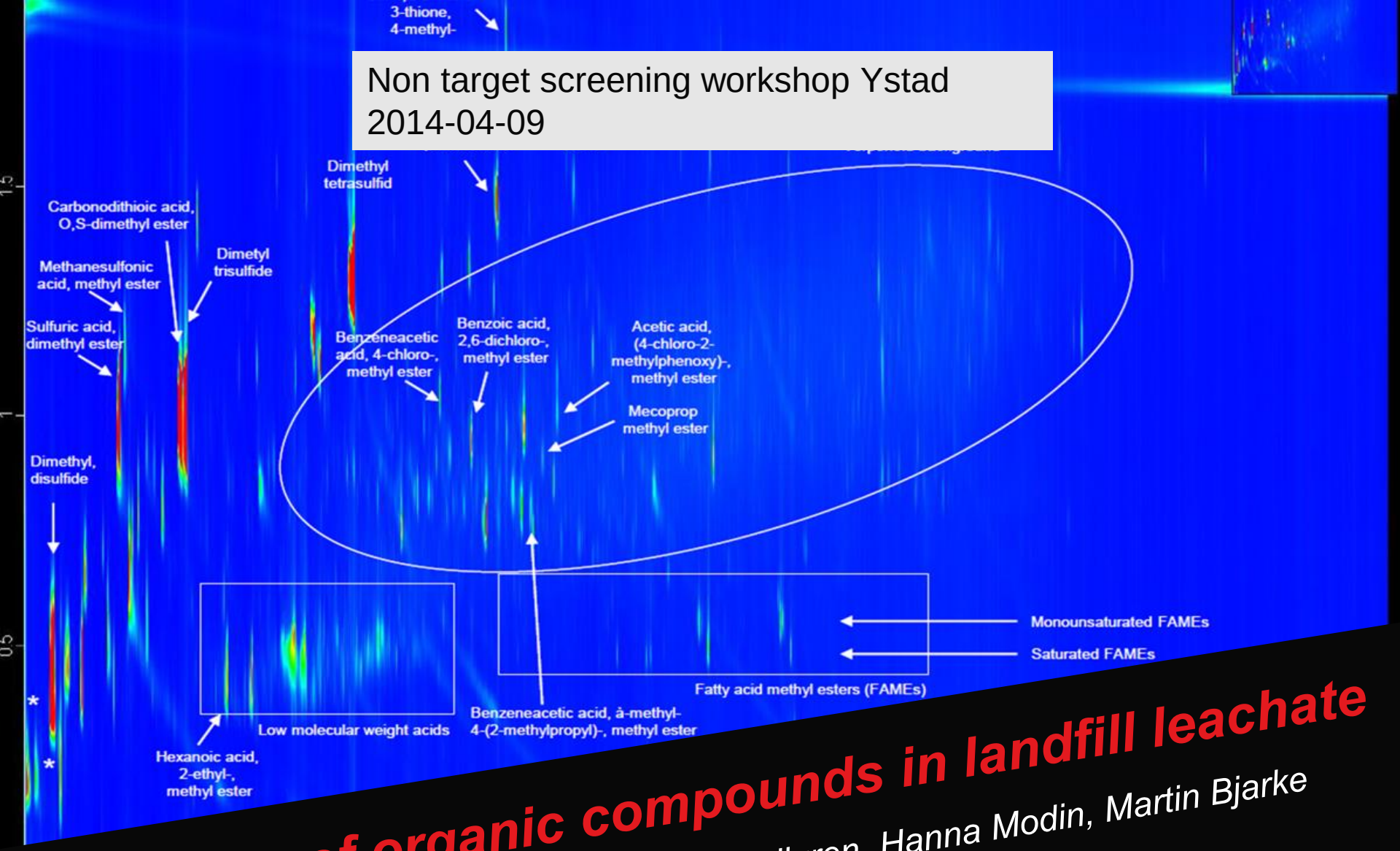
Non target screening workshop Ystad
2014-04-09



Screening of organic compounds in landfill leachate

Martijn van Praagh, Niklas Törneman, Pär Hallgren, Hanna Modin, Martin Bjarke

SWECO

Yesterday

Jaroslav reminded us yesterday that: Not measured Not regulated

Peter presented GCxGC screening from WWTP.

He also showed that many compounds are removed, possibly ending up in the sludge.

Jan was not comfortable with the term “removed” (right?).

- What if the WWTP receives leachate water from a landfill and wants to use the sludge on farmland? **EPA regulations for some “classic” compounds but what else?** Right Britta?

REVAQ (Swedish voluntary system for certification of sludge) stipulates that either:

1) the leachate stream should be separated from WWTP

or

2) measurements should include “organic compounds” that may stem from the leachate (or show with toxicity testing that the leachate is harmless)

Sounds good to me but what should they measure? TOC? EGOM? EOX?

In a landfill

has been buried for centuries.

In a landfill STUFF happens.

ITS SCREENING TIME!

Screening of organic compounds in landfill leachate

Results from two screening studies financed by Swedish EPA

”*Organiska ämnen i lakvatten från deponier*”

Available for download (in Swedish)

”*Detailed assessment of data from regional landfills*”

Approved and available soon

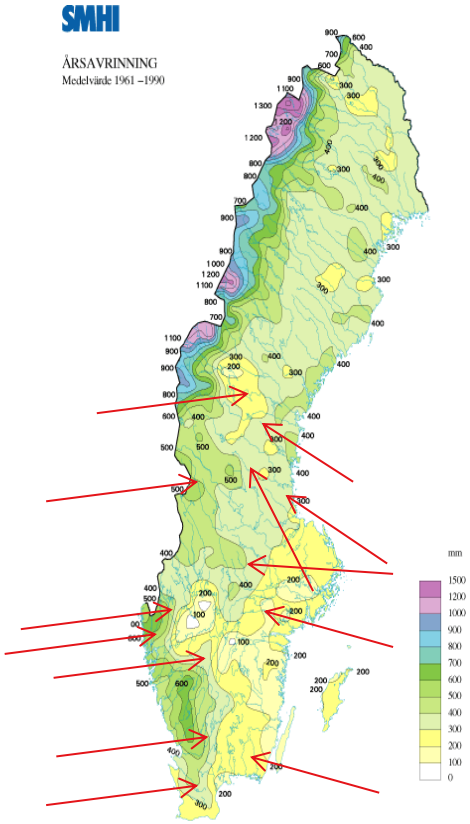
Axel Hullberg, Britta Hedlund, Erika Nygren, Maria Linderoth, Jan Christiansson (Naturvårdsverket)

Peter Haglund (Umeå Universitet)

Martijn van Praagh, Niklas Törneman, Pär Hallgren, Martin Bjarke, Hanna Modin (Sweco)

21 Landfills

(6 financed by Swedish EPA and 15 additionally joined in



(if possible) representing north to south

Mixed waste (industrial and household)

Different treatment systems

Different recipients (groundwater, streams, WWTP)

Analytical methods

Organic compounds

- GC*GC-MS

Toxicity

- Acute toxicity

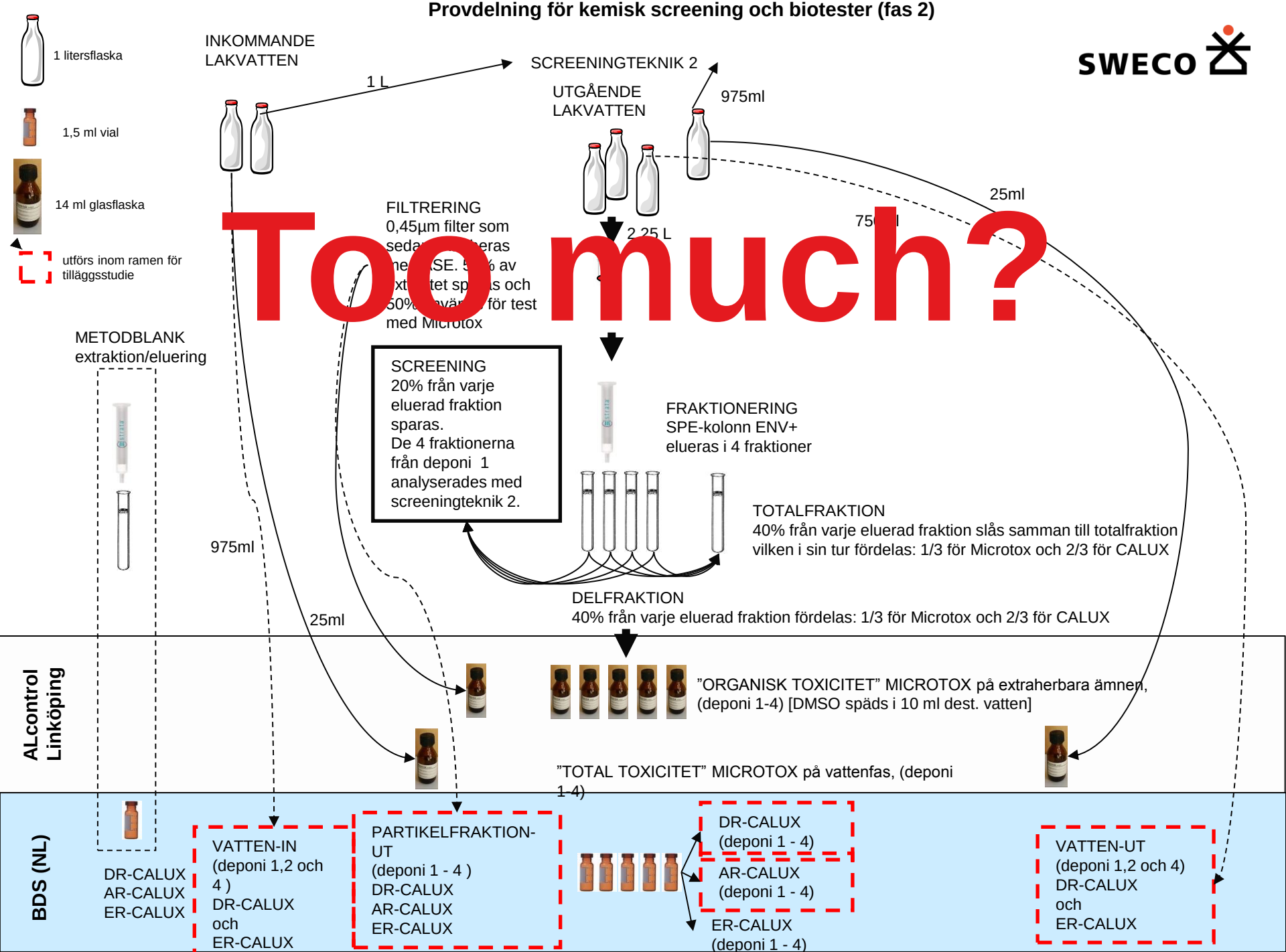
  → Microtox®

- Biochemical measurements

  → CALUX (**C**hemically **A**ctivated **L**uciferase e**X**pression)

