Selected plasticizers in the Nordic Environment

Mikael Remberger

Katarina Hansson

Lennart Kaj

Hanna Andersson

Eva Brorström-Lundén

IVL Swedish Environmental Research Institute

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a project financed and supported by

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through the Nordic Chemicals Group

and participating institutions in the different countries

Participating countries

- DK Denmark
- FI Finland
- FO Faroe Islands
- IS Island
- NO Norway
- SE Sweden

Plasticizers

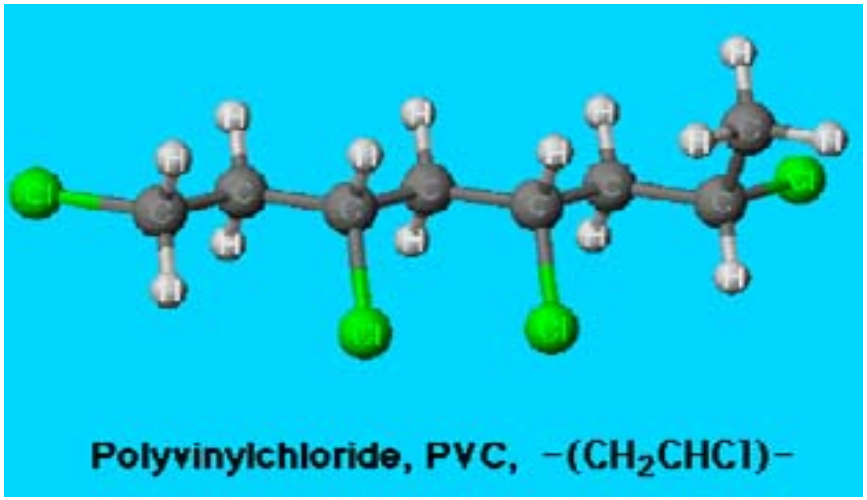
are used to increase the plasticity of a material, especially plastics

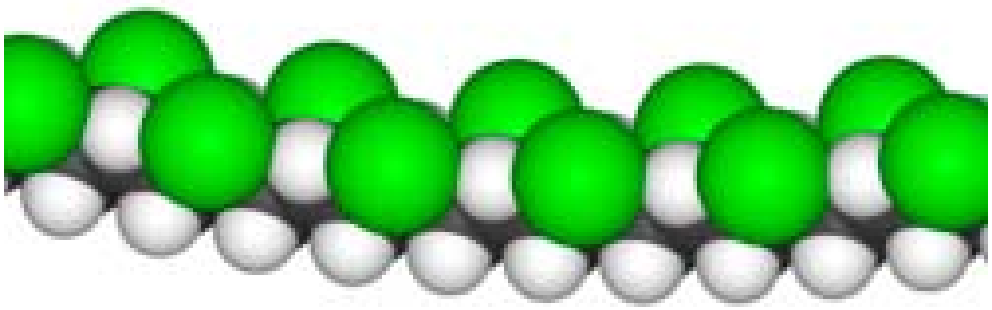
especially PVC (poly vinyl chloride)

most commonly used: phthalates

93% of the phthalates produced in Europe is used as additive for PVC

The plasticizers are not crosslinked into the PVC structure...

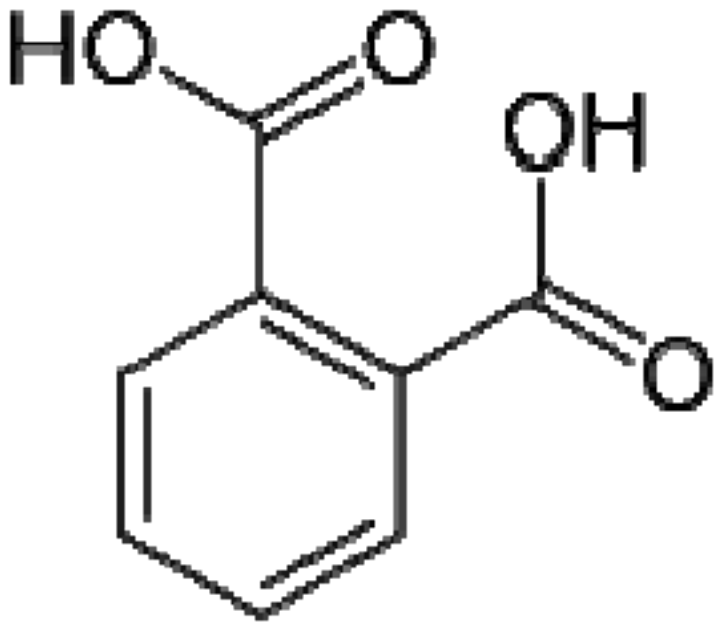


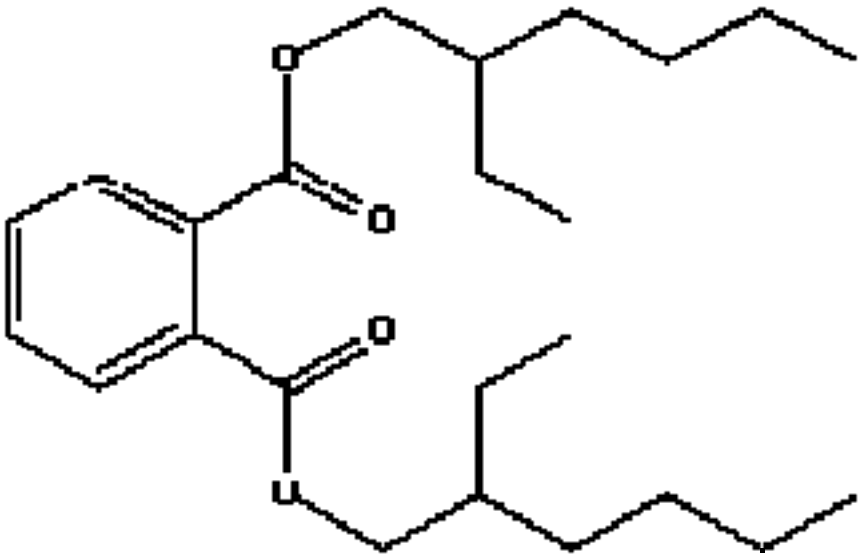


... will migrate to the surrounding environment

Phthalates

- esters of phthalic acid



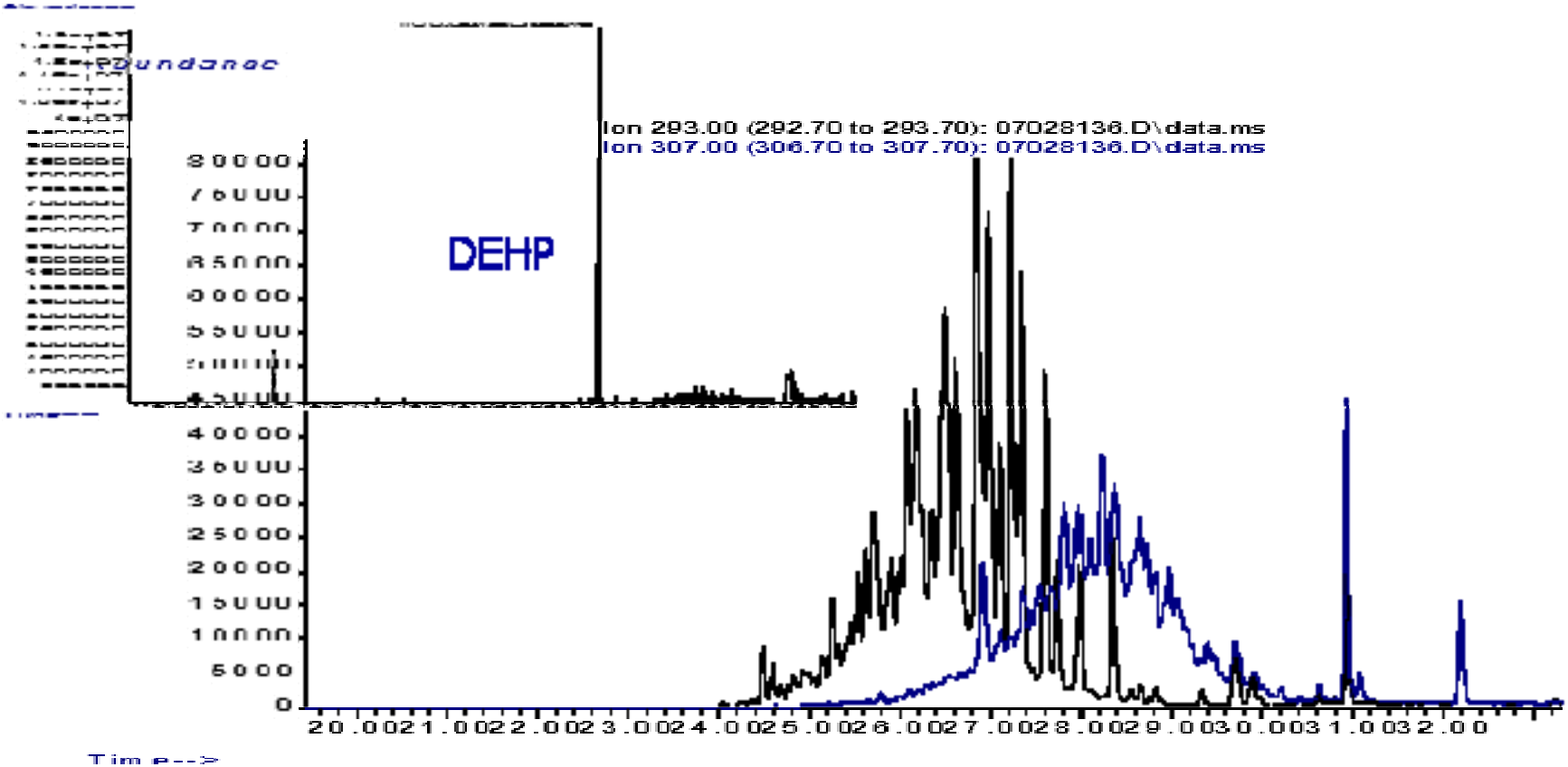


DEHP

Phthalates

- DBP R=R' = butyl
- BBP R= butyl R'= benzyl
- DEHP R=R' = 2-ethylhexyl
- L79P R=R' = heptyl, octyl, nonyl, branched IM
- DOP R=R' = octyl
- DINP R=R' = isononyl IM
- DIDP R=R' = isodecyl IM
- DUP R=R' = undecyl

