CVL100:Environmental Science(2-0-0)

Dr. Arun Kumar

Water Treatment-Mass Balance

Nov 9th and 10th, 2021

Re-cap

- Overall removal of pharmaceutical compounds in water treatment plants
  - Example approach

Understanding partitioning of contaminant in water and solids

- Hydrophilic compounds (more affinity to water)
- Hydrophobic compounds (less affinity to water)
- Octanol-water partition coefficient

Example 1

(read the paper from course web area)

Meta-Analysis of Mass Balances Examining Chemical Fate during Wastewater Treatment

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Mass balances are an instructive means for investigating the fate of chemicals during wastewater treatment. In addition

composition of biosolids is important because us
sewage sludge as fertilizer in agriculture, f

ere to search

TABLE 1. Chemical Abstract Service (CAS) Registry Number and Logarithmic 1-Octanol–Water Partitioning and Organic Carbon Normalized Sorption Coefficients (K_{OW} and K_{OC}, respectively) of Organic Wastewater Compounds Examined in This Review

compound	CAS no.	log K_{OW}	log K_{OC}
	Estrogens		
estrone	53-16-7	3.13 (*31*)	3.59 (*29*)
17β-estradiol	50-28-2	4.01 (*31*)	3.41 (*29*)
17α-ethinylestradiol	57-63-6	3.67 (*31*)	3.53 (*29*)
	Antimicrobials		
triclosan	3380-34-5	4.8 (*4*)	4.1[a]
triclocarban	101-20-2	4.9 (*4*)	4.5[a]
sulfamethoxazole	723-46-6	0.5[b]	2.77 (*29*)
trimethoprim	738-70-5	0.91(*31*)	2.7[c]
clarithromycin	81103-11-9	3.16 (*33*)	2.8[c]
ciprofloxacin	85721-33-1	−0.001[b]	4.23 (*29*)
norfloxacin	70458-96-7	−0.3[b]	4.6[d]
	Prescription Drugs		
carbamazepine	298-46-4	2.45 (*30*)	2.87 (*29*)
	Fragrances		
galaxolide (HHCB)	1222-05-5	5.9 (*34*)	5.22 (*29*)
tonalide (AHTN)	21145-77-7	5.7 (*34*)	5.36 (*29*)
	Surfactants and Industrial Chemicals		
nonylphenol	104-40-5	5.76 (*35*)	4.52 (*32*)
perfluorooctanesulfonate (PFOS)	1763-23-1[e]	6.3[b]	2.6 (*28*)
perfluorodecanesulfonate (PFDS)	335-77-3[e]	8.2[b]	3.5 (*28*)

A)Order antimicrobials and estrogens in chance of affinity to solids
B)Out of these, which will be found more in solids than in water?

TABLE 2. Concentrations of Compounds Reported in Wastewater Influent, Effluent, and Digested Sludge as Well as Their Corresponding Aqueous-Phase Removal Efficiency (Φ)[a]

compound	reference	influent (ng/L)	effluent (ng/L)	digested sludge (μg/kg)	Φ (%)	per-capita mass input (μg/person/day)
			Estrogens			
estrone	*9*	65.7	<1[c]	25.2	>*99*	*15*
	10	54.8	<0.1[b,c]	14.3[d]	100	*33*
17β-estradiol	*9*	15.8	<1 [c]	5.1	>*94*	*4*
	10	22.0	<0.1[b,c]	0.57[d]	*100*	*14*
17α-ethinylestradiol	*9*	8.2	<1 [c]	<1.5[c]	>*88*	*2*
	10	<5.0[c]	<0.1[b,c]	0.61[d]	>*98*	*NA*
			Antimicrobials			
triclosan	*14*	1200	51	1200	*96*	*620*
	15	4.700	70	30000	*98*	*2490*
triclocarban	*16*	6100	170	51000	*97*	*2870*
sulfamethoxazole	*11*	1700[e,h] (1400[g])	400[e,h] (10[g])	ND	*77*	*450*
trimethoprim	*11*	*290*[e]	*70*[e]	<0.1[c]	*76*	*100*
trimethoprim	*12*	*1373*[f]	*1424*[f]	ND	−4	*500*
clarithromycin	*11*	*380*[e]	*240*[e]	0.7	*37*	*180*
ciprofloxacin	*12*	*220*[f]	*48*[f]	*5970*[f]	*78*	*480*
ciprofloxacin	*13*	427	71	3100	*83*	*340*
norfloxacin	*12*	*293*[f]	*58*[f]	*6970*[f]	*80*	*610*
norfloxacin	*13*	431	51	2,900[f]	*88*	*350*

A)Which estrogen is removed more?
B) What does it say about their fate in water and in solids?
C) Compare maximum allowable values of these things with numbers here? Do they comply or not?
D) If not, how much removal do we have to further do?

- See previous table

- Provides information on conc. Of compons one can get in influent and in effluent

- Which compound has a higher chance of detection in liquid phase? In solid phase?

- This data is useful in deciding what to monitor in liquid line and in solid line

TABLE 3. Summary of Mass Balance Studies Indicating the Mass Fraction of Individual Compounds Found in Effluent or Digested Sludge or Lost from the System, Relative to the Total Loading (100%) Entering the Plant in Influent

compound	ref	mass in effluent (%)	mass in processed sludge (%)	mass lost (%)	label in Figure *3*
			Estrogens		
estrone + 17β-estradiol	*9*	<2	11	87	1 + 2
	10	12	4	84	3 + 4
17α-ethinylestradiol	*12*	<13	<6	>81	5
Antimicrobials					
ciprofloxacn	*12*	4	77	19	6
	13	12	83	5	7
clarithromycin	*12*	79	<1	>21	8
norfloxacin*12*	*12*	3	72	25	9
	13	8	75	17	10
sulfamethoxazole	*11*	38	<0.2	>62	11
triclocarban	*16*	3	76	21	12
triclosan	*14*	4	31	65	13
	15	2	50	48	14
trimethoprim	*11*	36	<0.2	>64	15
	12	104	NA	−4	
			Prescription Drugs		

- $A=Q\_inf * C\_in$=mass of compounds coming in
- $B=Q\_eff * C\_eff$=mass of compounds exit (i.e., B/A fraction of incoming compound has gone from liquid line)
- $D=Q_{\_solidwastage} * X\_solidwastage$=mass of compounds exiting during solid disposal (i.e., D/A fraction of incoming compound has gone from solid line)
- E=Some mass could be lost due to degradation or measurement error
- $A= B+D+E$

