 0.15	262	Soil	4.4–7.3	0.22–2.39	1.4–154	Strock et al. 2005
					Kaolinite	4.63		19.8	Strock et al. 2005
Desoxycarbadox (DCBX)	N/A	N/A	1.9 to 2.1	230	Soil	4.3–6.9	0.36–2.39	7.07–62.4[a]	Strock et al. 2005
					Clay	4.67	0	7.6	Strock et al. 2005
Tetracycline (TC)	3.3; 7.7; 9.7	231–52000	−1.97 to −0.47	444.4	Soil	3.8–7.5	0.48–2.91	3102–312447	Sassman and Lee 2005
					HS	7		1.0–5.7E4	Pils and Laird 2007
					Al or Fe oxide	5.3		41.8–133[a]	Gu and Karthikeyan 2005a
					MMLT	5.5		865[a]	Figueroa et al. 2004
					Clay	7		2.2–6.5E4	Pils and Laird 2007
Oxytetracycline (OTC)	3.27; 7.32; 9.11	300	−1.97 to −0.45	460	Soil	3.8–7.5	0.48–2.91	1229–269097	Sassman and Lee 2005
								950–7200	ter Laak et al. 2006a
					MMLT	1.5–11		2691–33884[a]	Kulshrestha et al. 2004
Sulfathiazole (STZ)	2.4; 7.1	590	1	255.3	MMLT	4–7.5		0.5–1.5	Kahle and Stamm 2007
					Ferrihydrite	5.3–7.2		3–20	Kahle and Stamm 2007
					Soil			0.4–3.5	ter Laak et al. 2006a
Sulfapyridine (SPY)	8.4	270	0.35	249.3	Whole soil	7	1.61	1.75[a]	Thiele-Bruhn et al. 2004
					Mineral			4	Gu and Karthikeyan 2005b
Sulfamethazine (SMZ)	2.3; 7.4	1500	0.8	278.33	Soil	7.2–7.5	0.94–1.8	2.4–4.2[a]	Accinelli et al. 2007
					Mineral			7.8–14.2[a]	Gao and Pedersen 2005
p-Aminobenzonic acid (pABA)	4.9	6100	0.83	137.1	Soil	7	1.61	0.47[a]	Thiele-Bruhn et al. 2004
					Coarse silt	6.4	0.1	1.82[a]	Thiele-Bruhn et al. 2004

S_w solubility in water, *MW* molecular weight, *N/A* not available, *MMLT* montmorillonite
[a] K_d was calculated at 10 ug/L if the data was provided as fitting results using the Freundlich or Langmuir model

Bo Pan (2009)

Sorption between PPCPs (VPs) and DOM

Johannes Tolls(2001)

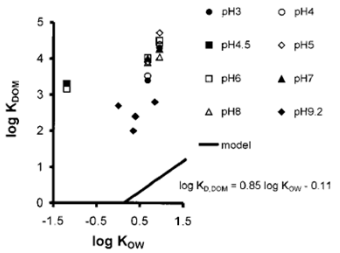


FIGURE 3. Plot of the log $K_{d,DOM}$ data against hydrophobicity expressed as log K_{ow}. The solid line is a regression line obtained for a wide range of neutral organic chemicals (*32*).

TABLE 3. Data on Sorption of VPs to DOM[a]

compound	corollary information	K_d (L/kg)	K_{oc} (L/kg)	ref
tetracycline	AHA, pH adjusted to 4.55, ED	2 060	6 059	*24*
	pH adjusted to 6.14, ED	1 430	4 206	*24*
oxolinic acid	AHA, pH range from 3 to 8, SPME	935−8 350	7 400−31 600	*25*
flumequine	AHA, pH range from 3 to 8, SPME	2 516−10 750	2 750−24 500	*25*
sarafloxacine	AHA, pH range from 3 to 8, SPME	18 700−52 700	55 000−155 000	*25*
enrofloxacin	HAS, pH 9.2, EM[b]	110		*26*
ciprofloxacin	HAS, pH 9.2, EM[b]	250		*26*
norfloxacin	HAS, pH 9.2, EM[b]	500		*26*
danofloxacin	HAS, pH 9.2, EM[b]	630		*26*
ofloxacin	HAS, pH 9.2, EM[b]	100		*26*
enro-CO_2	HAS, pH 9.2, EM[b]	250		*26*