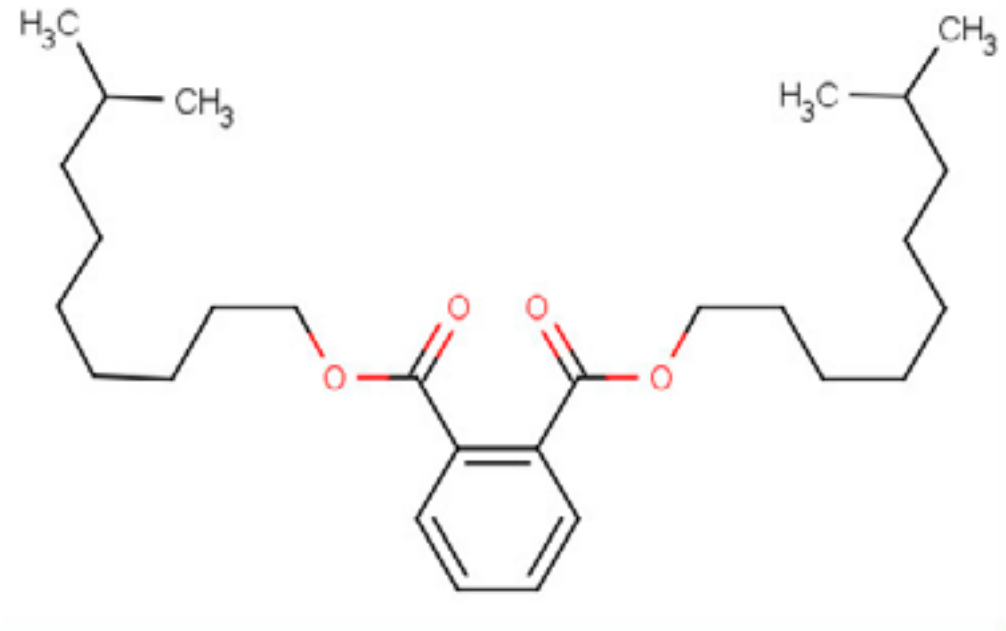
Isomeric mixtures

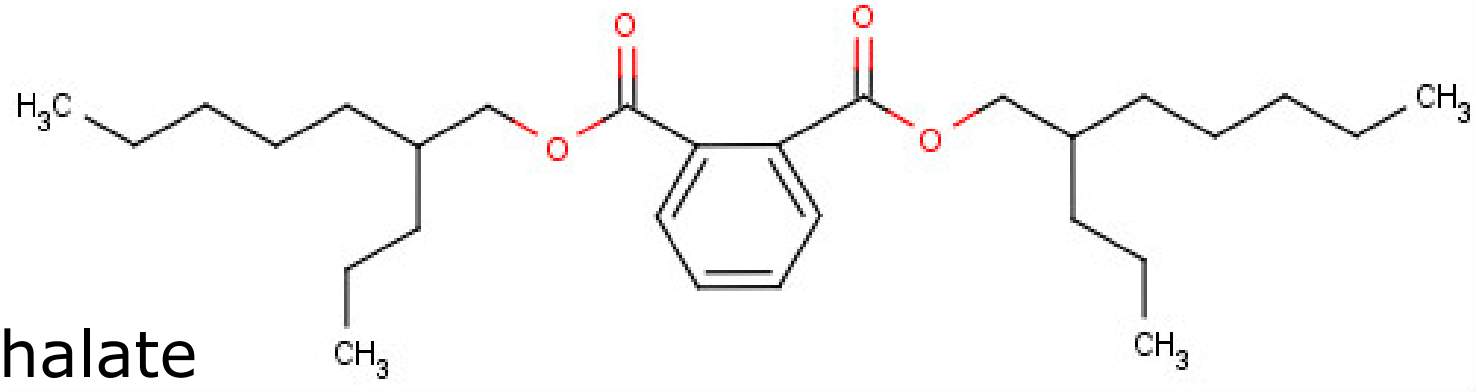


Chromatograms of DEHP (insert) DINP, and DIDP.

DINP, DIDP are more difficult to distinguish from background noise.

DIDP
Diisodecylphtalate
isomeric mixture, C10

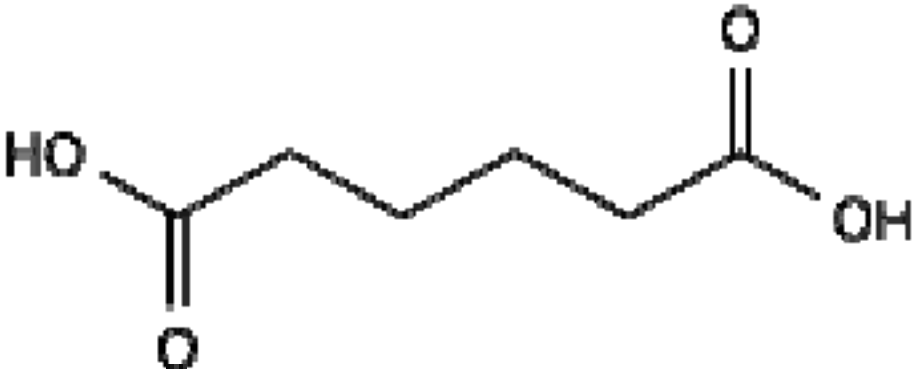


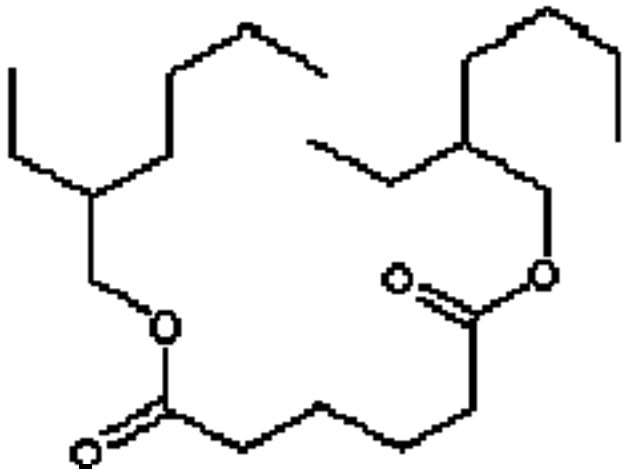


DPHP
Dipropylheptylphthalate
C10

Adipates

- offer enhanced low temperature properties
  - often used in blends with phthalates
    - esters of adipic acid





DEHA

Adipates

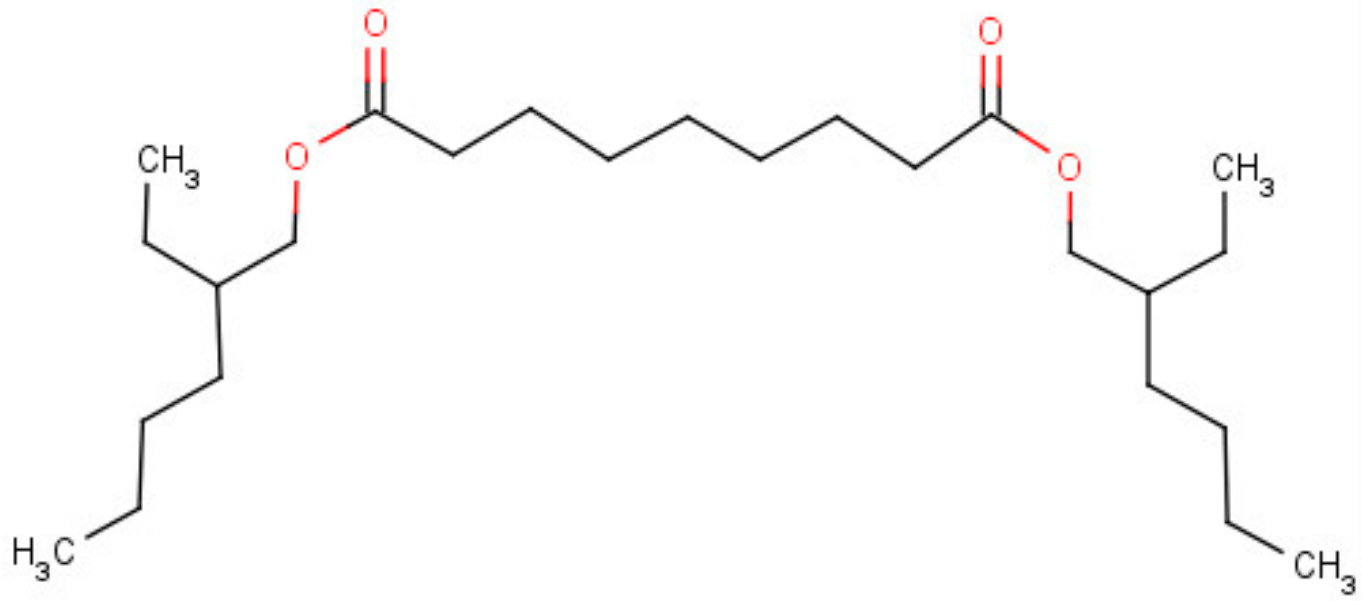
- DEHA R = R' = 2-ethylhexyl
- DINA R = R' = isononyl IM
- BOA R = Benzyl R'= octyl
- DBEEA R = R' = 2-butoxyethoxy