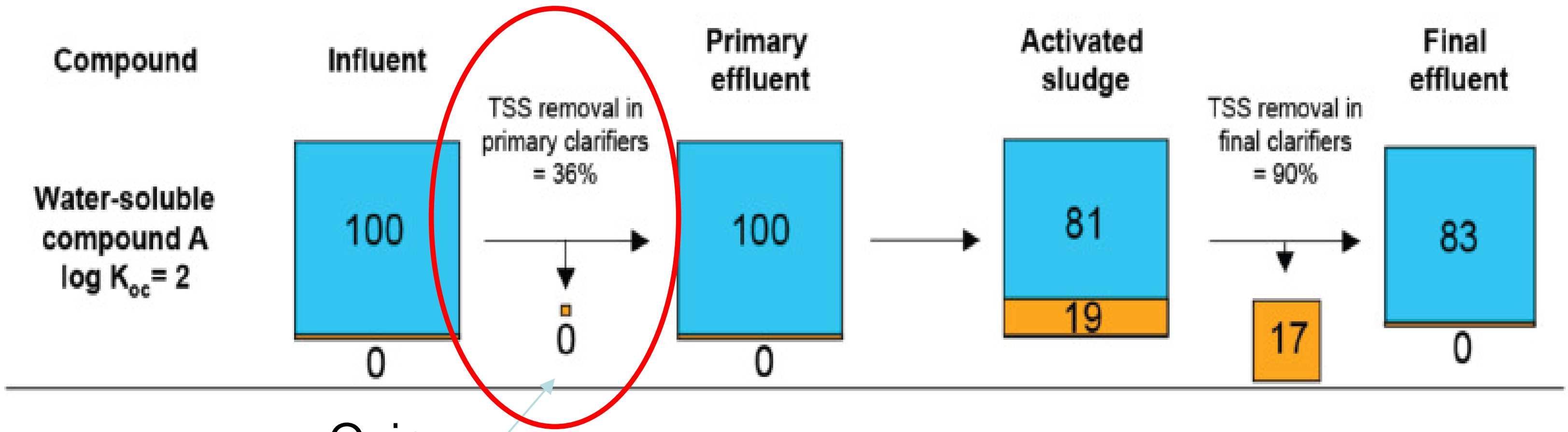
Mass balance calculation approaches

Generally, a mass balance can be described as a method to measure mass flows entering and leaving a system. In terms of wastewater treatment, this concept can be applied by determining the mass of a chemical entering the plant in raw wastewater, and the mass that exits the plant contained in treated wastewater, sewage sludge or both. A simple scheme for a mass balance is shown in equation S-1.

Equation S-1 $$M(i)_{enter} = M(i)_{exit} + M(i)_{lost}$$

with $M(i)_{enter}$ being the mass of chemical i entering the plant (mass/time), $M(i)_{exit}$ the mass of chemical i leaving the plant (mass/time) and $M(i)_{lost}$ (mass/time) the mass of chemical i being degraded or lost. A mass balance approach can be conducted for a plant as a whole (8,10),

FIGURE 2. Schematic illustrating the role of sorption in the fate of organic wastewater compounds during their hypothetical passage through a conventional activated sludge wastewater treatment plant assuming a lack of both transformation and loss processes. The partitioning of compounds between the dissolved phase (blue) and wastewater solids (orange) is shown for three organic wastewater compounds featuring logarithmic organic carbon normalized sorption coefficients (log K_{OC}) of 2, 4, and 6 (top, middle, and bottom panels, respectively).

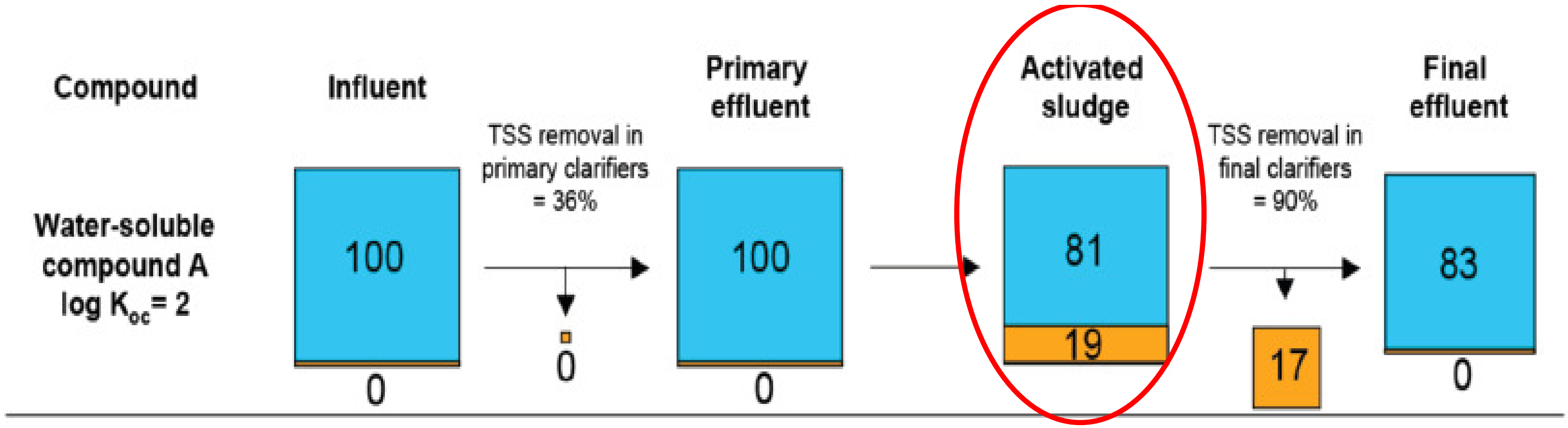


Q_in;
C_in

Q_in;
C_prim_eff=C_in

Solid is removed
But not organic compounds
⇒ 0 is shown for organic compounds

No removal of organics in primary unit
=> All present in water line



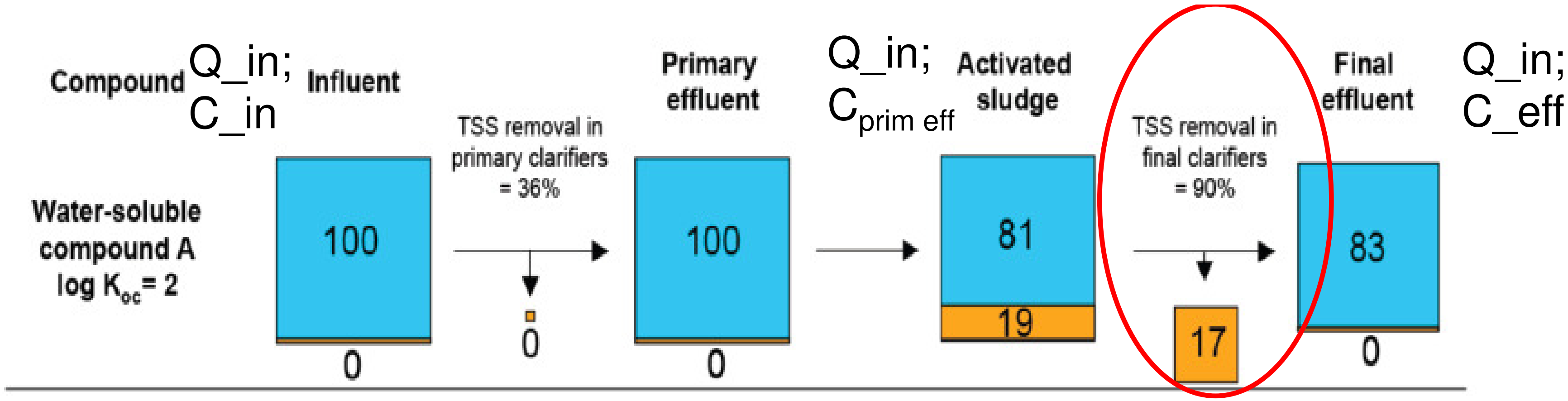
Q_in (MLD=million liters/day; 1gallon=3.78liters);
C_prim_eff=C_in (mg/L)
TSS=total suspended solids

