



# Miljögifter i slam och utgående vatten

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Seminarium: Slam och kretslopp - slam som produktionsresurs i svenska jord- och skogsbruk? Stockholm, 27 Februari 2013



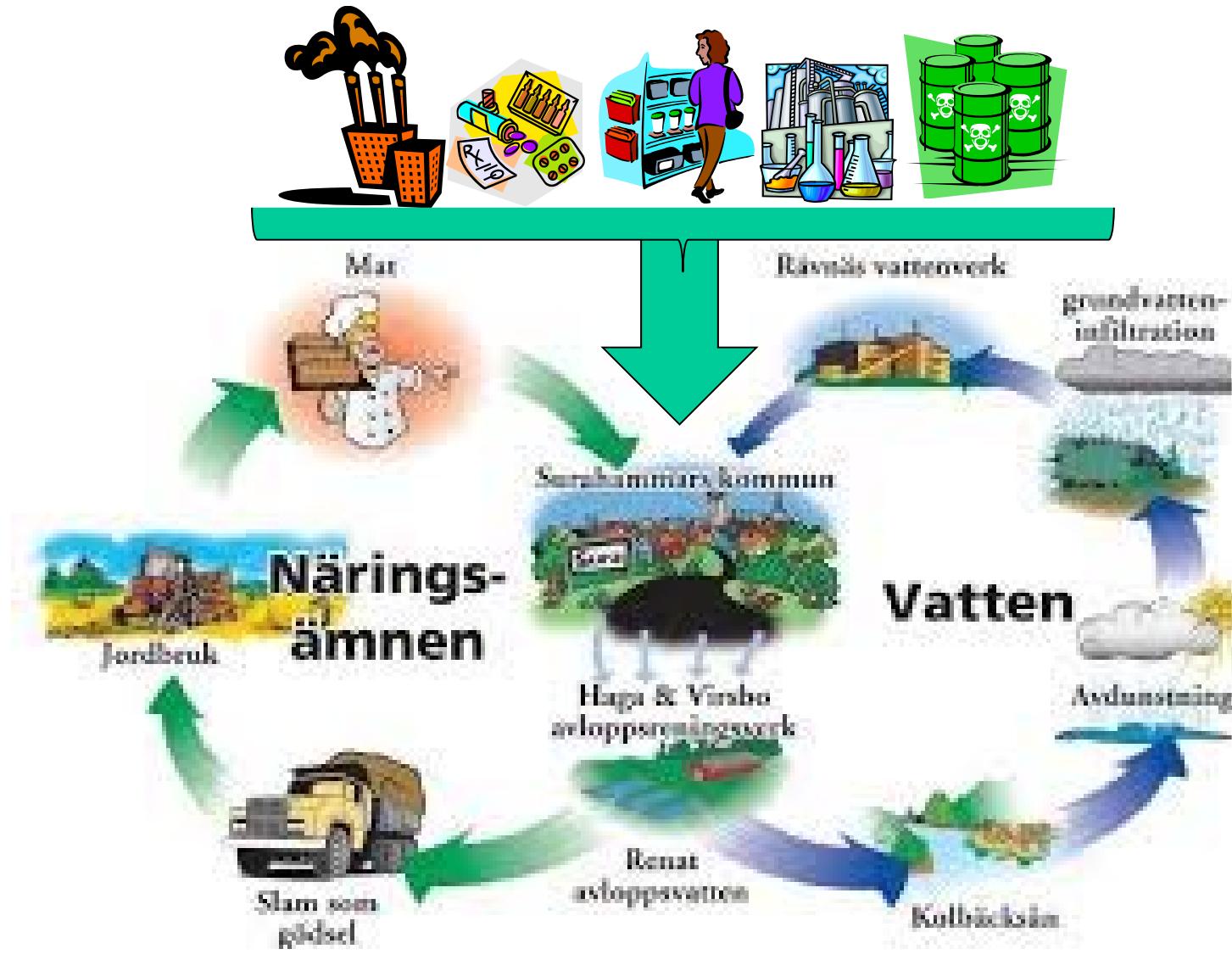
## Presentationen:

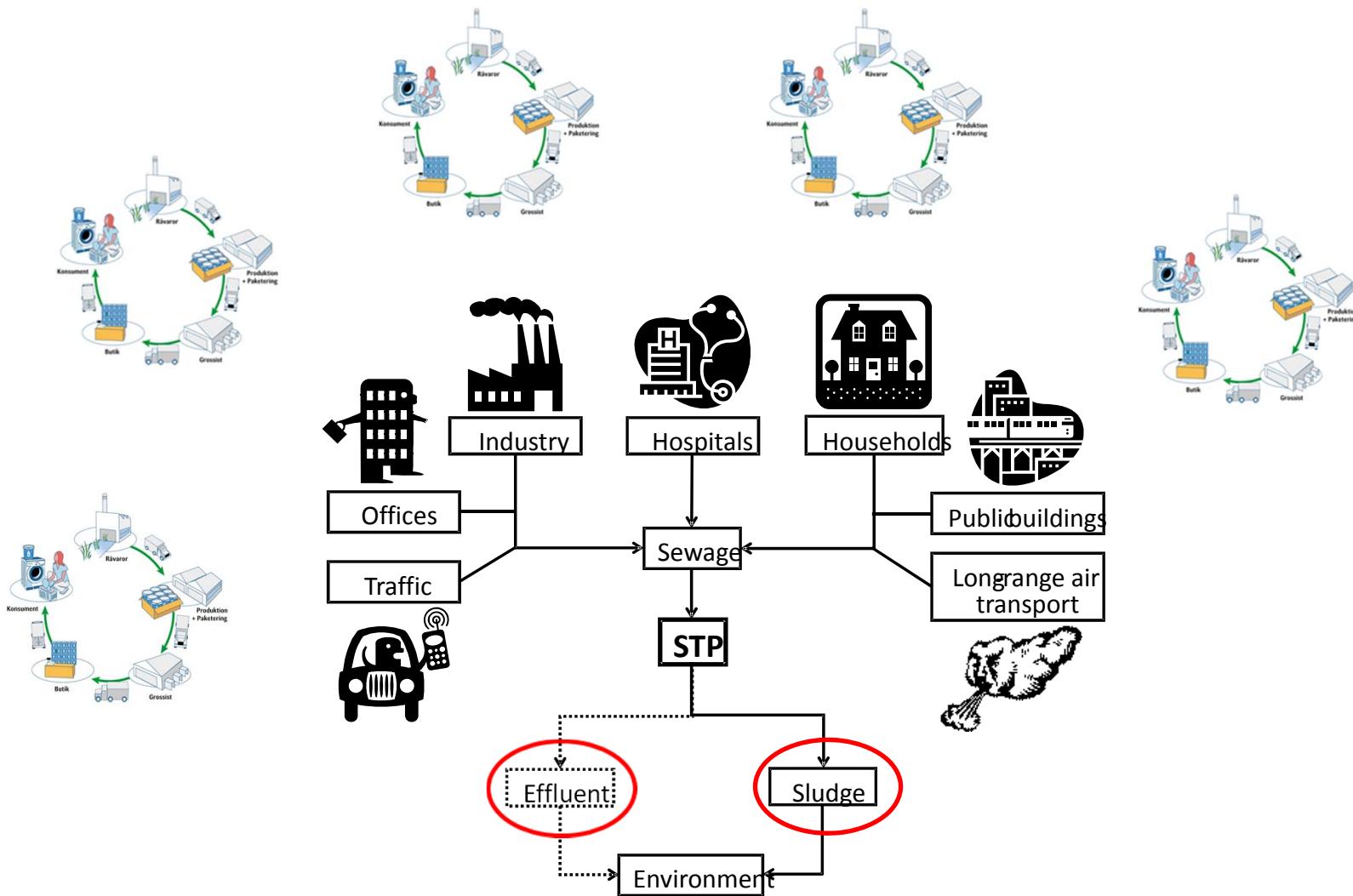
- Introduktion kemikalieflödet
- Substanser
- Flöden ARV – Avskiljning vs. Nedbrytning
- Tidstrender
- Slam jordsbruksmark & skogsmark
- Aspekter riskbedömning

# Vision om uthålliga kretslopp



# Vision om uthålliga kretslopp





# Emissioner tidigare, idag och i framtiden?

Klassiska emissioner



Produkter



# Några exempel – Kemikalieflödet

## Tillsatser i livsmedel:

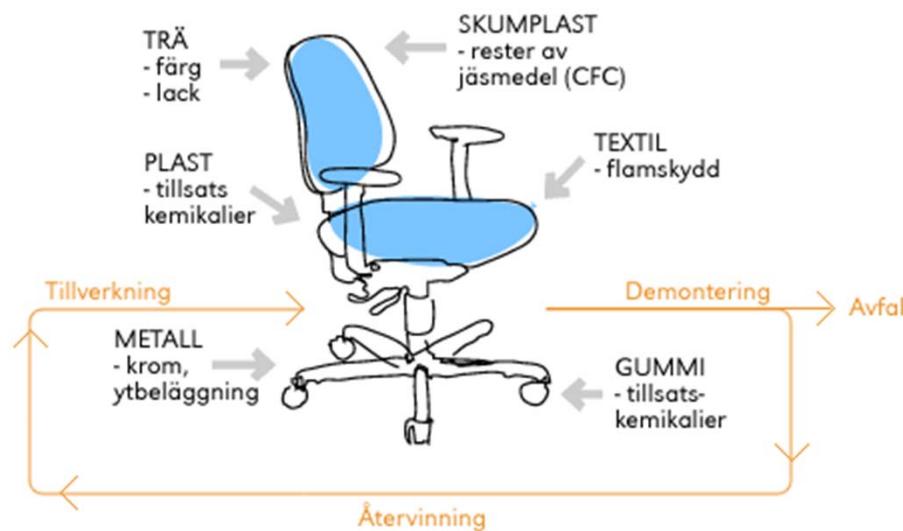
**Sukralos:** ca 10% rening/avskiljning i ARV (2 verk)

	Inkommande avloppsvatten (ng/l)	Utgående vatten (ng/l)	Ytvatten (ng/l)	Slam (ng/g våtvikt)
# prov	6	29	15	6
Sukralos	3 530-7 920	1 790-10 800	<4-3 560	<1-15
DF (%)	100	100	73	83

DF=Detektionsfrekvens

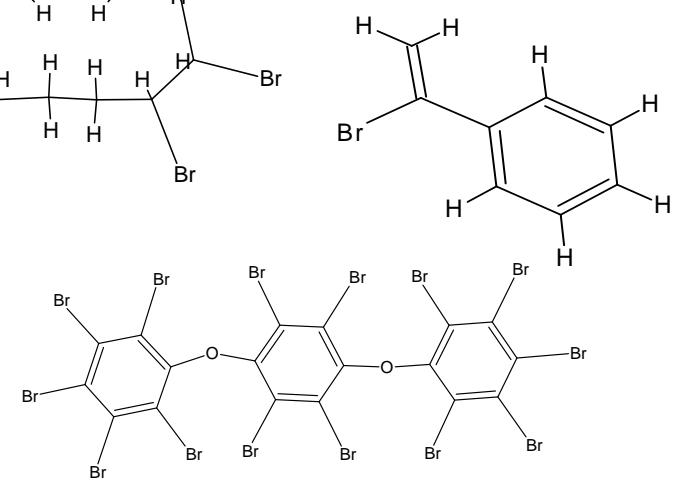
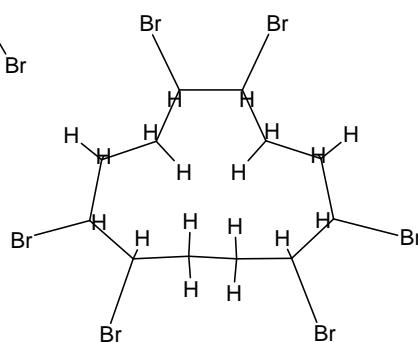
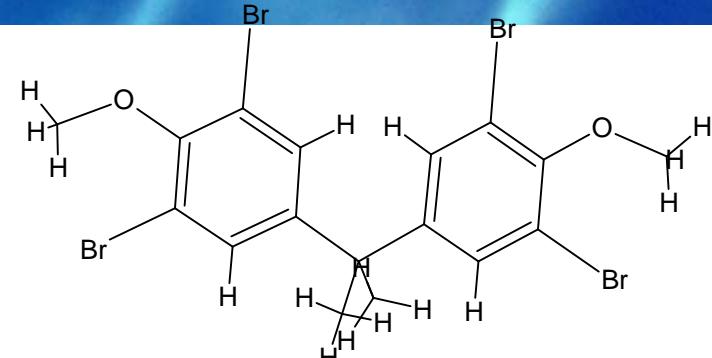
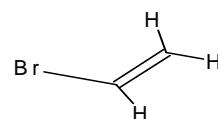
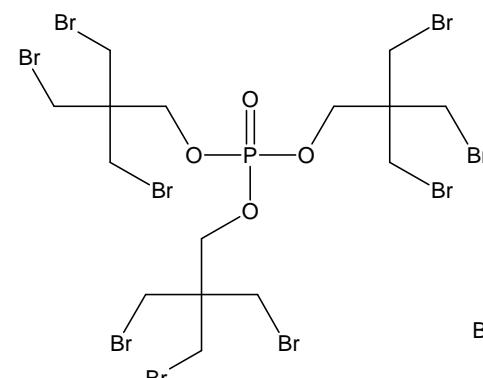
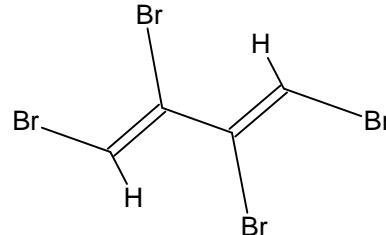
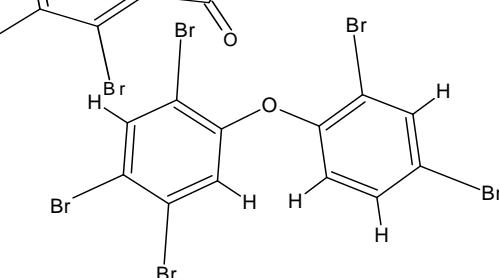
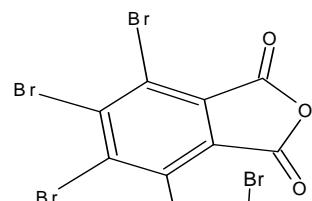
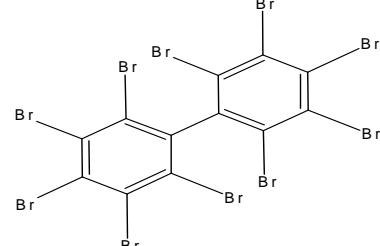
IVL Rapport B1769, Januari, 2008