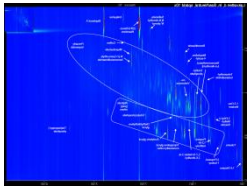
  - Estrogenic effects
  - Dioxin-like effects
  - Androgenic effects

Provdelning för kemisk screening och biotester (fas 2)



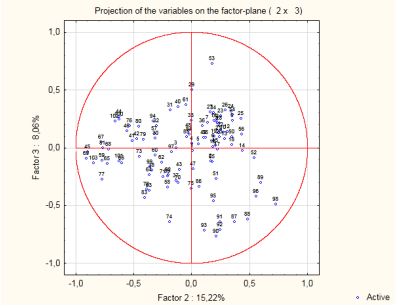
A taste of the data

1. A practical example of non-target screening followed by prioritization of the measured organic compounds



PEC/PNEC

2. A practical example of the use of multivariate statistics



3. Toxicity testing of landfill leachate
   - reduction after treatment
   - antagonistic effects

Background

Earlier literature study showed that:

- **930 organic compounds** have been detected in leachate
- ca 50% of these compounds are potentially **persistent** or very persistent
- Over 50 % of these compounds are potentially very **toxic** or toxic
- Some 20 different groups of chemicals in focus
- Little information available on efficiency of treatment methods

(Sweco, 2009)

Foto: VETAB, tagen från deponihandboken, Avfall Sverige, bilden har inget med studien att göra

Objectives

A. What organic compounds can be found?

B. In landfill leachate → and also in the recipient?

C. Reasons for inefficient reduction in treatment?

D. Contribute to relevant and cost efficient monitoring programs for landfills

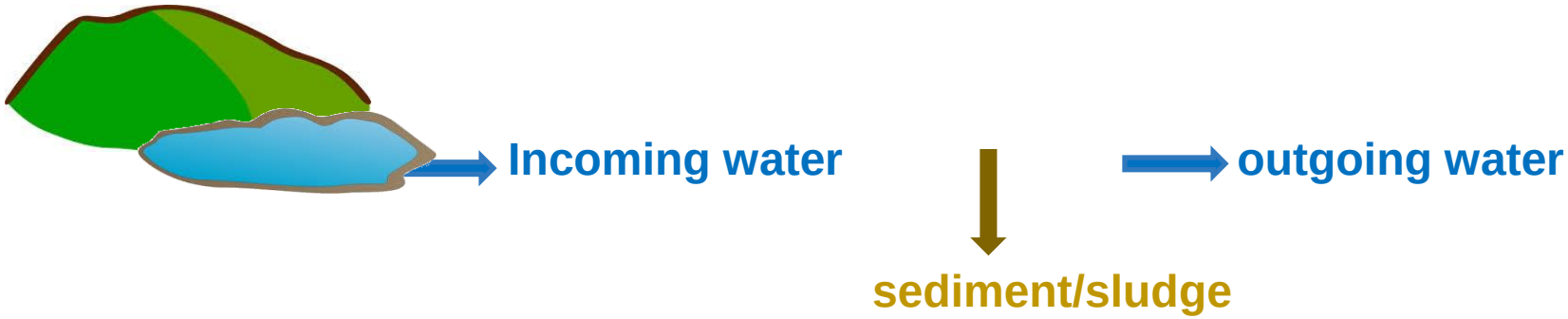
E. Support the evaluation of environmental risk from leachate in comparison to other emissions (e.g. WWTP)

F. Improve knowledge on local treatment techniques

Phase 1

<u>Organic compounds</u>

- GC*GC-MS



→611 organic compounds identified and semi-quantified (toluene equivalents)

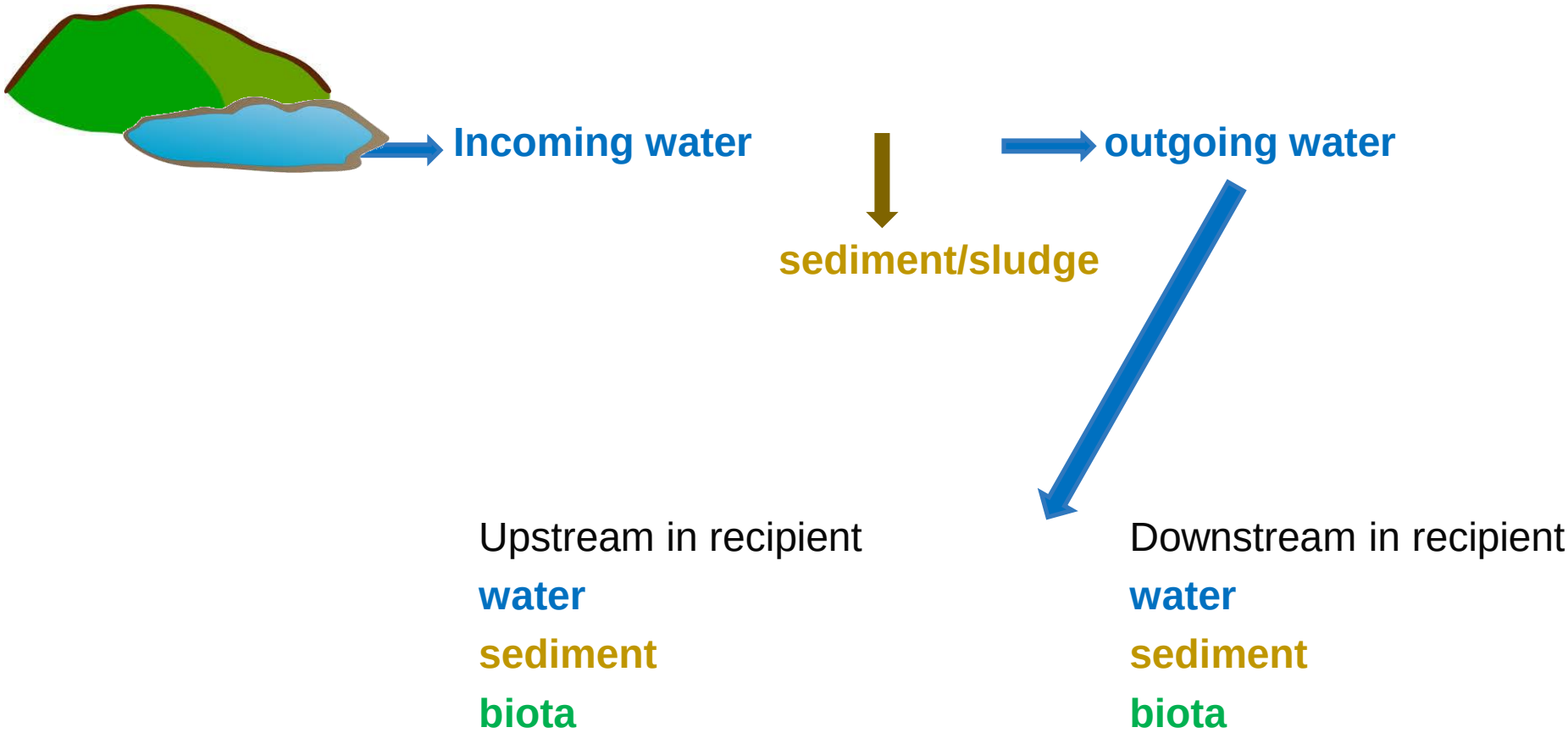
Over 100 ng/l in at least two samples + potentially PBT?
High concentrations in sediment + potentially PBT?

→300 organic compounds selected for phase 2

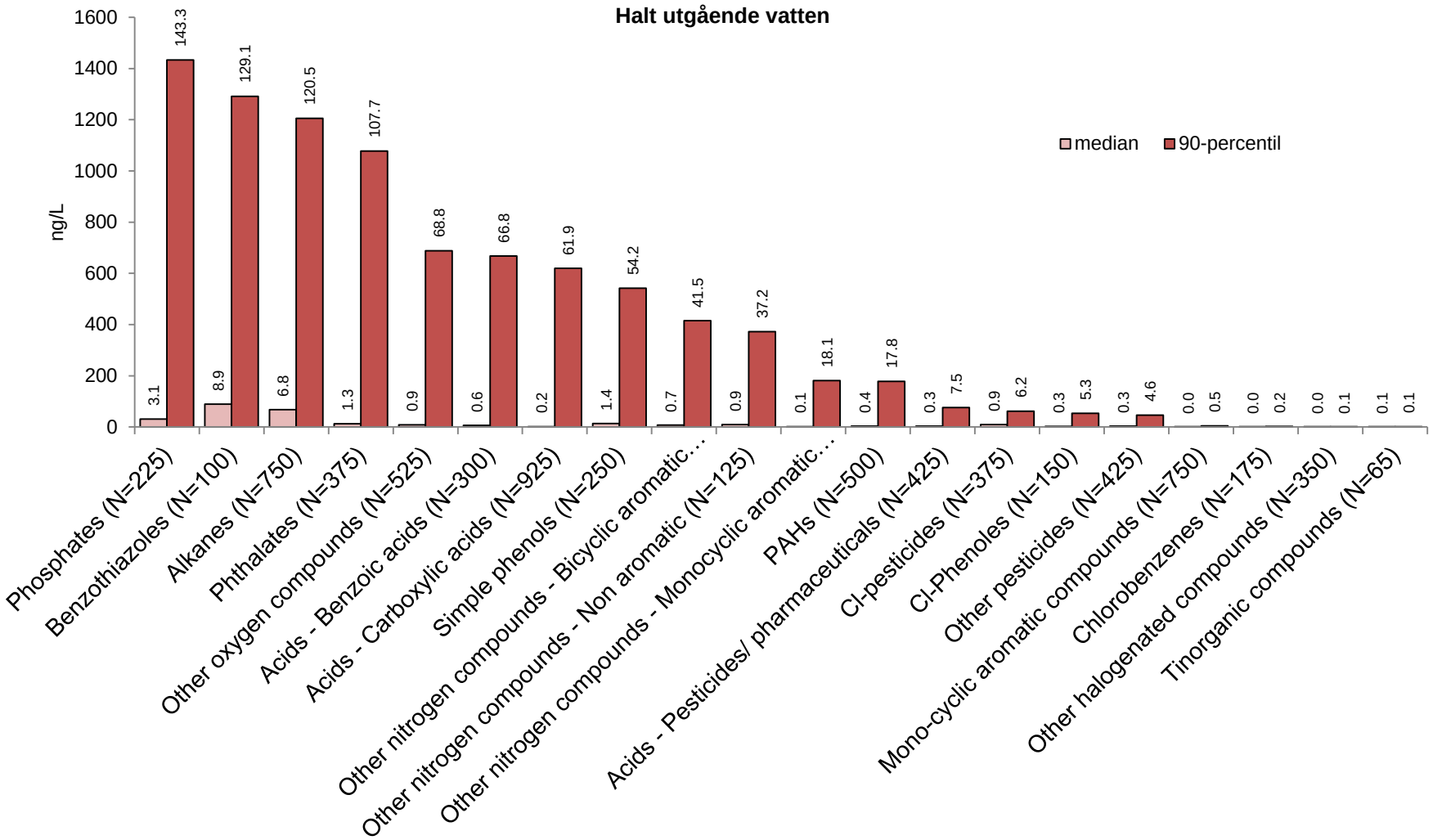
Phase 2, quantification

Organic compounds

- GC*GC-MS



Groups of organic compounds in leachate (phase 2)