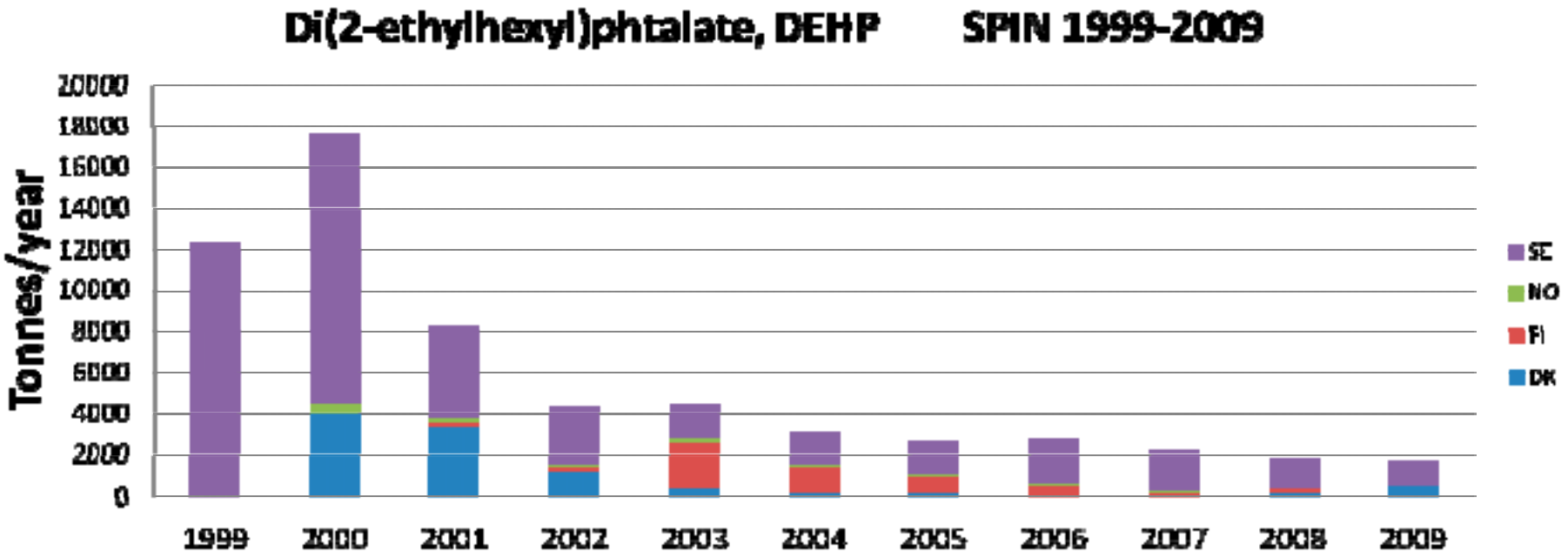
Azelates

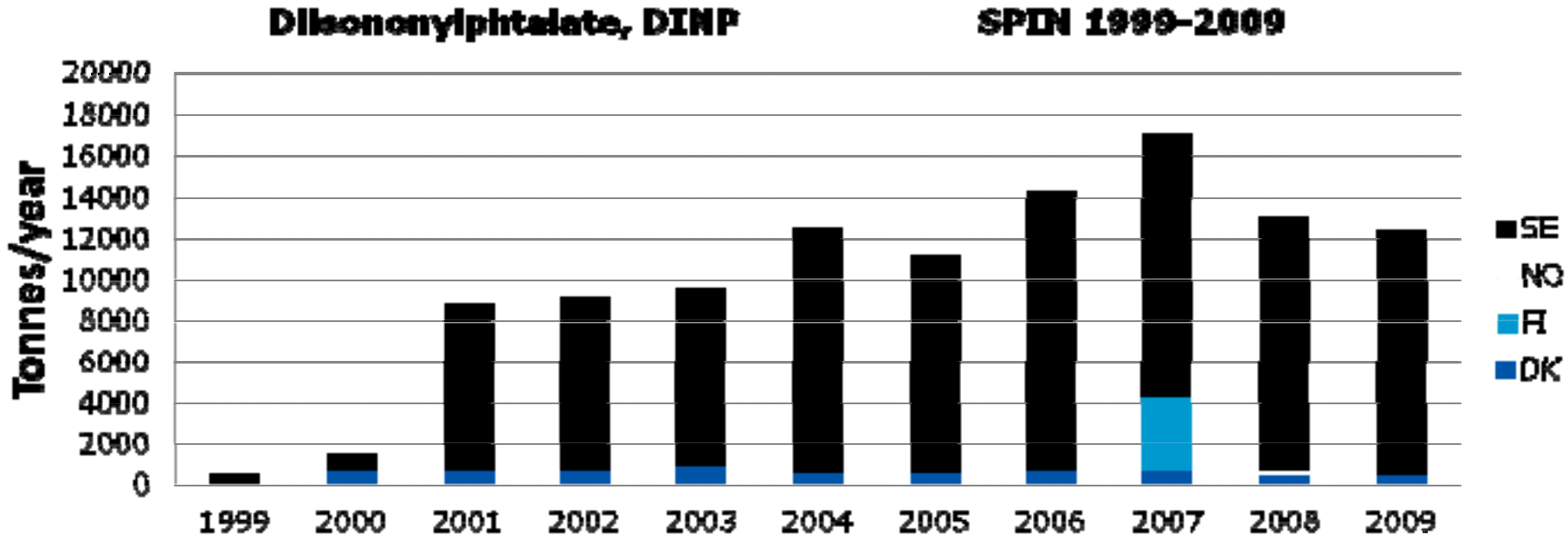
- Azelates have low temp performance superior to adipates
- higher prize
- esters of azelaic acid

Azelate

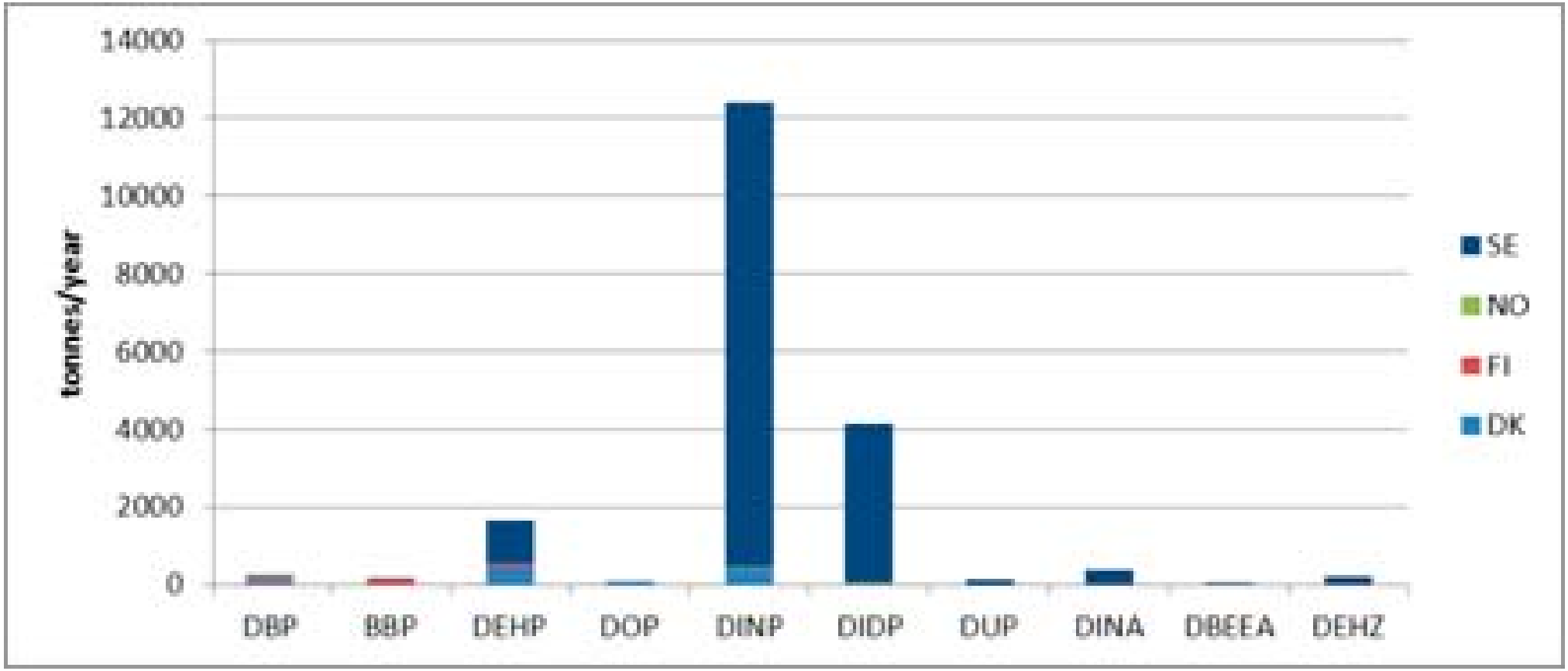
- DEHZ R = R' = 2-ethylhexyl




Di(2-ethylhexyl)phtalate, DEHP SPIN 1999-2009
Tonnes/year
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
SE
NO
FI
DK


Diisononylphtalate, DINP SPIN 1999-2009
Tonnes/year
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
SE
NO
FI
DK

Use of plasticizers in the Nordic countries
according to the SPIN database for the year 2009