## Kemikalier i varor:

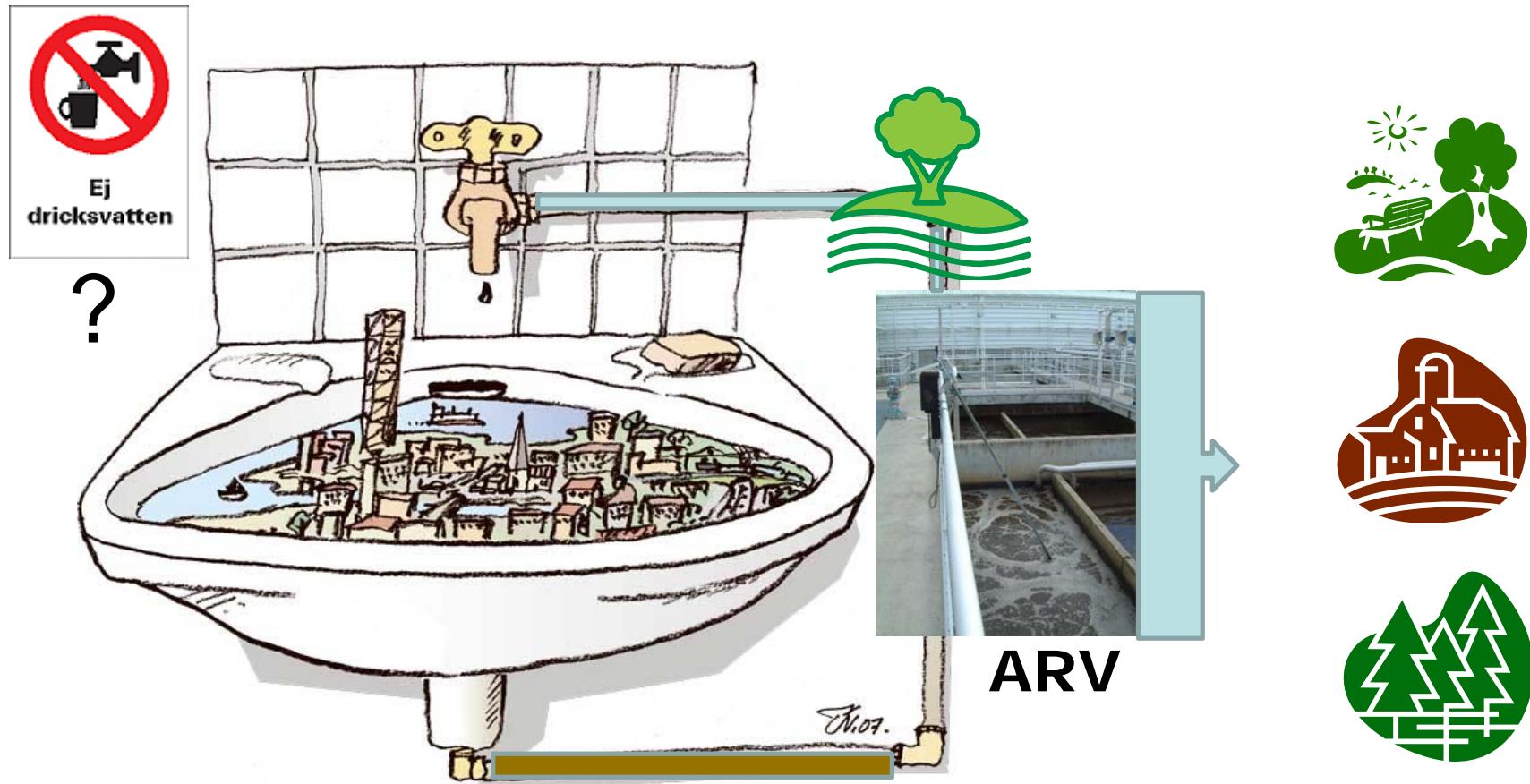


Källa: Keml

# Ex: Bromerade flamskyddsmedel



# Kemikalieflödet hot mot mark och vatten?

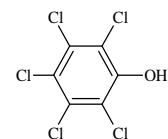


Teckning: Malmö kommun

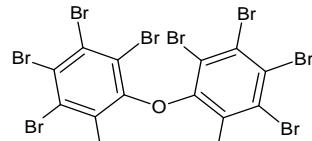
Vad klarar våra ARV? Var  
tar olika ämnen vägen?  
Nedbrytning/avskiljning?



## Olika tunga (Molekylvikt)

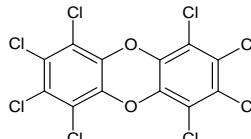


$M_w: 266.34$

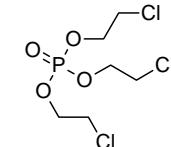


$M_w: 959.17$

## Vattenlösighet



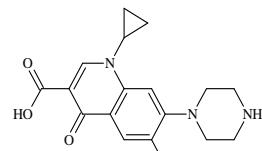
$S_w: 9.3 \cdot 10^{-6}$



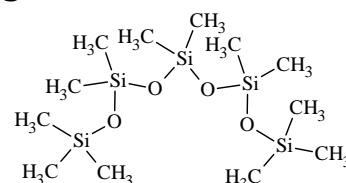
$S_w: 5\ 597$



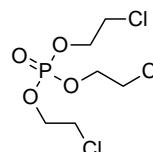
## Flyktighet



$H: 5.1 \cdot 10^{-19}$



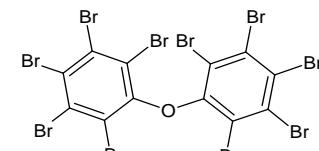
$H: 0.79$



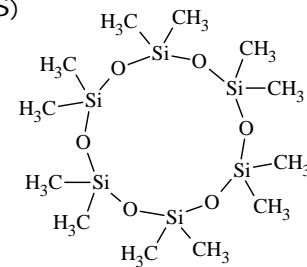
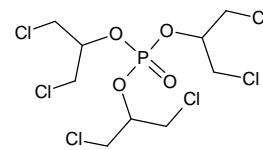
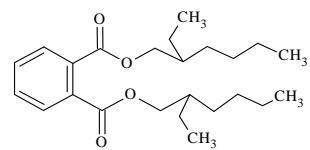
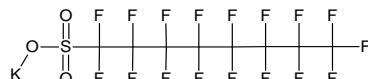
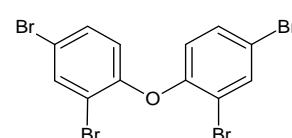
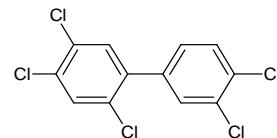
Tris(2-chloroethyl) phosphate  
 $\log K_{ow}: 1.63$



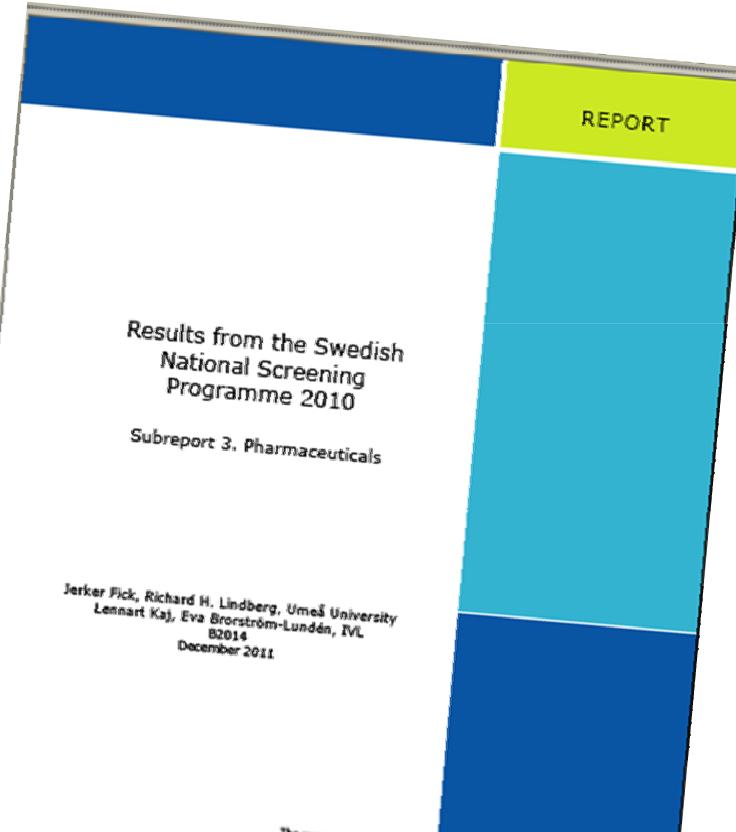
## Fettlösighet



$\log K_{ow}: 12.11$



# Naturvårdsverket – UmU och IVL screeningundersökning läkemedel (Dec. 2011)



## En del läkemedel hamnar i reningsverkens slam

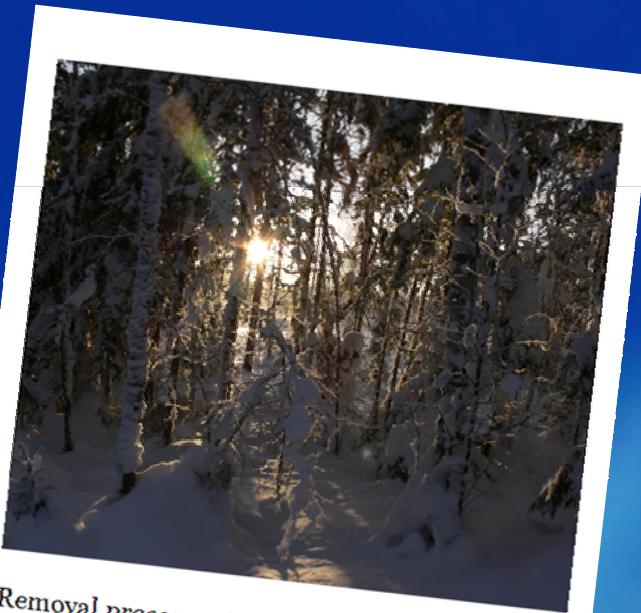
Eftersom studien är så bred och täcker in så många läkemedel är resultatet mycket informativt. Undersökningen visar att 92 av de 101 läkemedlen kunde detekteras (upptäckas) i inkommande avloppsvatten och att så många som 85 kunde detekteras i utgående, behandlat avloppsvatten. Slam analyserades från fyra avloppsreningsverk och då hittades 54 läkemedel i kvantifierbara halter.



Ulrika Olofsson.

"Reningsprocesser i  
avloppsreningsverk -  
Slamkvalitet och  
reningseffektivitet av  
strukturellt varierande  
organiska föreningar".

Doktorsavhandling Umeå  
universitet 2012.