Treatment effectiveness for some organic compounds in leachate

SWECO

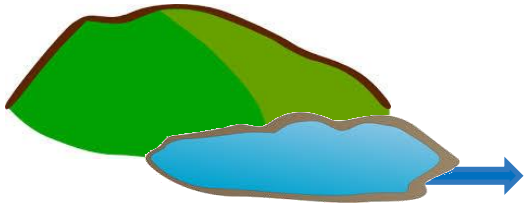
Compound	Origin/Use	Reduction median	Reduction 90 percentile
DEHP	Plasticizer	-77%	87%
Heptacosane	Greasing oil, wax	57%	96%
Tris(3-chloropropyl) phosphate	Flame retardant	55%	83%
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	Surface-active agent	13%	59%
Dibutyl phthalate – ftalat	Plasticizer	-89%	10%
Hexadecanoic acid (C16:0)	Degradation product	1%	58%
Dodecane	Solvent	99%	100%
Tri(2-chloroethyl) phosphate	Flame retardant	-57%	-8%
5H-1-Pyridine	Additive, flavor	96%	100%
Diisobutyl phthalate	Plasticizer	-36%	14%
Nonanal - aldehyd	Fragrance	33%	73%
Phenanthrene - PAH	Tires, asphalt	86%	99%
3/4-methylphenol (m/p-cresol)	Solvent, disinfectant, tar	65%	98%
5,6,7,7a-tetrahydro-4,4,7a-trimethyl-2(4H)Benzofuranone	Fragrance, tobacco	58%	95%
Benzothiazole	Flavor, color, rubber additive	67%	95%

Prioritizing, ranking

As for the NORMAN methodology PBT was considered

In the NORMAN methodology the ratio MEC/PNEC is calculated

Here the ratio downstream-/upstream concentration was calculated



Upstream in recipient	Downstream in recipient
water	**water**
sediment	**sediment**
biota	**biota**

Like in the NORMAN methodology ranking was done by considering:

- Frequency (increased concentration in how many landfills?)
- Extent (how large increase?)

Prioritizing, ranking

Nr	Ämne	CAS	Ytvatten	Sediment	Biota
1	Heptacosane*	593-49-7	**Y**	**S**	**B**
2	Pentacosane*	629-99-2	**Y**	**S**	**B**
3	Dodecane*	112-40-3		s	**B**
4	Tetradecane*	629-59-4	**Y**	s	**B**
5	5H-1-Pyridine	270-91-7	**Y**	s	**B**
6	Dibutyl phthalate	84-74-2		**S**	**B**
7	Tricosane*	638-67-5	**Y**	**S**	
8	Phenanthrene	85-01-8	**Y**	s	b
9	Pentadecane	629-62-9	**Y**	s	b
10	Nonacosane*	630-03-5	y	s	**B**
11	*Octanoic acid (C8:0)***	*124-07-2*	***Y***		
12	Diethyl Phthalate	84-66-2		s	**B**
13	Heneicosane*	629-94-7	**Y**	**S**	
14	Dimethyl phthalate	131-11-3	**Y**	**S**	
15	Hexacosane*	630-01-3	y	**S**	b
16	3-ethyl-4-methyl-1H-Pyrrole-2,5-dione	20189-42-8	y	**S**	
17	5,6,7,7a-tetrahydro-4,4,7a-trimethyl-2(4H)Benzofuranone	15356-74-8	y	s	b
18	Fluoranthene	206-44-0		**S**	b
19	p,p'-DDE	72-55-9			**B**
20	Tridecane*	629-50-5			**B**
21	Benzothiazole	95-16-9		**S**	b

OBS! Bara utdrag ur listan…

Organic compounds from leachate a risk to the recipient?

- Leachate volumes and recipient flow were considered to calculate dilution
- Large variation (3-3000 times dilution according to data from landfill owners)
- Risk was calculated for the 20 “top ranks”
- Concentrations > PNEC in outgoing water is diluted to < PNEC at some sites but not all

Environmental concentration and risk

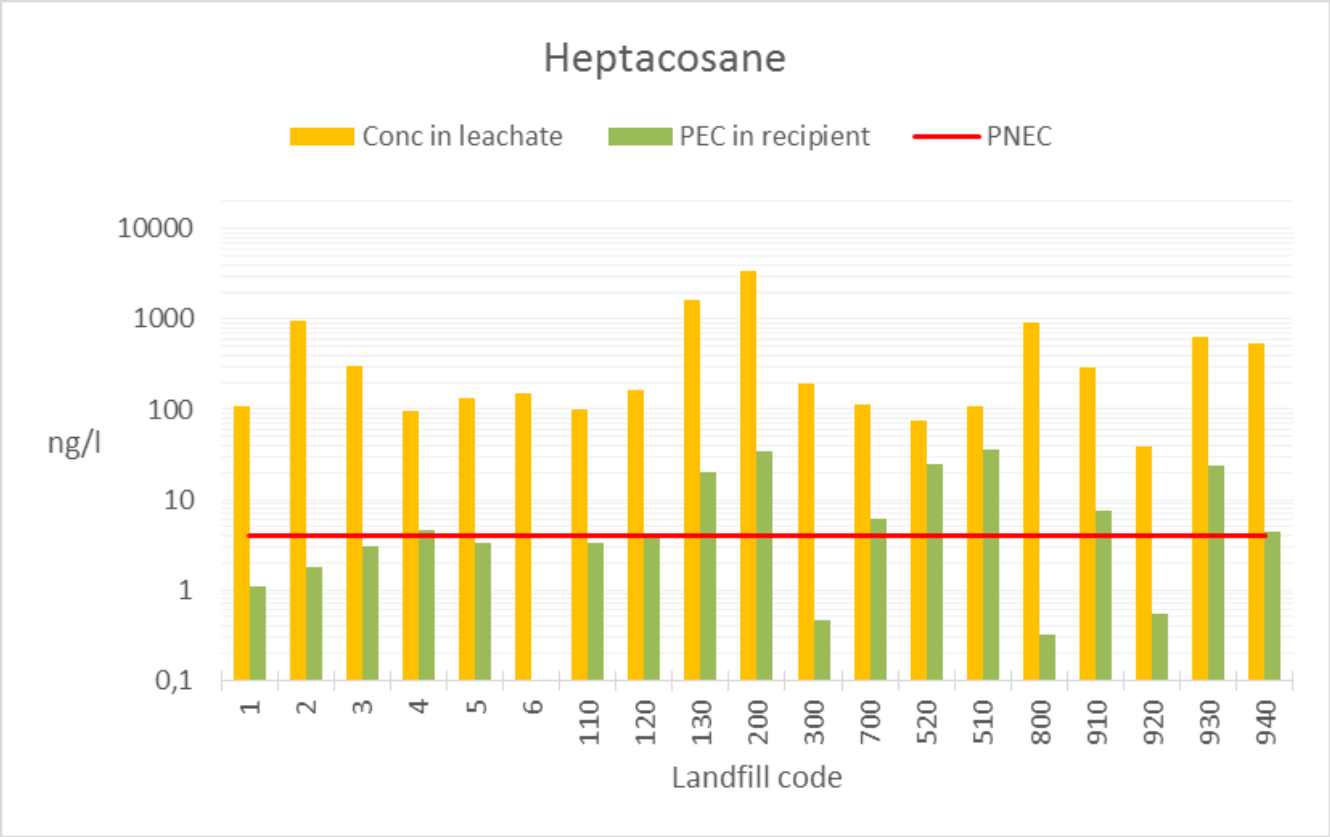
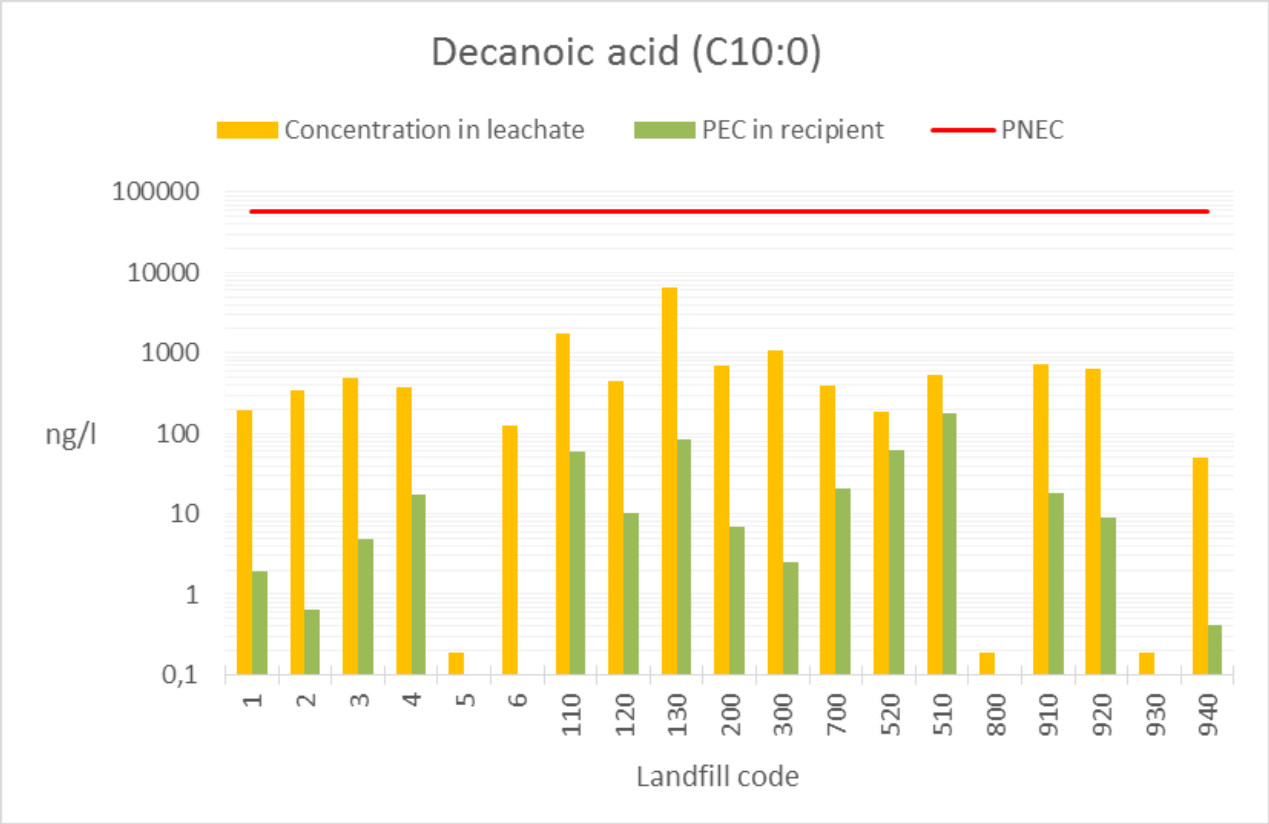