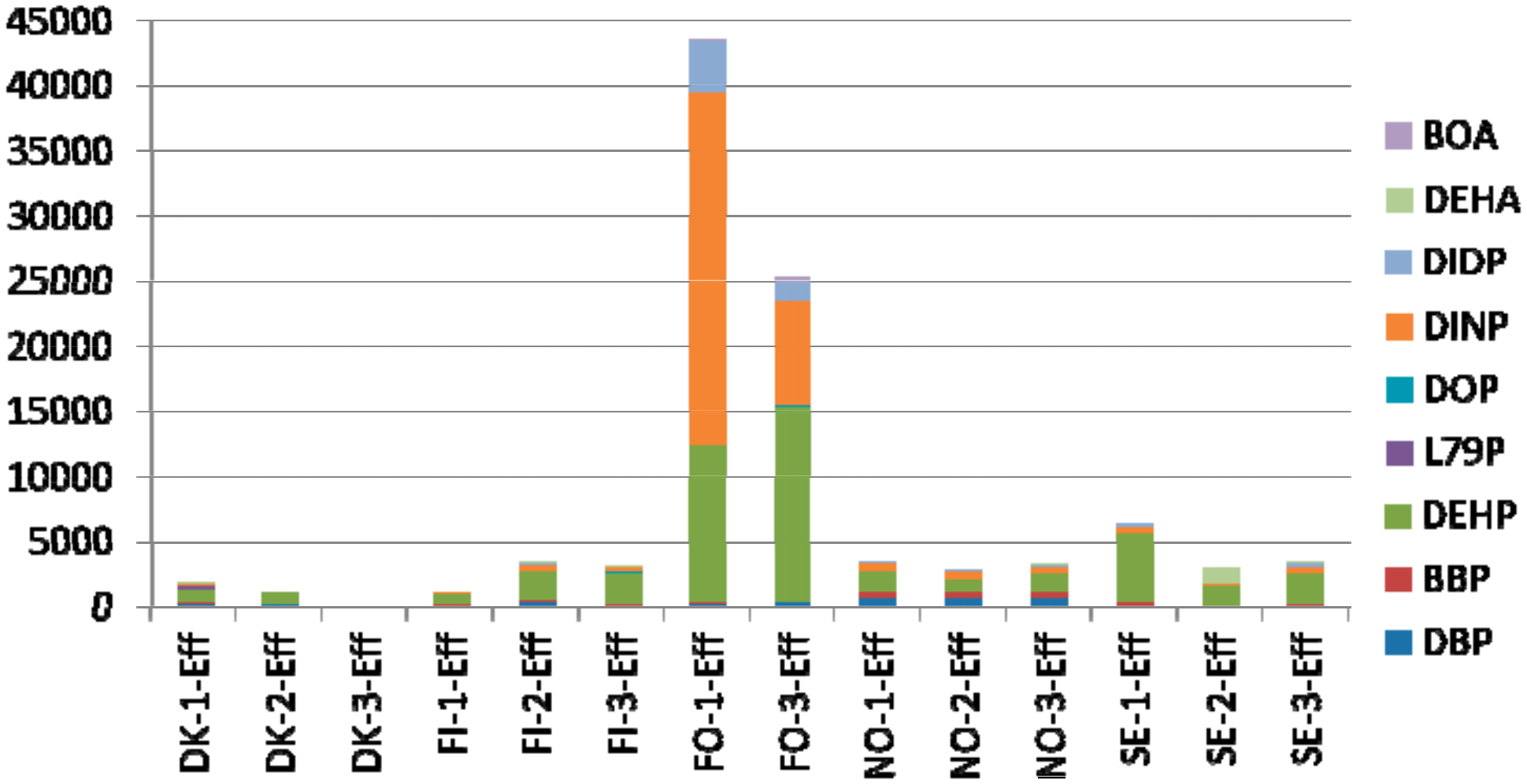
Sample types

- WWTP Effluent water
- WWTP Sludge
- Sediment
- Fish muscle
- Guillemot Eggs

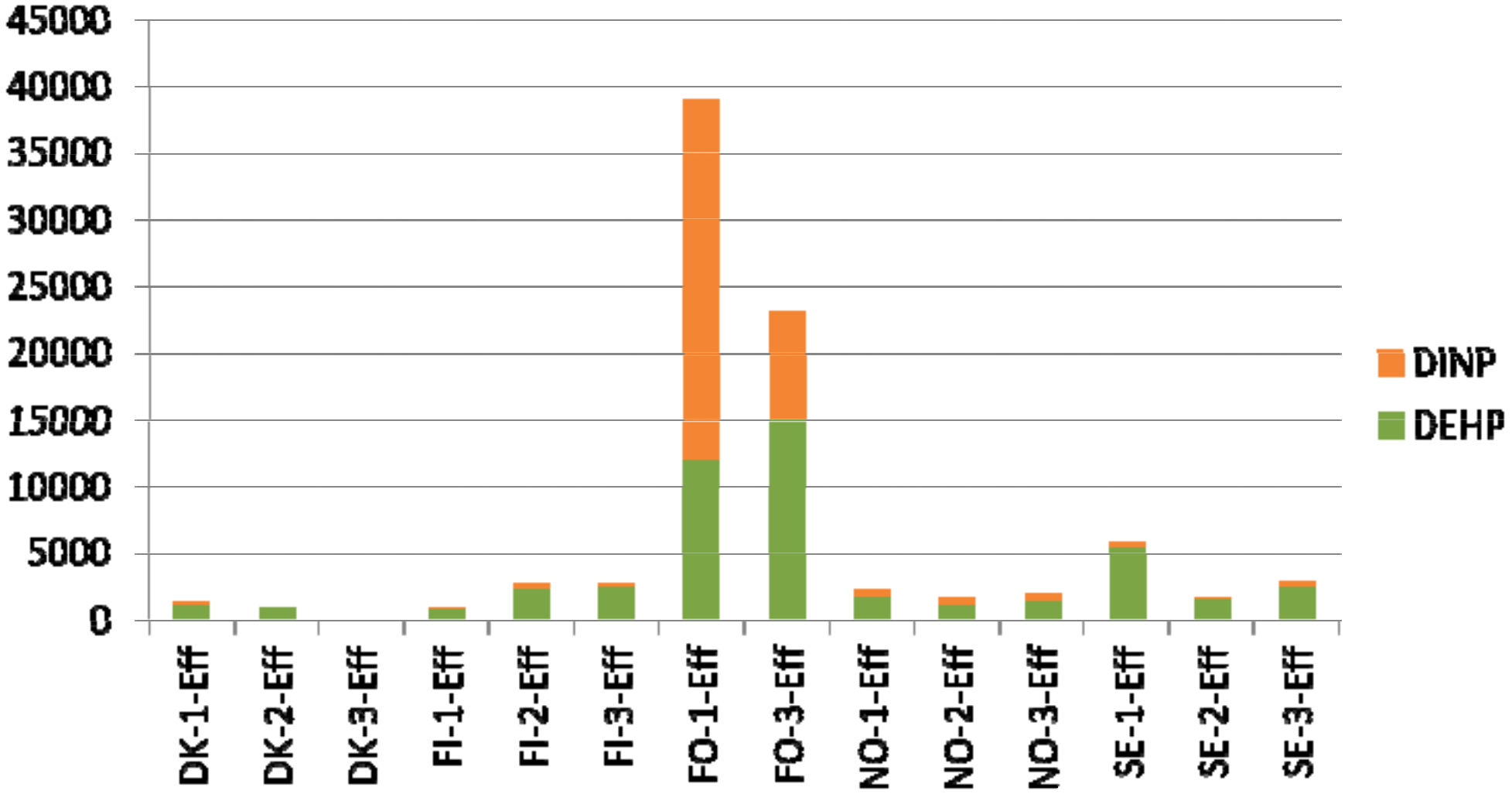
Analysis

- Avoid contamination!
- Glassware wrapped in Al-foil, heat treated (400 deg C)
- Other equipment solvent washed
- Everything kept covered
- Frits in SPE-columns soxlet extracted or exchanged for glass fibre filters
- SPE column washed with MTBE, acetone, MeOH, water
- All bottles of solvents and water checked before use.
- GC-MS-MS system checked
- A lot of laboratory blanks run

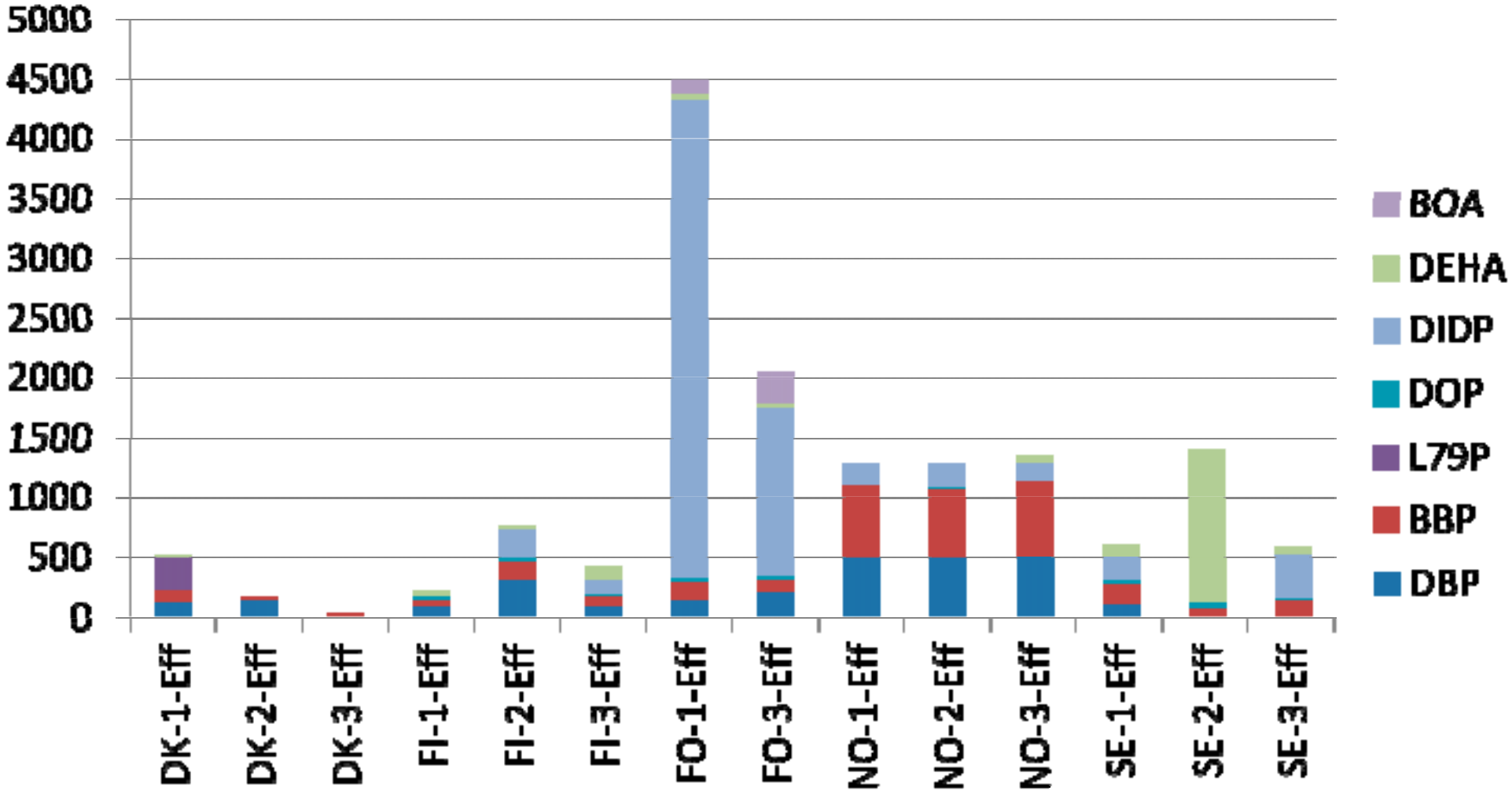
Effluents, ng/l



Effluents, ng/l
DEHP, DINP only



Effluents, ng/l
DEHP, DINP excluded



Toxicity, effluents

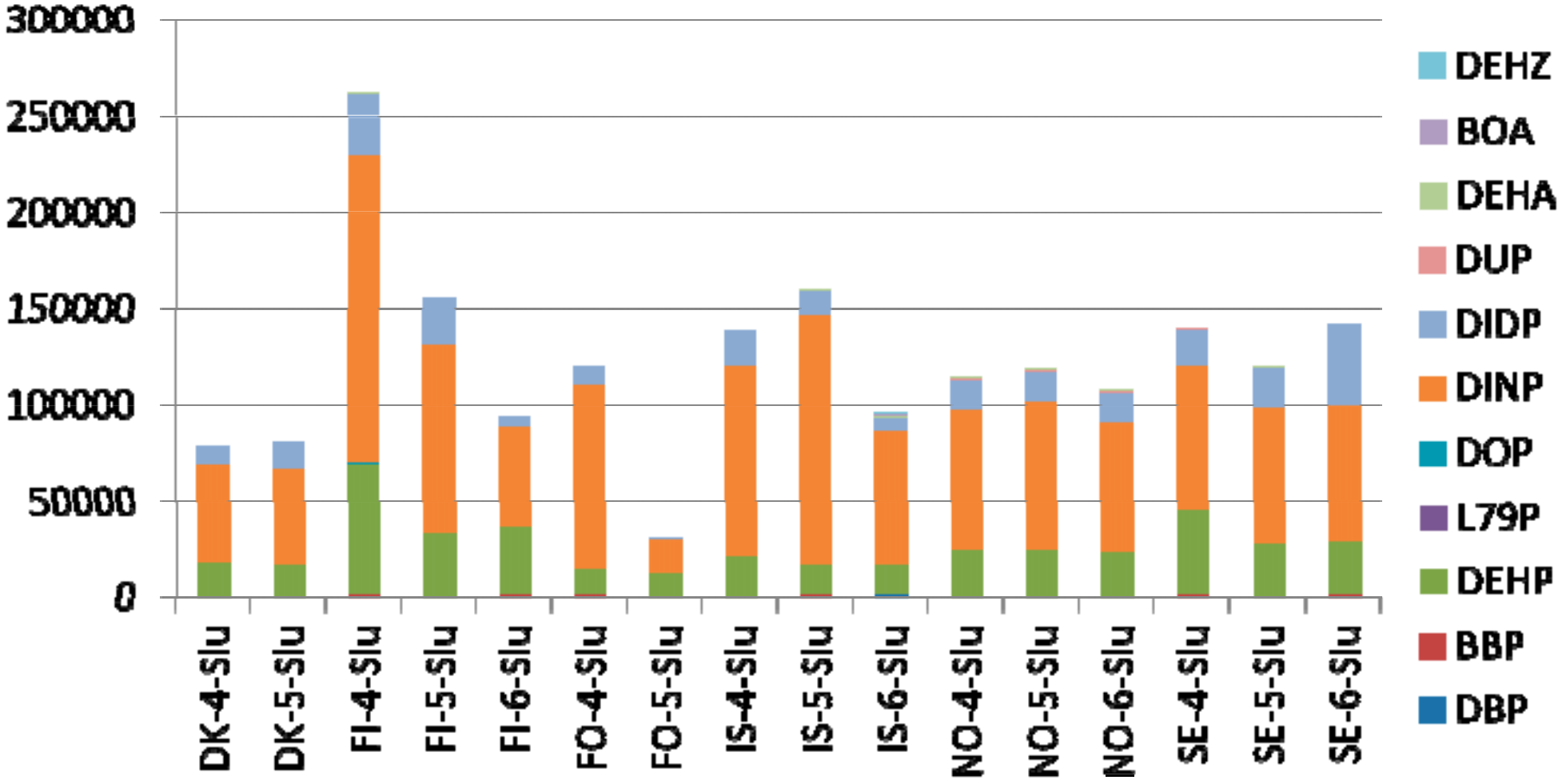
	PNEC, ug/l	Effluent, max, ug/l
DBP	10	0.5
BBP	7.5 (0.75)	0.6
DUP est	4	<0.02
DEHA est	0.5	1.3