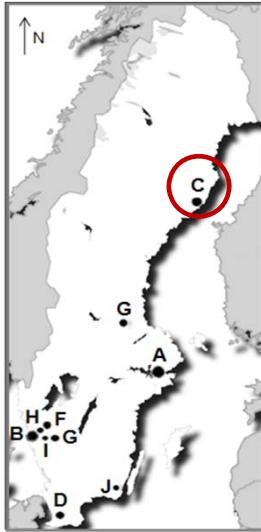
Removal processes in sewage treatment plants -  
Sludge quality and treatment efficiency of structurally  
diverse organic compounds

Ulrika Olofsson

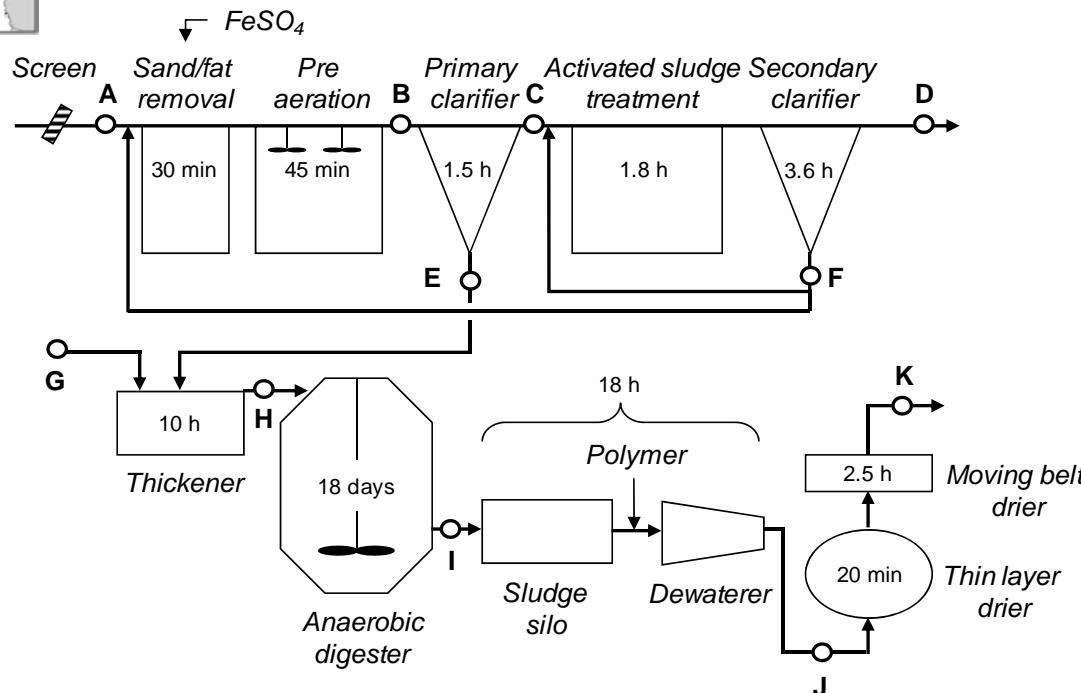


Department of Chemistry  
Doctoral Thesis 2012





# Avloppsreningsverken inte avsedda för att rena industri- och hushållskemikalier!



- **Sampling location**
- **A** Raw sewage water
- **B** Aerated effluent
- **C** Primary effluent
- **D** Final effluent
- **E** Sludge, primary clarification
- **F** Sludge, secondary clarification
- **G** External sludge
- **H** Raw sludge
- **I** Digested sludge
- **J** Dewatered (digested) sludge
- **K** Pellet

# Resultat nationella screenningen (NV) 2011

In ARV Ytvatten

Ut ARV Fisk

Name	(ng/L)	(ng/L)	(ng/L)	(µg/Kg)	Diphenhydramine	203,5	54,2	11,4	0,1	Memantine	86,3	30,7	15,3	0,8
Alfuzosin	224,1	106,3	32,6	<LOQ	Dipyridamole	6945,3	<LOQ	<LOQ	<LOQ	Metformin	1534,8	<LOQ	<LOQ	<LOQ
Alprazolam	59,7	14,3	<LOQ	<LOQ	Donepezil	70,1	22,2	<LOQ	<LOQ	Metoprolol	6831,3	1959,6	1198,8	<LOQ
Amiodiarone	<LOQ	<LOQ	<LOQ	<LOQ	Duloxetine	11,4	2,1	<LOQ	<LOQ	Mianserin	65,2	34,6	6,3	<LOQ
Amitriptyline	47,4	16,3	<LOQ	<LOQ	Eprosartan	935,1	98,3	20,8	<LOQ	Miconazole	47,6	<LOQ	<LOQ	<LOQ
Atenolol	4884,3	597,7	355,1	<LOQ	Erythromycin	2065,8	94,4	<LOQ	<LOQ	Mirtazapine	866,2	412,3	213,3	<LOQ
Atorvastatin	260,6	<LOQ	<LOQ	<LOQ	Estradiol	<LOQ	<LOQ	<LOQ	<LOQ	Naproxen	411,9	125,3	76,8	<LOQ
Atracurium	28,7	26,5	0,7	<LOQ	Ethinyl estradiol	<LOQ	<LOQ	<LOQ	<LOQ	Nefazodone	217,6	16,2	<LOQ	<LOQ
Azelastine	40,5	9,8	<LOQ	<LOQ	Etonogestrel	<LOQ	609,6	166,0	<LOQ	Norfloxacin	<LOQ	<LOQ	<LOQ	<LOQ
Azithromycin	44,1	22,7	<LOQ	<LOQ	Ezetimibe	240,2	<LOQ	<LOQ	<LOQ	Oflloxacin	<LOQ	<LOQ	<LOQ	<LOQ
Beclomethazone	<LOQ	<LOQ	<LOQ	<LOQ	Felodipine	<LOQ	<LOQ	<LOQ	<LOQ	Orphenadrine	183,5	81,4	28,5	2,2
Biperiden	70,1	26,5	<LOQ	0,5	Fentanyl	8,4	4,9	0,9	<LOQ	Oxazepam	1776,4	726,3	577,4	9,6
Bisoprolol	563,8	108,5	59,1	<LOQ	Fexofenadine	1090,4	371,5	146,1	<LOQ	Paracetamol	536730,8	405,7	51,8	<LOQ
Bromocriptine	13,1	<LOQ	<LOQ	<LOQ	Finasteride	28,0	<LOQ	<LOQ	<LOQ	Paroxetine	128,9	32,6	<LOQ	17,2
Buprenorphine	1001,0	37,8	<LOQ	<LOQ	Flecainide	705,6	226,5	130,3	0,2	Perphenazine	88,5	<LOQ	<LOQ	<LOQ
Bupropion	81,6	21,4	14,2	<LOQ	Fluconazole	2070,2	517,5	287,7	<LOQ	Pizotifen	34,7	18,9	1,0	4,5
Carbamazepine	2621,5	1079,5	756,0	<LOQ	Flunitrazepam	16,6	<LOQ	<LOQ	<LOQ	Promethazine	188,7	60,6	<LOQ	<LOQ
Chlorprothixen	77,6	<LOQ	<LOQ	<LOQ	Fluoxetine	239,8	81,3	31,7	6,7	Ranitidine	379,2	152,6	108,8	<LOQ
Chlorpromazine	68,5	10,3	<LOQ	<LOQ	Flupentixol	71,6	8,6	12,1	<LOQ	Repaglinide	143,6	39,6	15,7	<LOQ
Cilazapril	41,9	8,3	<LOQ	<LOQ	Fluphenazine	127,3	<LOQ	<LOQ	<LOQ	Risperidone	275,0	134,4	1,6	0,4
Ciprofloxacin	30,4	11,5	14,0	<LOQ	Flutamide	114,1	34,1	<LOQ	<LOQ	Rosuvastatin	525,4	14,6	<LOQ	<LOQ
Citalopram	1015,4	345,0	192,5	<LOQ	Glibenclamide	74,1	40,6	<LOQ	19,4	Roxithromycin	366,5	90,3	<LOQ	<LOQ
Clarithromycine	476,0	46,9	2,1	<LOQ	Glimepiride	<LOQ	11,3	<LOQ	<LOQ	Sertraline	96,3	25,0	28,1	13,6
Clemastine	4,2	2,9	<LOQ	<LOQ	Haloperidol	69,0	7,1	1,4	0,4	Sulfamethoxazole	1475,7	280,8	147,4	12,8
Clindamycin	232,6	200,9	138,0	<LOQ	Hydroxyzine	61,4	21,8	2,1	8,3	Tamoxifen	928,6	12,2	<LOQ	6,3
Clomipramine	72,4	28,7	1,0	8,1	Ibuprofen	1932,4	139,9	117,6	<LOQ	Telmisartan	1421,0	181,8	106,5	<LOQ
Clonazepam	<LOQ	<LOQ	<LOQ	<LOQ	Irbesartan	2618,4	1104,9	431,6	1,3	Tetracycline	4514,4	<LOQ	<LOQ	<LOQ
Clotrimazol	59,3	28,2	1,9	13,6	Ketoconazole	1233,0	122,7	<LOQ	<LOQ	Tramadol	6069,7	2783,0	1840,1	<LOQ
Codeine	4242,9	583,1	343,7	<LOQ	Ketoprofene	157,3	166,1	108,0	<LOQ	Trihexyphenidyl	109,0	46,6	1,4	<LOQ
Cyproheptadine	49,2	<LOQ	<LOQ	<LOQ	Levomepromazine	<LOQ	<LOQ	<LOQ	<LOQ	Trimethoprim	1373,3	346,4	213,8	<LOQ
Desloratidin	172,7	81,1	6,0	<LOQ	Levonorgestrel	<LOQ	<LOQ	<LOQ	<LOQ	Venlafaxine	2234,2	658,9	445,0	<LOQ
Diclofenac	6976,1	3858,1	876,7	<LOQ	Loperamide	20,9	13,9	1,6	<LOQ	Verapamil	110,0	17,9	<LOQ	<LOQ
Dicycloverin	8,0	<LOQ	<LOQ	<LOQ	Maprotiline	51,8	17,9	<LOQ	<LOQ	Zolpidem	44,4	19,0	6,0	<LOQ
					Meclozine	21,9	<LOQ	<LOQ	<LOQ					

UNIVERSITET



= >200ng/l

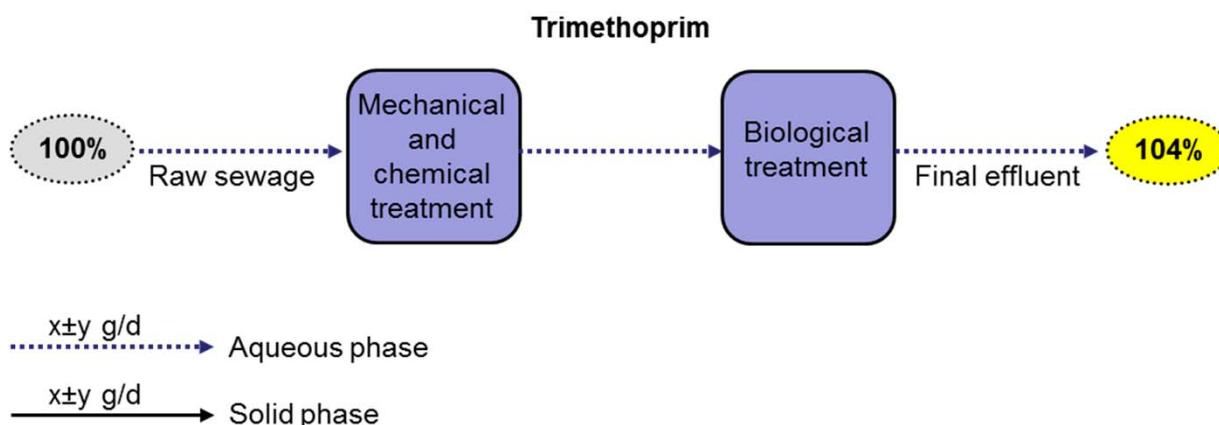
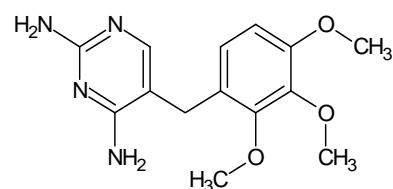
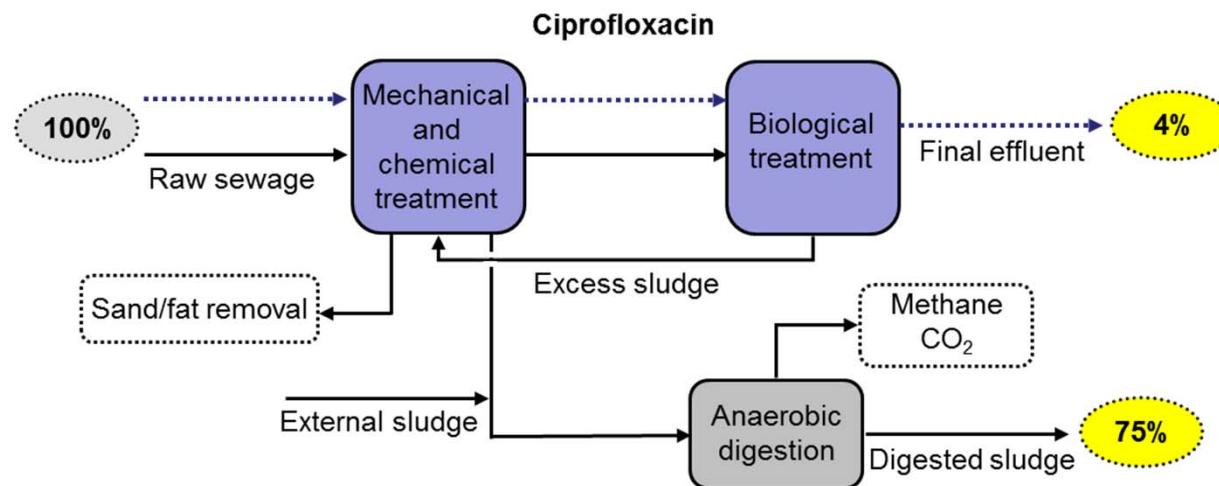
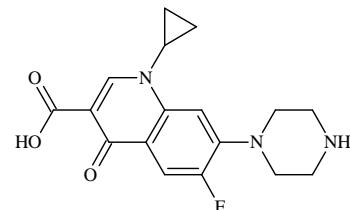