Figure 3-4. Measured concentrations in Leachate and PEC and PNEC of heptacosane. If the PEC (green bar) exceeds the PNEC value (red line) an ecotoxicological risk may be present in the recipient water.

Environmental concentration and risk



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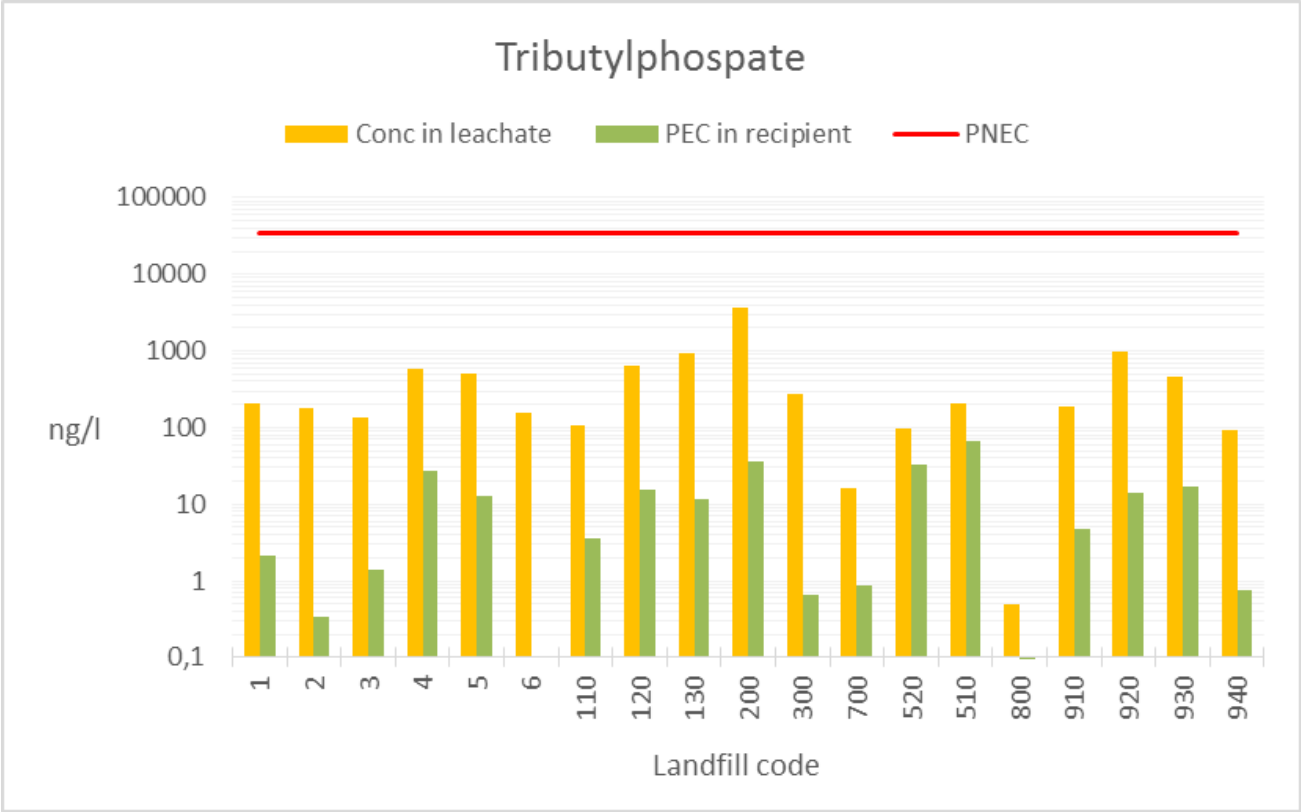
Environmental concentration and risk



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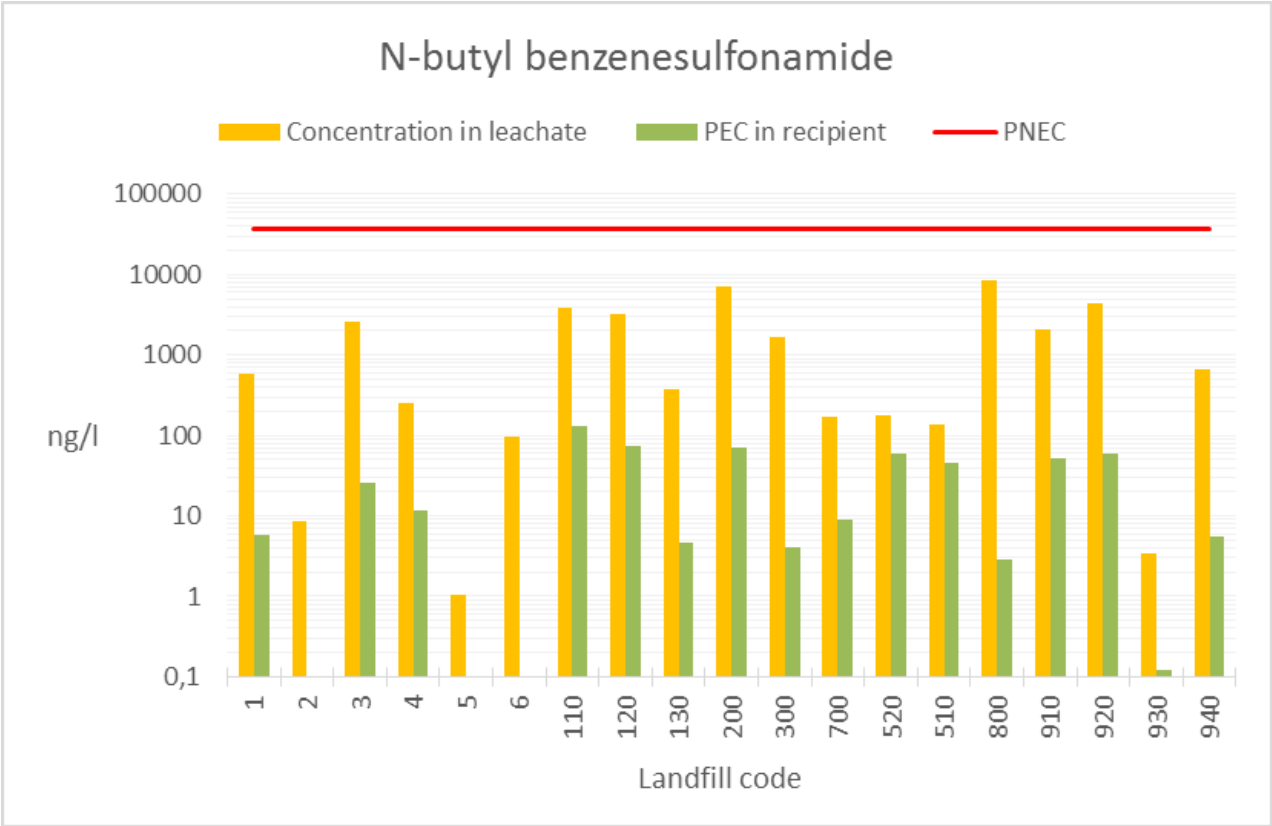
Environmental concentration and risk