With 10 times dilution koncentrations well below PNEC

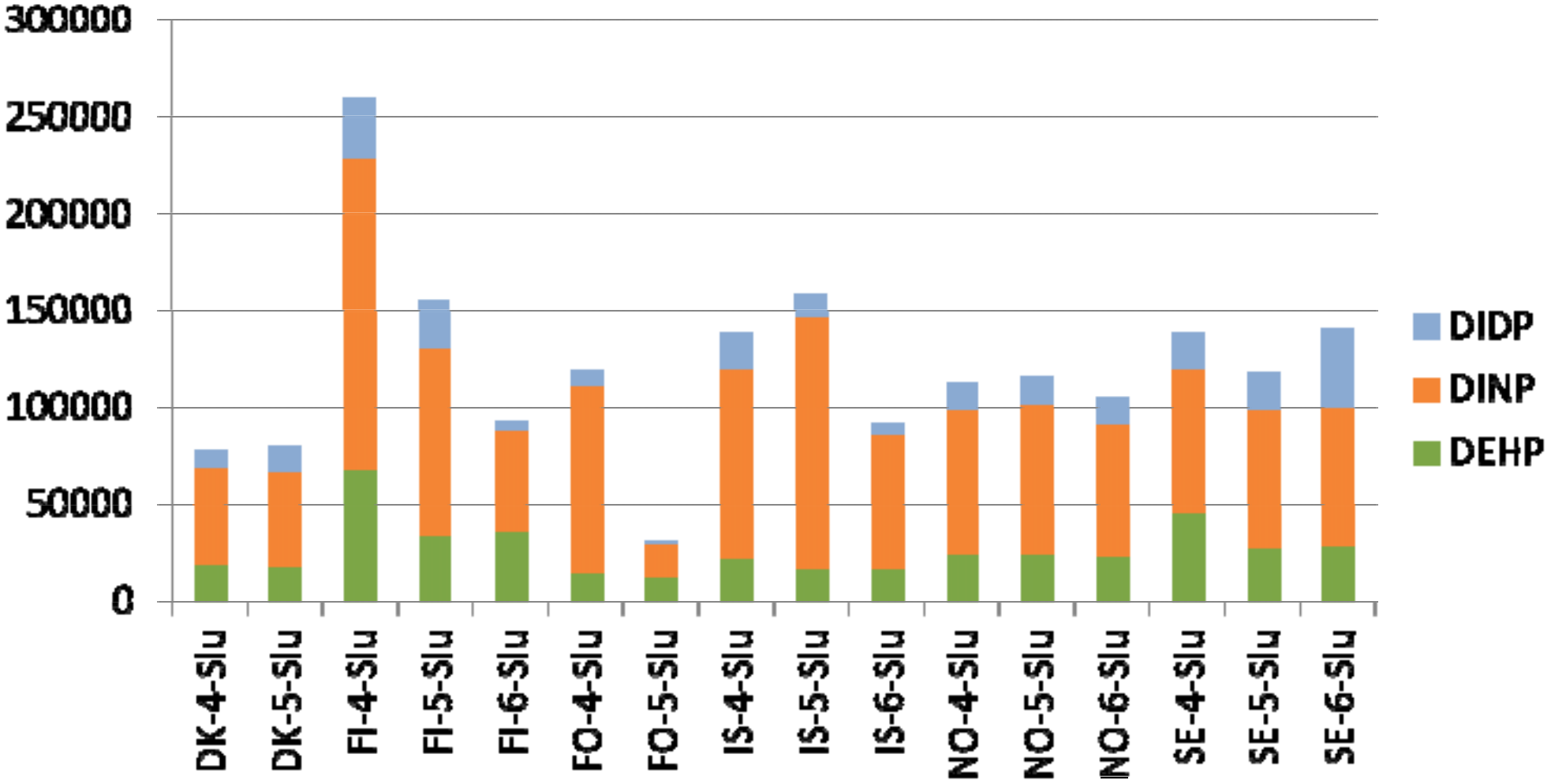
DEHP: PNEC could not be specified, no reliable long-term studies below water solub.