Mass of organic entering into activated sludge tank =Q_in*C_prim_eff=Say (F) (mg)

Reactor volume=V_as (L); solids in AS tank = (AA) mg/L
81% is in liquid phase and rest in solid phase

Organic conc. In liquid phase in AS =C_AS=(0.81*F/V_as) (mg/L)

Organc conc on solids in AS (mg organic/mg solids)=X_AS
=(0.19*F)/(AA*V_as) (mg/mg)

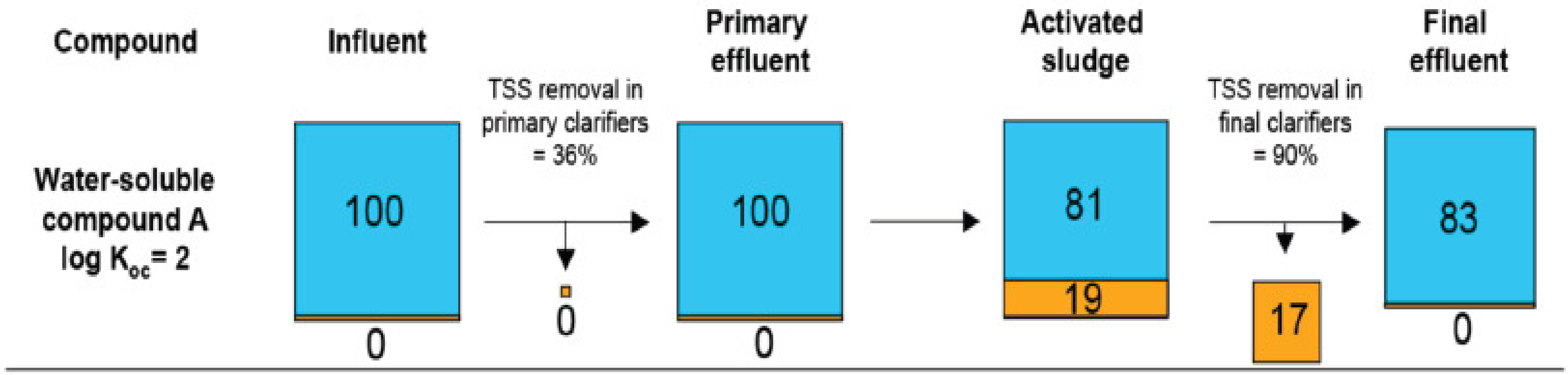


Q_in (MLD=million liters/day; 1m^3=3.78liters??/);
Organic conc. In liquid phase in AS =C_AS=(0.81*F/V_as) (mg/L)
Organc conc on solids in AS (mg organic/mg solids)=X_AS
=(0.19*F)/(AA*V_as) (mg/mg)

Now 90% solids removed in secondary clarifier. Amount of solids removed in secondary clarifier= X_wastage_Secondary tank= 0.9*X_AS
(17=0.9*19 => so amount of organic on solids wasted per day =90% of solids present in AS suspension)

⇒ Organic going out in effluent=C_eff_final=10% contribution from organic present on solids and organic in AS (i.e., C_AS)

FIGURE 2. Schematic illustrating the role of sorption in the fate of organic wastewater compounds during their hypothetical passage through a conventional activated sludge wastewater treatment plant assuming a lack of both transformation and loss processes. The partitioning of compounds between the dissolved phase (blue) and wastewater solids (orange) is shown for three organic wastewater compounds featuring logarithmic organic carbon normalized sorption coefficients (log K_{OC}) of 2, 4, and 6 (top, middle, and bottom panels, respectively).



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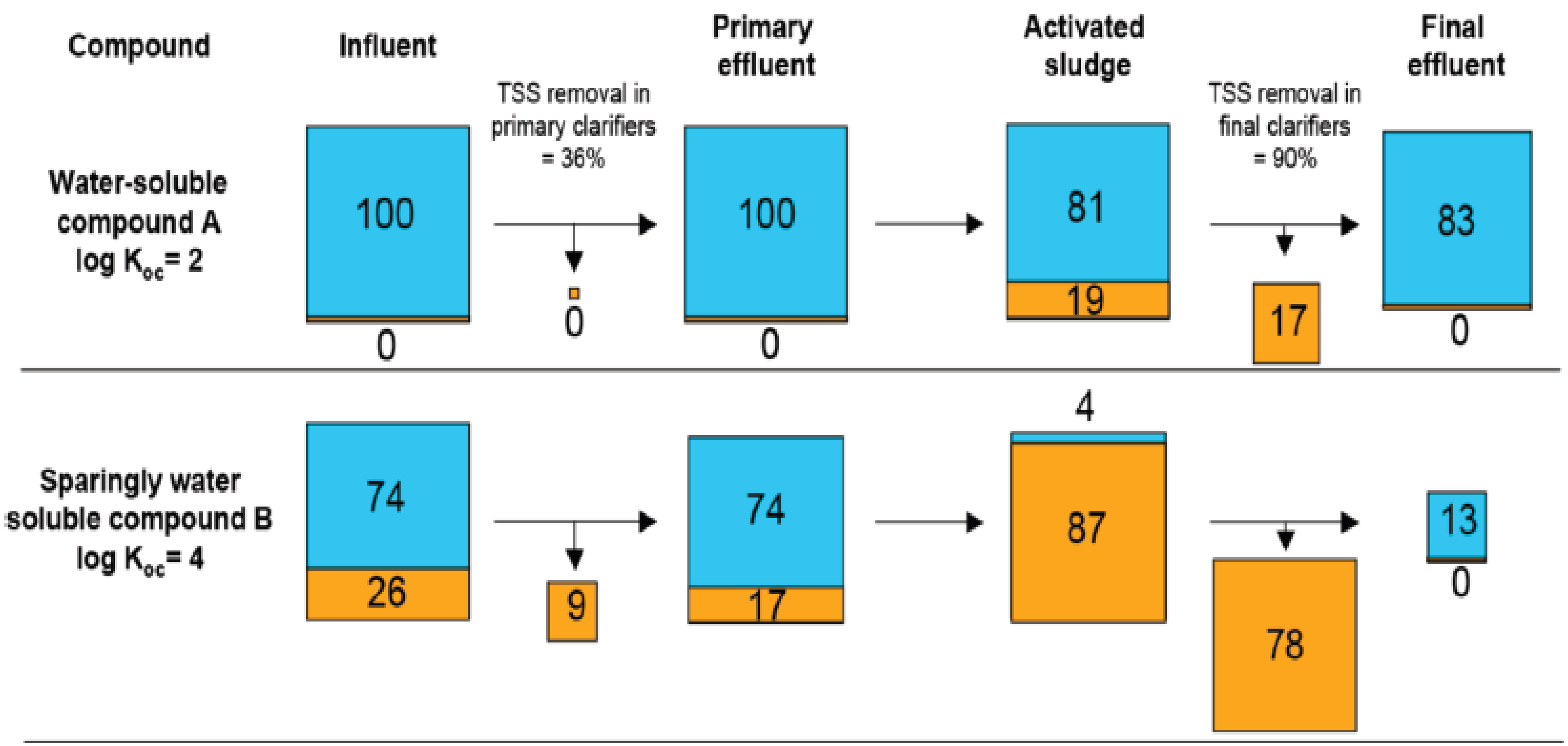