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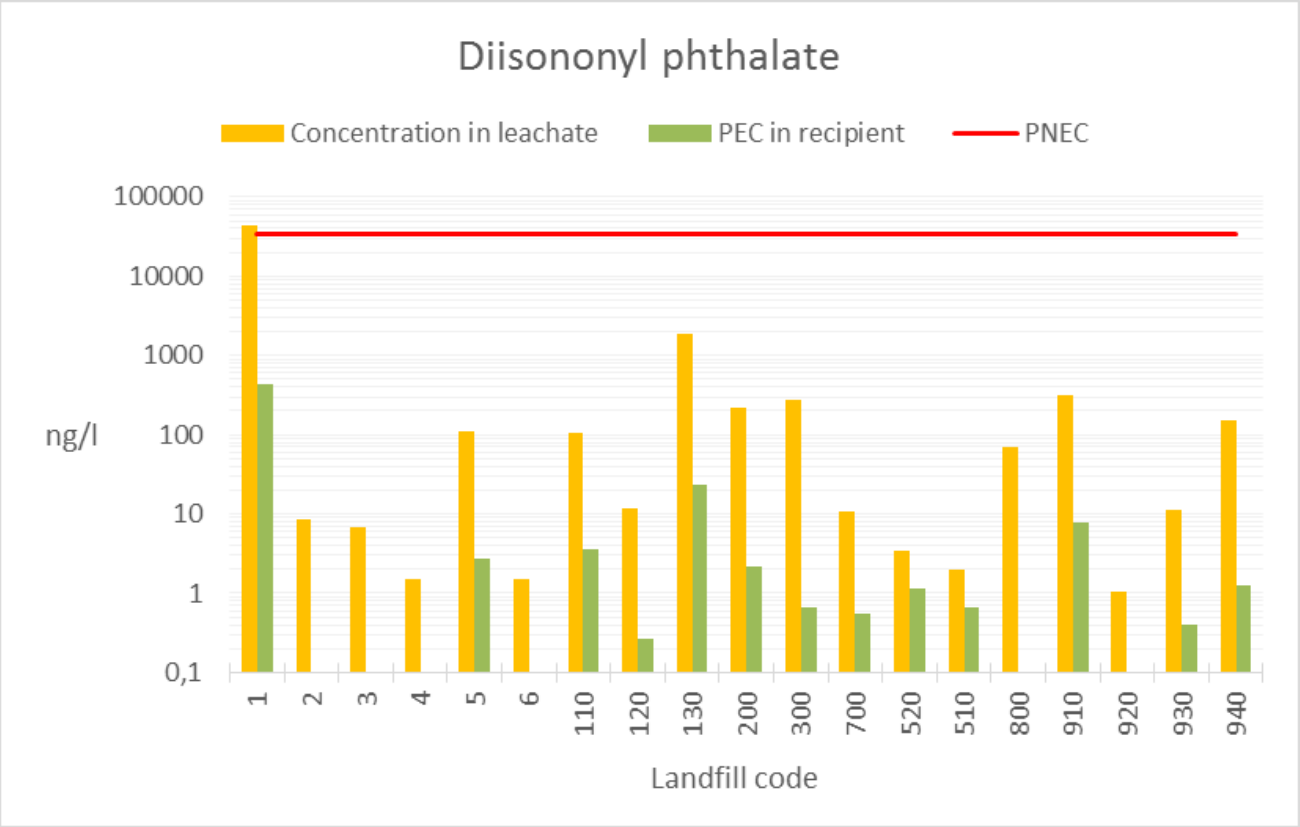
Environmental concentration and risk



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Environmental concentration and risk

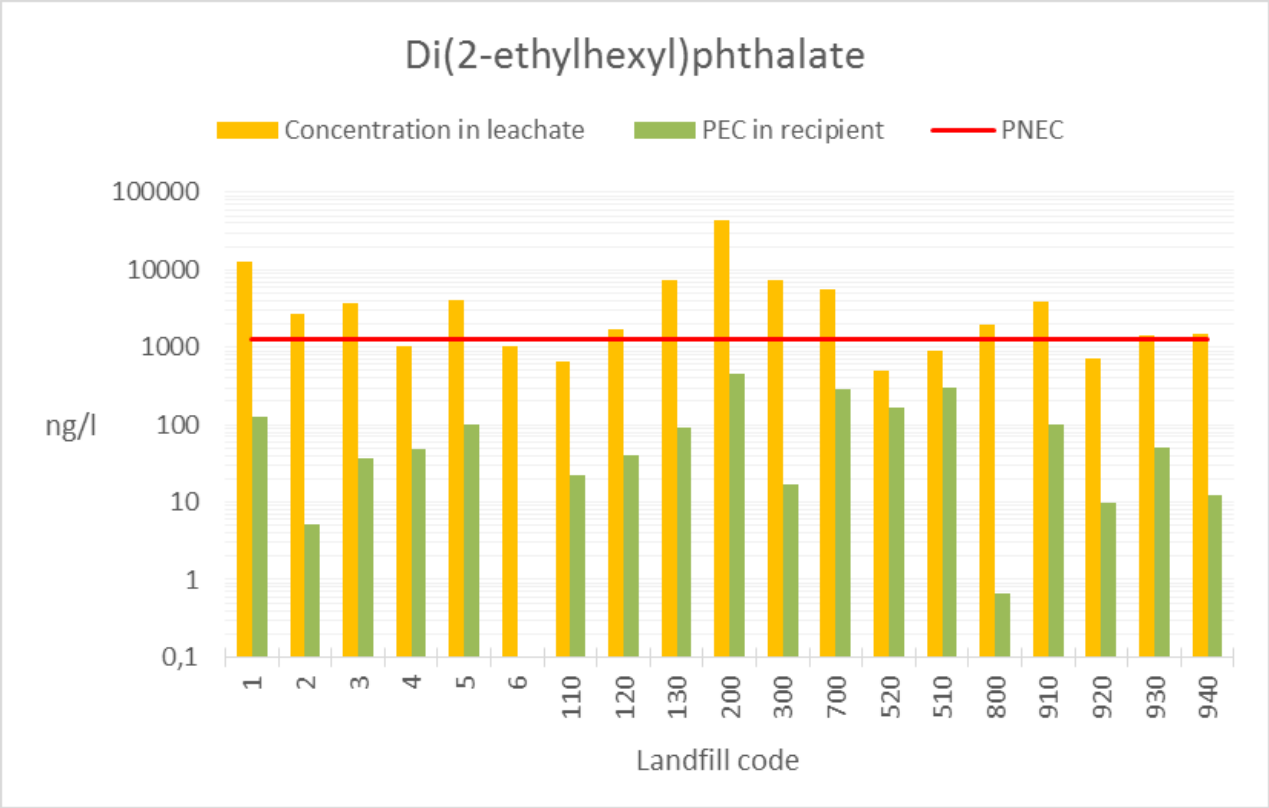


Figure 3-4. Measured concentrations in Leachate and PEC and PNEC. If the PEC (green bar) exceeds the PNEC value (red line) an ecotoxicological risk may be present in the recipient water.

Notes and uncertainties

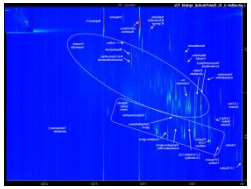
- plume behaviour of the leachate
- limited data on the actual ecotoxicity
- uncertain dilution factors which may vary considerably during the year
- Synergistic ecotoxicological effects

Summary of Results – organic compounds in leachate

- **>600 compounds detected** (300 compounds detected at all 21 sites)
- ca 50% has **potentially harmful properties**
- Toxic untreated leachate, but **fairly good reduction** after treatment
- **Advanced treatment → better reduction** of concentration and effects
- Risk ratios **>> 1 for a few compounds** (outgoing concentration/no effect concentration)
- Compounds identified that could be included in monitoring

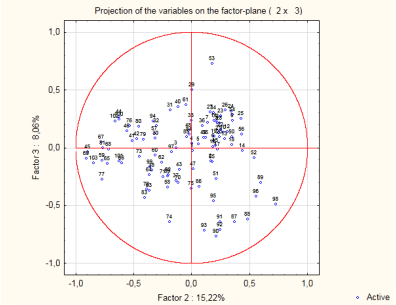
Old v.s new landfill

1. A practical example of non-target screening followed by prioritization of the measured organic compounds



PEC/PNEC

2. **A practical example of the use of multivariate statistics**



3. Toxicity testing of landfill leachate
   - reduction after treatment
   - antagonistic effects

Old v.s new landfill

- Study of untreated leachate
- 18 landfills compared
- 304 common organic compounds
- 201 compounds removed from comparison (>20 % cases below LOQ)
- 103 compounds included in multivariate evaluation

Data treatment

- Log normalized
- Divided by standard deviation for each compound
- Subtracted by the average for each compound

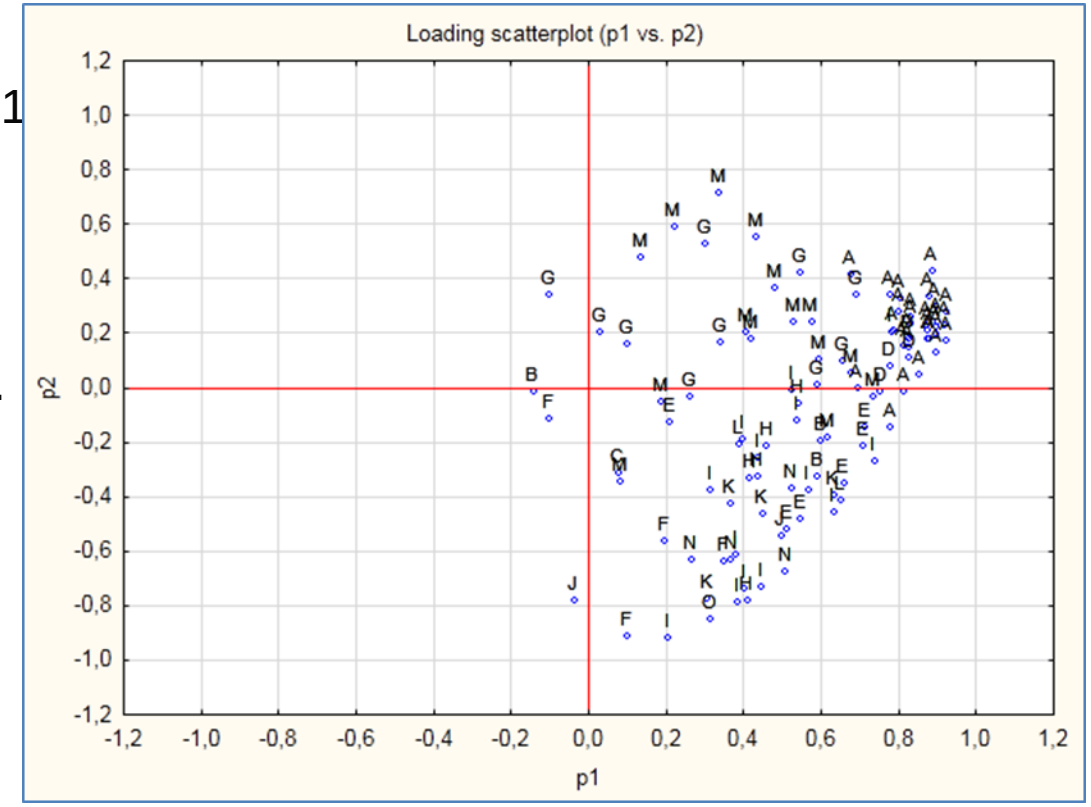
Results

The contribution from each principal component to the original variance:

