



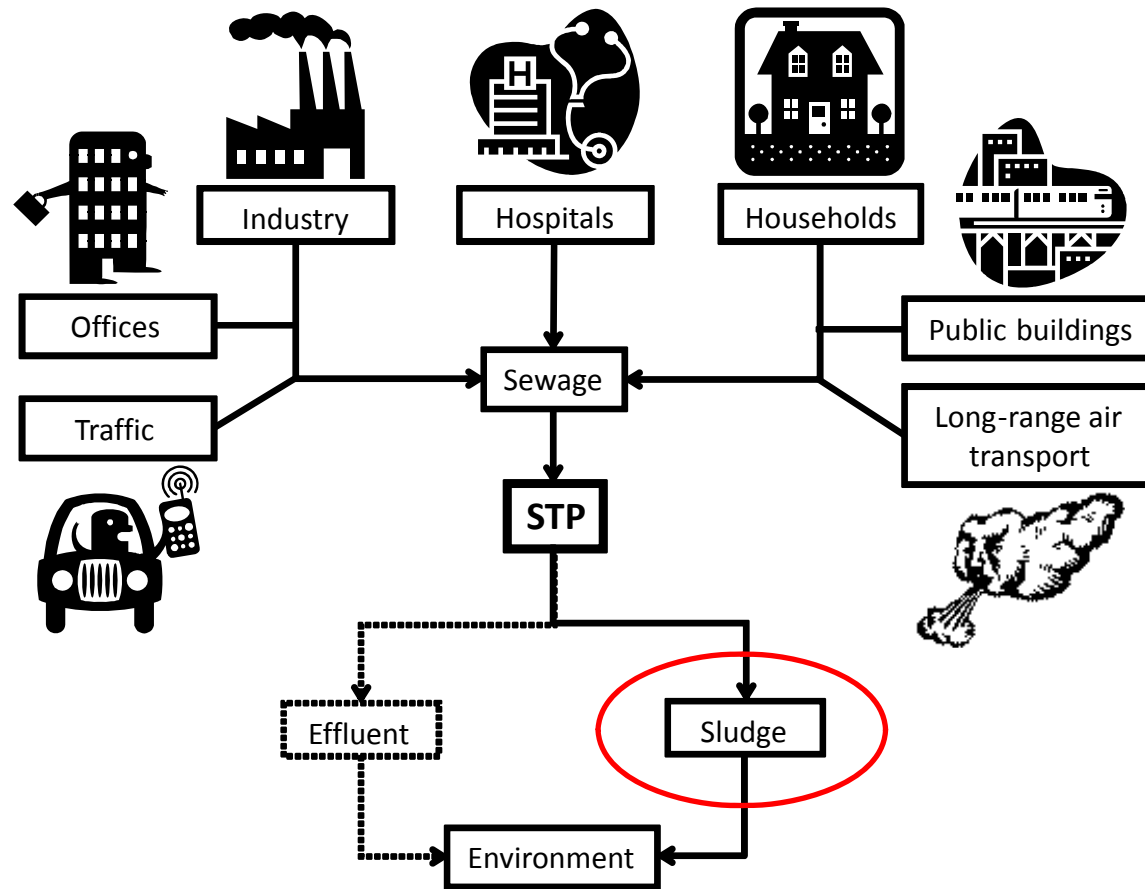
# Förekomst och trender av miljögifter i slam

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## Presentationen:

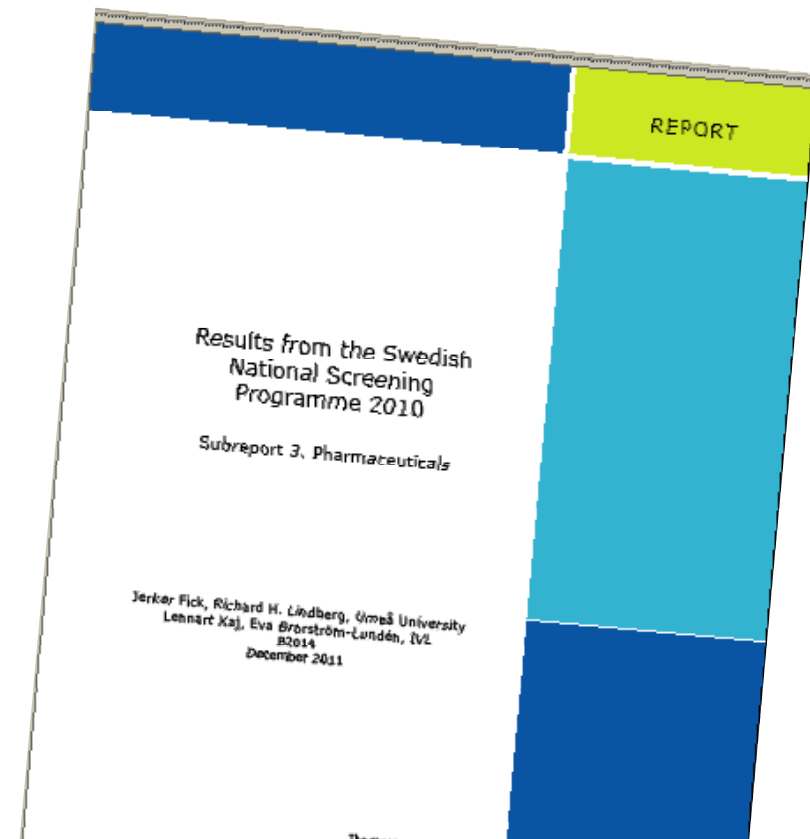
- Substanser
- Flöden ARV – Avskiljning vs. Nedbrytning
- Tidstrender
- Slam jordsbruksmark & skogsmark
- Aspekter riskbedömning



Schematic diagram of the mass flows of chemical substances derived from both internal and external milieus, via sewage systems to a sewage treatment plant (STP), then through effluent and sludge into the environment.



# 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.

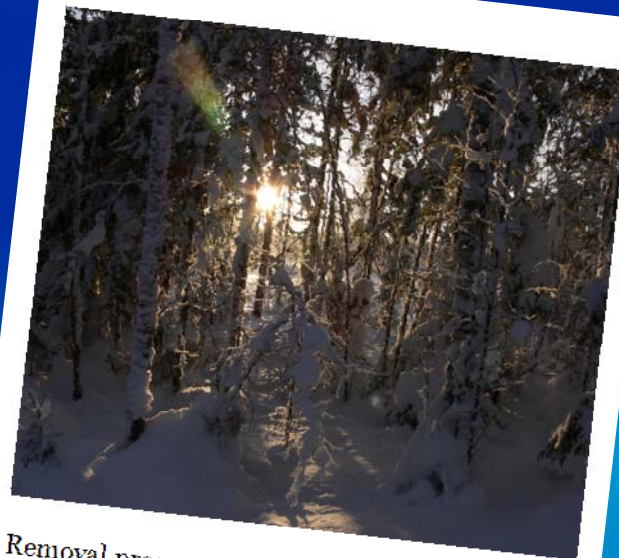




Ulrika Olofsson.

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

Doktorsavhandling Umeå  
universitet 2012.

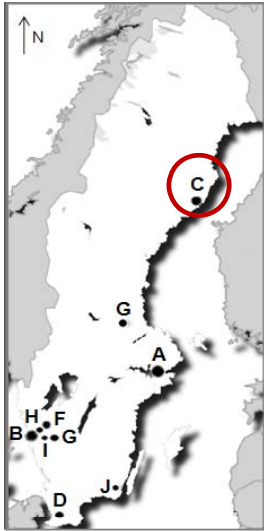


Removal processes in sewage treatment plants -  
Sludge quality and treatment efficiency of structurally  
diverse organic compounds