= 21-200 ng/L

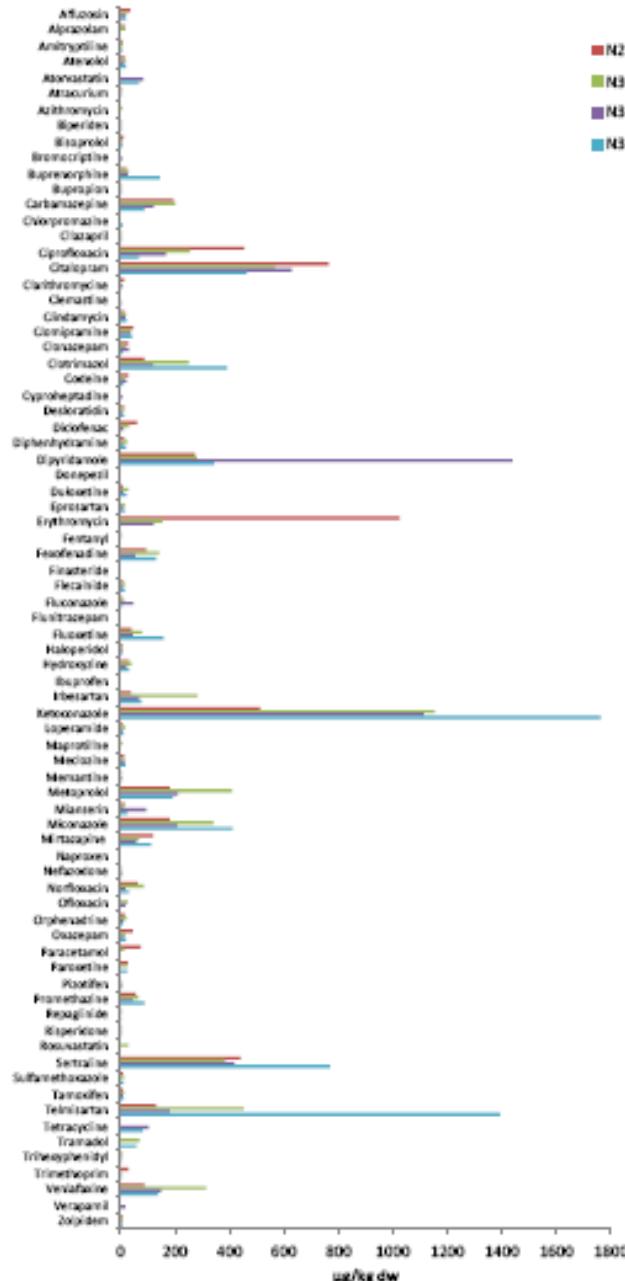


= <20 ng/L

# Mass flöde av antibiotika (Umeå ARV)



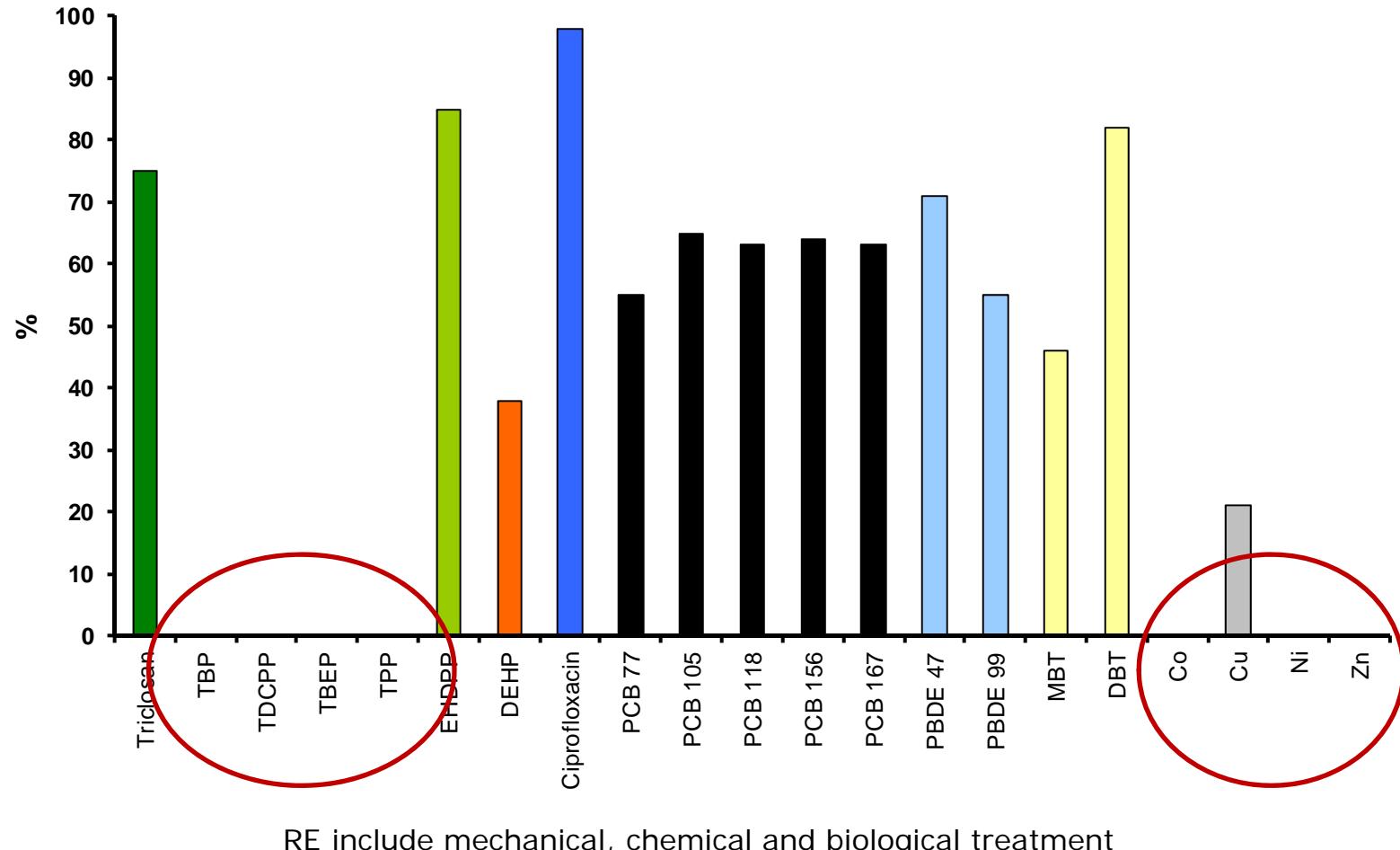
# Läkemedel detekterade i slam från fyra ARV (Skövde, Stockholm, Uppsala, Umeå). Rapport dec 2011



**Figure 3.** Detected pharmaceuticals ( $\mu\text{g}/\text{Kg}$ ) in dewatered digested sludge from the WWTPs Stadskvarn Skövde (N29), Henriksdal, Stockholm (N30), Ön, Umeå (N31) and Kungsängsverket, Uppsala (N32).

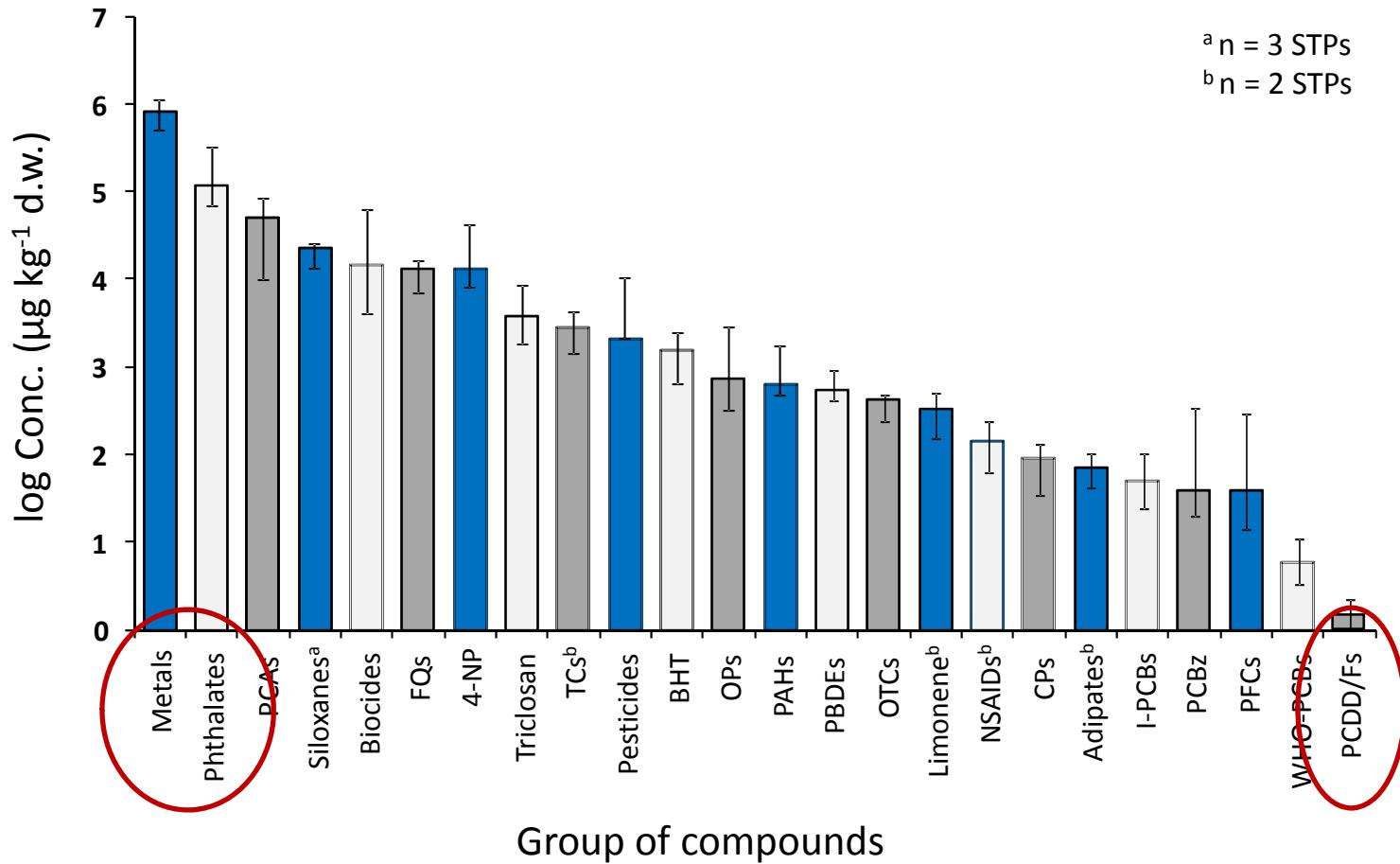
# Avskiljningseffektivitet (RE)

$$RE (\%) = 100 - \left( \frac{C_{\text{Effluent, tot}}}{C_{\text{Influent, tot}}} \cdot 100 \right)$$