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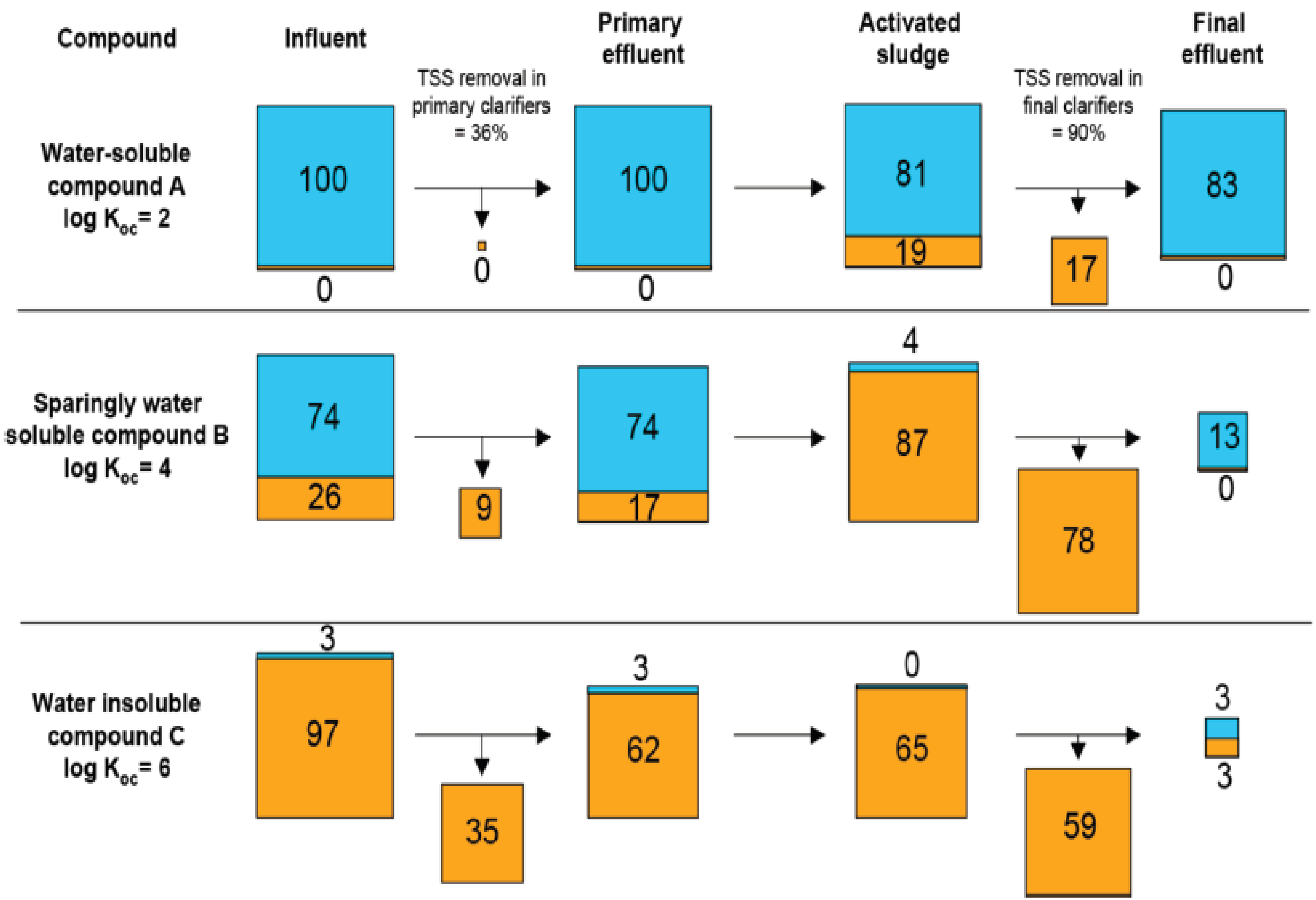