DINP, DIDP: PNEC could not be specified, no toxic effects in long-term tests

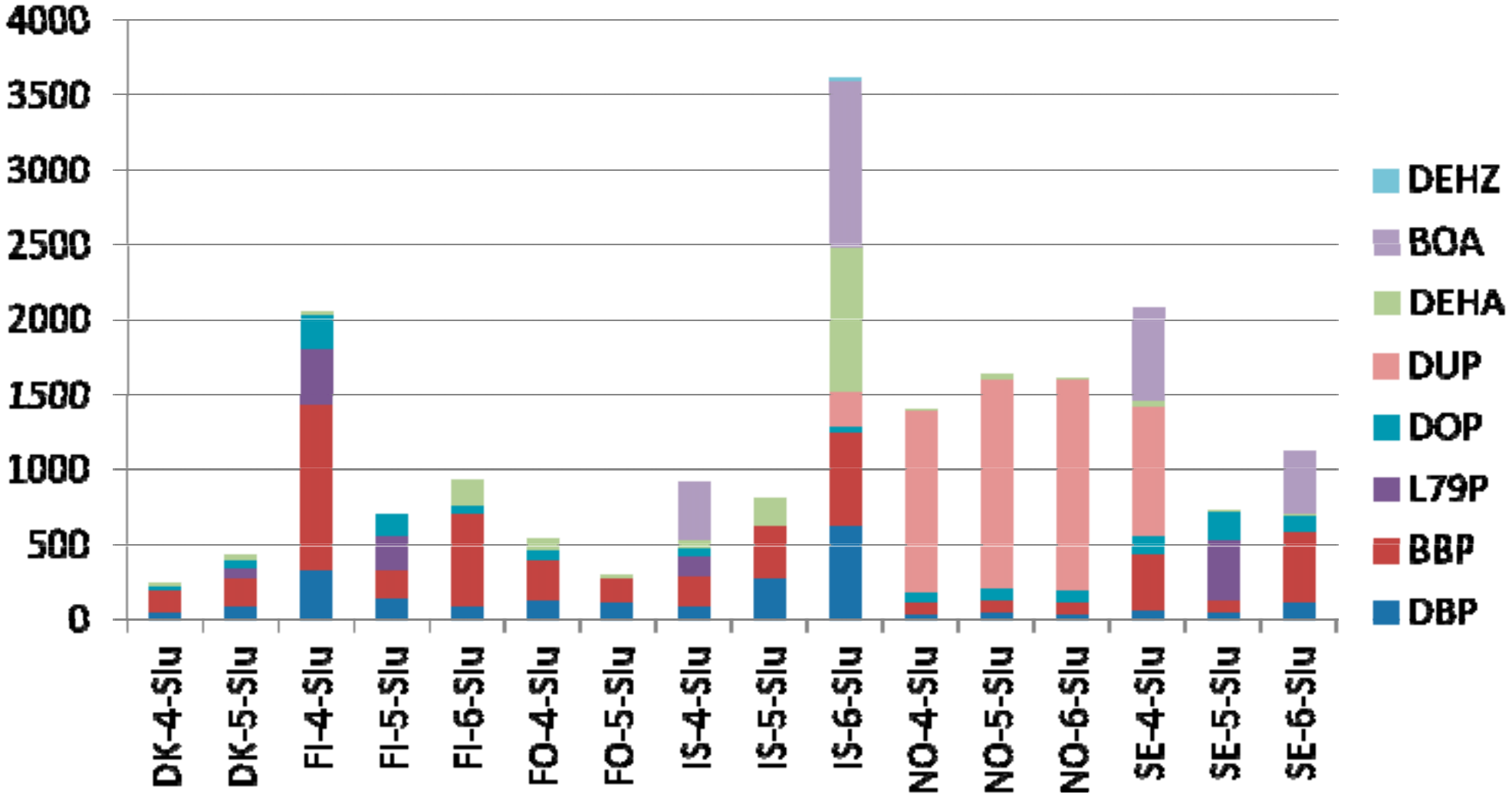
Sludge, µg/kg dw



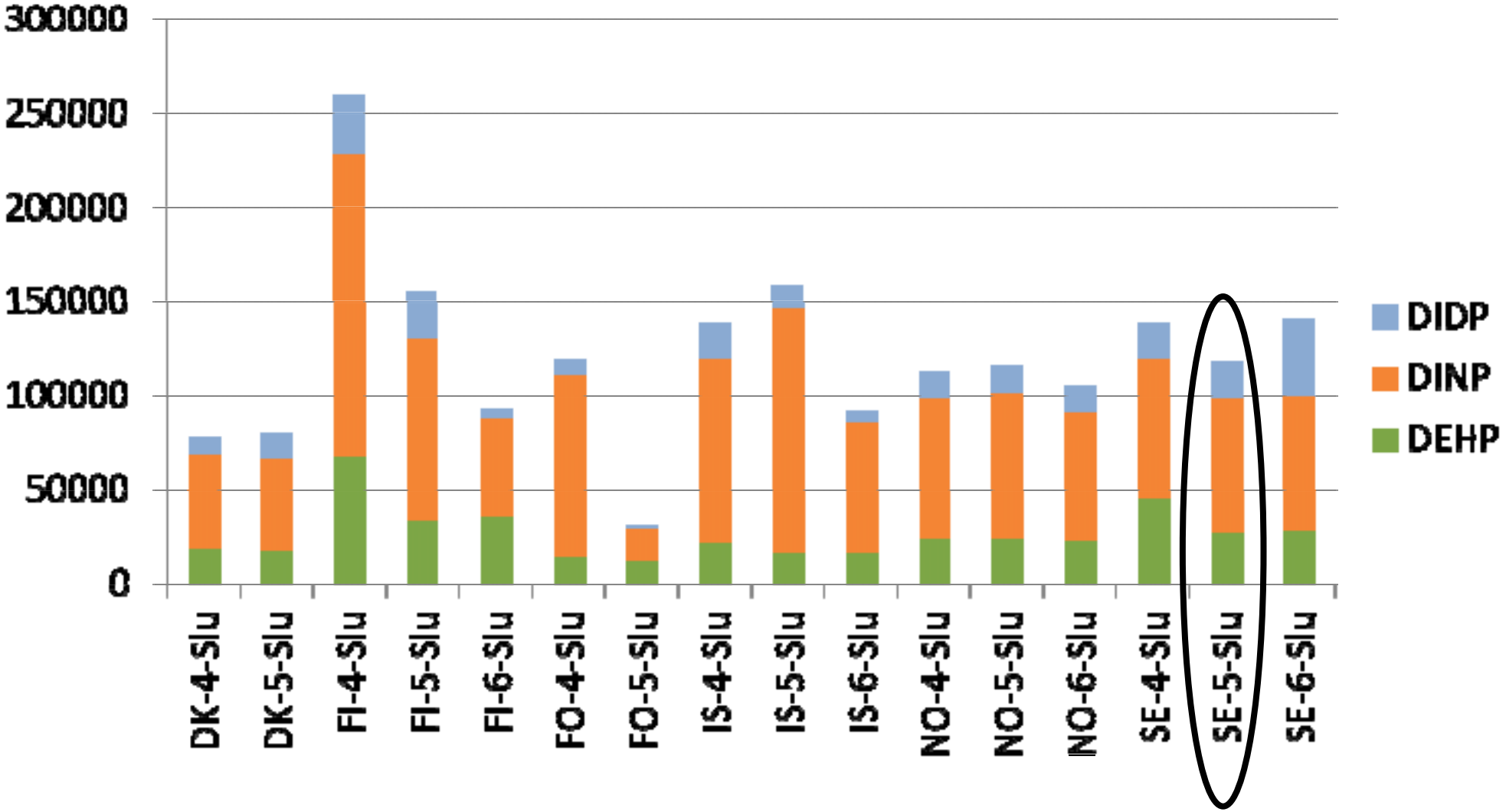
Sludge, µg/kg dw
DEHP, DINP, DIDP only



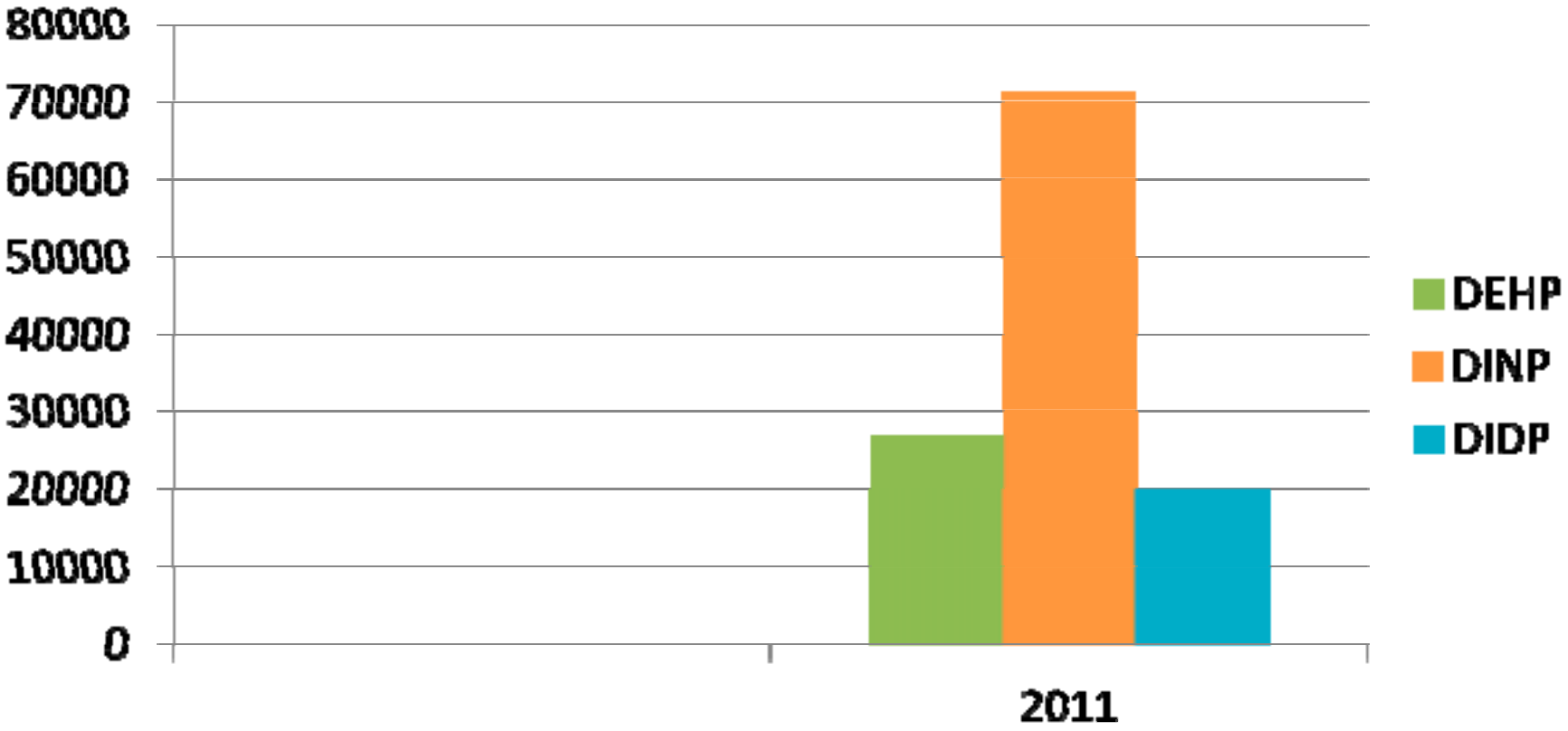
Sludge, µg/kg dw
DEHP, DINP, DIDP excluded