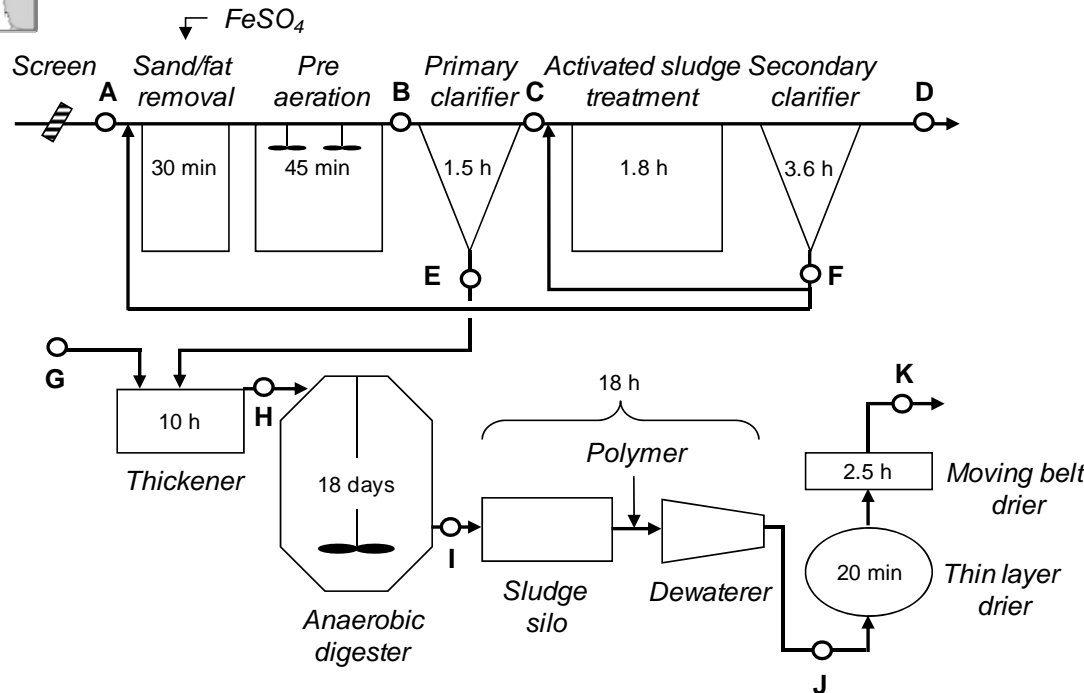
Ulrika Olofsson



Department of Chemistry  
Doctoral Thesis 2012



# Avloppsreningsverket 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

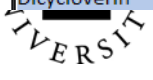




# Resultat nationella screeningen (NV) 2011

In ARV      Ytvatten  
Ut ARV      Fisk

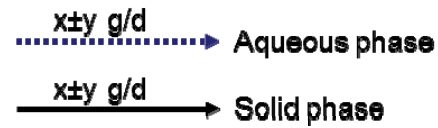
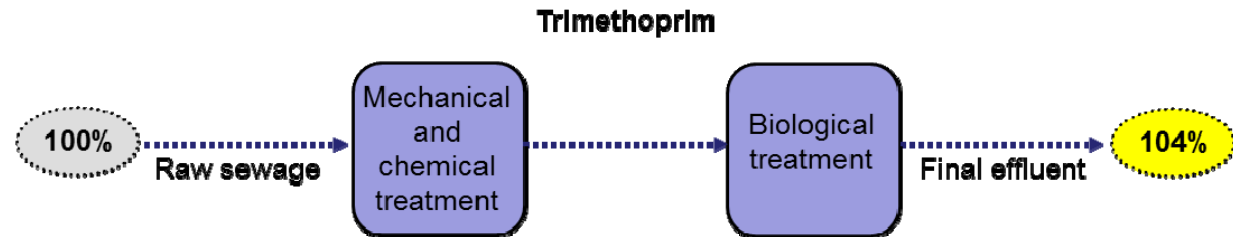
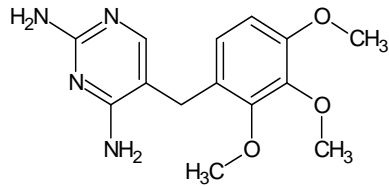
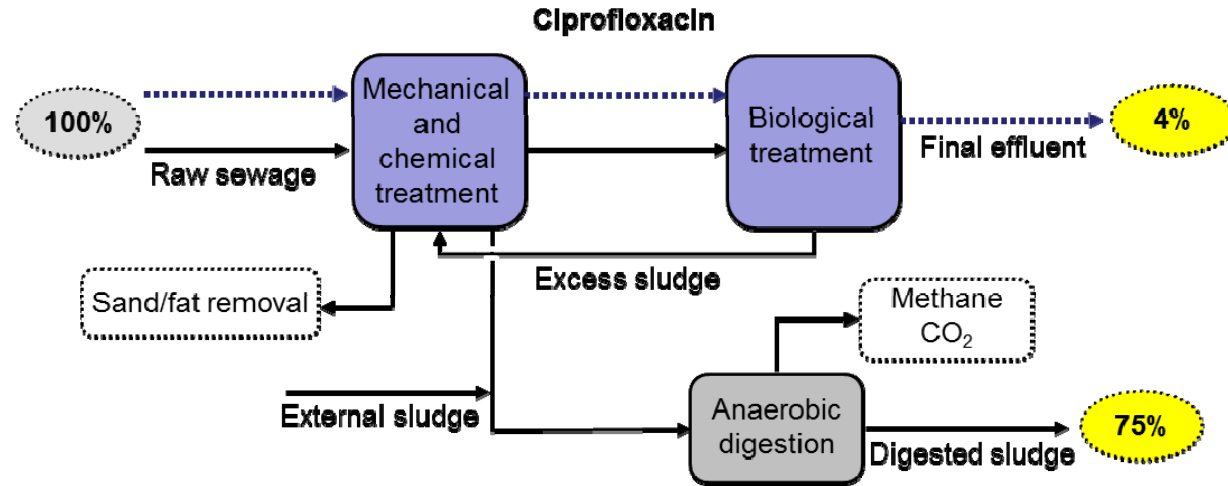
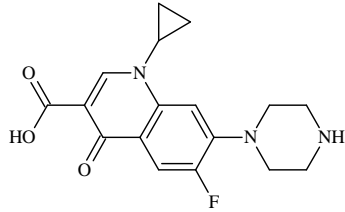
Name	(ng/L)	(ng/L)	(ng/L)	(µg/Kg)
Alfuzosin	224,1	106,3	32,6	<LOQ
Alprazolam	59,7	14,3	<LOQ	<LOQ
Amiodiarone	<LOQ	<LOQ	<LOQ	<LOQ
Amitryptiline	47,4	16,3	<LOQ	<LOQ
Atenolol	4884,3	597,7	355,1	<LOQ
Atorvastatin	260,6	<LOQ	<LOQ	<LOQ
Atracurium	28,7	26,5	0,7	<LOQ
Azelastine	40,5	9,8	<LOQ	<LOQ
Azithromycin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



= >200ng/L     
  = 21-200 ng/L     
  = <20 ng/L



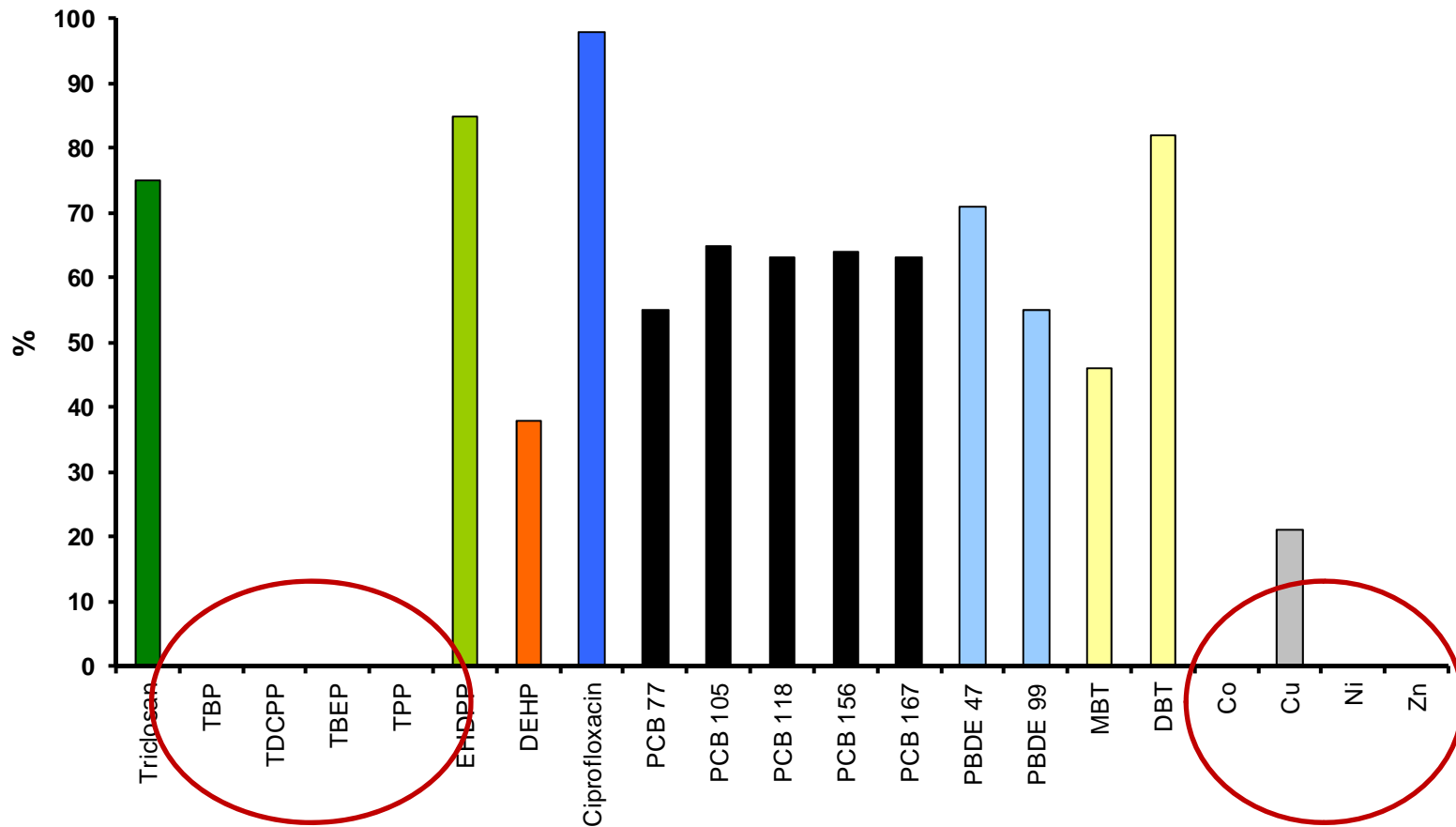
# Mass flöde av antibiotika (Umeå ARV)





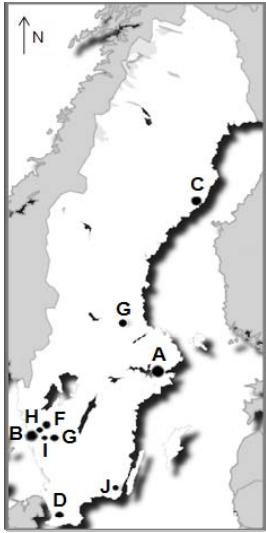
# Avskiljningseffektivitet (RE)