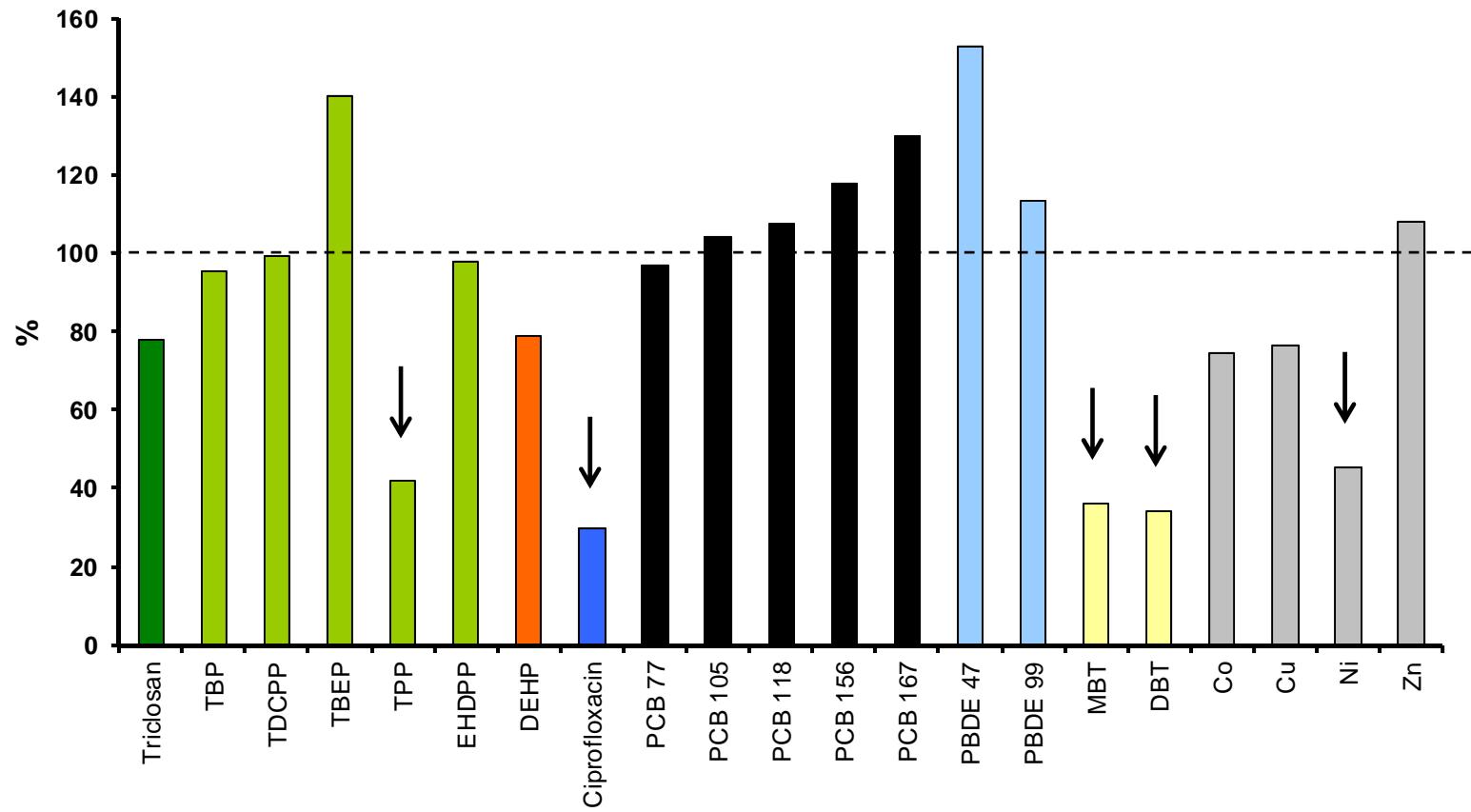




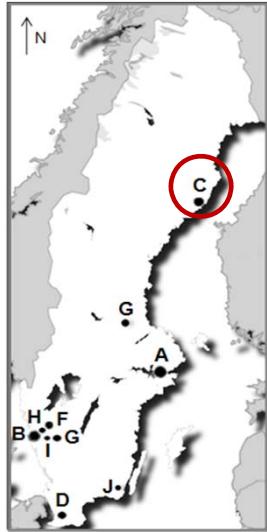
## Oönskade ämnen i slam



# Anaerob rötning

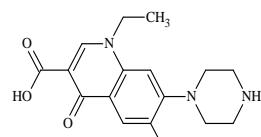


>100% means higher concentration in dewatered digested sludge than in primary sludge

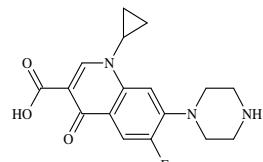


## Generellt ARV

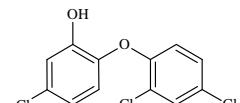
- ARV har generellt högre avskiljningseffektivitet för s k hydrofoba ämnen (lipofila) än fallet för mer vattenlösliga (väntat)
- Hög RE (>70%) – norfloxacin, ciprofloxacin, triclosan, PBDE 47, EHDPP and DBT