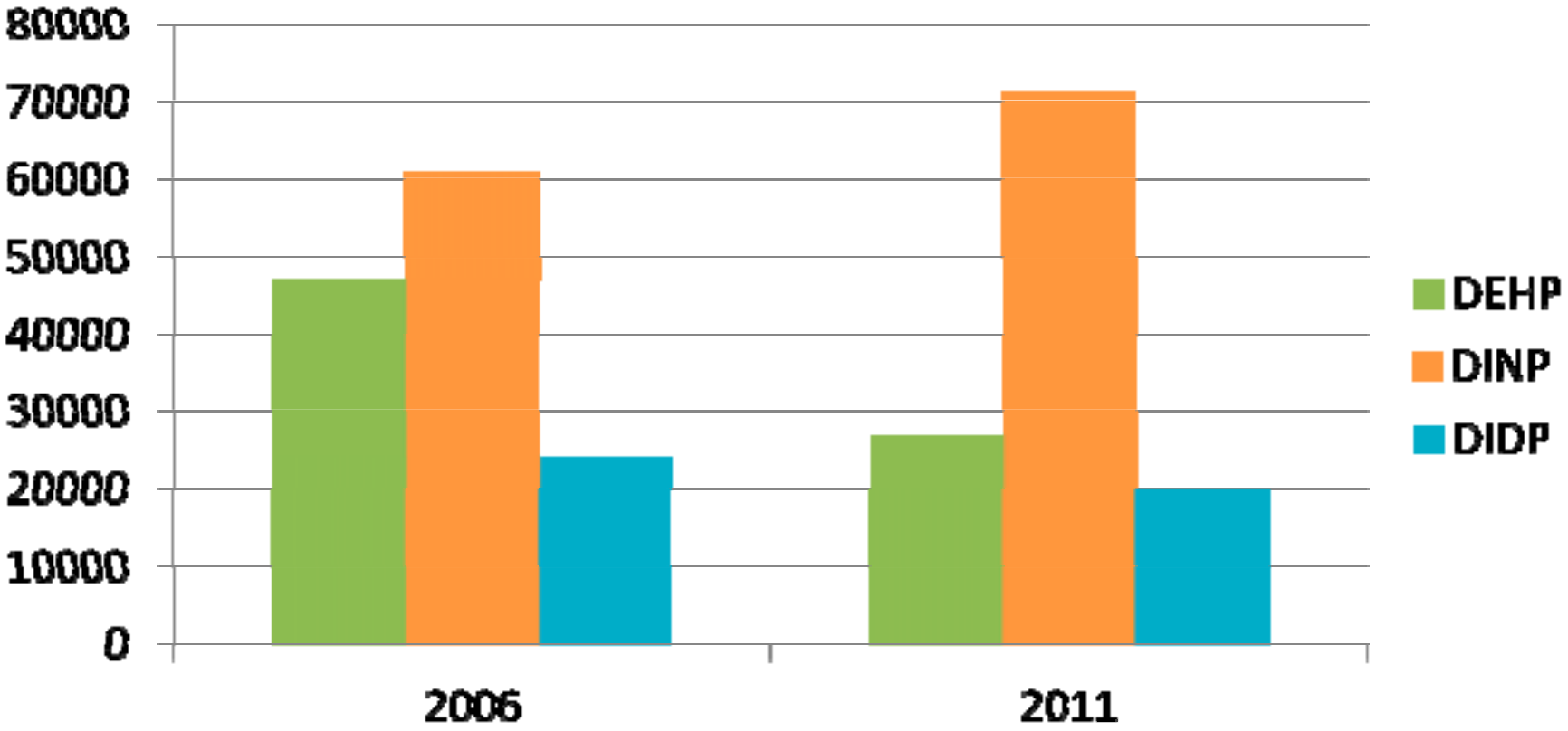
Sludge, µg/kg dw
DEHP, DINP, DIDP only



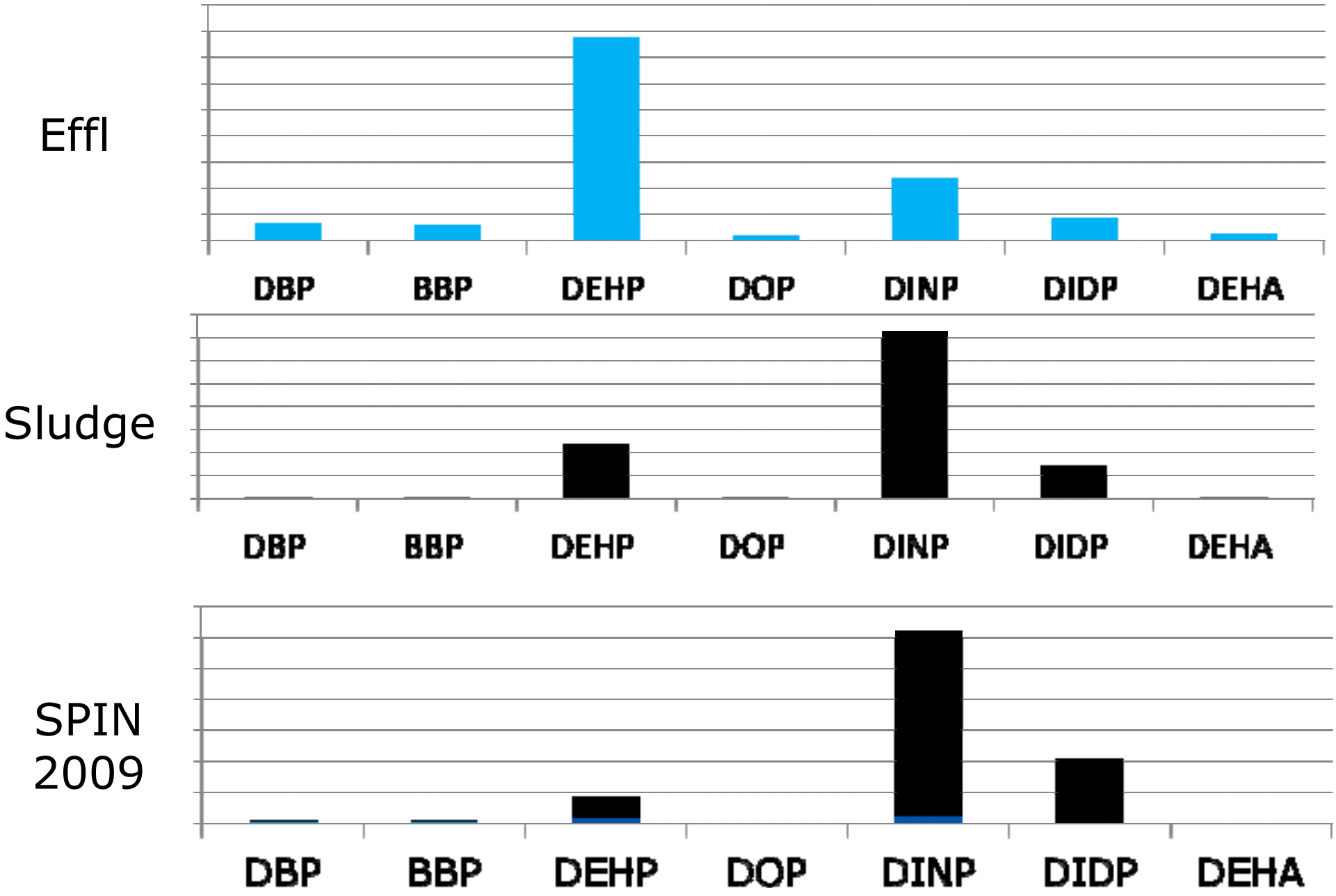
Sludge, µg/kg dw
Ryaverken, Göteborg



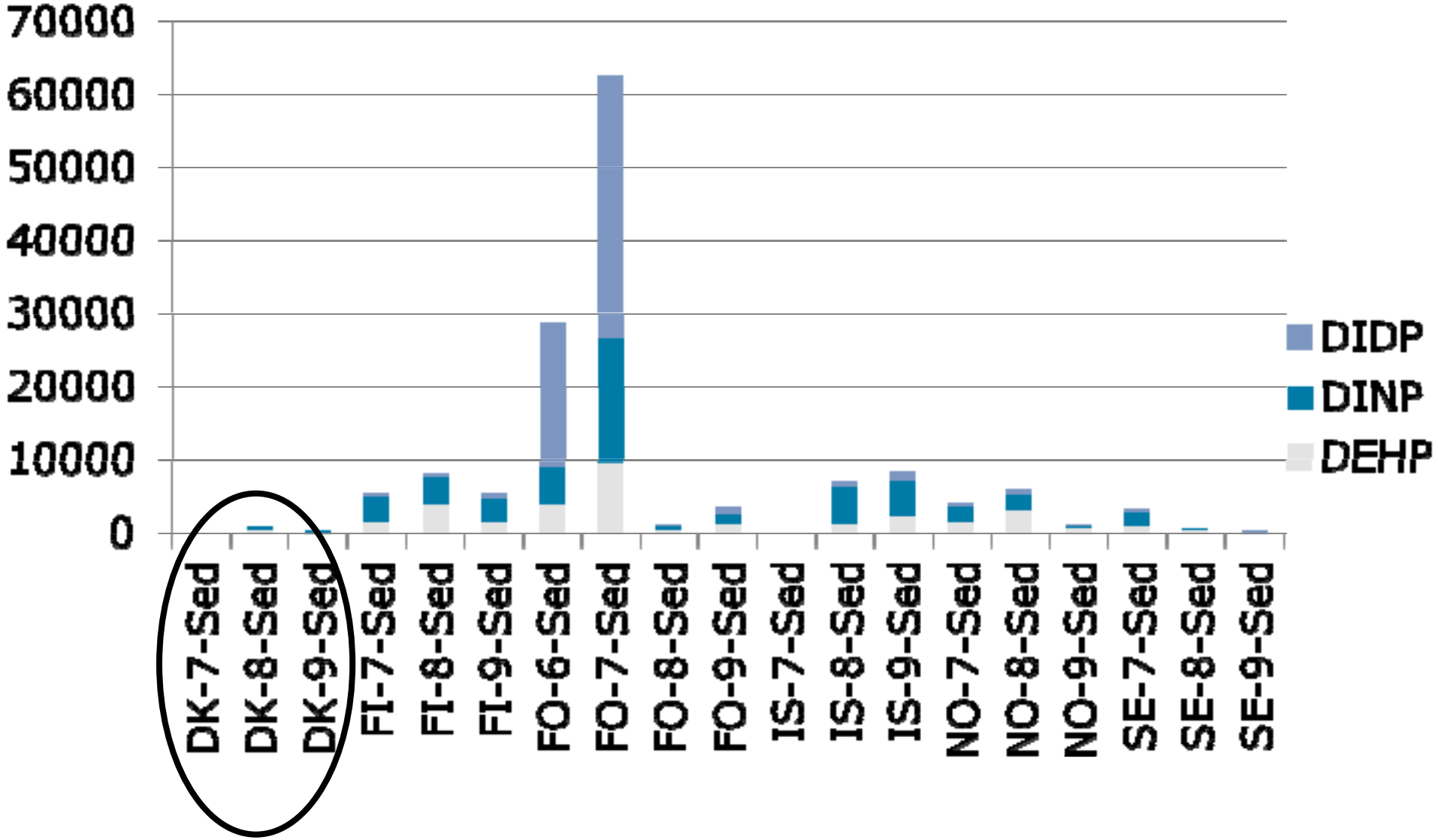
Sludge, µg/kg dw
Ryaverken, Göteborg



-17% +3% -3% / year


Effl
DBP
BBP
DEHP
DOP
DINP
DIDP
DEHA
Sludge
DBP
BBP
DEHP
DOP
DINP
DIDP
DEHA
SPIN
2009
DBP
BBP
DEHP
DOP
DINP
DIDP
DEHA

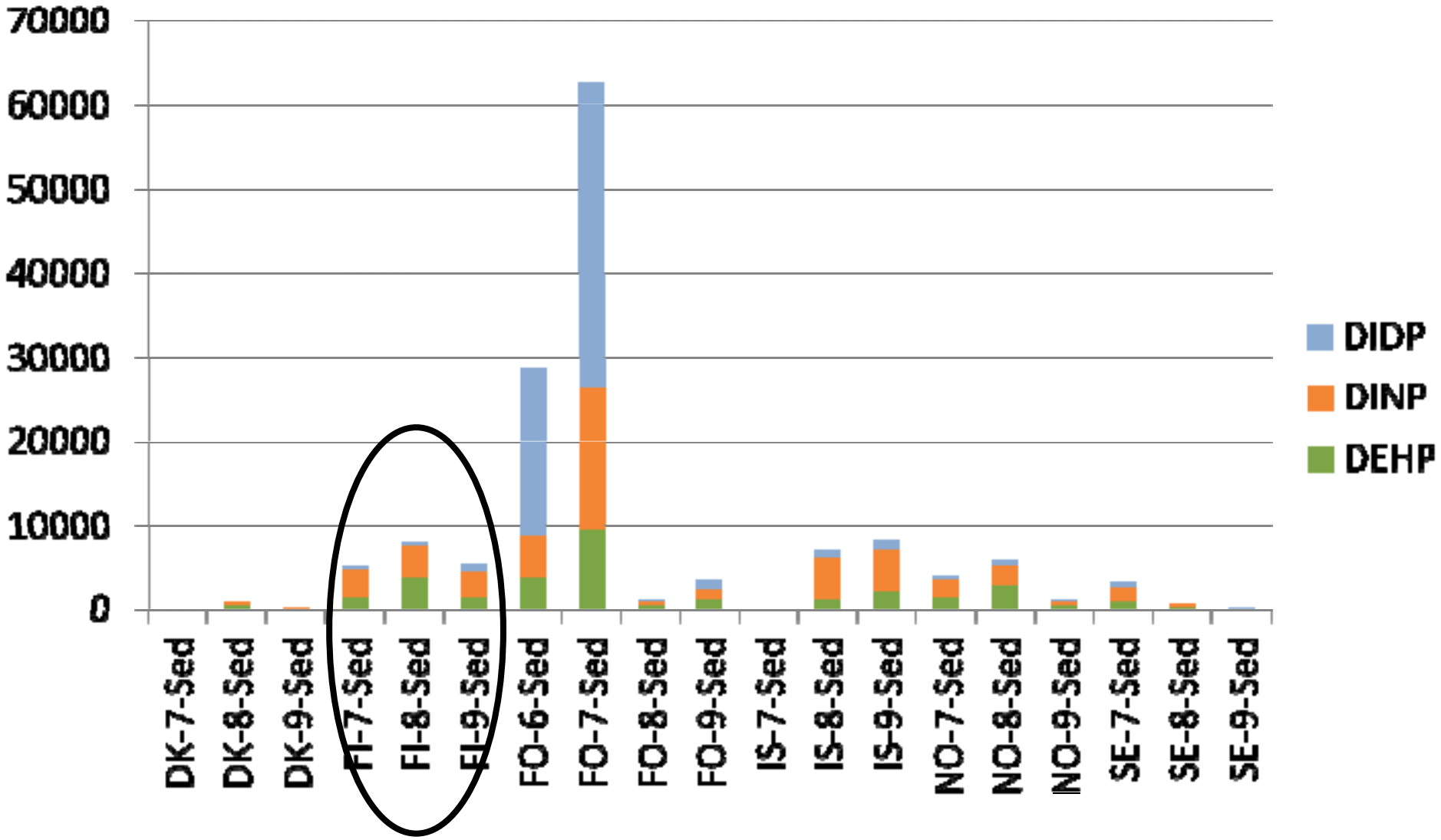
Sediment, µg/kg dw
DEHP, DINP, DIDP only



Sample type

- Effluent
- Fish, muscle
- Sediment
- Sludge

Sediment, µg/kg dw
DEHP, DINP, DIDP only



Sample type

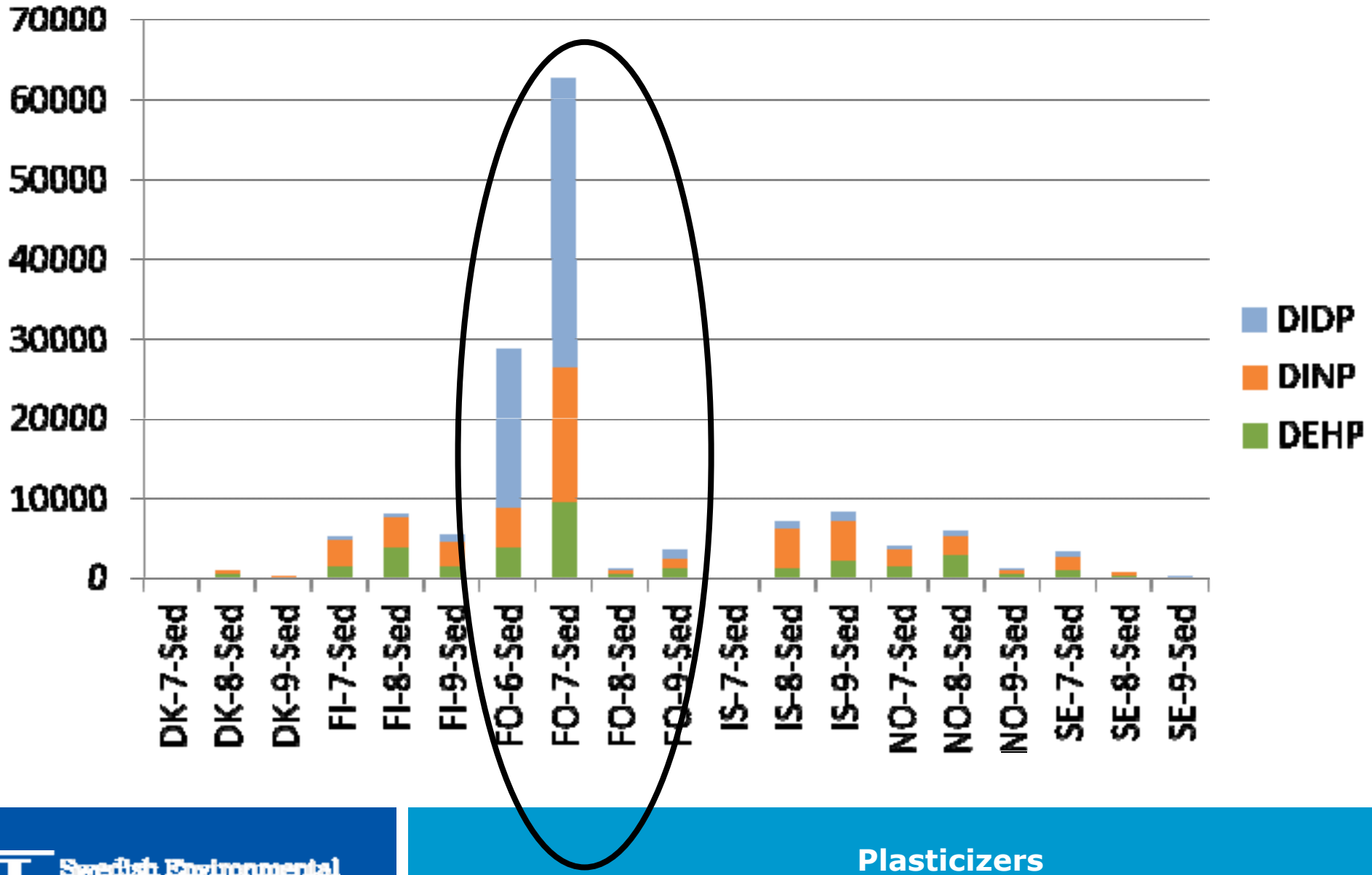
- Effluent
- Fish, muscle
- Sediment
- Sludge