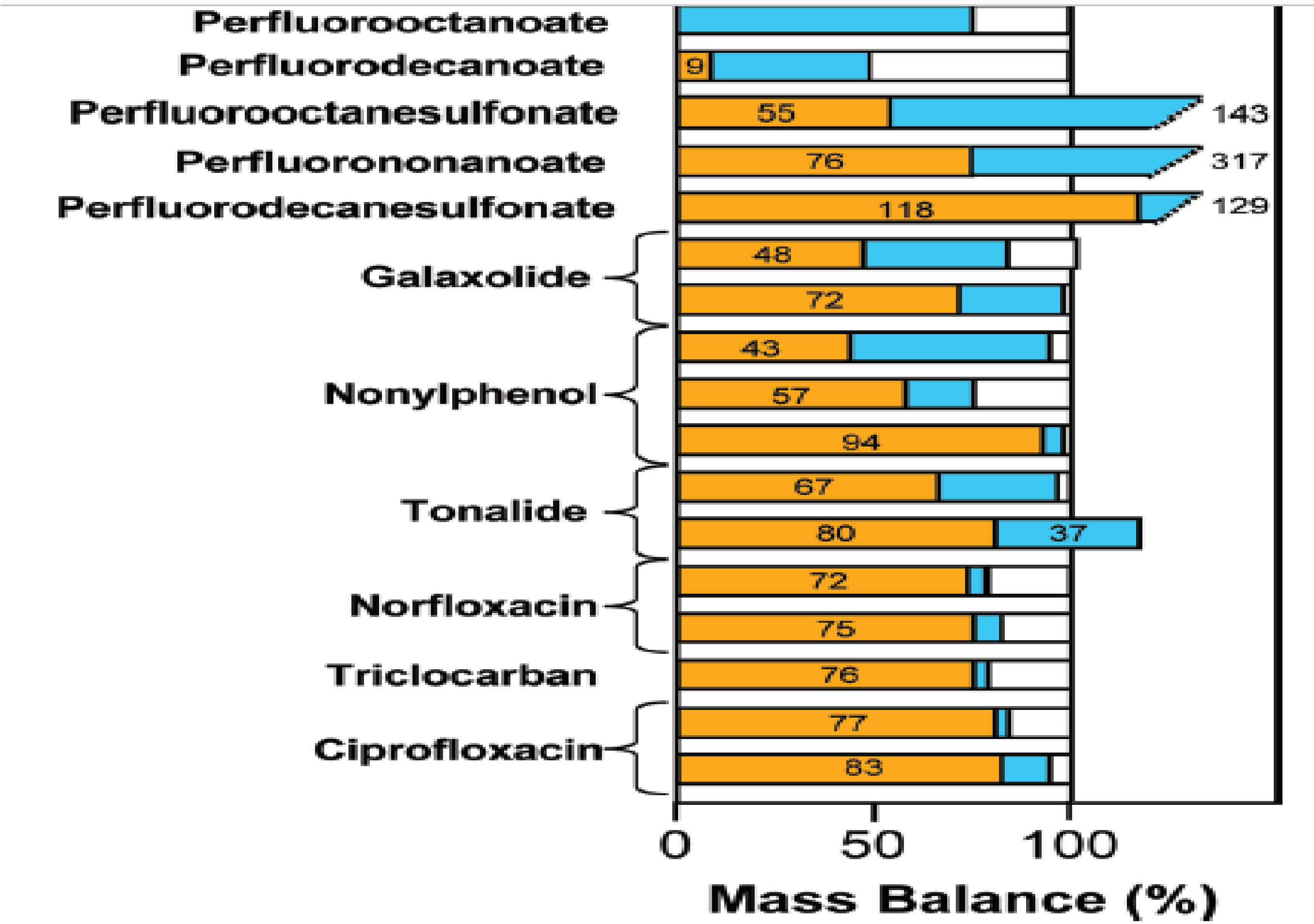


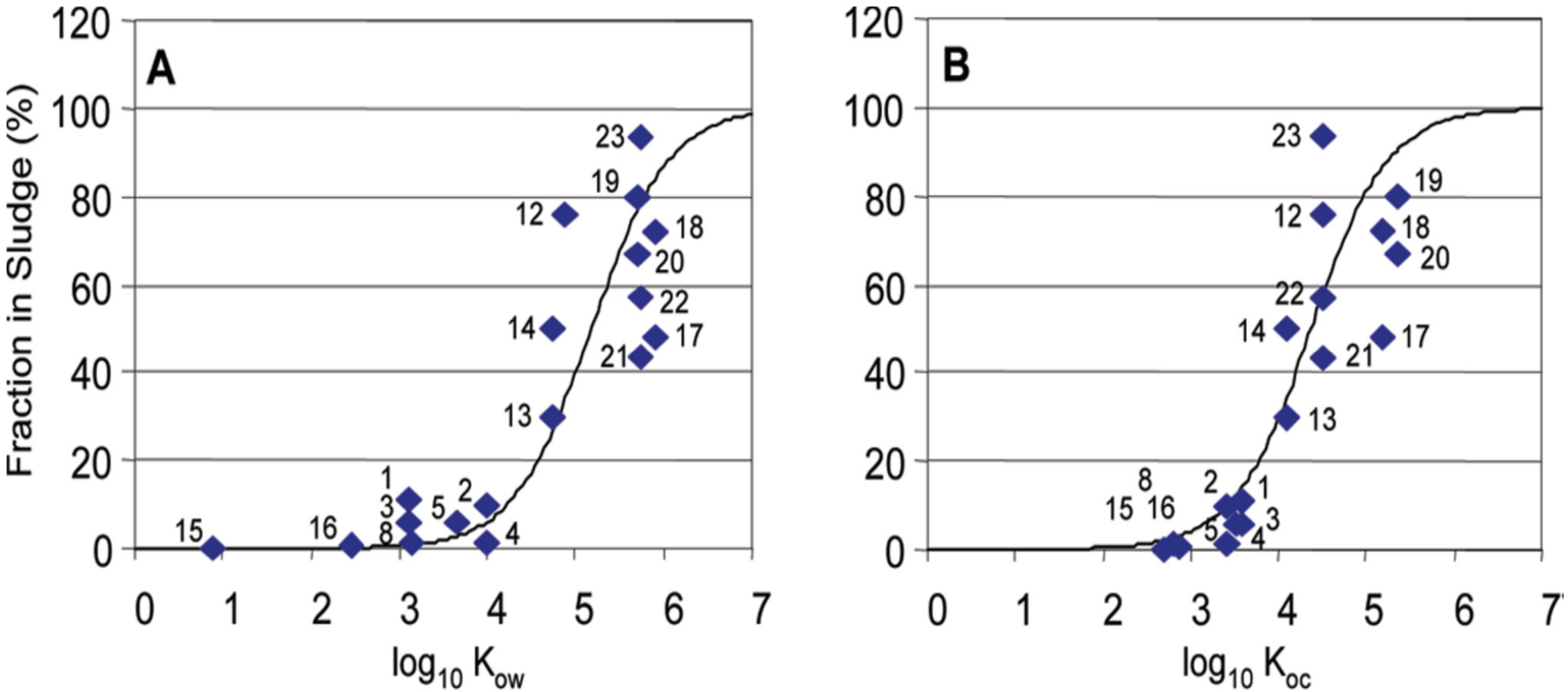
FIGURE 1. Compilation of select mass balances for organic wastewater compounds published in the peer-reviewed literature. Shown for each compound are the mass fractions emitted by the plant in effluent (blue), lost to degradation or otherwise unaccounted for (white), and persisting in sludge after digestion of wastewater solids (orange). Compounds are grouped based on structural similarities and sorted according