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

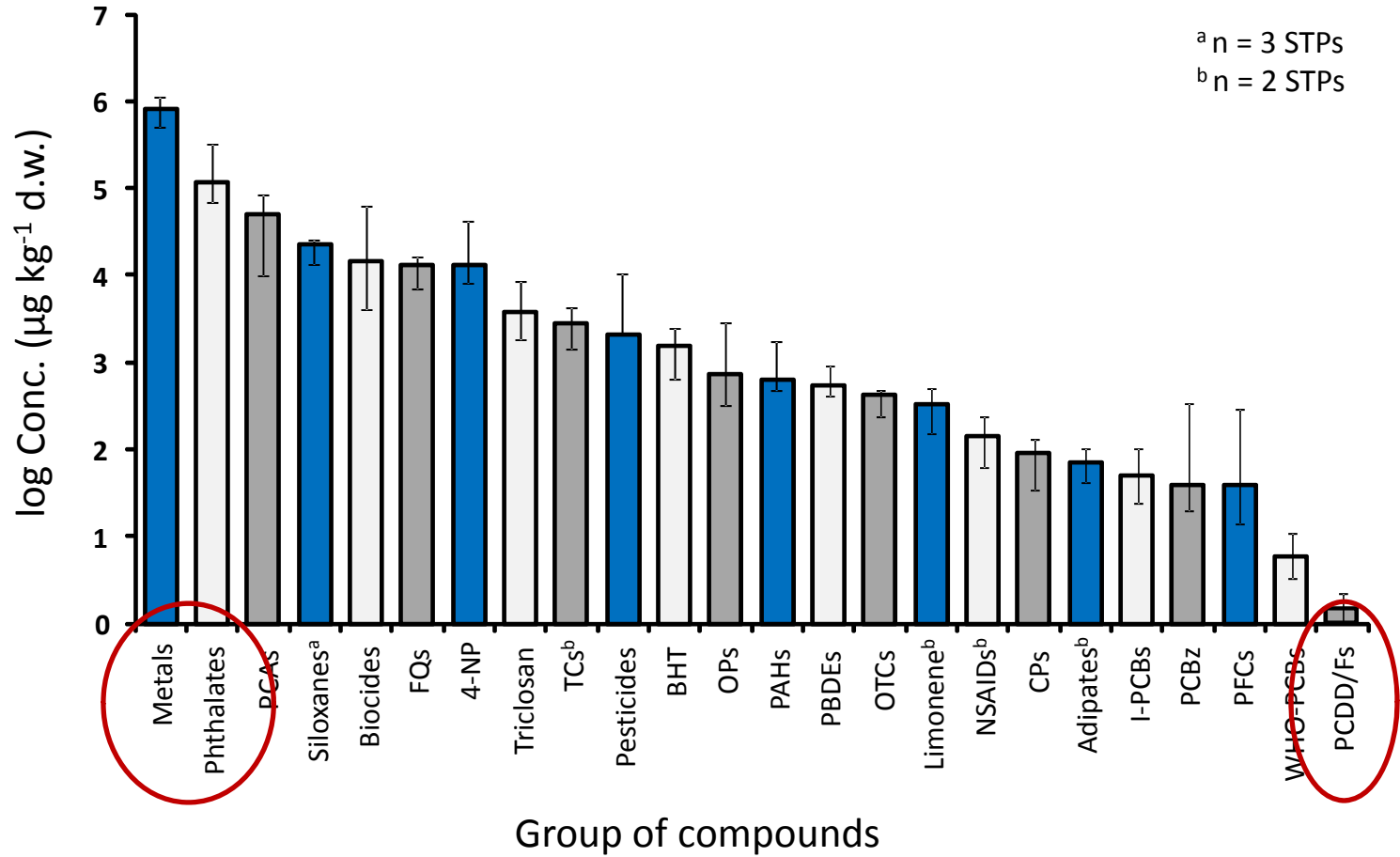


RE include mechanical, chemical and biological treatment

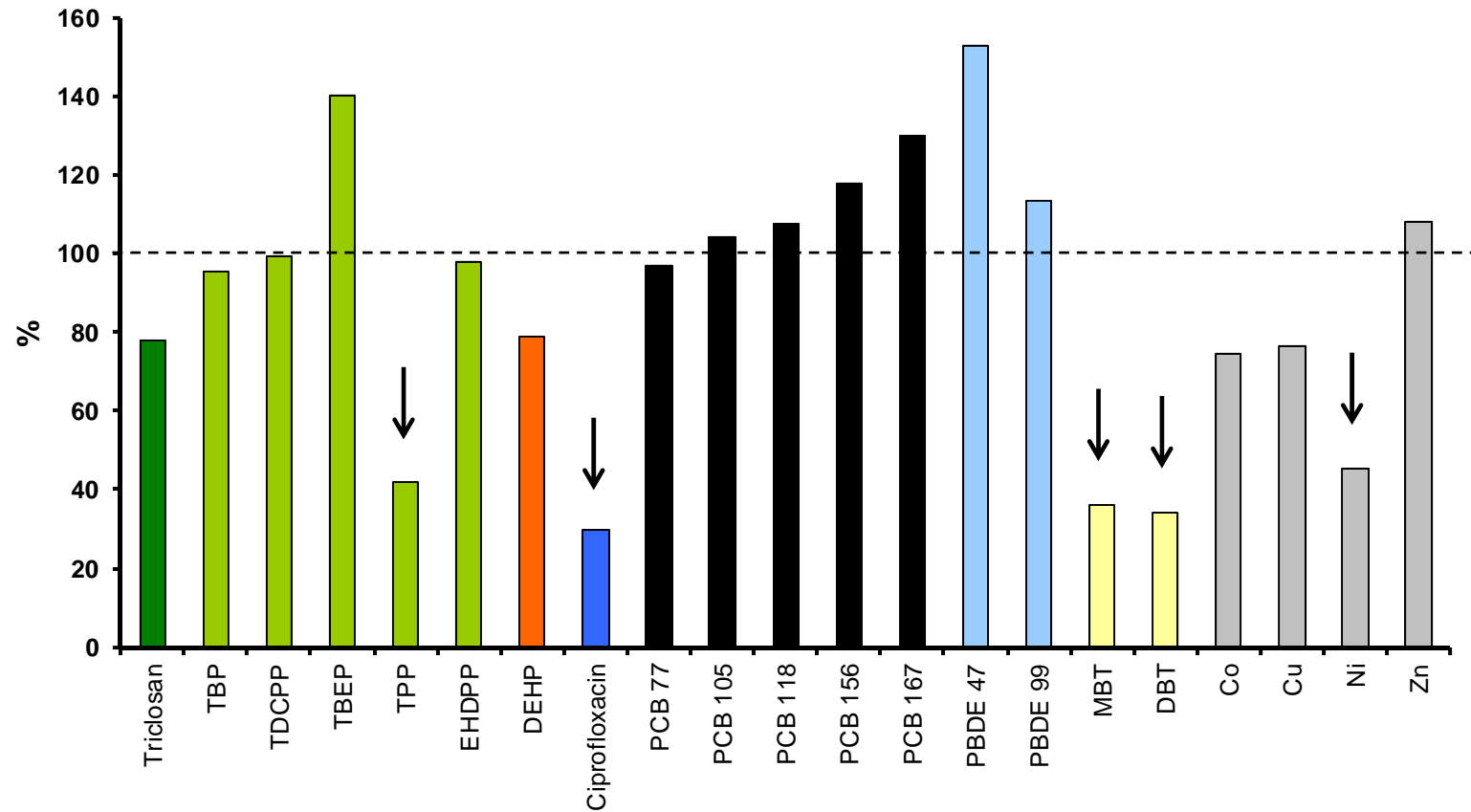




# Oönskade ämnen i slam

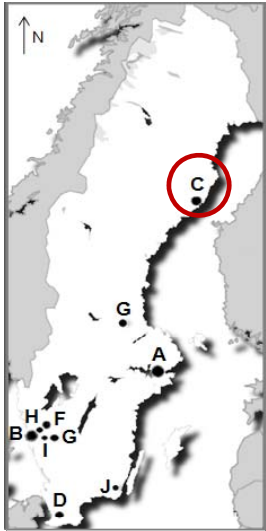


# Anaerob rötning



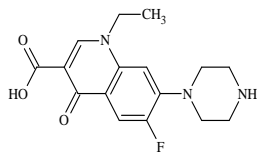
>100% means higher concentration in dewatered digested sludge than in primary sludge



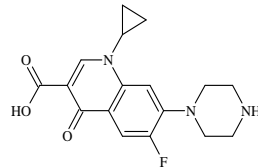


## Generellt ARV

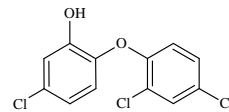
- ARV har generellt högre avskiljningseffektivitet för s k hydrofoba ämnen (lipofila) än fallet för mer vattenlösliga (väntat)
- Hög RE (>70%) – norfloxacin, ciprofloxacin, triclosan, PBDE 47, EHDPP and DBT