- PC1: 35 %
- PC2: 15 %
- PC3: 8 %
- PC4: 8 %

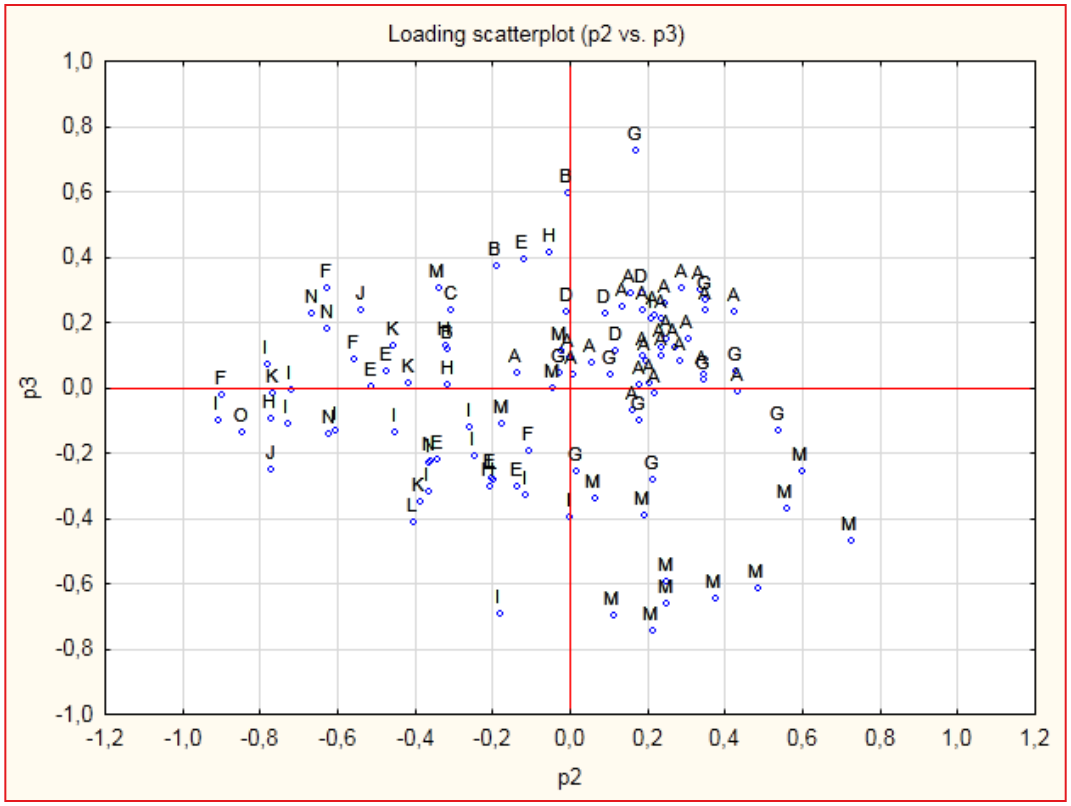
Results: PC1 vs. PC2

All parameters (compounds) in PC1 are on the same side.
This shows that PC1 is demonstrating a common process that is universal for all compounds.
This most likely describes how diluted the leachate is.
This is not the difference we are interested in. Forget about PC1!



Results: PC2 vs. PC3

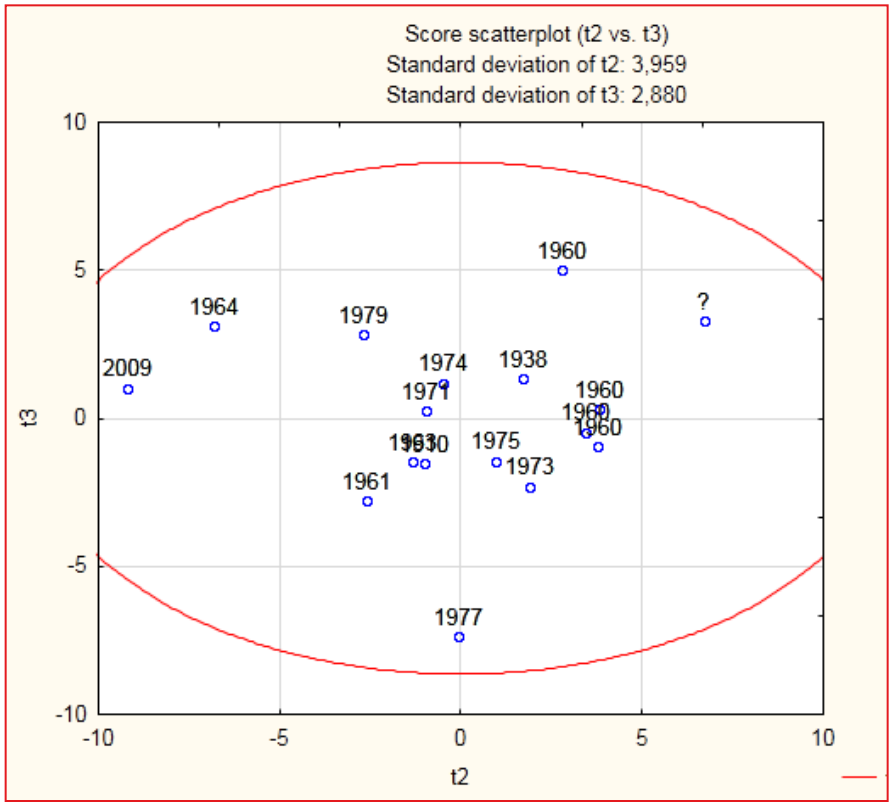
Differences are now visible and no longer obscured by differences in dilution of leachate samples.



Results: PC2 vs PC3

What year was the landfill opened?

<u>No pattern, does not seem important</u>

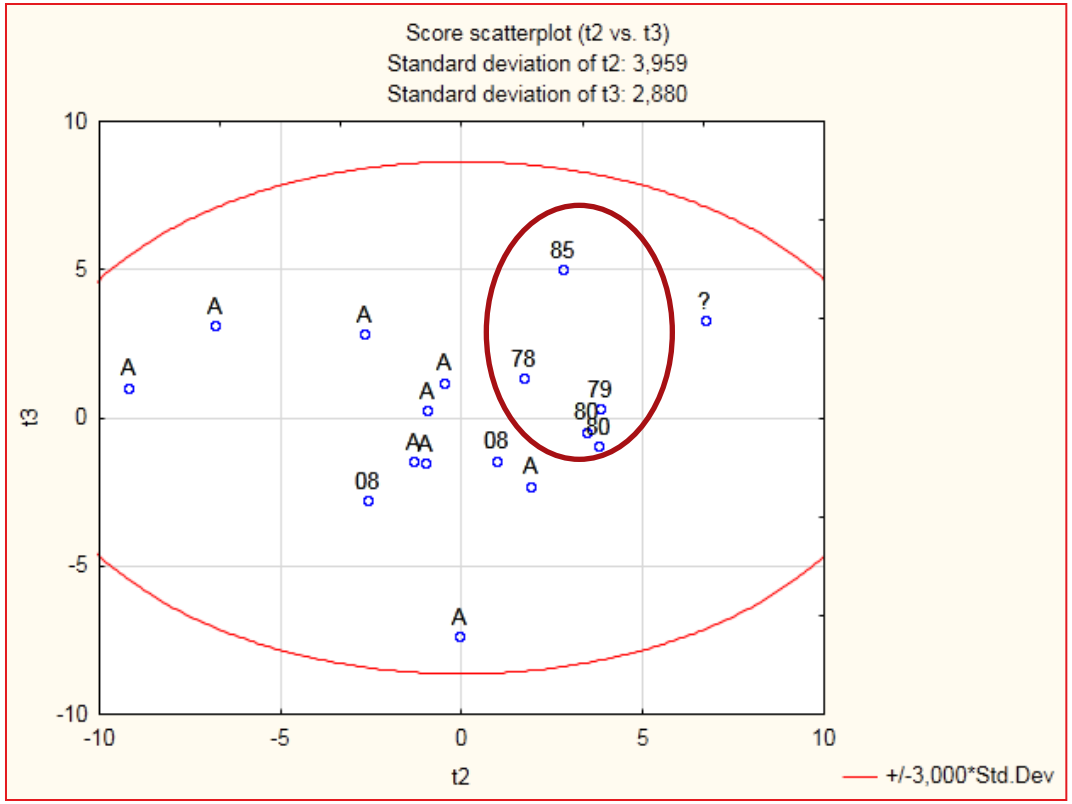


Results: PC2 vs. PC3

What year did the landfill stop receiving waste?

A = active

There is a pattern! Old landfills (closed in the 70´s and 80´s) are clustered in the top right corner

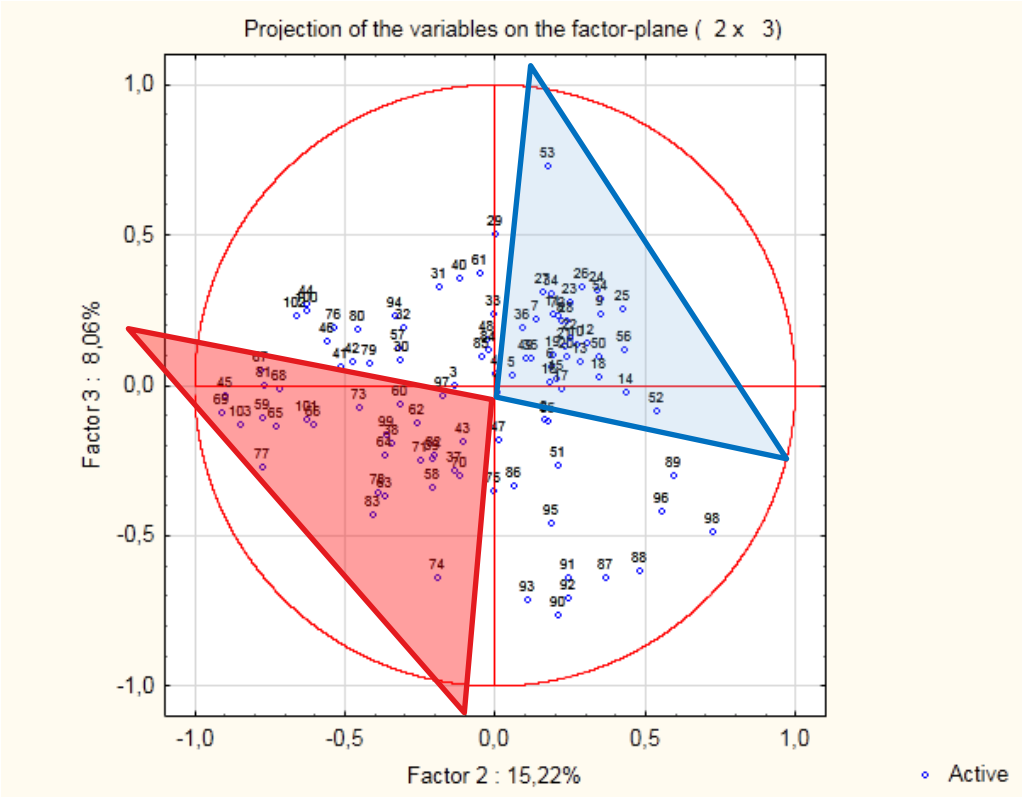


”?” = industrial landfill

What variables can point out the old landfills?