e here to search

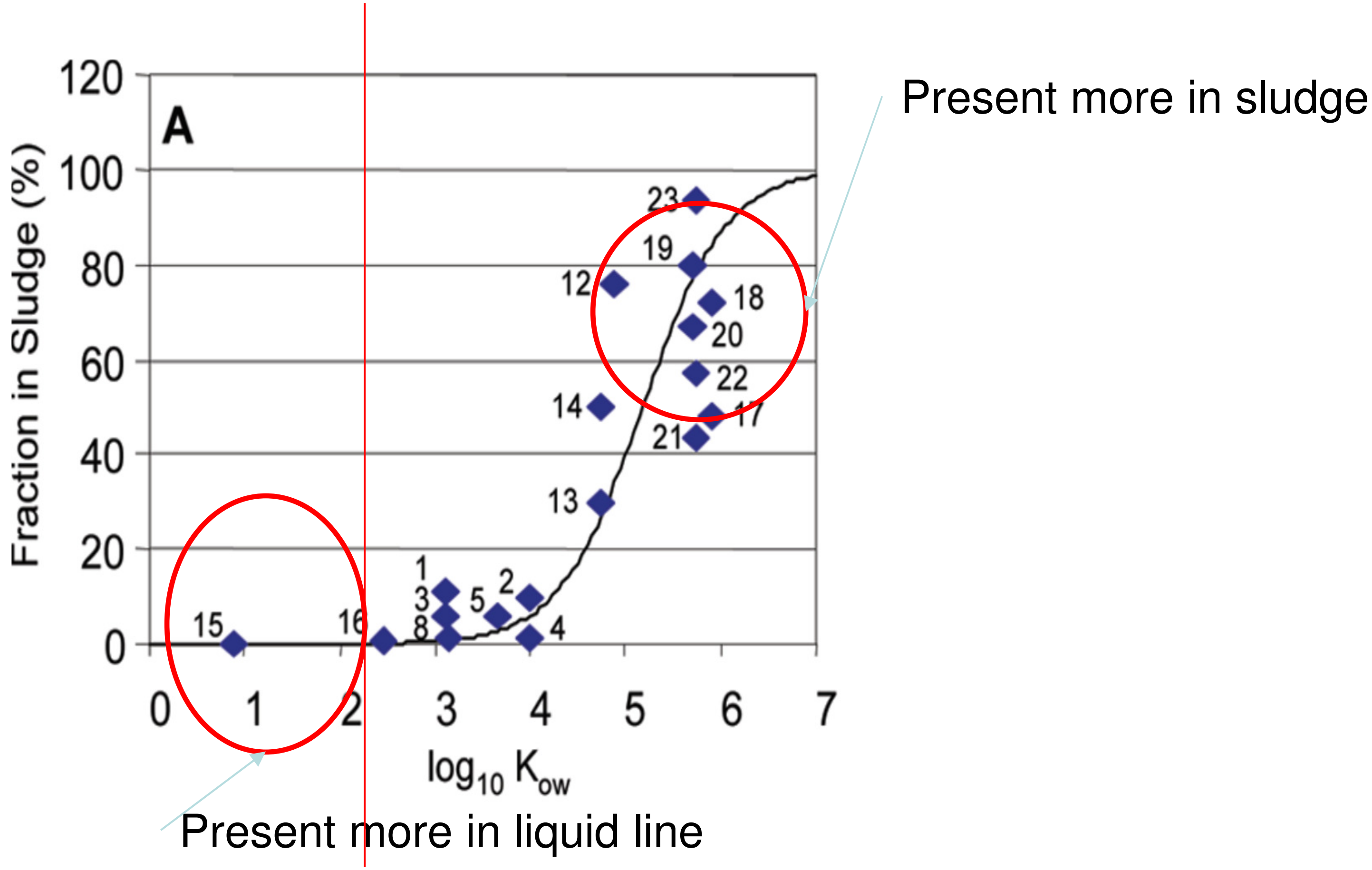
- See previous figure 1
- What does the fraction information tell about K_OW of compounds?
- Which compound has a higher chance of detection in liquid phase? In solid phase?

- This data is useful in deciding what to monitor in liquid line and in solid line

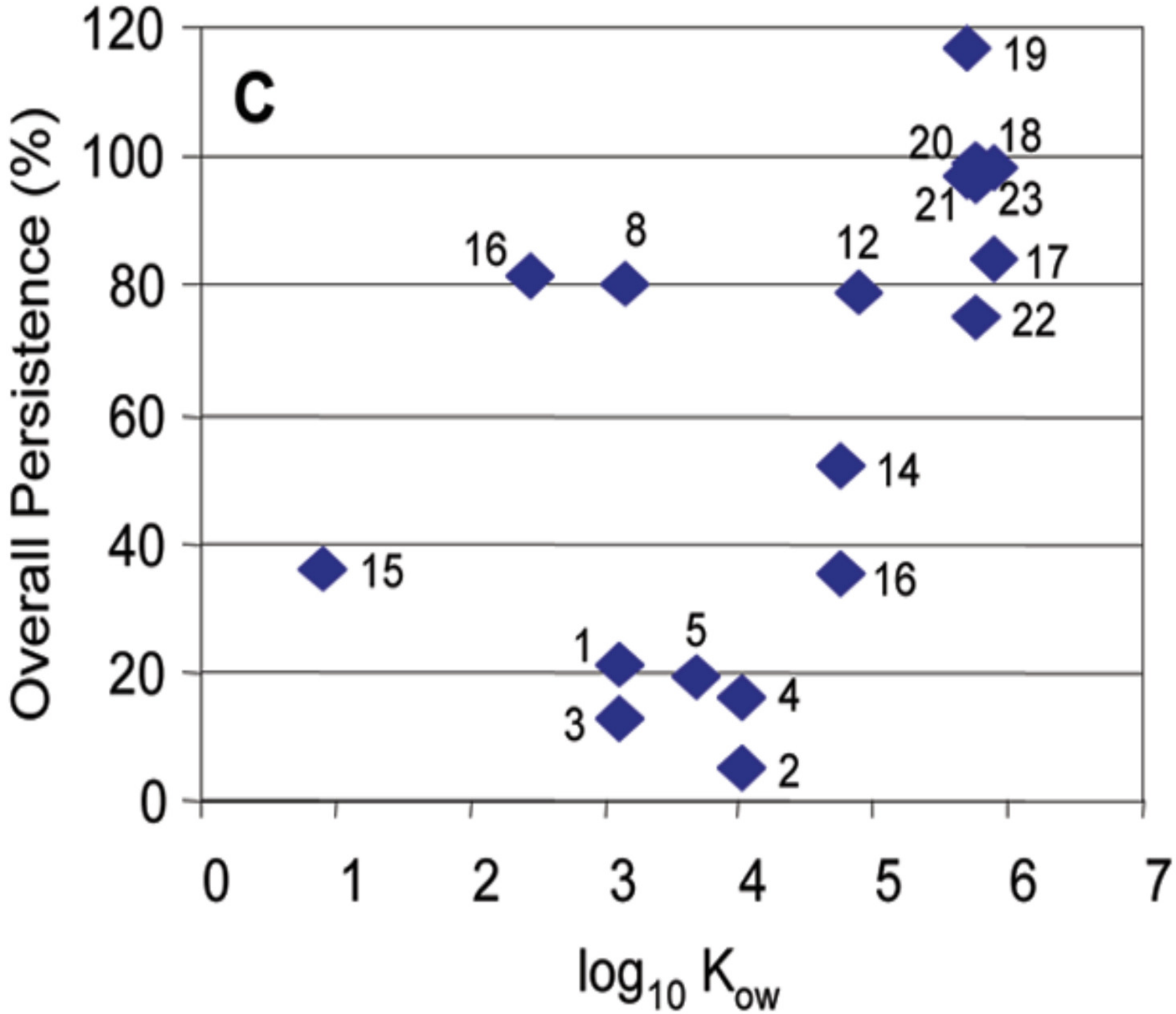
Fraction in sludge =f(K_{ow};K_{oc})