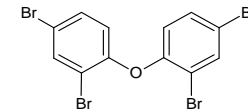
Norfloxacin



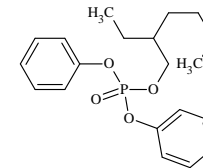
Ciprofloxacin



Triclosan



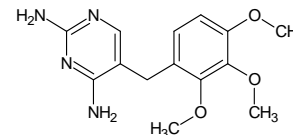
PBDE 47



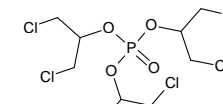
EHDPP

### *Lipophilic compounds*

- Låg RE – trimethoprim, de flesta organofosfater och vissa metaller

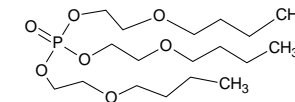


Trimethoprim



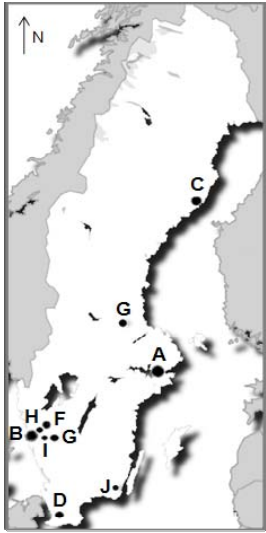
TDCPP

### *Water soluble compounds*

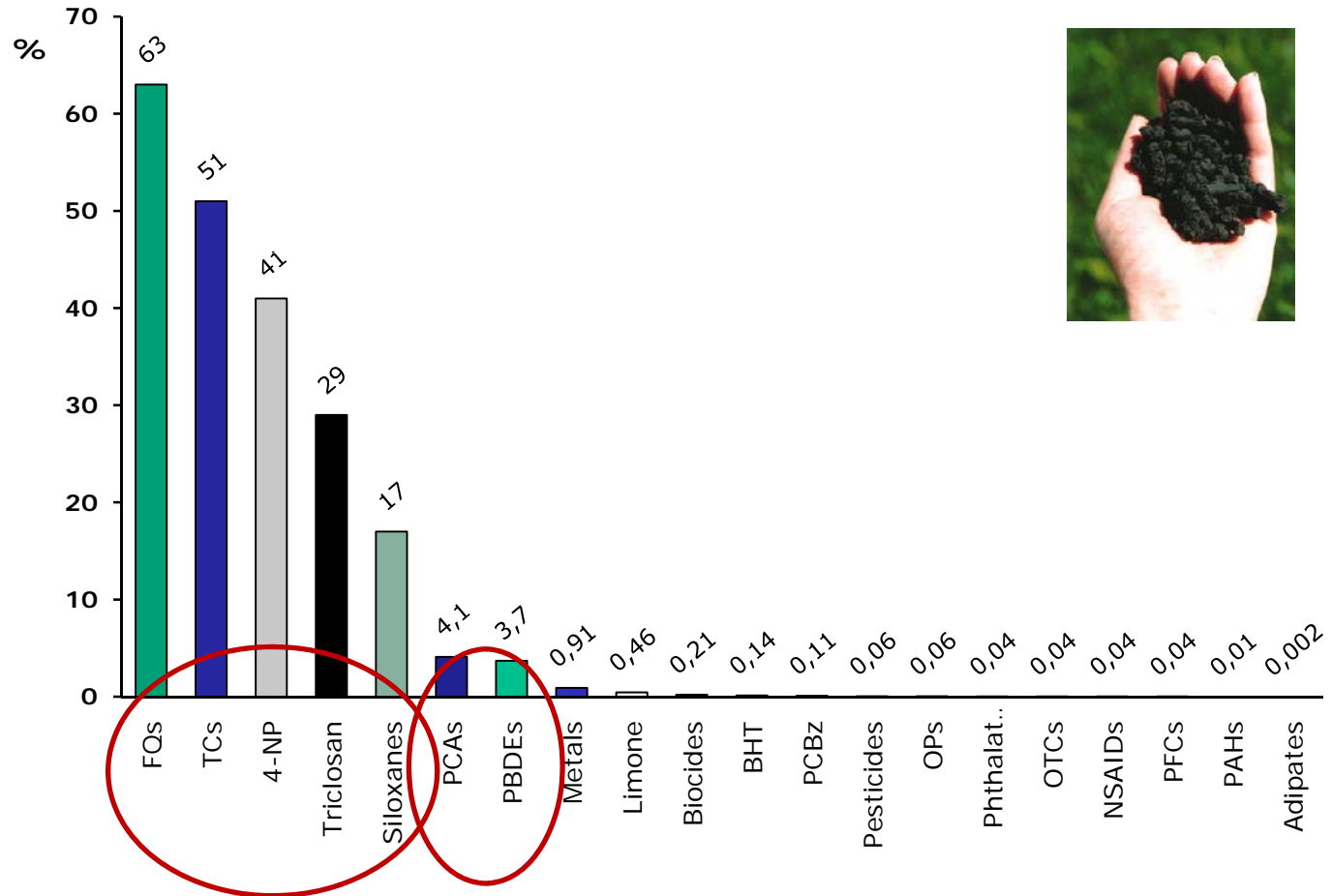


TBEP

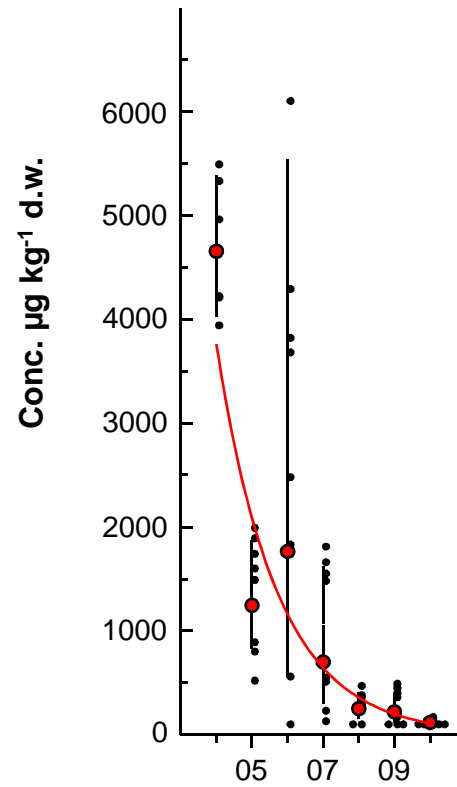




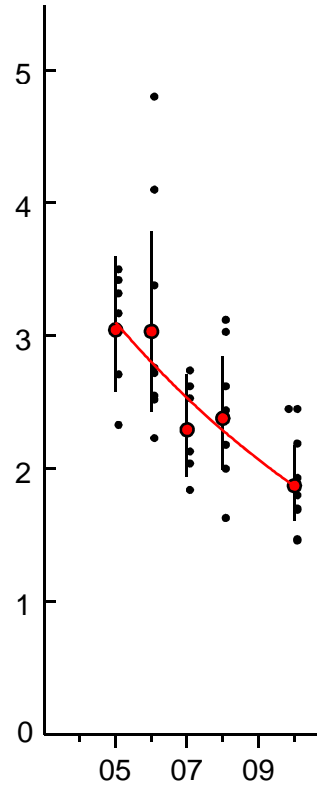
## Återfinning av substanser i slam relativt användningsvolymen i samhället