[a] AHA and HAS stand for Aldrich humic acid and for humic acid from a soil, respectively. The experimental techniques employed were equilibrium dialysis (ED), solid-phase microextraction (SPME), and electrophoretic mobility. K_d and K_{oc} are the sorption and organic carbon-normalized sorption coefficients, respectively. [b] Organic carbon content of humic acid is not reported.

Hydrophobicity (Cont.)

- Karickhoff (1979) reported that K_d of environmental chemicals are strongly correlated to the organic carbon content (f_{oc}(%))

- During(2002), Bowman(2002), Holthaus(2002), Loffredo(2006), Maskaoui(2007), and Uslu(2008) reported that both Freundlich sorption parameter K_F and Linear sorption parameter K_d of PPCPs are found to be positively related to organic carbon content

- Most of PPCPs are moderately hydrophobic compounds (Bo Pan;2009)

So,

$$K_{OC} = \frac{K_d}{f_{oc}}$$

K_{oc} : organic carbon partition coefficient (L/kg)

K_d : linear sorption coefficient (L/kg)

f_{oc} : fraction of organic carbon (%)

Hydrophobicity (Cont.)

- Franco(2008) and Karickhoff (1979) reported the K_{oc} is correlated to the K_{ow} (Octanol-water distribution coefficient)
  - Log K_{ow} = positive : Hydrophobic
  - Log K_{ow} = negative : Non-hydrophobic

- Sablijic (1995) found that the K_{oc} for non-hydrophobic and ionisible compounds is pH-dependent

- And, Sablijic (1995) determined the correlation between the K_{oc} and the K_{ow} depending on physical and chemical properties of organic compouns

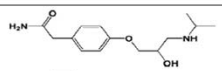
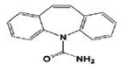
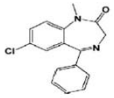
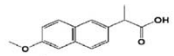
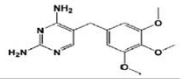
Table 5. List of all derived QSAR models for soil sorption with their chemical domains.

Model #	Regression Equation	Chemical Domain
1	$\log K_{oc} = 0.70 + 0.52^{*1}\chi$	Predominantly hydrophobics
2	$\log K_{oc} = 0.10 + 0.81^{*}\log K_{ow}$	Predominantly hydrophobics
3	$\log K_{oc} = 1.02 + 0.52^{*}\log K_{ow}$	Nonhydrophobics
4	$\log K_{oc} = 0.90 + 0.63^{*}\log K_{ow}$	Phenols, anilines, benzonitriles, & nitrobenzenes
5	$\log K_{oc} = 1.09 + 0.47^{*}\log K_{ow}$	Acetanilides, carbamates, esters, phenylureas, phosphates, triazines, triazoles, & uracils
6	$\log K_{oc} = 0.50 + 0.47^{*}\log K_{ow}$	Alcohols & organic acids
7	$\log K_{oc} = 1.12 + 0.40^{*}\log K_{ow}$	Acetanilides
8	$\log K_{oc} = 0.50 + 0.39^{*}\log K_{ow}$	Alcohols
9	$\log K_{oc} = 1.25 + 0.33^{*}\log K_{ow}$	Amides
10	$\log K_{oc} = 0.85 + 0.62^{*}\log K_{ow}$	Anilines
11	$\log K_{oc} = 1.14 + 0.365^{*}\log K_{ow}$	Carbamates
12	$\log K_{oc} = 1.92 + 0.38^{*}\log K_{ow}$	Dinitroanilines
13	$\log K_{oc} = 1.05 + 0.49^{*}\log K_{ow}$	Esters
14	$\log K_{oc} = 0.55 + 0.77^{*}\log K_{ow}$	Nitrobenzenes
15	$\log K_{oc} = 0.32 + 0.60^{*}\log K_{ow}$	Organic acids
16	$\log K_{oc} = 1.08 + 0.57^{*}\log K_{ow}$	Phenols & benzonitriles
17	$\log K_{oc} = 1.05 + 0.49^{*}\log K_{ow}$	Phenylureas
18	$\log K_{oc} = 1.17 + 0.49^{*}\log K_{ow}$	Phosphates
19	$\log K_{oc} = 1.50 + 0.30^{*}\log K_{ow}$	Triazines
20	$\log K_{oc} = 1.405 + 0.47^{*}\log K_{ow}$	Triazoles