Variables in blue triangle are positively correlated with old landfills (higher concentrations of these compounds in old landfills)

Variables in red triangle are negatively correlated with old landfills (lower concentrations of these compounds in old landfills)



Organic compounds in old landfills

High concentration

- Alkanes (23 substances, tetradecane – heptatriacontane)
- PAHs (phenanthrene and pyrene)
- some phthalates
  - *Diisobutyl phthalate,*
  - *Dihexyl phthalate,*
  - *Benzyl butyl phthalate*
  - *Di(2-ethylhexyl)adipate,*
  - *Di(2-ethylhexyl)phthalate*
  - *Diisononyl phthalate*
- terpenoid (13-Isopropylpodocarpa-8,11,13-trien-19-al)

Low concentration

- simple phenols and cresols
- benzothiazoles
- organic phosphates
- p-methyl-Cumene
- D-Limonene
- Pentobarbital
- Bisphenol A
- N,N,4-trimethyl benzenesulfonamide
- Caffeine
- Ibuprofen

General remarks on differences between old and new landfills?

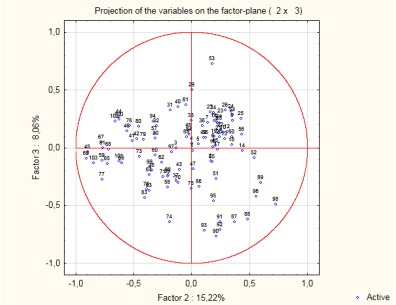
- Same number of compounds
- Typical concentrations are different
- A few compounds are more exclusively found in only new or old
- Generally lower load to recipients from new landfills
- Similar load from old landfills to that from WWTP.
- Lower load from old landfills than from WWTP when compounds such as DEHP and Tris-butoxyetyl-fosfat are considered.

Toxicity testing of fractionated samples

1. A practical example of non-target screening followed by prioritization of the measured organic compounds

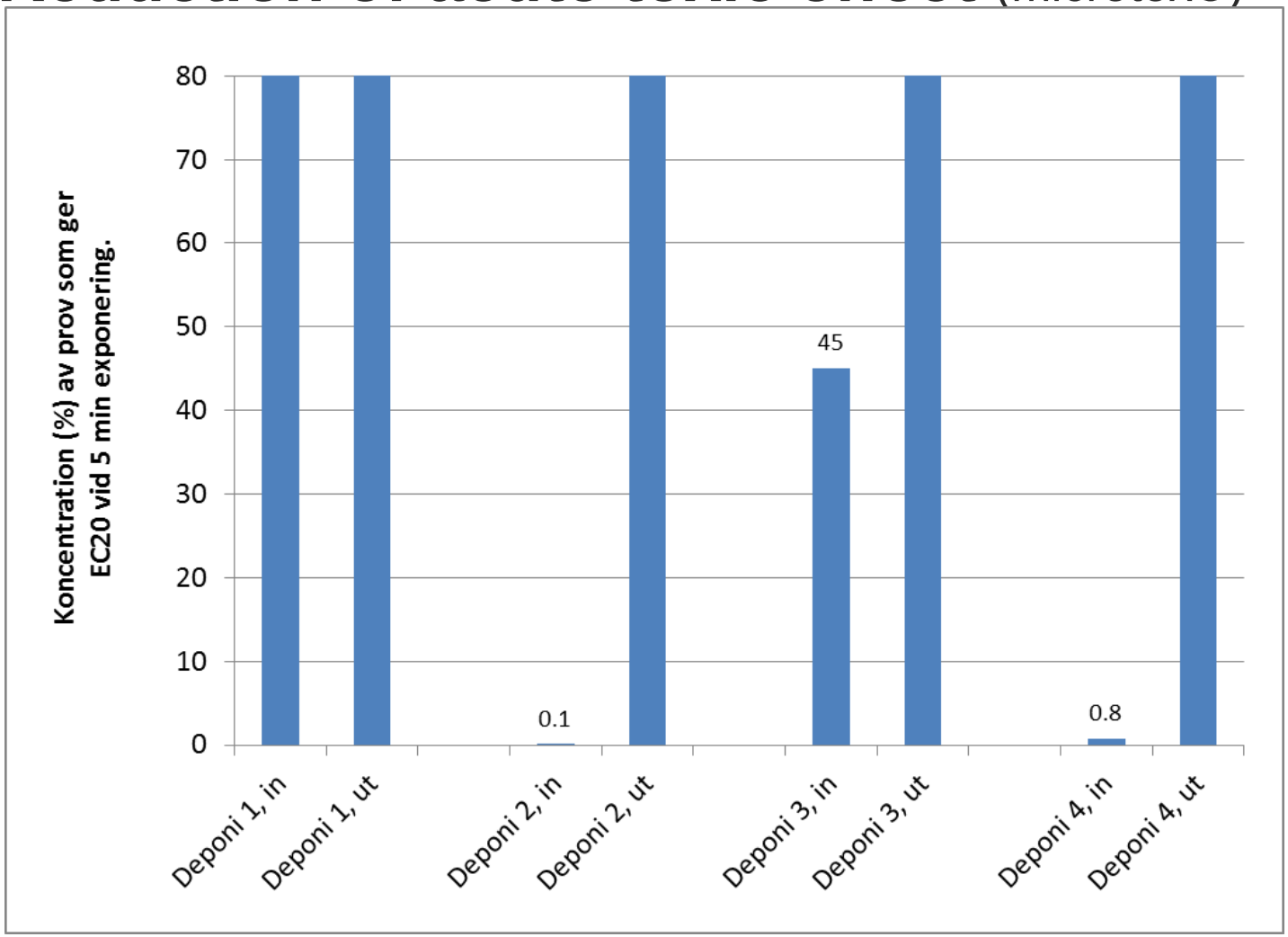
PEC/PNEC

2. **A practical example of the use of multivariate statistics**

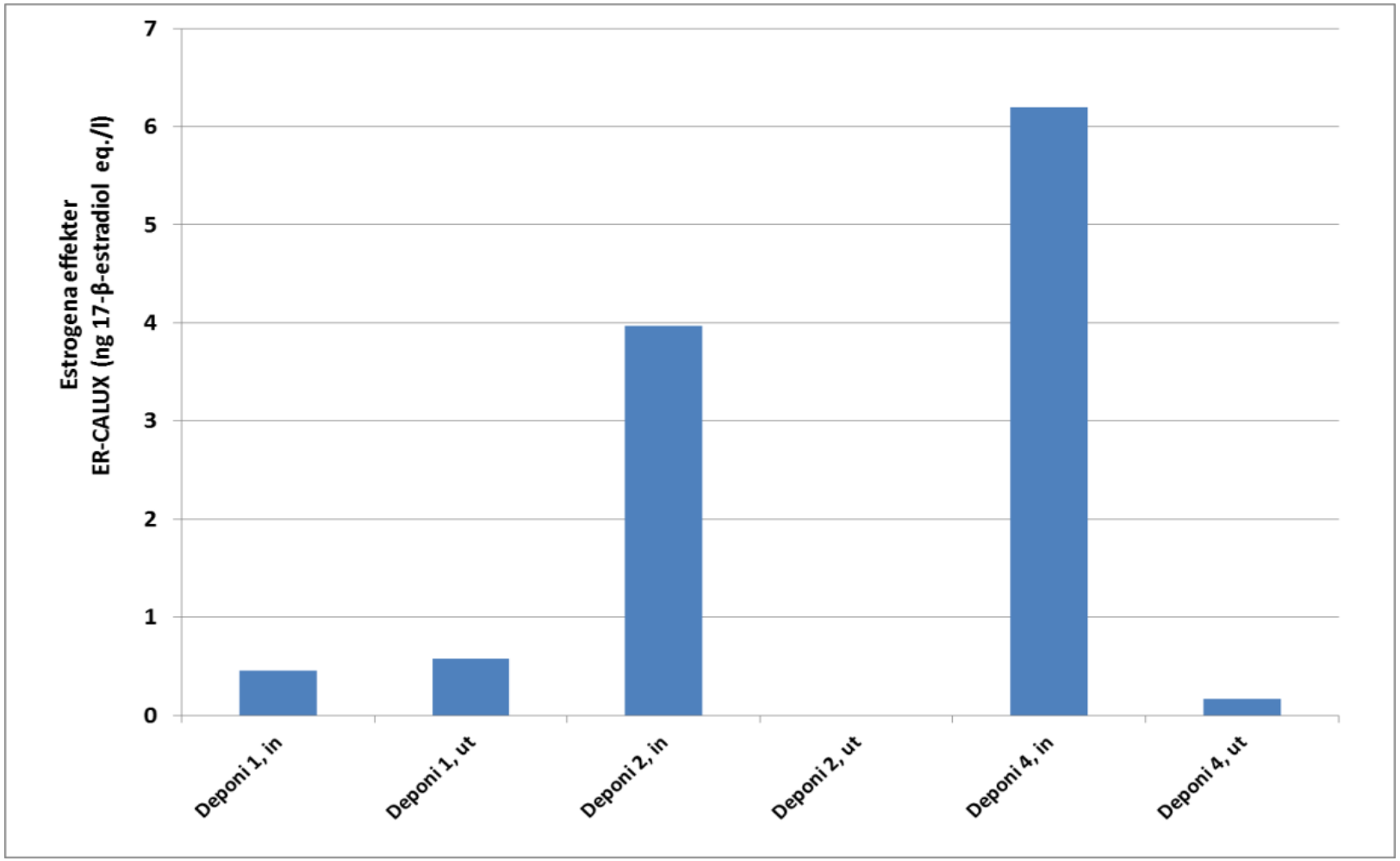


3. **Toxicity testing of landfill leachate**
   - **reduction after treatment**
   - **antagonistic effects**