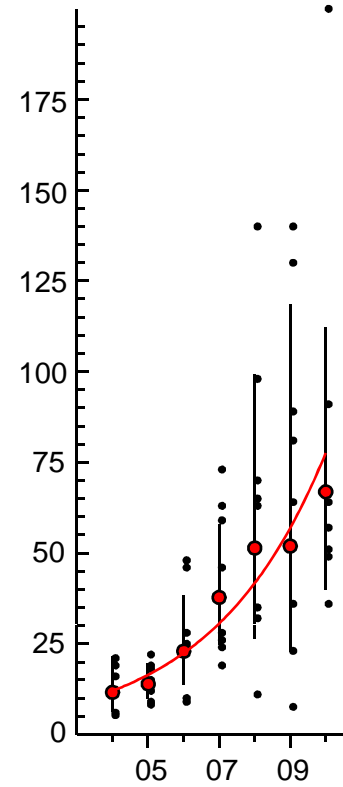
# Tidstrender



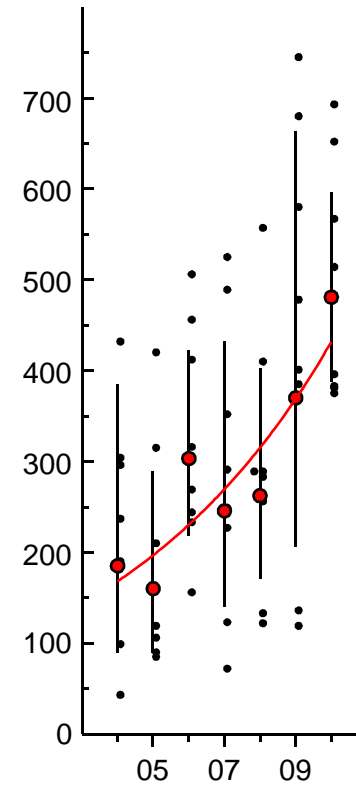
Norfloxacin



PBDE 154  
Hexabrominated  
diphenylether



MD2M  
Decamethyltetrasiloxane



PBDE 209  
Decabrominated  
diphenylether

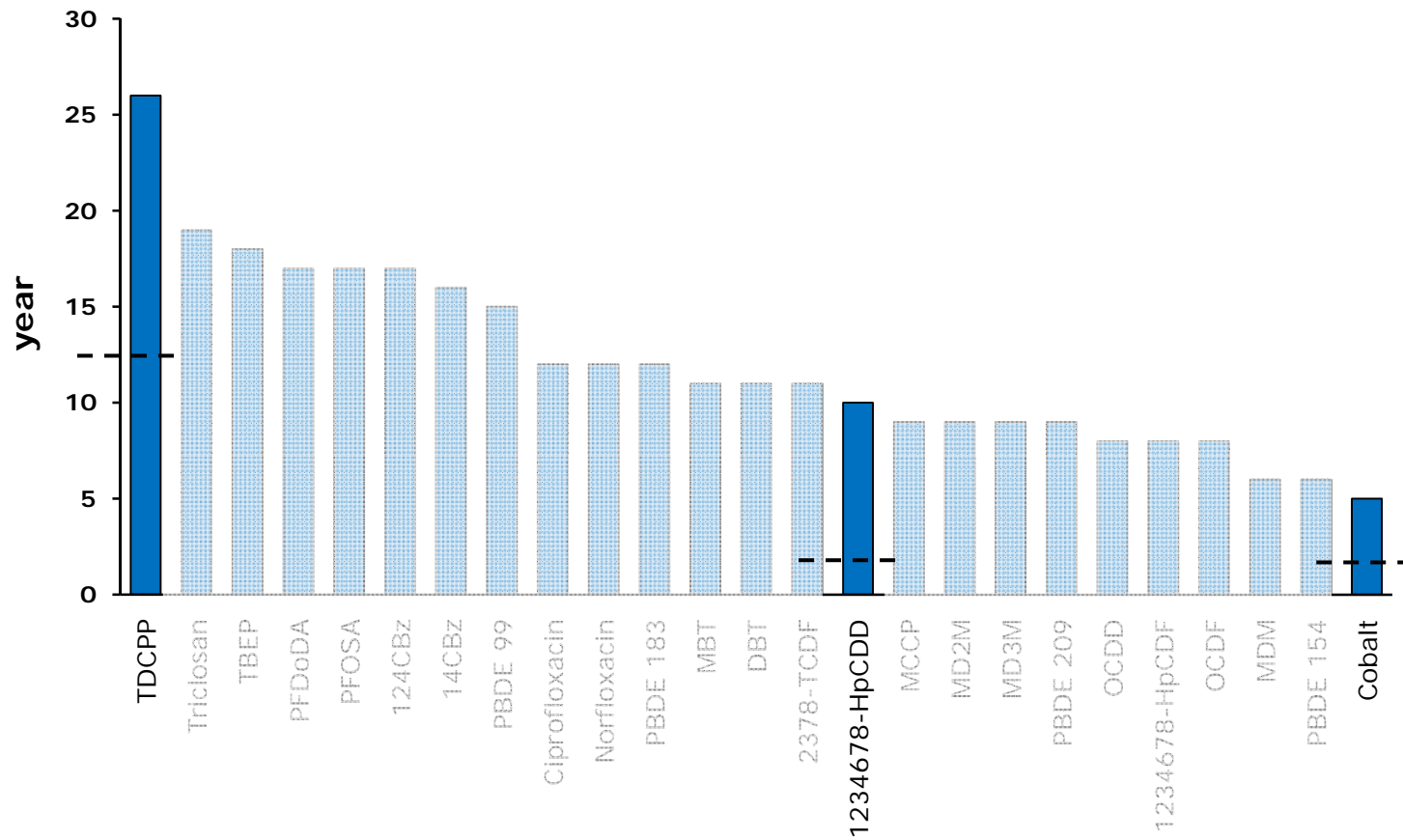


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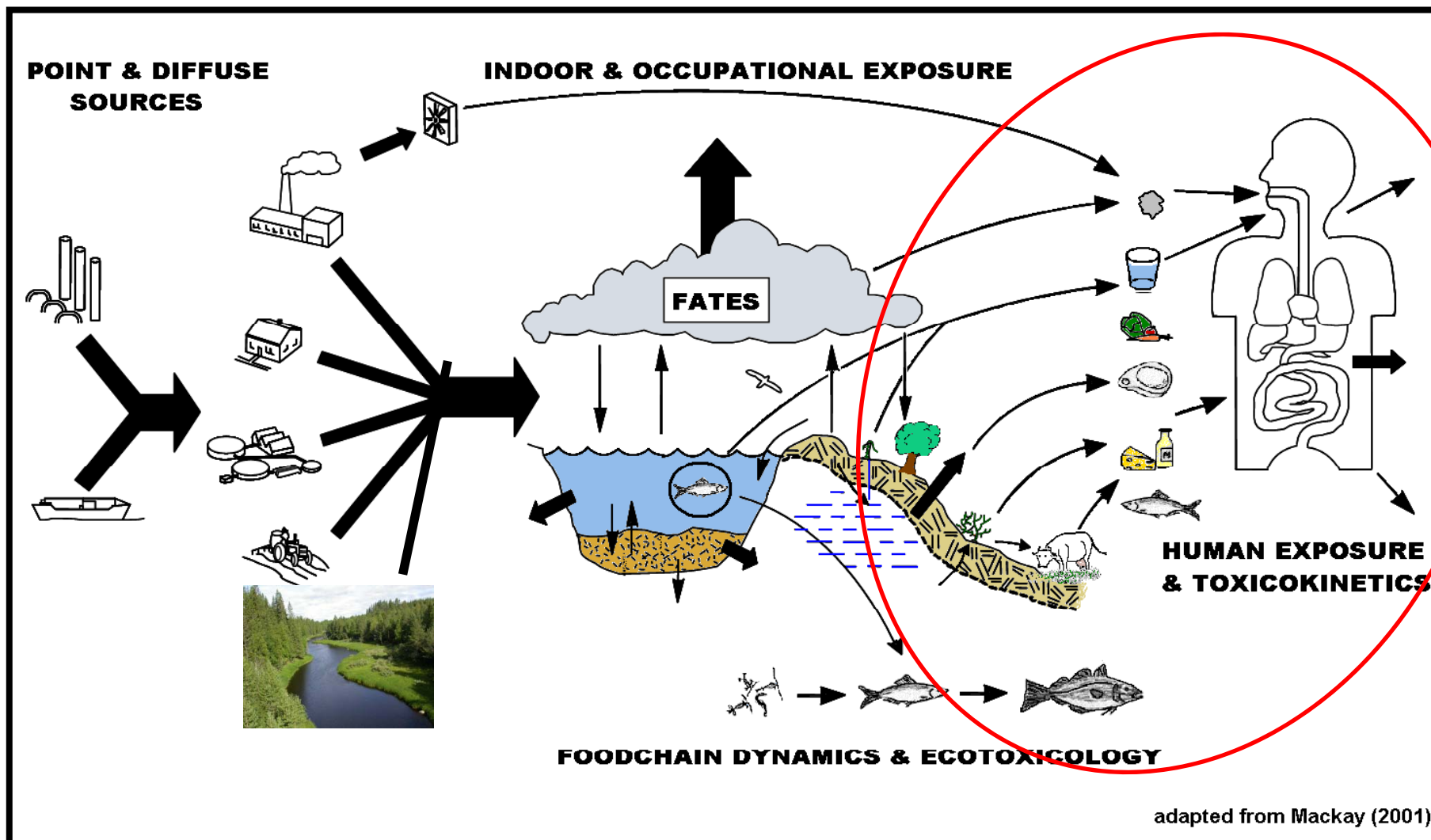
## Tidstrender - Estimated years to see time-trends

- Varies from 5 to 26 years

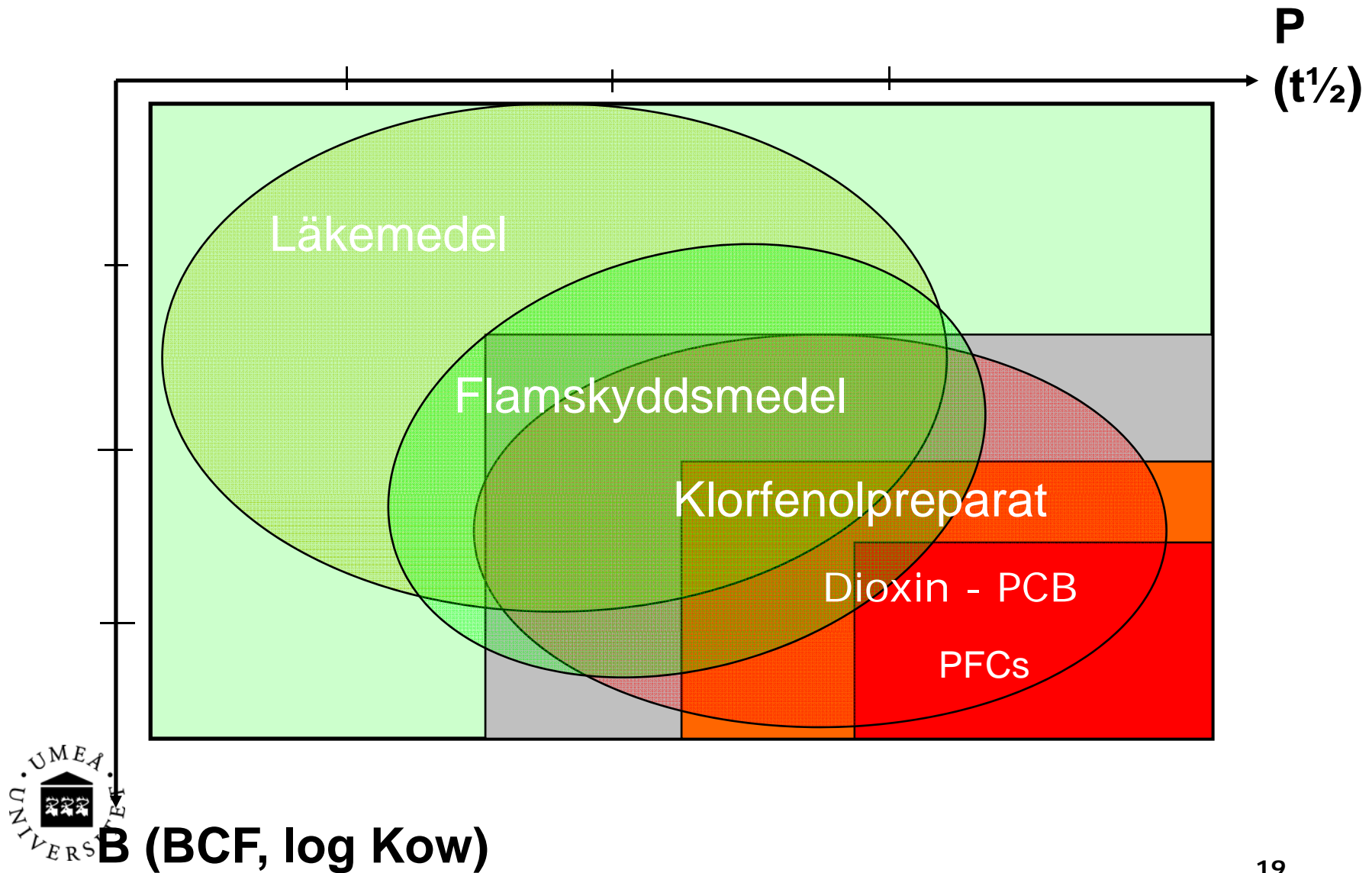
- Natural fluctuations → variability between STPs/years
- Variations in the analytical determination (analytical uncertainty)