Aleksandar Sabljic (1995)

Sorption of pH-dependent non-hydrophobic PPCPs

Table 1
Chemical properties, structures and speciation of the sorbates.

Compound (Detection, wavelength λ)	Structure	pK_a[a] (character[c])	log K_{OW}[b]	Species[d] at pH =		
				4	6	8
Atenolol (λ = 227 nm)		9.2 ± 0.4[e] (B)	0.1 ± 0.28	+	+	+, 0
Carbamazepine (λ = 232 nm)		−0.49 ± 0.2[e] (B)	2.67 ± 0.38	0	0	0
Diazepam (λ = 232 nm)		3.4 ± 0.1[e] (B)	2.96 ± 0.55	+, 0	0	0
Naproxen (λ = 215 nm)		4.8 ± 0.3 (A)	3.0 ± 0.24	0, –	–	–
Phenobarbital (λ = 243 nm)		7.6 ± 0.1 (A)	0.53 ± 0.26	0	0	–
Primidone (λ = 215 nm)		12.3 ± 0.4 (A)	0.4 ± 0.52	0	0	0
Trimethoprim (λ = 225 nm)		7.2 ± 0.1[e] (B)	0.79 ± 0.38	+	+	+, 0

Schaffer (2012)

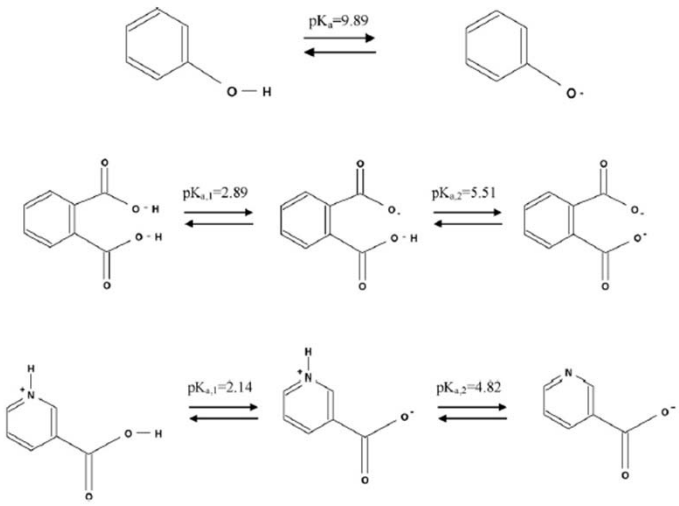
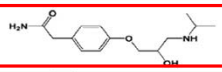
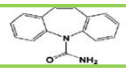
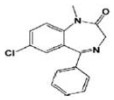
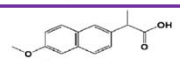
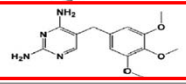


Fig. 1. Chemical structures and conjugated species of phenol, o-phthalic acid, and nicotinic acid used in this study. The pK_a values indicated are those in pure water ($^{W}_{W}pKa$).

Fabrice Gritti (2009)

Sorption of pH-dependent non-hydrophobic PPCPs

Table 1
Chemical properties, structures and speciation of the sorbates.