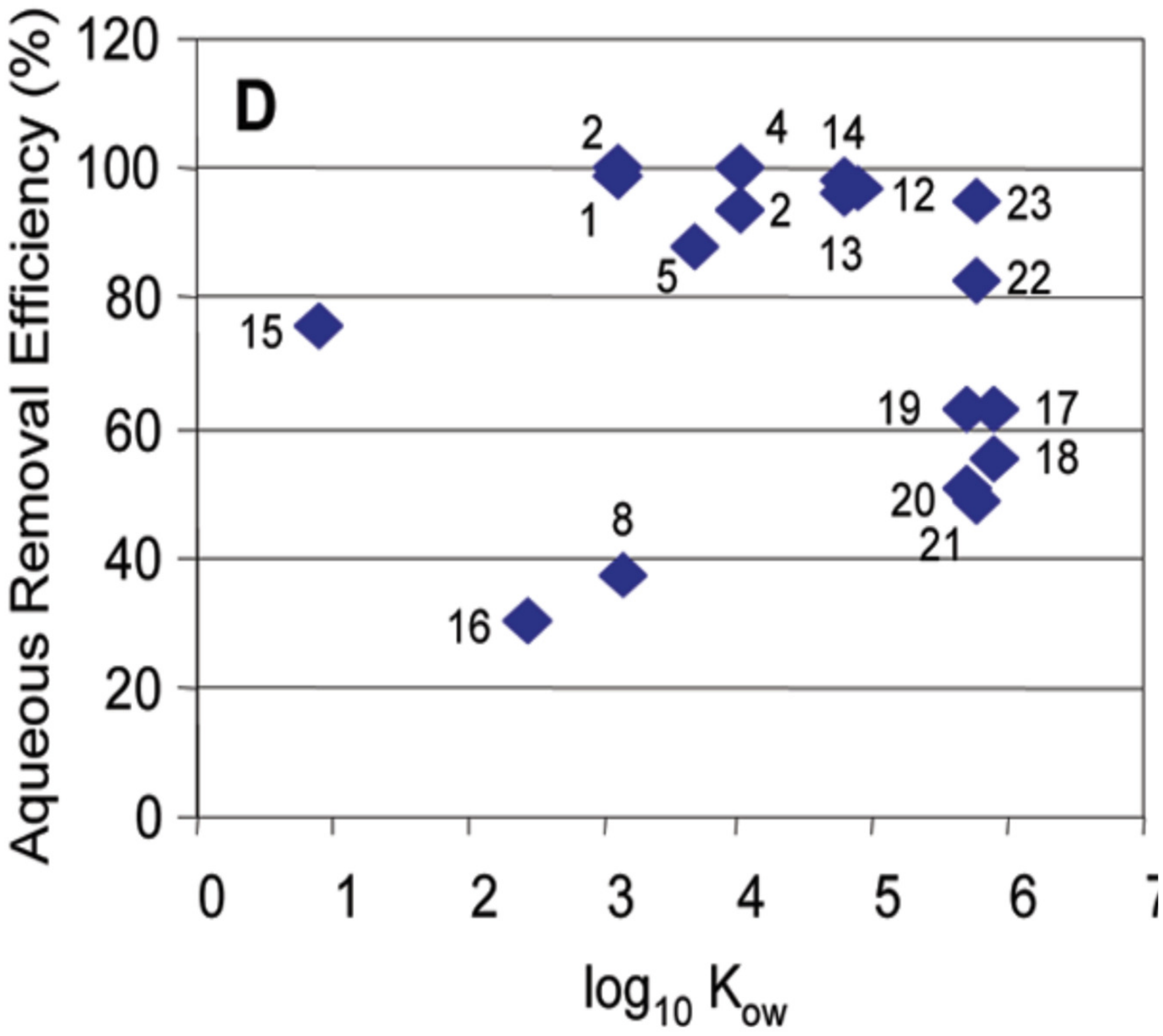


Role of K_OW in partitioning to sludge part



The trend is similar to that of fraction in sludge =f(K_ow)





D
Aqueous Removal Efficiency (%)
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
log10 Kow
2
1
4
2
5
14
12
13
23
22
15
19
17
18
20
21
8
16

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Occurrence of pharmaceuticals in a municipal wastewater treatment plant: Mass balance and removal processes

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ABSTRACT

Occurrence and removal efficiencies of fifteen pharmaceuticals were investigated in a conventional municipal wastewater treatment plant in Michigan. Concentrations of these pharmaceuticals were determined in both wastewater and sludge phases by a high-performance liquid chromatograph coupled to a

Table 2
Mass flux of the investigated pharmaceuticals at different treatment units.

Pharmaceuticals	Mass flux (g d^{-1})									Mass in effluent (%)	Mass in dewatered sludge, R_{sor} (%)	Mass lost in WWTP, R_{bio} (%)
	Raw influent	Pretreatment effluent	Primary effluent	Aeration effluent	Secondary effluent	Final effluent	Primary sludge	Waste sludge	Dewatered sludge			
CTC	8.1 ± 8.2	7.7 ± 1.8	5.5 ± 1.1	2.4 ± 0.9	NA	NA	0.2	NA	NA	NA	NA	100
DMC	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DOC	34 ± 25	22 ± 16	20 ± 16	26 ± 25	15 ± 18	17 ± 17	2.3 ± 1.5	1.3 ± 1.3	1.0 ± 0.5	50	3.0	47
OTC	1.3 ± 0.8	0.9 ± 0.6	1.2 ± 0.3	0.9 ± 0.2	0.6 ± 0.4	0.8 ± 0.2	0.1 ± 0.01	0.1 ± 0.03	0.03 ± 0.02	61	2.2	37
TC	14 ± 4.2	5.7 ± 2.0	7.0 ± 2.4	7.0 ± 3.9	NA	NA	NA	3.1 ± 1.7	1.0 ± 0.5	NA	7.1	93
SDZ	1.7 ± 0.5	1.6 ± 0.4	1.6 ± 0.3	2.0 ± 0.3	1.3 ± 0.1	1.2 ± 0.6	0.2 ± 0.04	0.2 ± 0.2	0.1 ± 0.03	73	5.2	22
SMR	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SMZ	1.2 ± 0.1	NA	NA	NA	NA	NA	NA	0.03 ± 0	0.01 ± 0	NA	0.5	99
SMX	71 ± 26	58 ± 24	59 ± 23	75 ± 32	22 ± 3.9	8.1 ± 6.9	0.1 ± 0.1	0.3 ± 0.2	0.1 ± 0.03	11	<0.1	>89
ERY	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
TYL	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
LCM	2.6 ± 3.6	6.1 ± 7.6	3.4 ± 5.1	2.6 ± 3.5	2.6 ± 2.0	1.6 ± 0.5	0.04 ± 0.05	0.2 ± 0.04	0.03 ± 0.02	60	1.0	39
CBZ	5.0 ± 1.2	5.4 ± 1.2	6.0 ± 1.8	7.7 ± 2.7	7.1 ± 2.2	7.0 ± 2.5	0.1 ± 0.1	0.1 ± 0.05	0.03 ± 0.02	141	0.6	-41
AMP	2800 ± 1493	2644 ± 1099	2561 ± 1238	145 ± 134	3.2 ± 1.6	4.5 ± 3.9	0.3 ± 0.1	0.5 ± 0.3	0.2 ± 0.1	<0.2	<0.01	>99
CAF	1871 ± 550	1737 ± 538	2436 ± 794	138 ± 205	3.3 ± 2.1	3.4 ± 2.7	0.3 ± 0.1	0.4 ± 0.6	0.1 ± 0.05	<0.2	<0.01	>99

NA, not currently available. Mass flux was calculated according to Eqs. (1) and (2). R_{bio} and R_{sor} were calculated using Eqs. (4) and (5), respectively.