# “From source to exposure”



# Persistens (P) – Bioackumulation (B)



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



## Slutrapport

STEM P30686-1: 2007-2009

Mars 2010

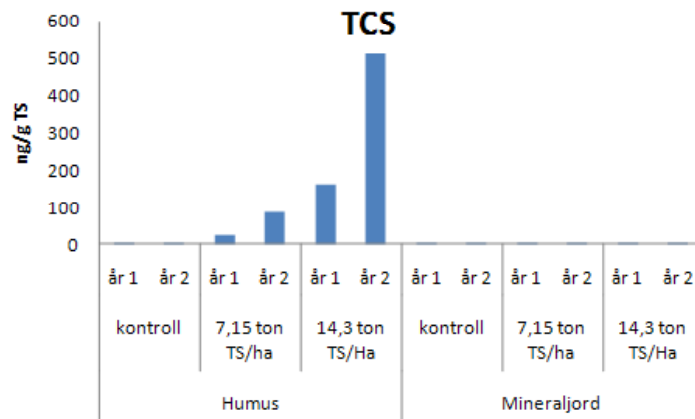
Dr Richard Lindberg, Kemiska Institutionen, Umeå universitet

Professor Mats Tysklind, Kemiska Institutionen, Umeå universitet

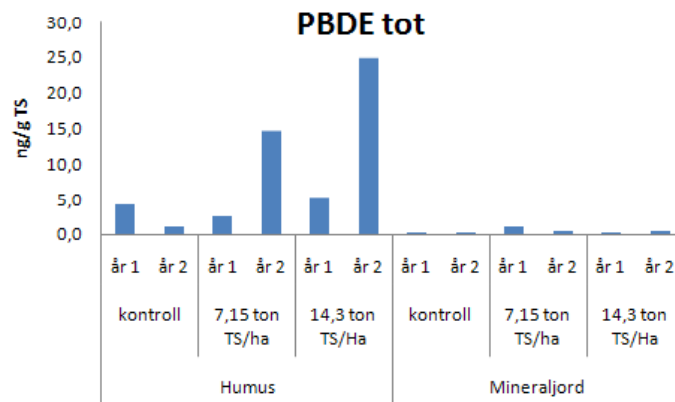
Docent Kenneth Sahlén, Inst f skogens ekologi och skötsel, SLU, Umeå







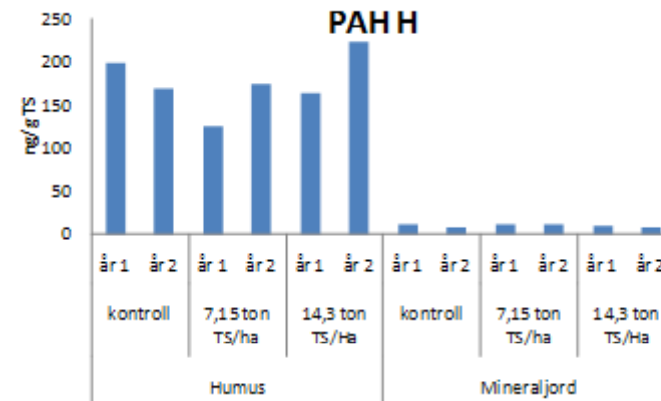
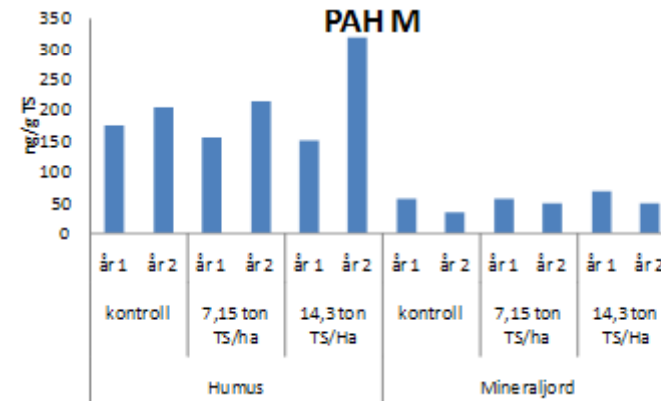
Figur 1. Halter av TCS i kontrolltytor och handgödslade provtytor.



Figur 2. Totalhalt PBDE i kontrolltytor och handgödslade provtytor.

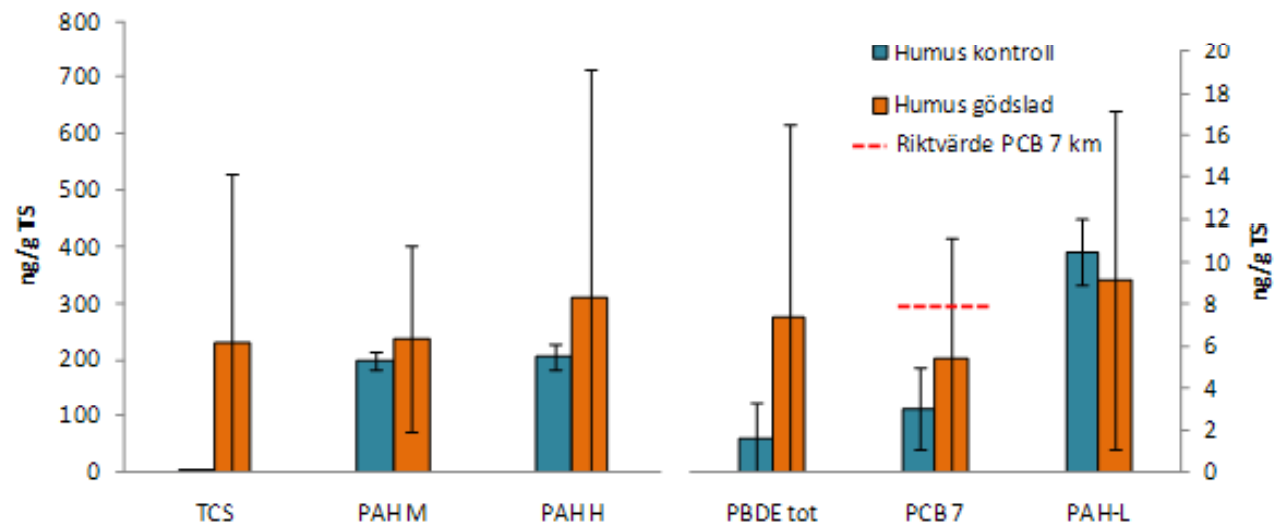
Tabell 3 Halter (i ng/g TS) av organiska ämnen i torkat granulerat slam.

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 kontrolltytor och handgödslade provtytor.

# Organiska ämnen i skogsgödslad mark



Figur 5. Medelkoncentrationer och standardavvikelse hos de organiska substanserna i gödslade (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.