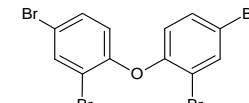
Norfloxacin



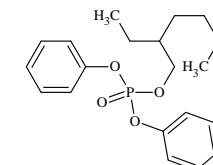
Ciprofloxacin



Triclosan



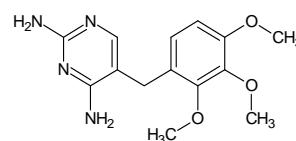
PBDE 47



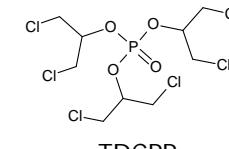
EHDPP

*Lipophilic compounds*

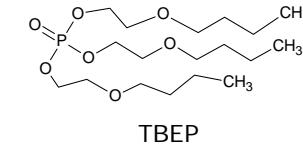
*Water soluble compounds*



Trimethoprim



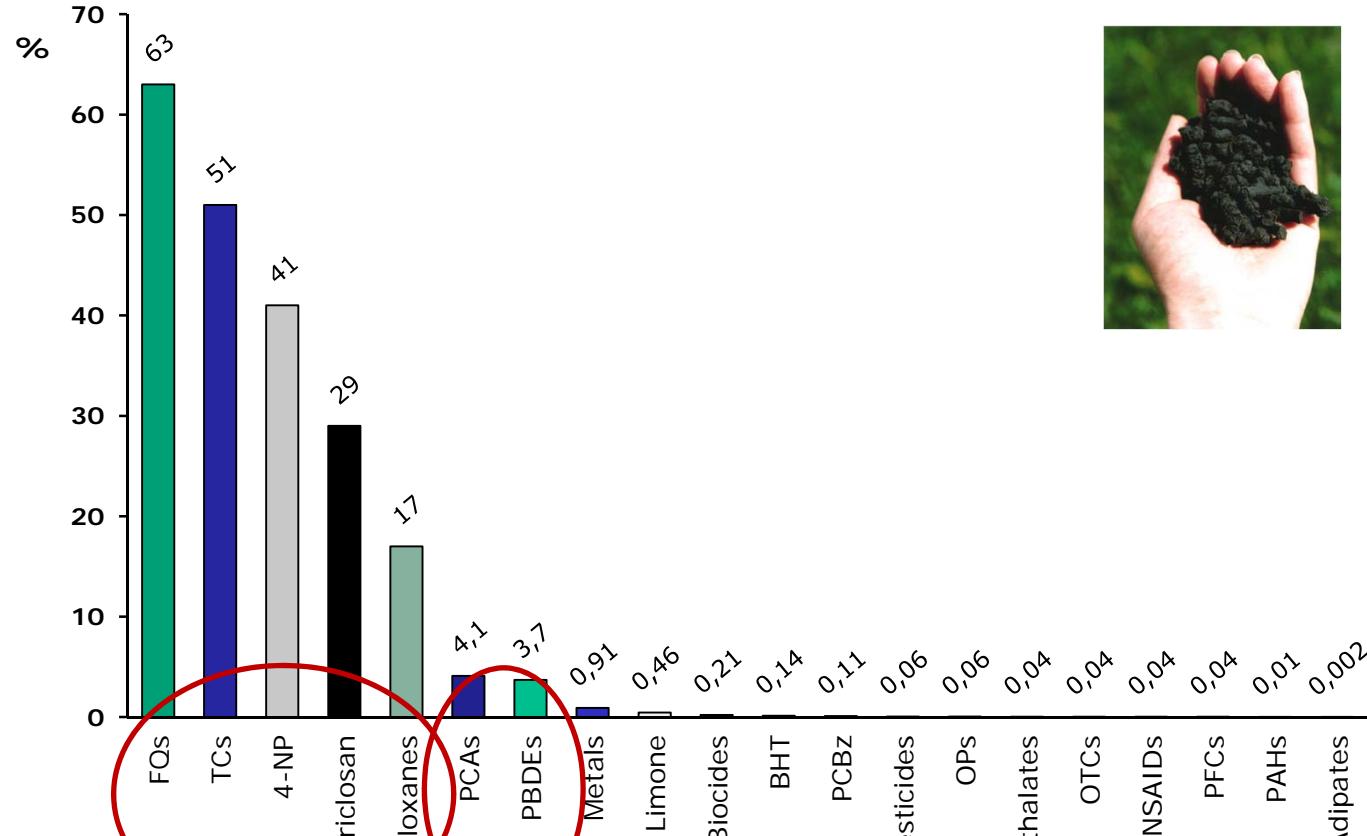
TDCPP



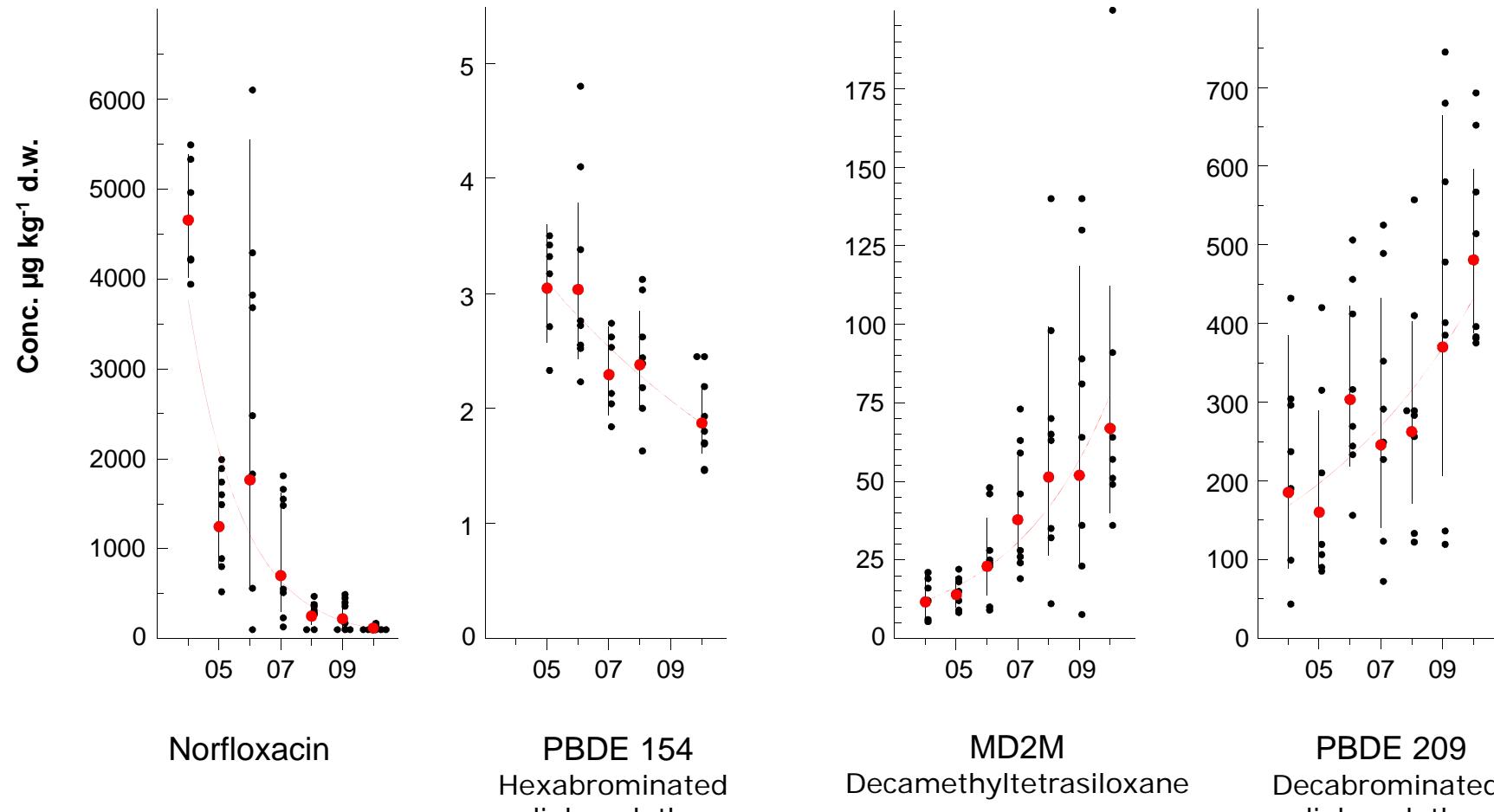
TBEP



## Återfinning av substanser i slam relativ användningsvolym i samhället



# Tidstrender



Norfloxacin

PBDE 154  
Hexabrominated  
diphenylether

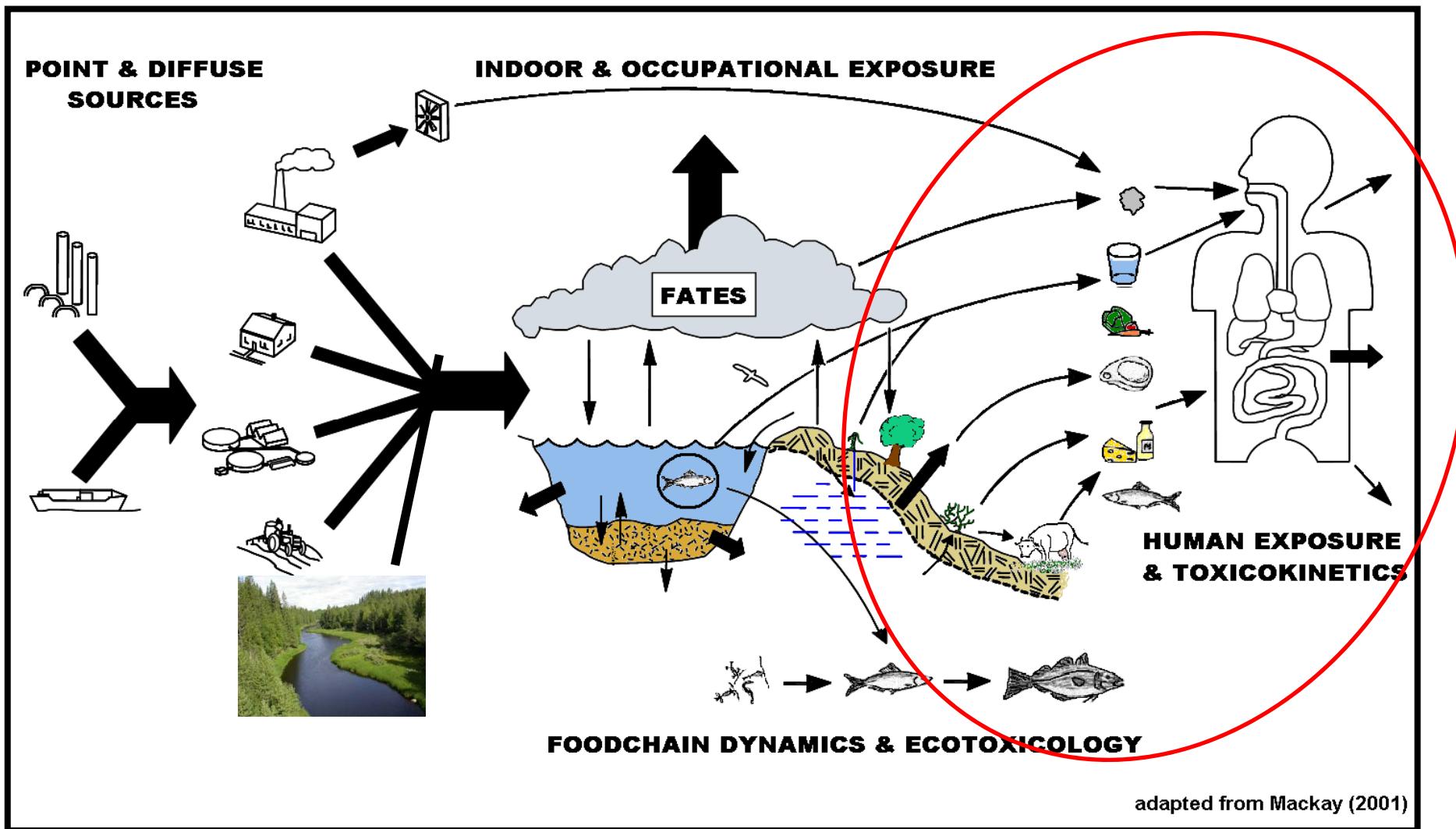
MD2M  
Decamethyltetrasiloxane

PBDE 209  
Decabrominated  
diphenylether



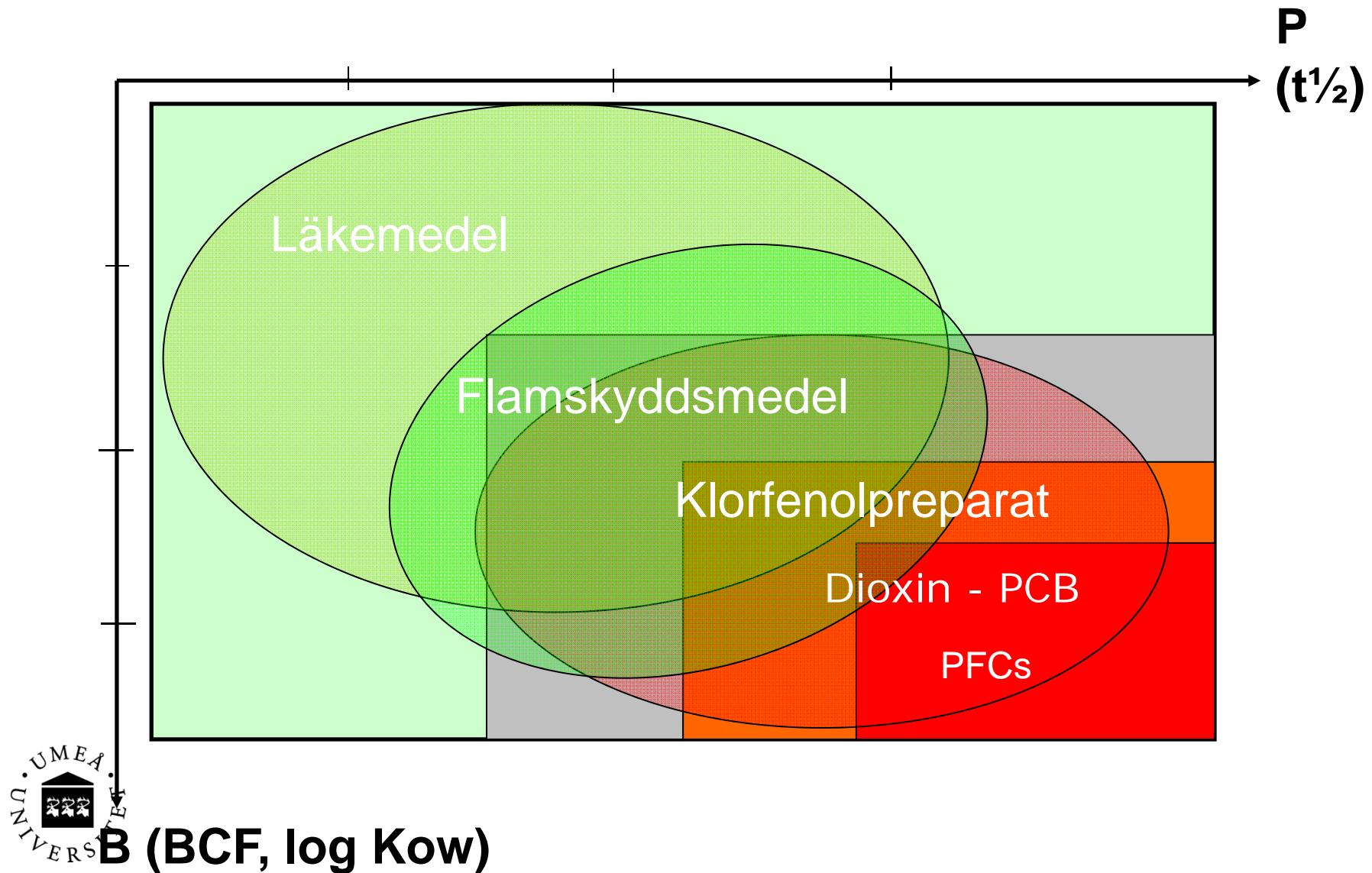
Olofsson et al 2012

# “From source to exposure”



adapted from Mackay (2001)

# Persistens (P) – Bioakkumulation (B)



# **Miljöriskbedömning av skogsgödsling med pelleterat/granulerat avloppsslam – syntetiska organiska ämnen**



## **Slutrapport**

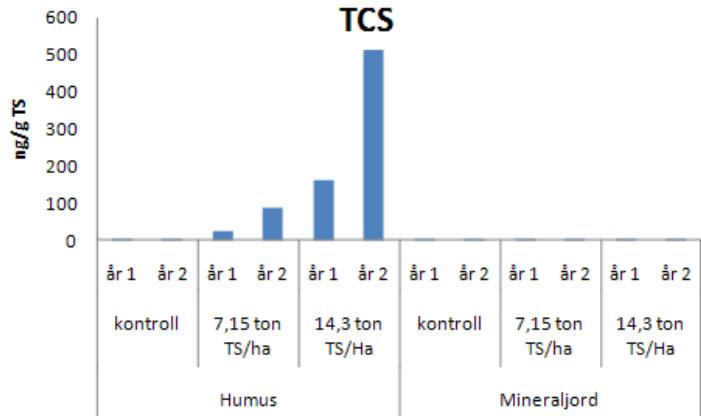
STEM P30686-1: 2007-2009

Mars 2010

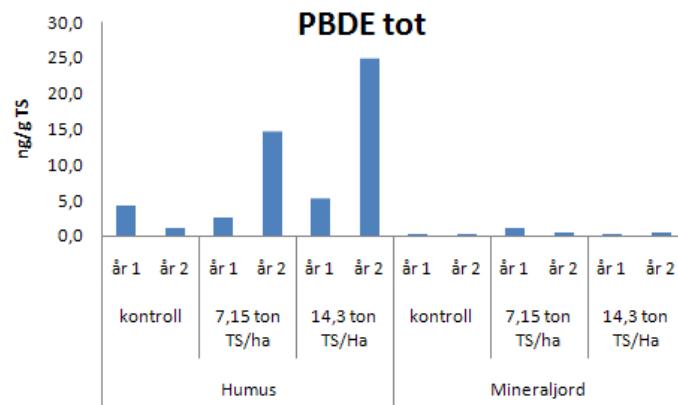
Dr Richard Lindberg, Kemiska Institutionen, Umeå universitet

Professor Mats Tysklind, Kemiska Institutionen, Umeå universitet

Docent Kenneth Sahlén, Inst f skogens ekologi och skötsel, SLU, Umeå



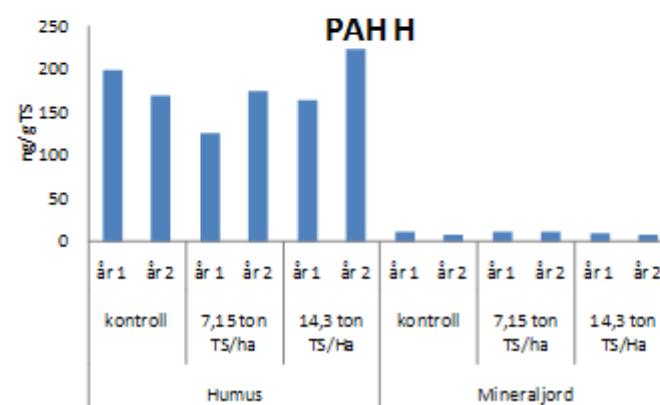
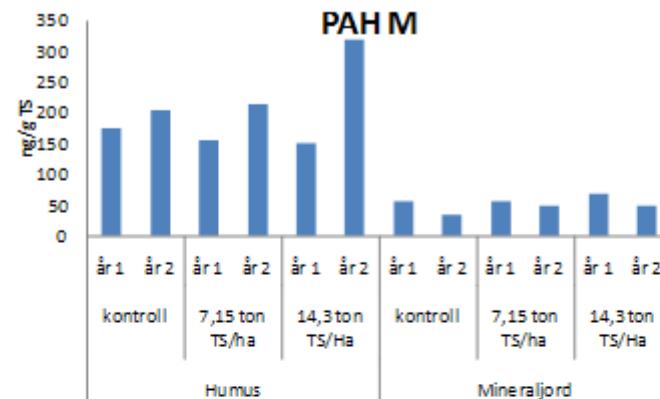
Figur 1. Halter av TCS i kontrolllytor och handgödslade provytor.



Figur 2. Totalhalt PBDE i kontrolllytor och handgödslade provytor.