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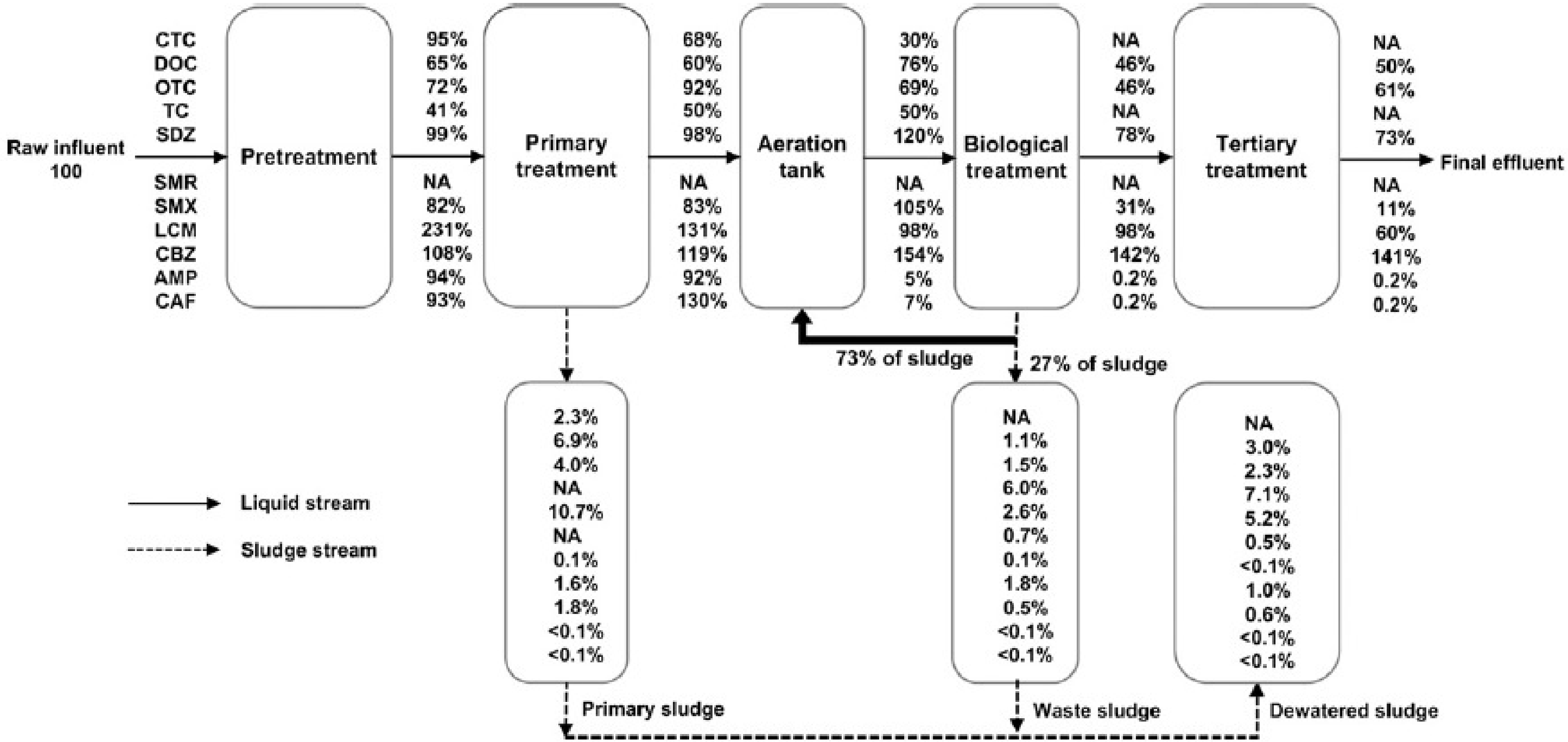

Fig. 4. Percentage (R_i, %, calculated applying Eq. (6)) of detected pharmaceuticals along the WWTP.

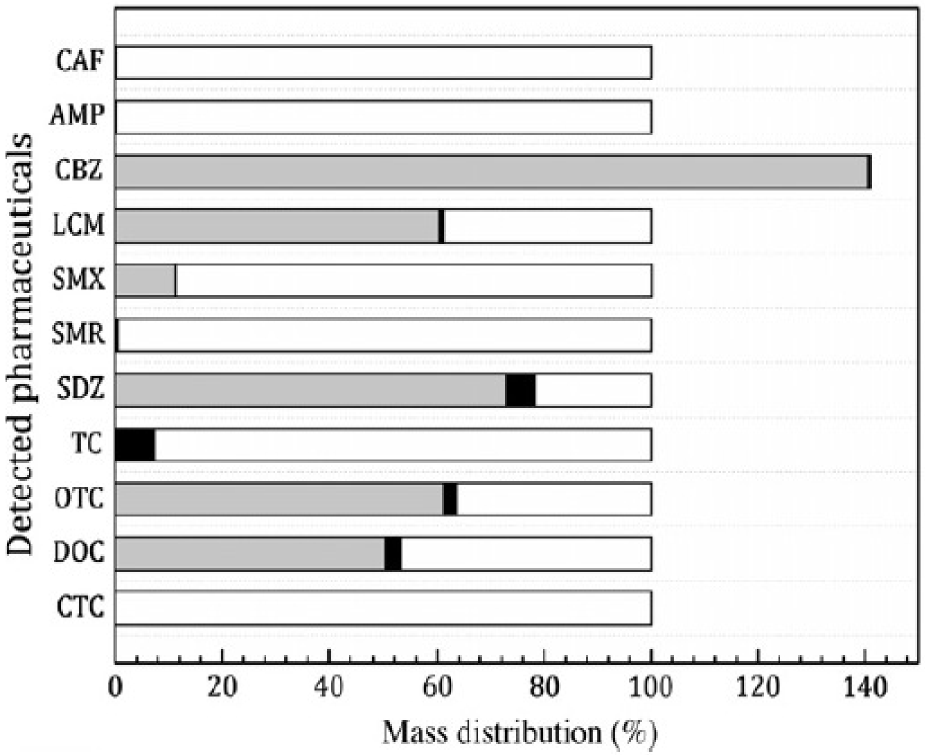

Fig. 3. Mass distribution of the detected pharmaceuticals in the WWTP. The grey-colored bar represents the mass fraction in the final effluent, the black-colored bar represents the fraction in the dewatered sludge, and the white bar represents the loss of pharmaceuticals due to biodegradation.

- Write Name entry number on a paper
- Q1: Order chemicals in decreasing order of their potential occurrence in final effluent?
- Q2: Which compound is expected to have smallest K_{OW}?