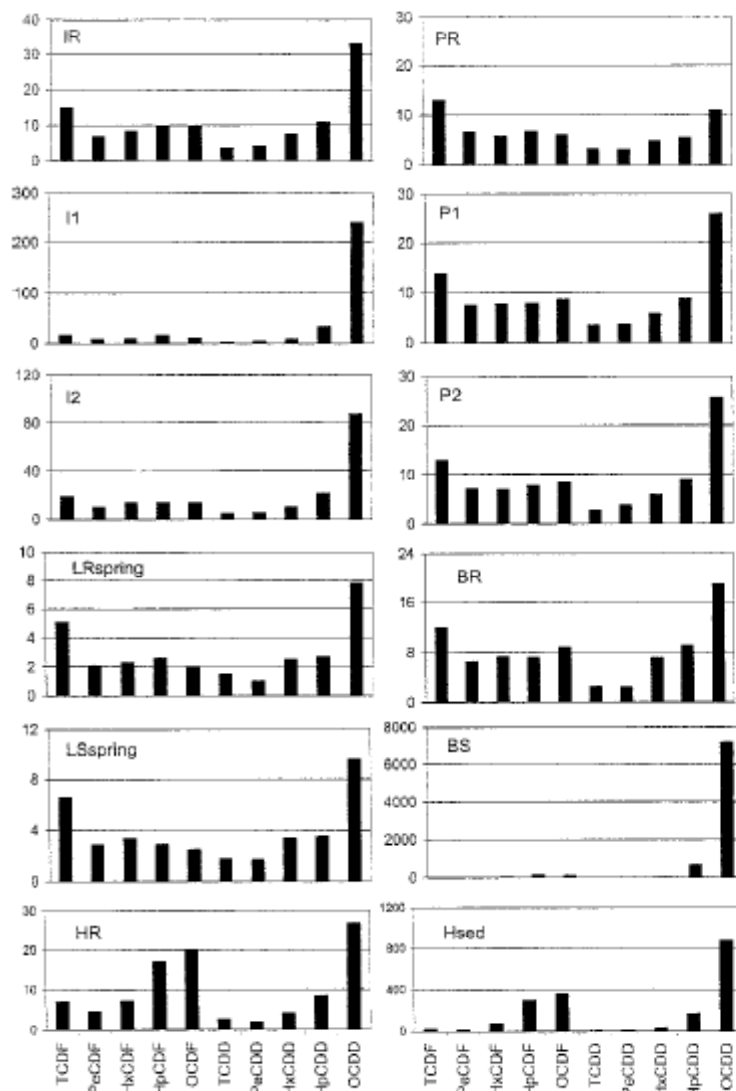


Fig. 1. Profiles of sums tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-*p*-dioxins/dibenzofurans (-CCDs/CDFs) in soil (pg/g dry matter [DM]). Meanings of the designations for the sites are given in Table 1; see Table 3 for definitions. TCDD = tetrachlorinated dibenzo-*p*-dioxin; PeCDD =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

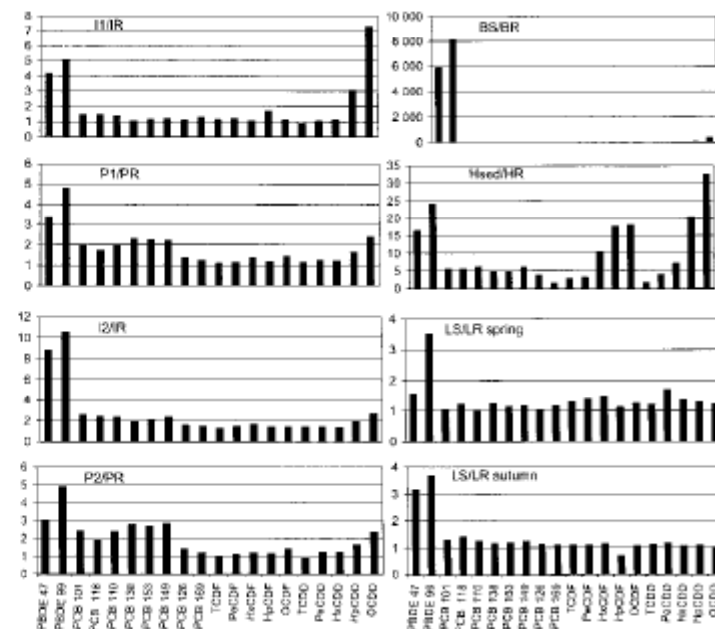


Fig. 2. Ratios of concentrations of polybrominated diphenylethers (PBDEs), polychlorinated diphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) in soil with and without application of sludge. Meanings of the designations are listed in Table 1; see Table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



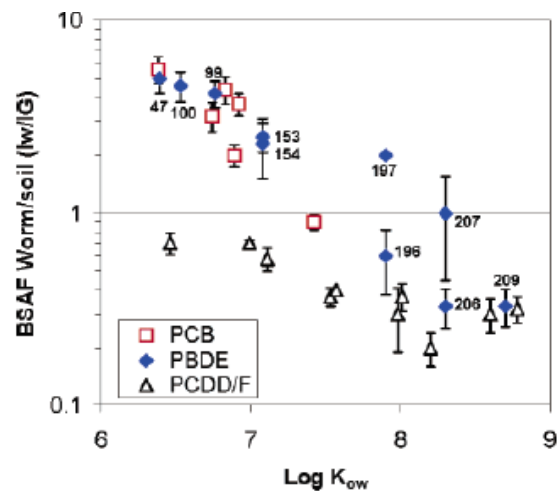


FIGURE 2. Relationships between Log  $K_{ow}$  values and biota-soil accumulation factors (BSAFs) for PCBs, PCDD/Fs (from ref 7), and PBDEs (from this study). Values are given as means  $\pm$  standard error. The BDE congener numbers are given in the figure.

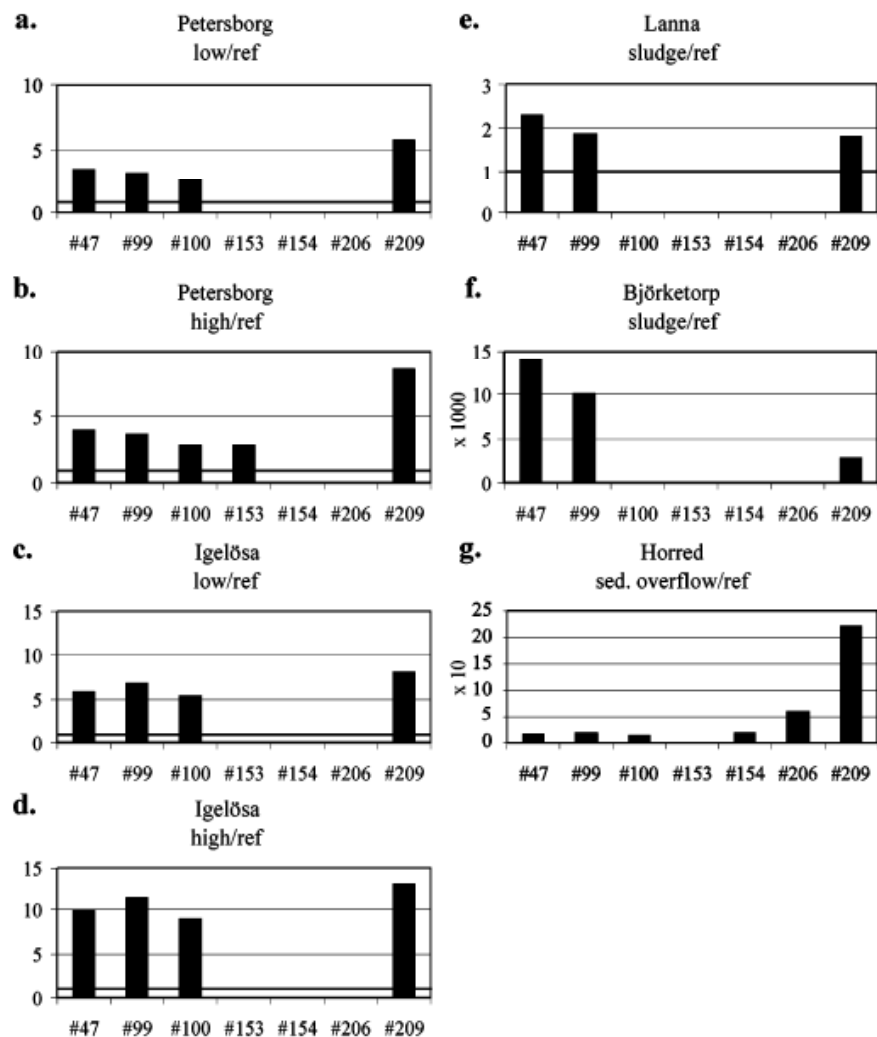
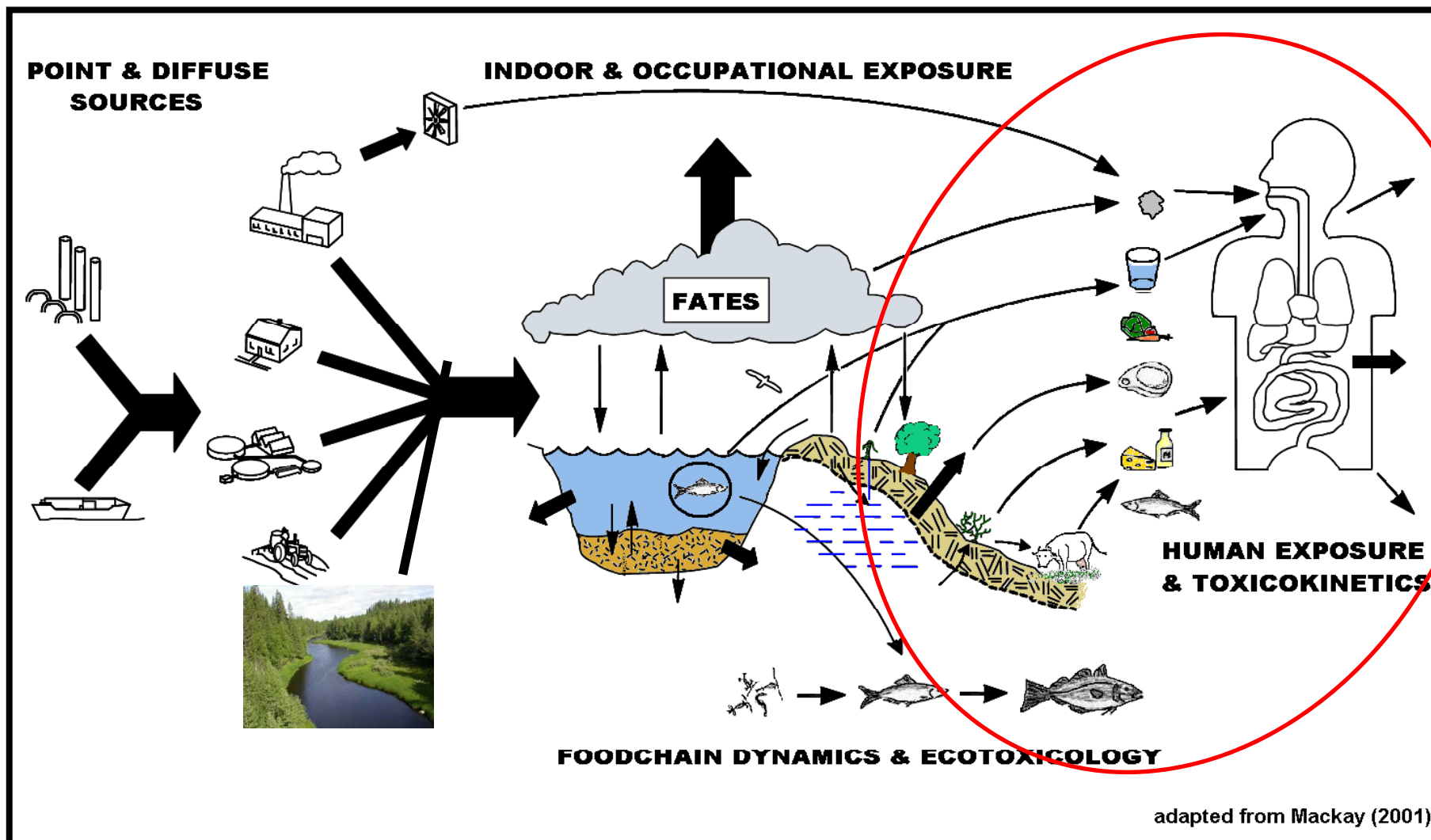