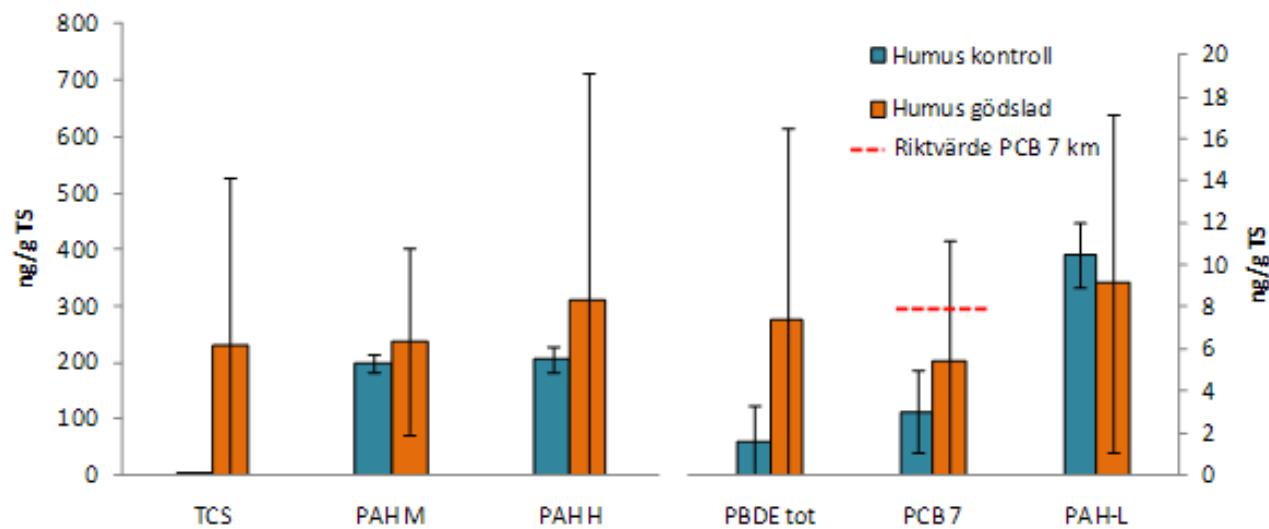
Tabell 3 Halter (i ng/g TS) av organiska ämnen i torkat gränulerat släm.

FQ tot	6920	PCB7	41
TCS	1173	PAH-L	13
EE2	1,4	PAH-M	768
PBDE tot	56	PAH-H	747



Figur 4. Totalhalt PAH-L, -M och -H i kontrolllytor och handgödslade provytor.

# Organiska ämnen i skogsgödslad mark



**Figur 5. Medelkoncentrationer och standardavvikelse hos de organiska substanserna i ogödslade (kontrollområden) och slamgödslade områden.**

**TABLE 1. Data about Sites and Sampling**

site and type of field in Sweden (reference or applied with sludge)	first – last year of sludge application	total amount of dry sludge applied (tonnes/ha)	date of sampling	condition at time of sampling	clay type
Petersborg, P			April 6, 2000	plowed autumn 1999, harrowed and sowed	light clays
P ref, reference		0			
P low, lower sludge dosage	1981–1997	20			
P high, higher sludge dosage	1981–1997	60			
Igelösa, I			April 6, 2000	plowed autumn 1999, not harrowed or sowed	medium clays
I ref, reference		0			
I low, lower sludge dosage	1981–1997	20			
I high, higher sludge dosage	1981–1997	60			
Lanna, L			April 3, 2000	before sowing	slightly clayey soils
L ref, reference		0			
L slu., sludge applied	1998	2.3			
Björketorp, B			September 20, 2000	plowed grassland (B ref), clover cover (B slu)	not classified
B ref, reference		0			
B slu., sludge applied	1978–1982	25			
Horred, H			September 20, 2000	not harvested, covered with oat and clover	not classified
H ref, reference					
H sed, sediment overflow					

\* Adapted from ref 7. Copyright 2002 Society of Environmental Toxicology and Chemistry, used by permission of Alliance Communications Group, a division of Allen Press, Inc.



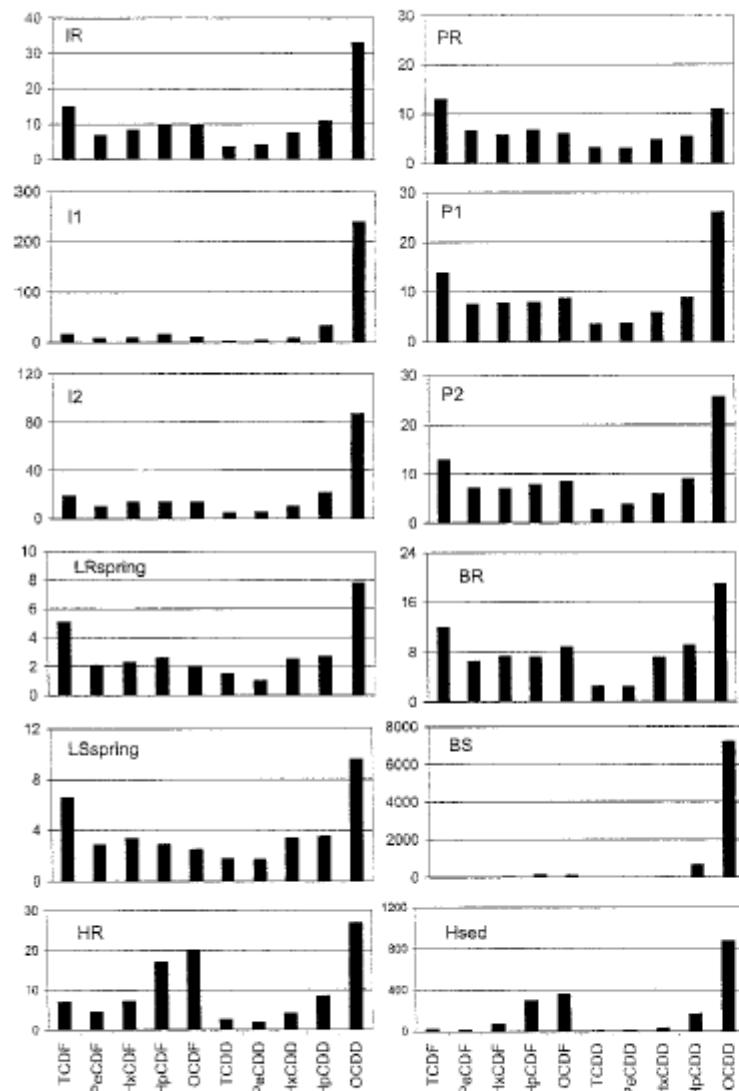


Fig. 1. Profiles of sums tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-*p*-dioxins/dibenzofurans (-CCDs/CDFs) in soil (pg/g dry matter [DM]). Meanings of the designations for the sites are given in Table 1; see Table 3 for definitions. TCCD = tetrachlorinated dibenzo-*p*-dioxin; PeCDD = pentachlorinated dibenzo-*p*-dioxin.

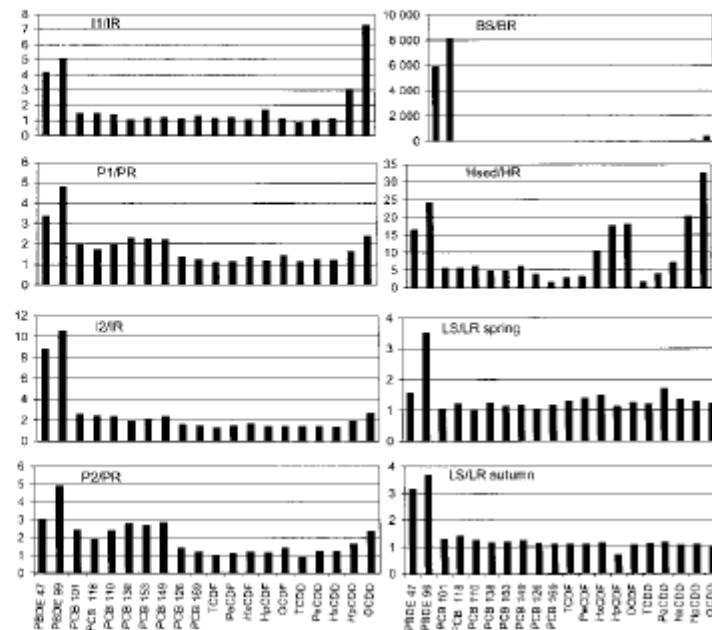
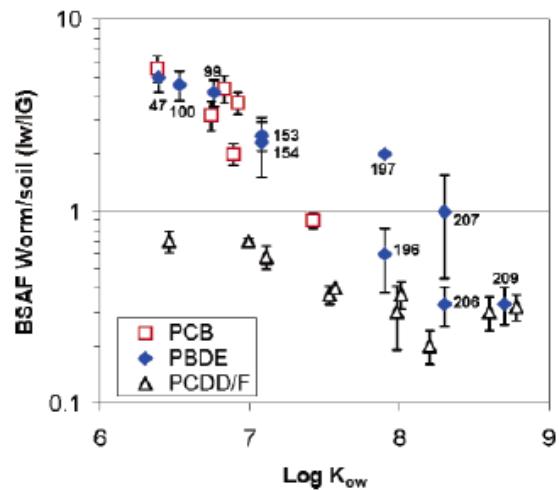


Fig. 2. Ratios of concentrations of polybrominated diphenylethers (PBDEs), polychlorinated diphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) in soil with and without application of sludge. Meanings of the designations are listed in Table 1; see Table 3 for definitions. TCCD = tetrachlorinated dibenzo-*p*-dioxin; PeCDD = pentachlorinated dibenzo-*p*-dioxin.

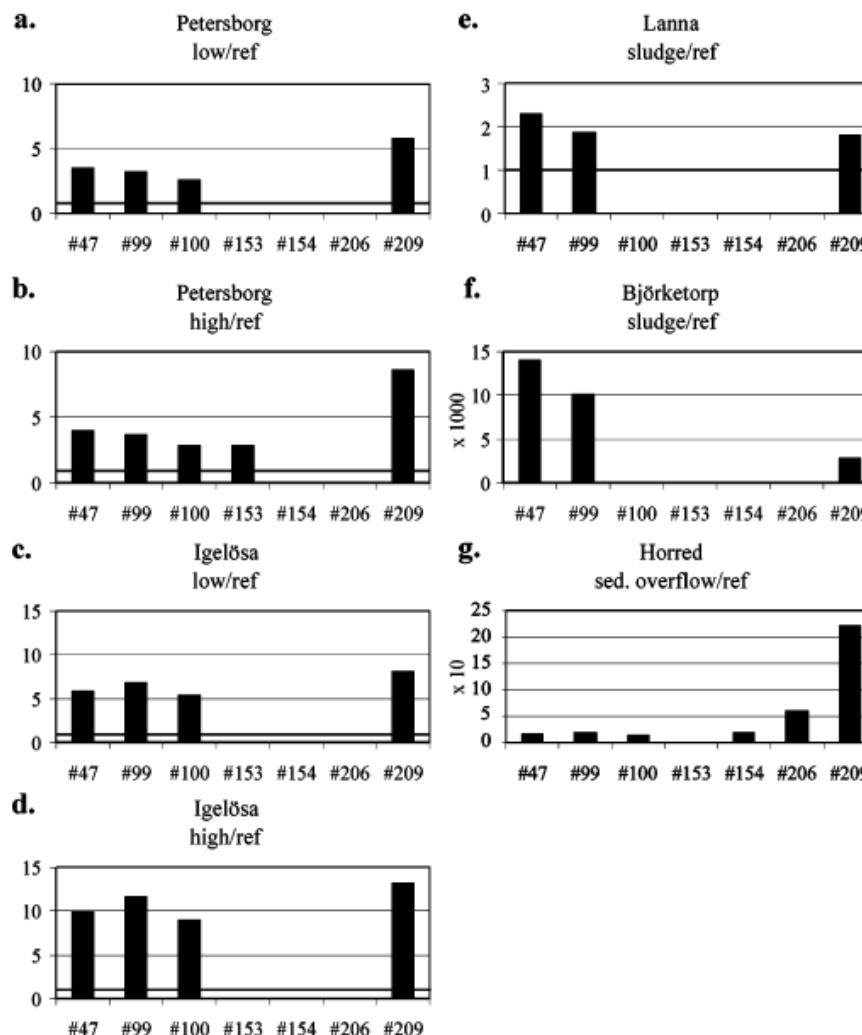
average 20 times higher concentrations than the soil further away from the river Viskan.

Because of the high levels of PBDEs in the soil with sludge from Björketorp and the low levels in the reference soils, the concentration varies by a factor of approximately 400,000. None of the soils from the research sites had concentrations of PBDEs above 1 ng/g DM, whereas the lowest concentration in Björketorp soil was 0.8 ng/g (for PBDE 28). All congeners searched for were found in this soil.