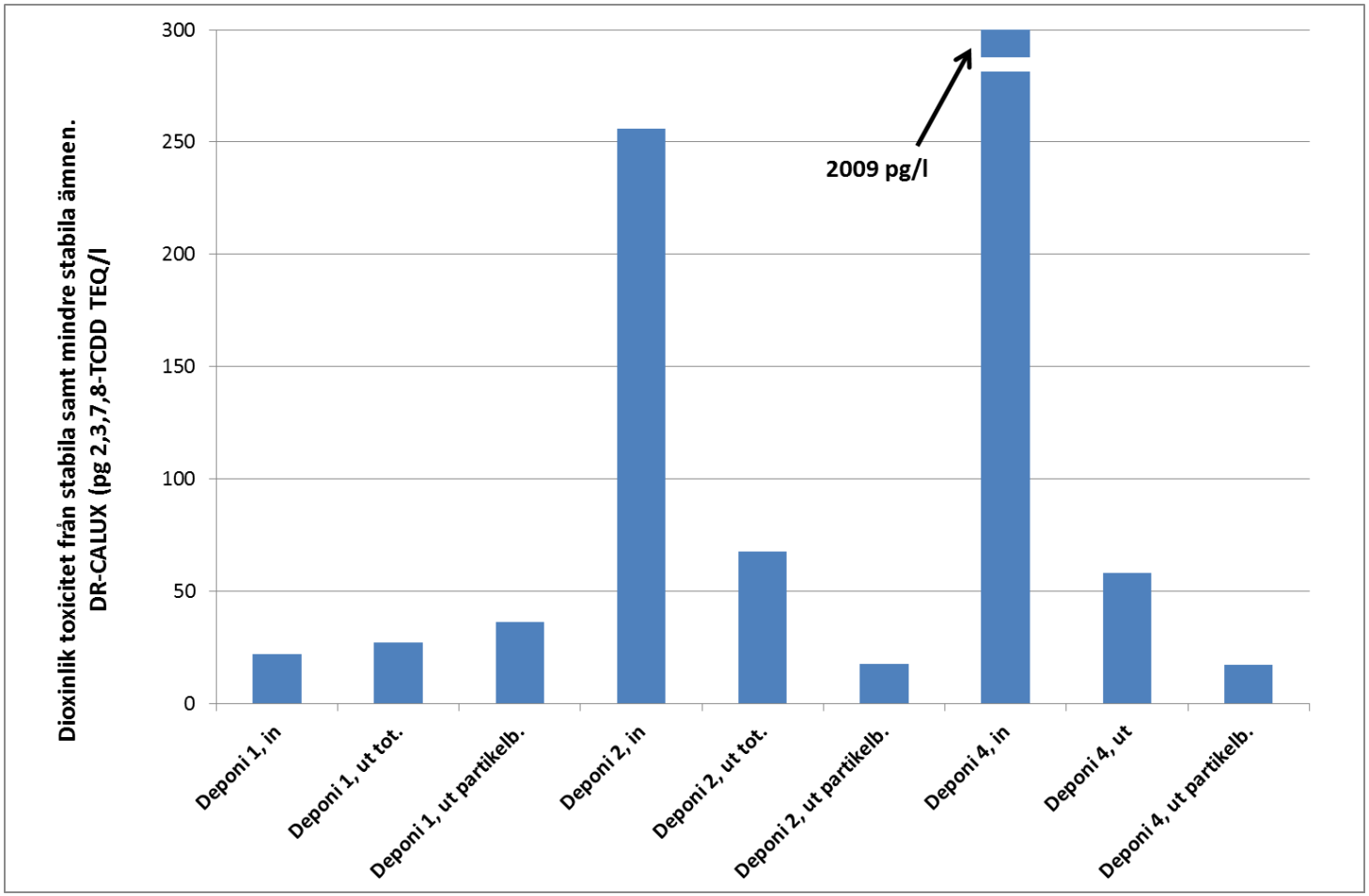
Reduction of acute toxic effect (microtox®)



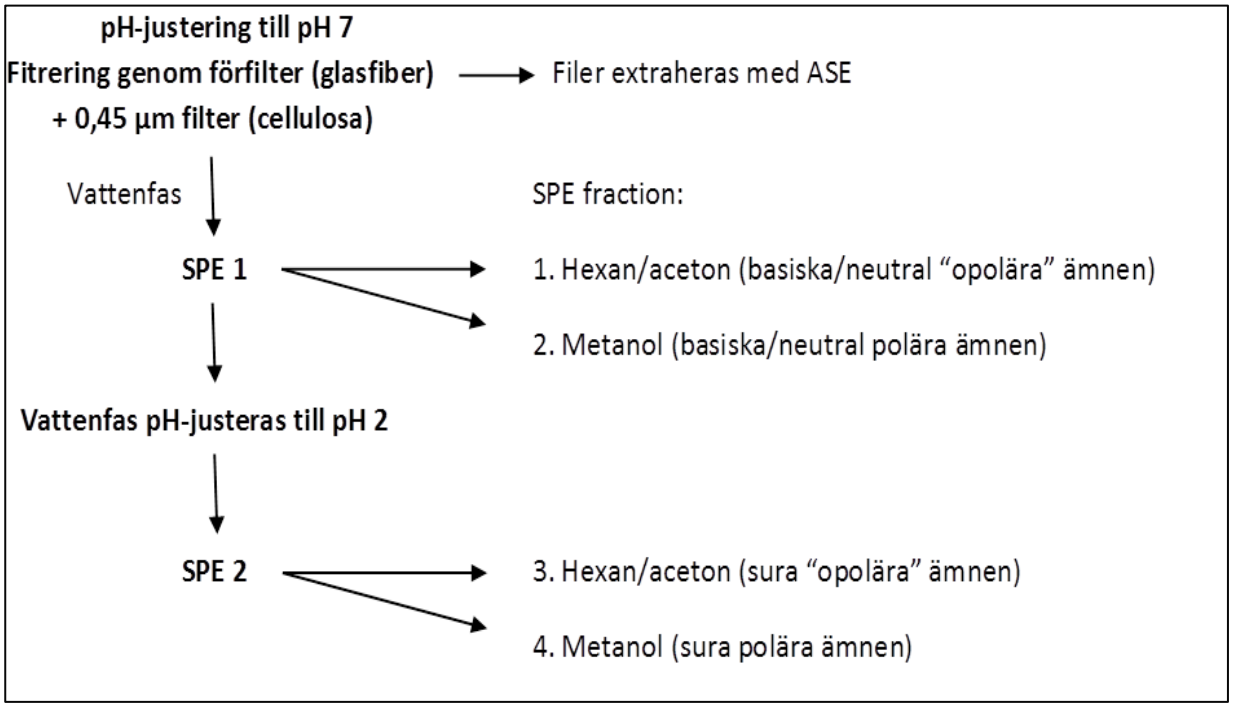
Reduction of estrogenic effect (ER-CALUX)



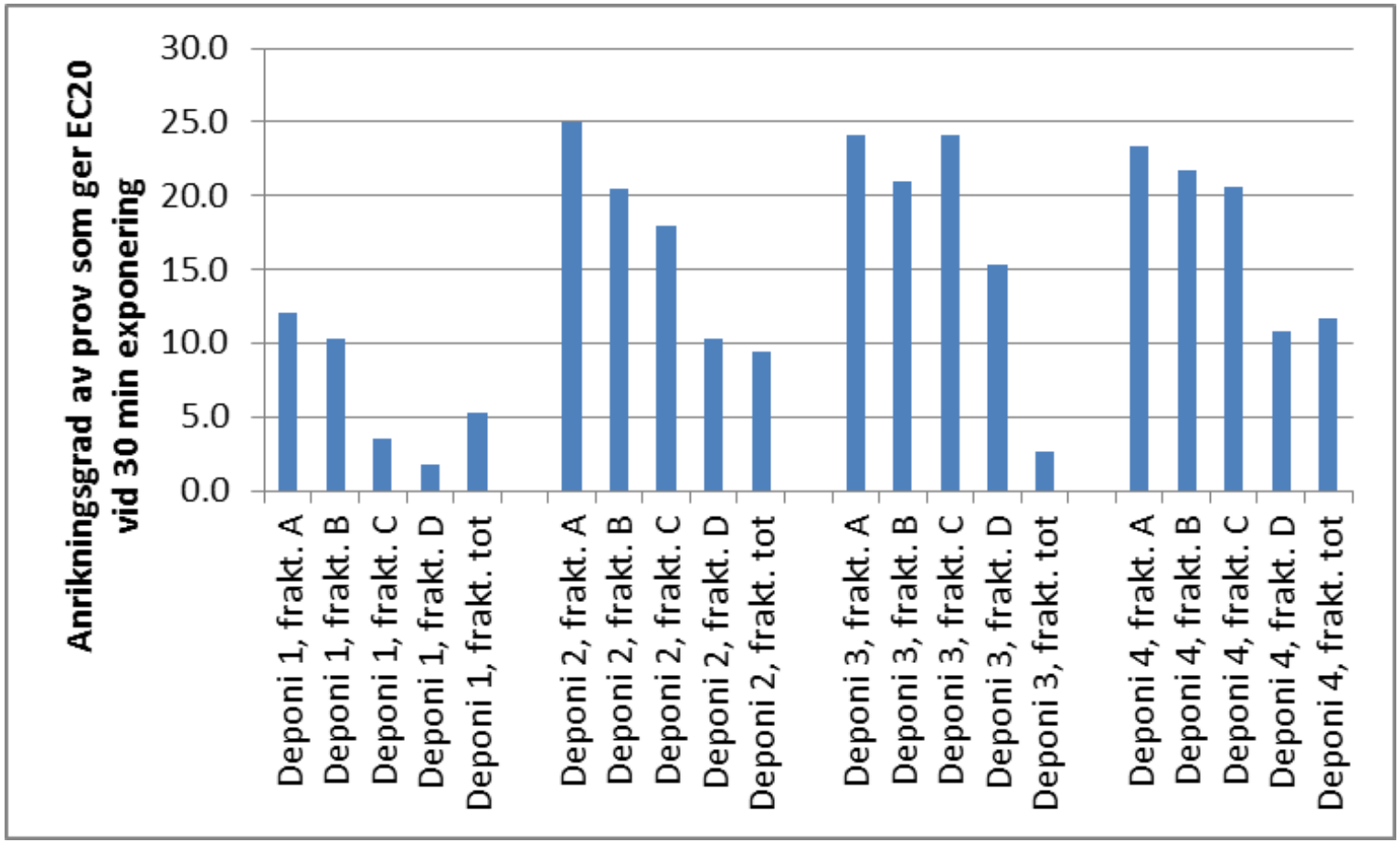
Reduction of dioxin-toxicity (DR-CALUX)



Fractionation of outgoing leachate water



Antagonistic effects in outgoing leachate water - Microtox



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Questions/contact

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