FIGURE 1. Sludge-amended/flooded soil to reference soil (S/R) ratios for dry weight concentrations of single polybrominated diphenyl ether congeners. See Table 1 for site information. The ratio showing no difference (S/R = 1) is indicated as a darker horizontal line. Note the different scales for f and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

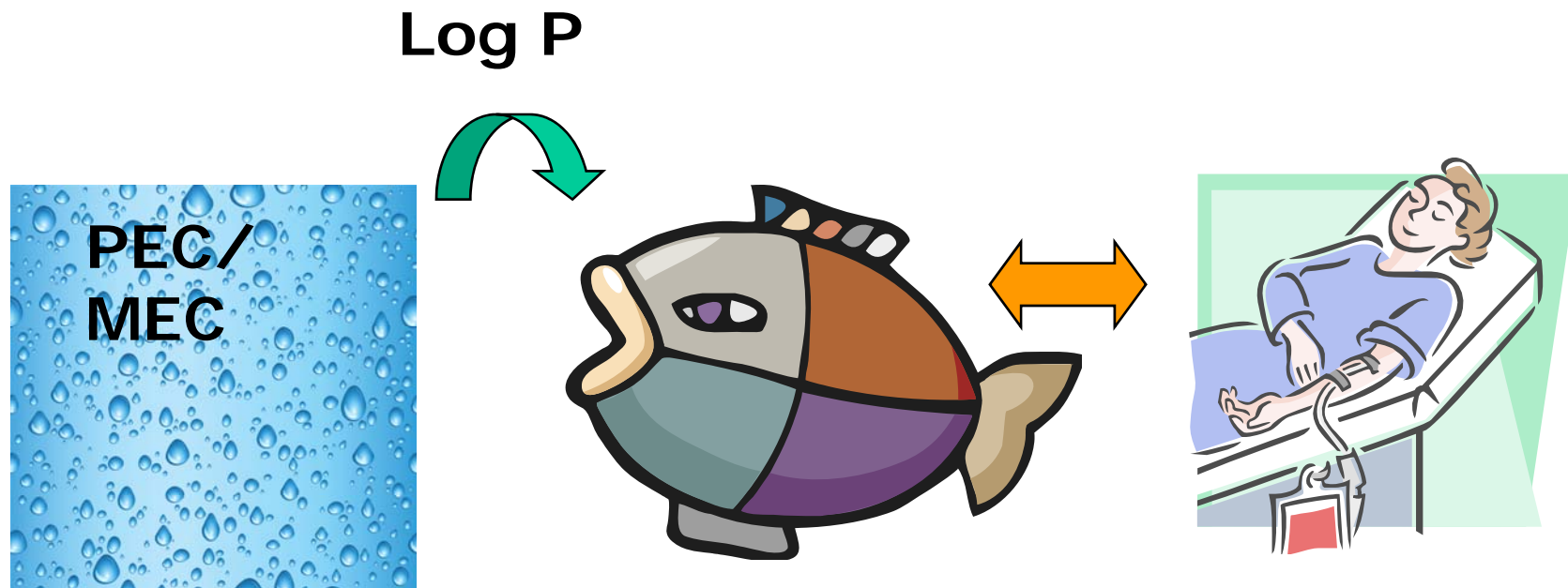


# “From source to exposure”





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

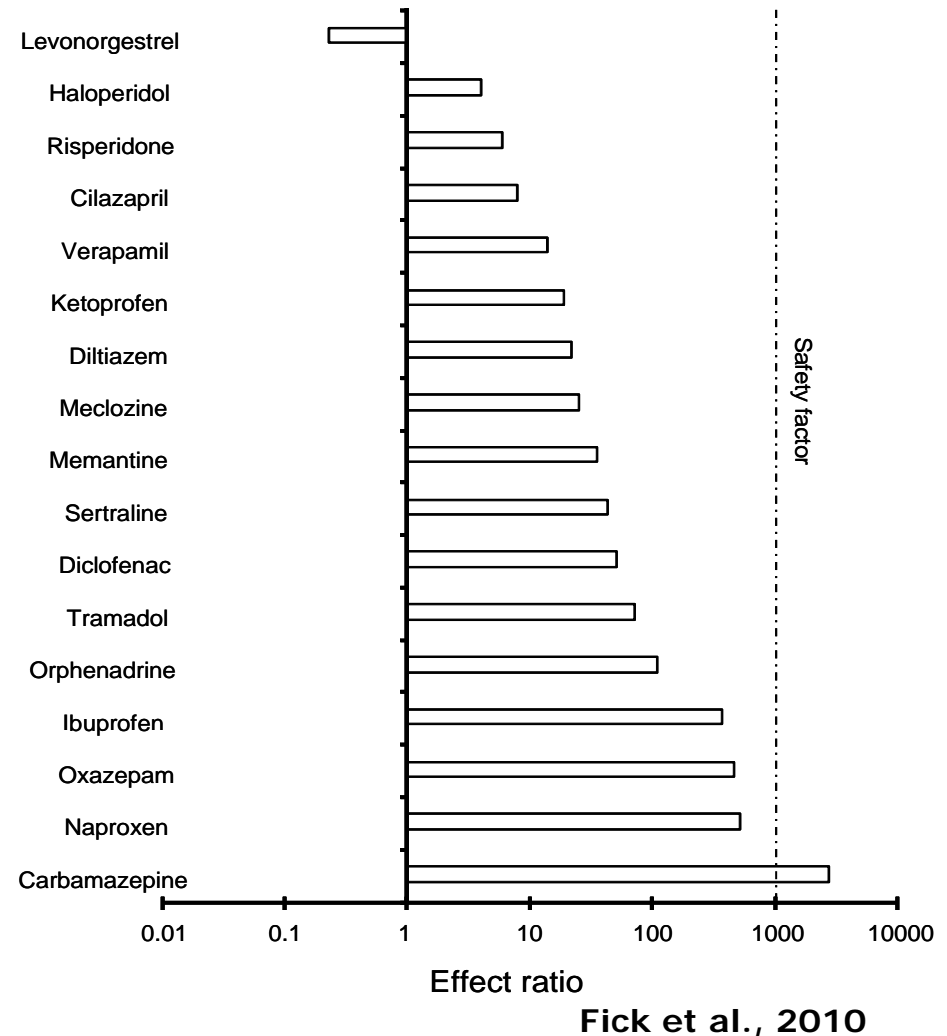


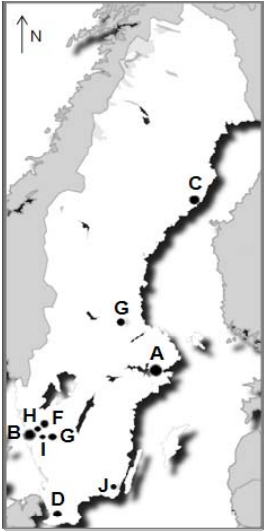
Ratio: Human terap. konc./  
Fiskplasma konc.

# Results BCF-studies – Effekt ratio

Levonogestrel:

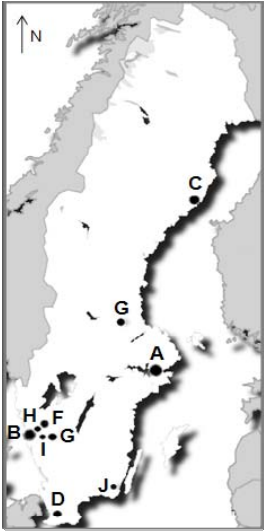
- syntetisk progesteron
- p-piller
- uppmätt vatten 12 resp 8,5 ng/L
- effekter fisk ca 1 ng/L





## Slutsatser

- Sammansättning och fördelning mellan slam/vatten generellt likartad hos alla ARV
  - Oberoende av plats, storlek och anslutna verksamheter
- Önskade 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



## Slutsatser fortsättning

- Tidsserieanalyser är möjliga för slam
- Tidstrender kan kopplas till användning i samhället
- Stora kunskaps luckor om organiska ämnens öde i markmiljön