#### *Concentrations of PCDD/Fs, PCBs, and PBDEs*

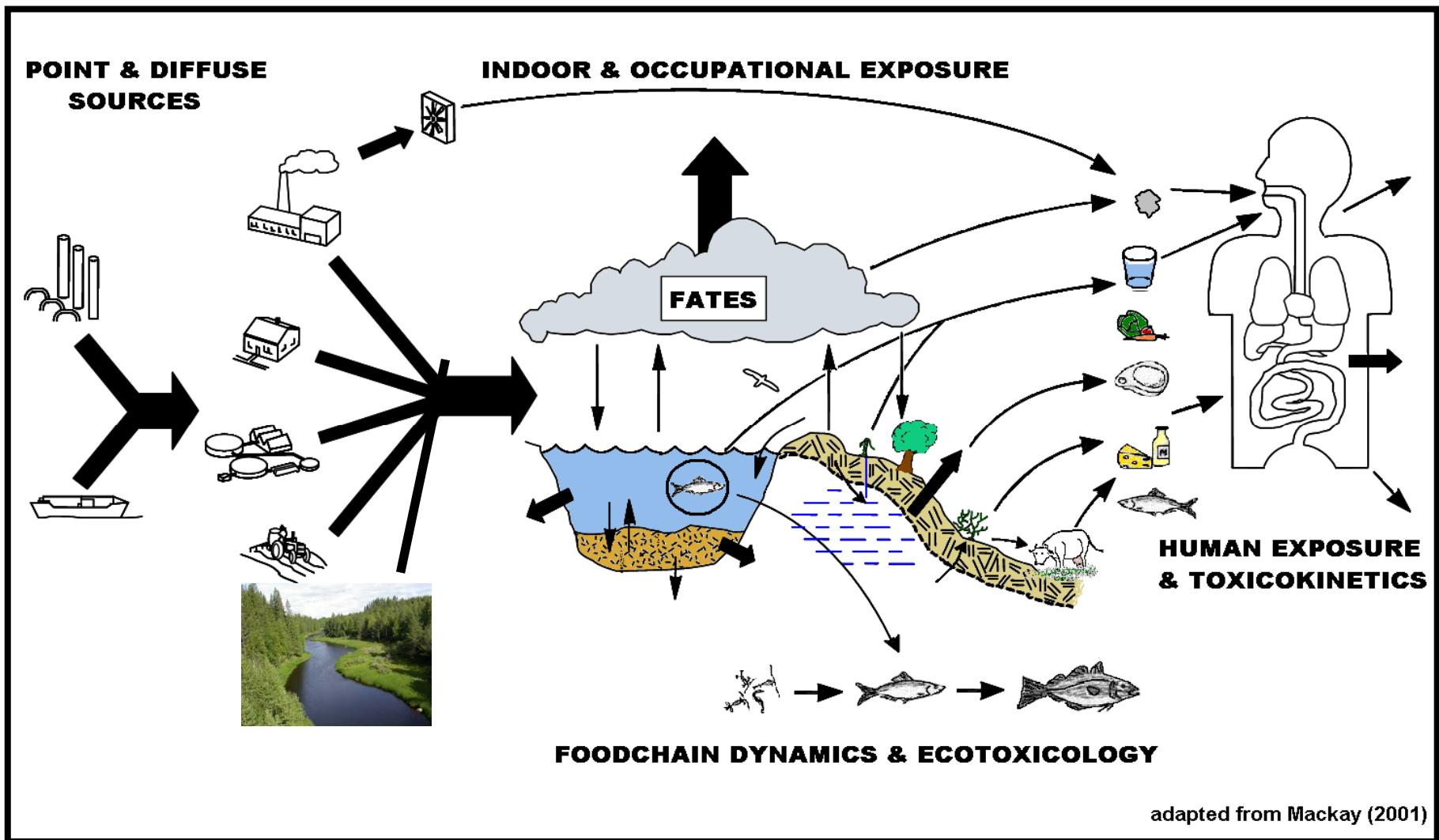


**FIGURE 2.** Relationships between Log  $K_{ow}$  values and biota–soil accumulation factors (BSAFs) for PCBs, PCDD/Fs (from ref 7), and PBDEs (from this study). Values are given as means  $\pm$  standard error. The BDE congener numbers are given in the figure.

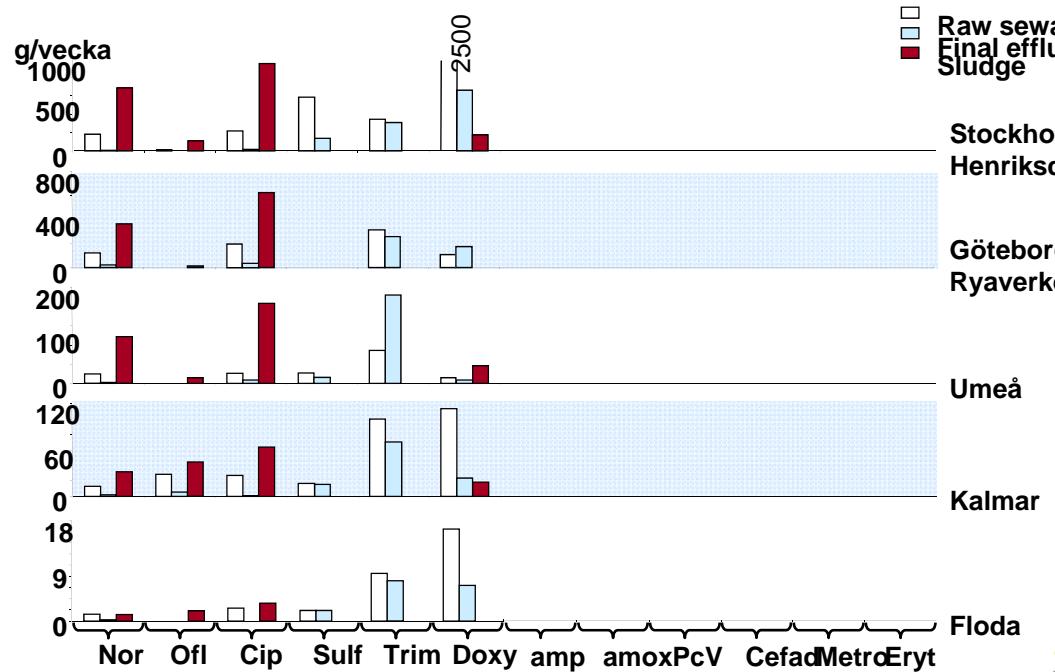


**FIGURE 1.** Sludge-amended/flooded soil to reference soil (S/R) ratios for dry weight concentrations of single polybrominated diphenyl ether congeners. See Table 1 for site information. The ratio showing no difference (S/R = 1) is indicated as a darker horizontal line. Note the different scales for f and g.

# “From source to exposure”



# Läkemedel passerar ARV!



Lindberg et al. 2005



Källa: Aftonbladet

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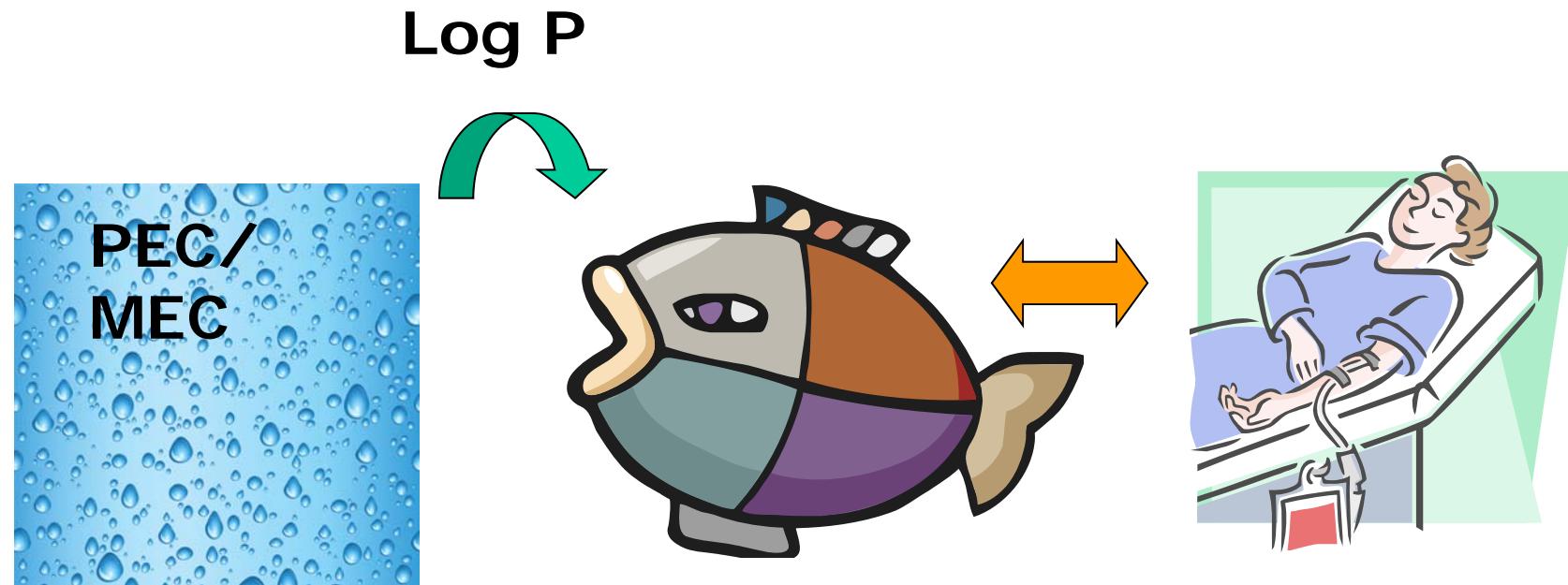
**Sobril i avloppet påverkar abborrar**

Dagens Nyheter

**The Wall Street Journal**

**THE AUSTRALIAN**

# "Fiskplasmamodellen" (Hugget et al., 2003)

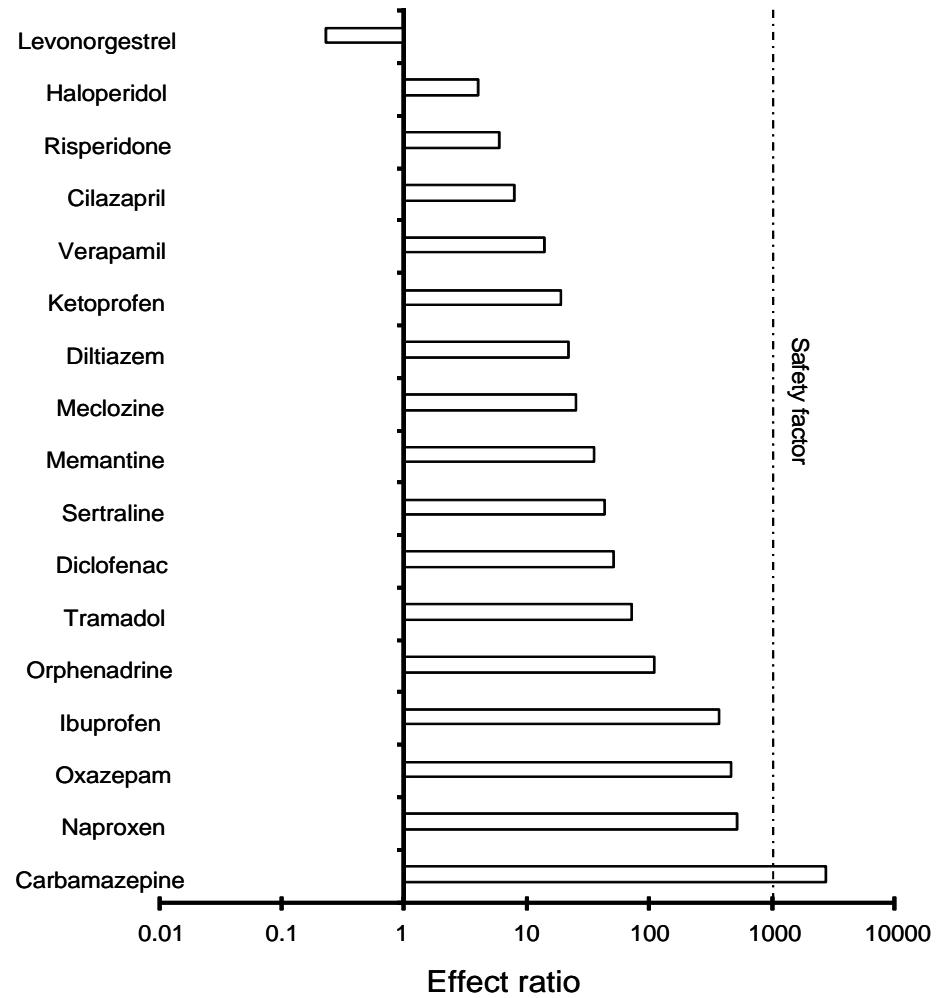


Ratio: Human terap. konc./  
Fiskplasma konc.

# Results BCF-studies – Effekt ratio

Levonogestrel:

- syntetisk progesteron
- p-piller
- uppmätt vatten 12 resp 8,5 ng/L
- effekter fisk ca 1 ng/L





## Slutsatser

- Sammansättning och fördelning mellan slam/vatten generellt likartad hos alla ARV
  - Oberoende av plats, storlek och anslutna verksamheter
- Oönskade ämnen från många diffusa källor snarare än tydliga punktkällor
  - Dock, förekomst av perfluorerade ämnen varierar mellan olika ARV (Textilindustri kan påverka halter i slam)
  - Dock, ARV med högra andel hushållsavloppsvatten har högre halter triclosan (Hushållens produkter är viktiga för triklosan och andra ämnen förekomst i slam)
- Tidsserieanalyser är möjliga för slam och tidstrender kan kopplas till användning i samhället
- Stora kunskapsluckor om organiska ämnens öde i markmiljön

# Vision om uthålliga kretslopp