Compound (Detection. wavelength λ)	Structure	pKa[a] (character[c])	log Kow[b]	Species[d] at pH = 4	6	8
Atenolol (λ = 227 nm)		9.2 ± 0.4[e] (B)	0.1 ± 0.28	+	+	+, 0
Carbamazepine (λ = 232 nm)		−0.49 ± 0.2[e] (B)	2.67 ± 0.38	0	0	0
Diazepam (λ = 232 nm)		3.4 ± 0.1[e] (B)	2.96 ± 0.55	+, 0	0	0
Naproxen (λ = 215 nm)		4.8 ± 0.3 (A)	3.0 ± 0.24	0, –	–	–
Phenobarbital (λ = 243 nm)		7.6 ± 0.1 (A)	0.53 ± 0.26	0	0	–
Primidone (λ = 215 nm)		12.3 ± 0.4 (A)	0.4 ± 0.52	0	0	0
Trimethoprim (λ = 225 nm)		7.2 ± 0.1[e] (B)	0.79 ± 0.38	+	+	+, 0

Schaffer (2012)

Sorption of pH-dependent non-hydrophobic PPCPs at pH = 8.23

Table 3
Sorption model variables and model fitting adjustments.

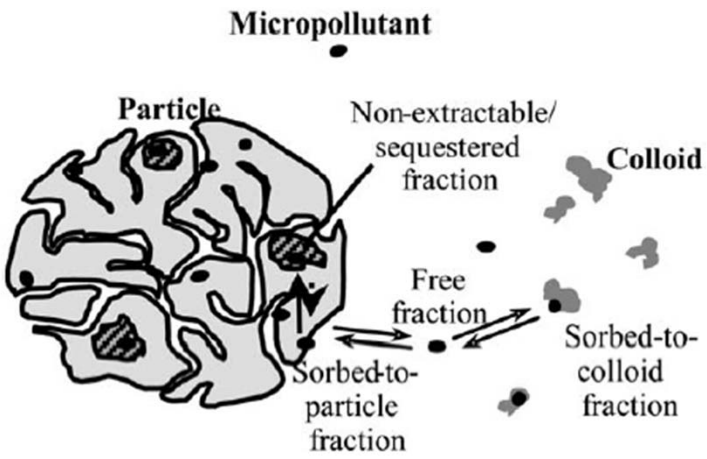
Compound	Character (charge)	Linear K_d	STD	Freundlich K_F	K_L	C_{max}	Langmuir R^2	n	R^2	HI
CBZ	Base (N)	0.40	0.55	0.97	0.34	5.62	0.88	0.37	0.97	-
ACP	Acid (N)	0.50	0.16	0.68	0.02	32.93	0.98	0.87	0.97	-
ATN	Base (+)	7.93	4.01	11.00	0.08	189.01	0.99	0.76	0.99	−0.66
CAF	Base (+)	17.86	6.10	20.00	0.09	221.17	0.98	0.87	0.99	−0.30
NPX	Acid (−)	1.86	1.27	3.38	0.07	68.68	0.97	0.70	0.99	4.46
SXZ	Acid (−)	4.25	1.61	6.20	0.03	218.78	1.00	0.79	0.99	13.81

K_d expressed in L kg^{-1}; K_F expressed in $\mu g^{1-n} L^n kg^{-1}$; K_L expressed in L μg^{-1}; C_{max} expressed in $\mu g\ kg^{-1}$. STD: Standard deviation. HI: Hysteresis Index.
N: Neutral (+): Positively charged (−): Negatively charged.

Martinez-Hernandez (2014)

- Basic compounds : Highest K_d by strong interactions with negatively-charged surface
- Acidic compounds : Moderate K_d by ion exchange with cations on surface or physical interaction among polar molecules
- Neutral compounds : Lowest K_d by negligible sorption affinity

K_d in sludges



Barret (2011)

K_d in sludges

German WWTP consists of a biological treatment unit with two denitrifying tanks, a nitrifying tank and a secondary clarifier with the sludge recycle going to the inlet of the first denitrification tank

	Location	TOC/TSS	COD/TSS	P/TSS	Fe(III)/TSS	N/TSS	VSS/TSS
Primary	After Grit	35%	146%	3%	<1%		
Secondary	Nitrification tank	34%	112%	3%	4%	5.8%	60%

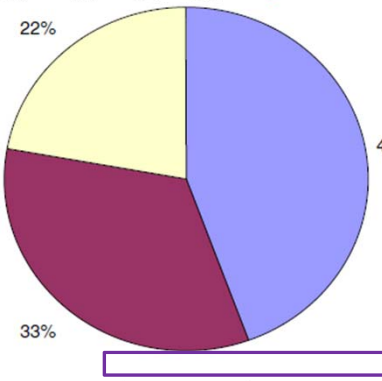
Table 1.3: Sorption coefficients for sludge of municipal wastewater treatment, measured in batch experiments and octanol-water partitioning coefficients (according to Ternes *et al.* 2004).

	Primary sludge K_d [L kg_{SS}^{-1}]	Secondary sludge K_d [L kg_{SS}^{-1}]	log K_{OW}
Acidic pharmaceuticals	**I.**	**II.**	**III.**
Diclofenac	459±32	16.0±3.1	4.6
Ibuprofen	-- (< 20)	7.1±2.0	3.5
Clofibric acid	-- (< 30)	4.8±2.5	2.57
Neutral pharmaceuticals			
Ifosfamide	21.8±13.8	1.4±0.4	0.86
Cyclophosphamide	55.4±19.6	2.4±0.5	0.63
Carbamazepine	-- (< 20)	1.2±0.5	2.45
Diazepam	43.9±26.1	21.1±7.6	2.82
Musk fragrances			
Galaxolide (HHCB)	4919±2073	1807±534	5.9
Tonalide (AHTN)	5299±1905	2372±958	5.7
Iodinated contrast media			
Iopromide	-- (<5)	11±1	-2.33
Estrogens			
17α–Ethinylestradiol	278±3	349±37	3.9

Thomas A. Ternes (2004)

Removal of PPCPs in WWTP

	Biological removal (g day^{-1})						Level of removal by biodegradation[a]
	Day 1	Day 3	Day 9	Day 10	Average	Standard deviation	
Diclofenac	−23.1	−4.1	−47.5	−24.1	−24.7	17.8	Low
Etofenamate	−0.3[b]	−1.1	−2.6	12.4	2.1	6.9	Medium
Ibuprofen	45.1	0.5	0.4	−0.3	11.4	22.5	High
Ketoprofen	83.3	−0.2					
Fluoxetine	0.0[b]	0.0[b]					
Clorazepate	0.0[b]	0.2					
Hydroxyzine	−2.3[b]	−1.6[b]					
Indapamide	−0.9[b]	−0.1[b]					
Enalapril	0.0[b]	−0.3					
Captopril	2.1	−0.6					
Atenolol	12.8	2.8					
Clofibric acid	49.9	0.2					
Ampicillin	−0.1[b]	0.0[b]					
Galaxolide	−0.4	−3.7					
Tonalide	0.2	−0.3					
Cashmeran	−0.8	−3.8					
Celestolide	0.5	−0.3					
Traseolide	0.2	−0.1					



	Standard deviation	Theoretical logK_{ow}	Level of removal by adsorption[a]
	7.3	4.0–4.7	Medium
	1.3	4.2	Medium
	0.5	3.5–4.0	Low
	0.1	3.0–3.2	Low
	0.0	1.8	Low
	0.4	2.1	Low
	1.3	2.4	Medium
	3.2	2.7	High
	0.2	2.4	Low
	0.1	1.7	Low
	0.0	0.2–1.4	Low
	0.3	2.6–3.6	Low
	0.0	1.4	Low
	7.3	4.6–5.9	High
Tonalide	1.0	4.8–5.7	High
Cashmeran	14.0	4.8	High
Celestolide	0.9	4.4	High
Traseolide	0.2	6.3	High

R. Salgado (2011)


To next lecture
Thank You
EE 697Z – Lecture #24