Swedish Environmental Research Institute

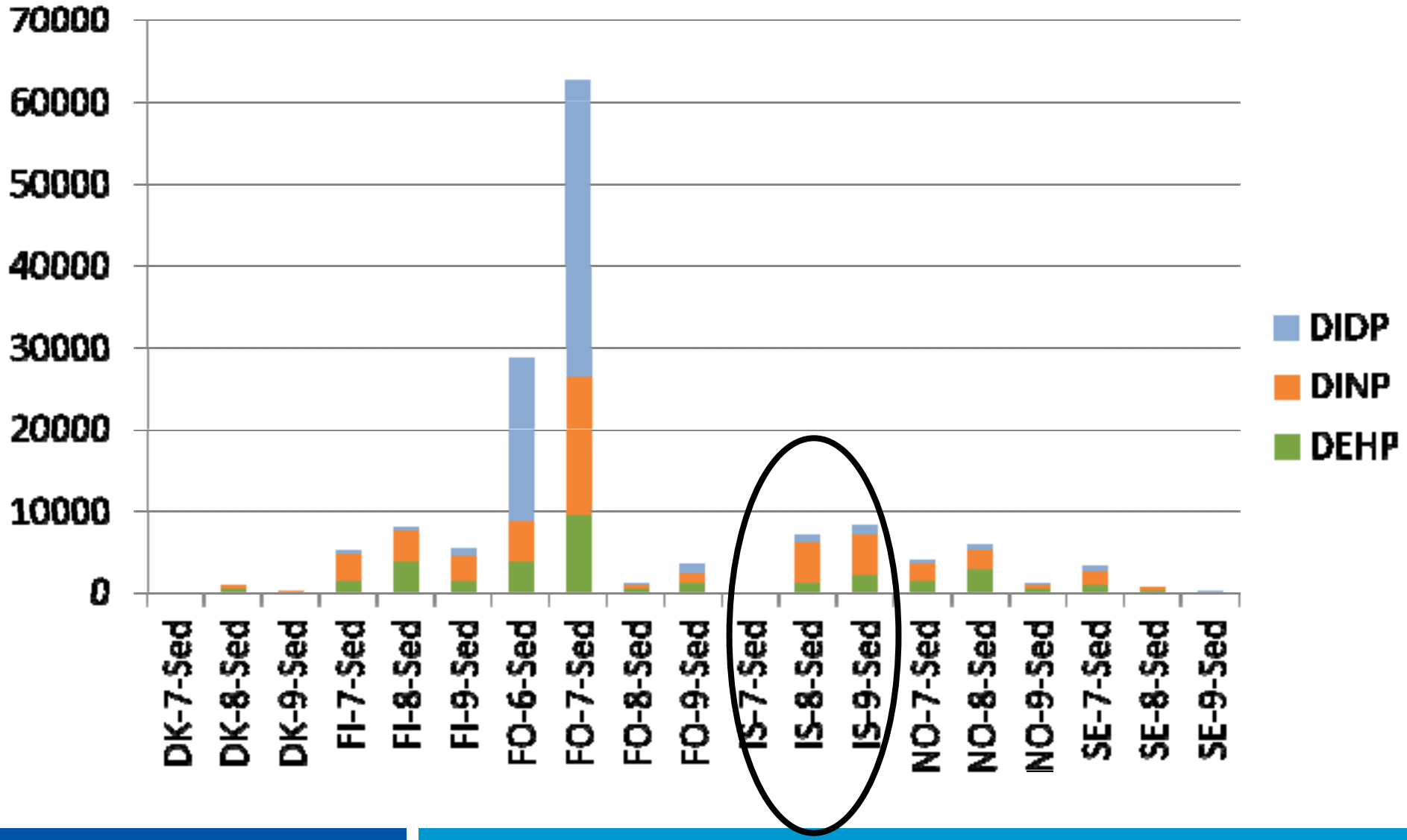
Plasticizers

Lennart Kaj, 2012-05-07

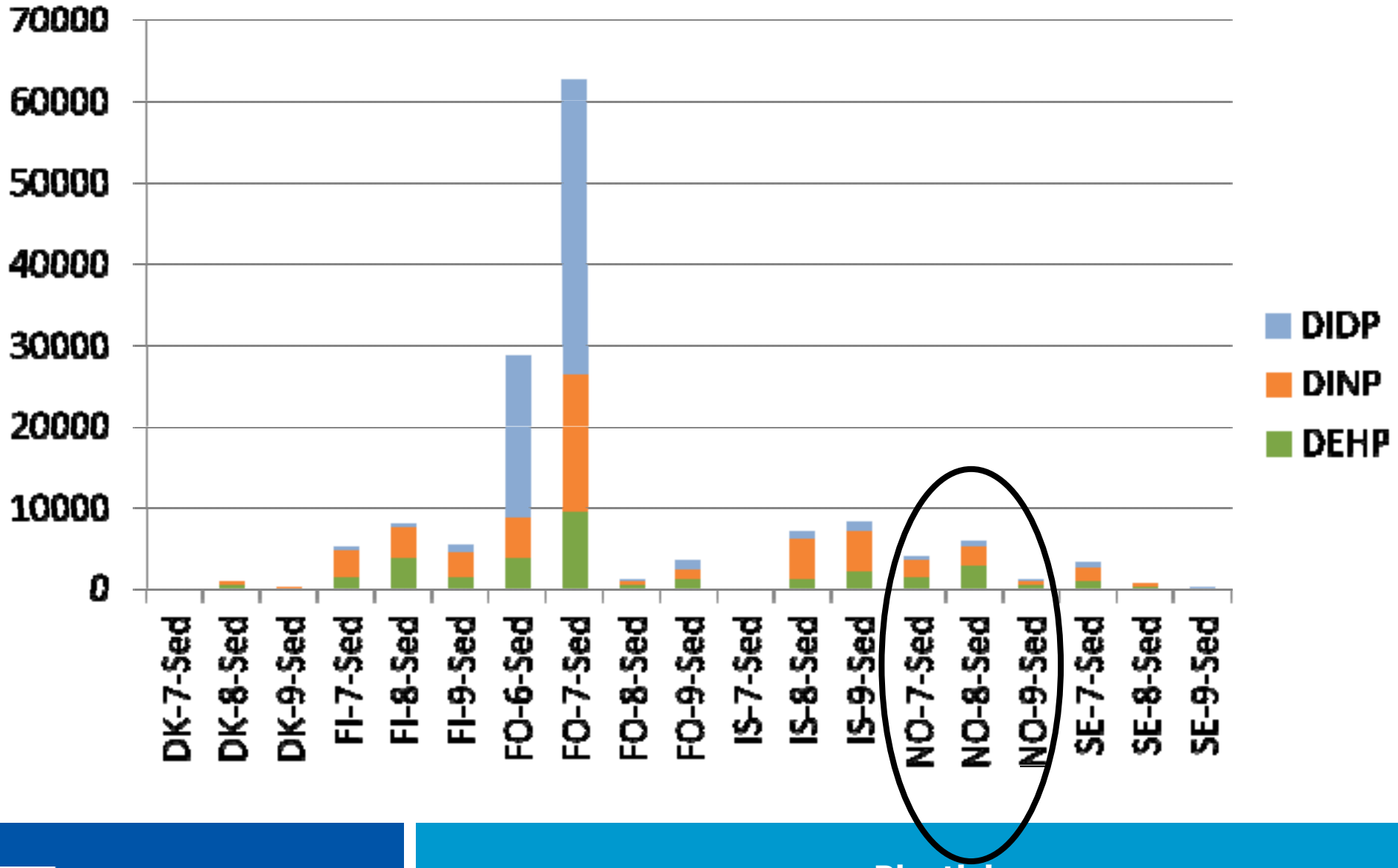
Sediment, µg/kg dw
DEHP, DINP, DIDP only



Sediment, µg/kg dw
DEHP, DINP, DIDP only

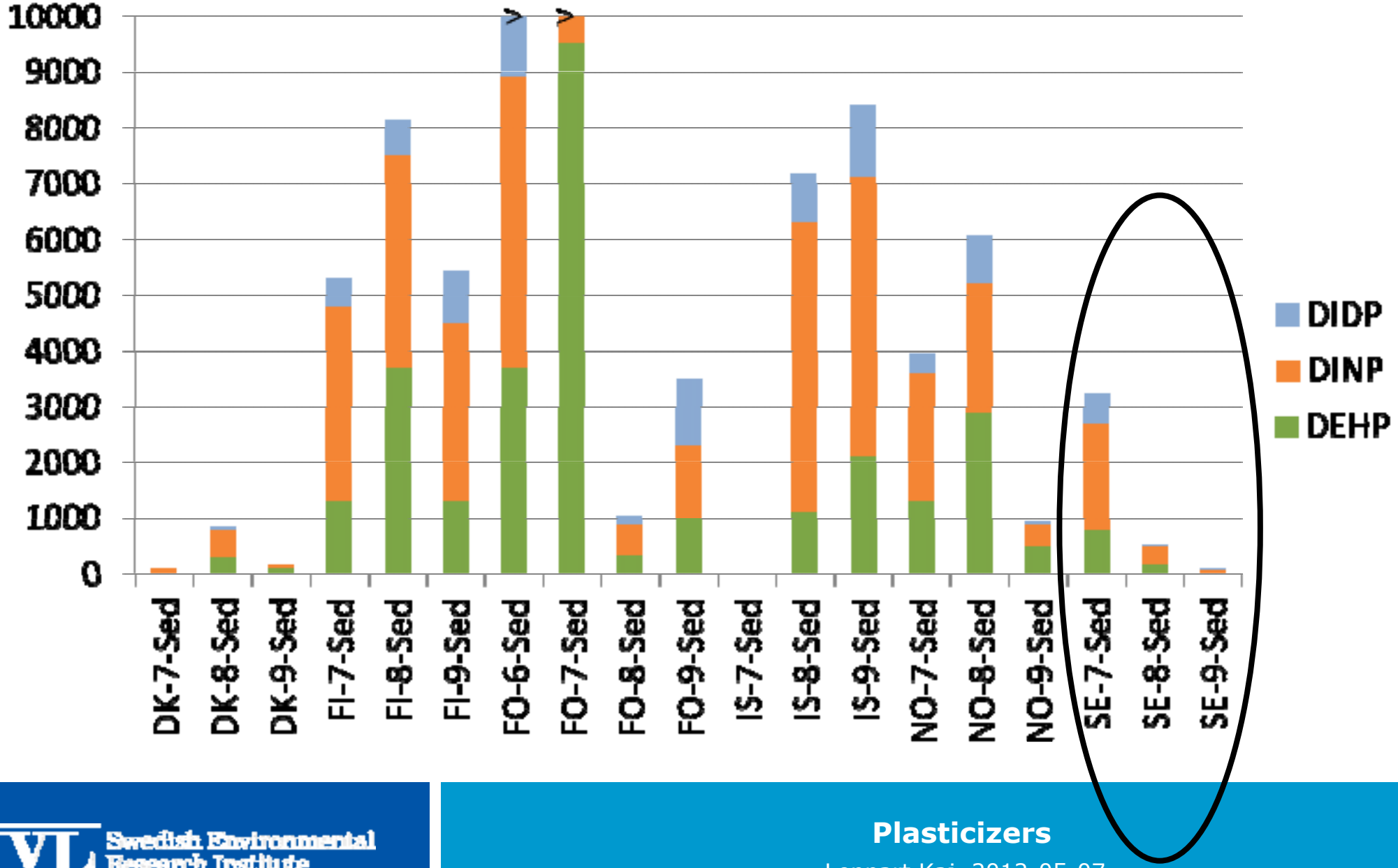


Sediment, µg/kg dw
DEHP, DINP, DIDP only

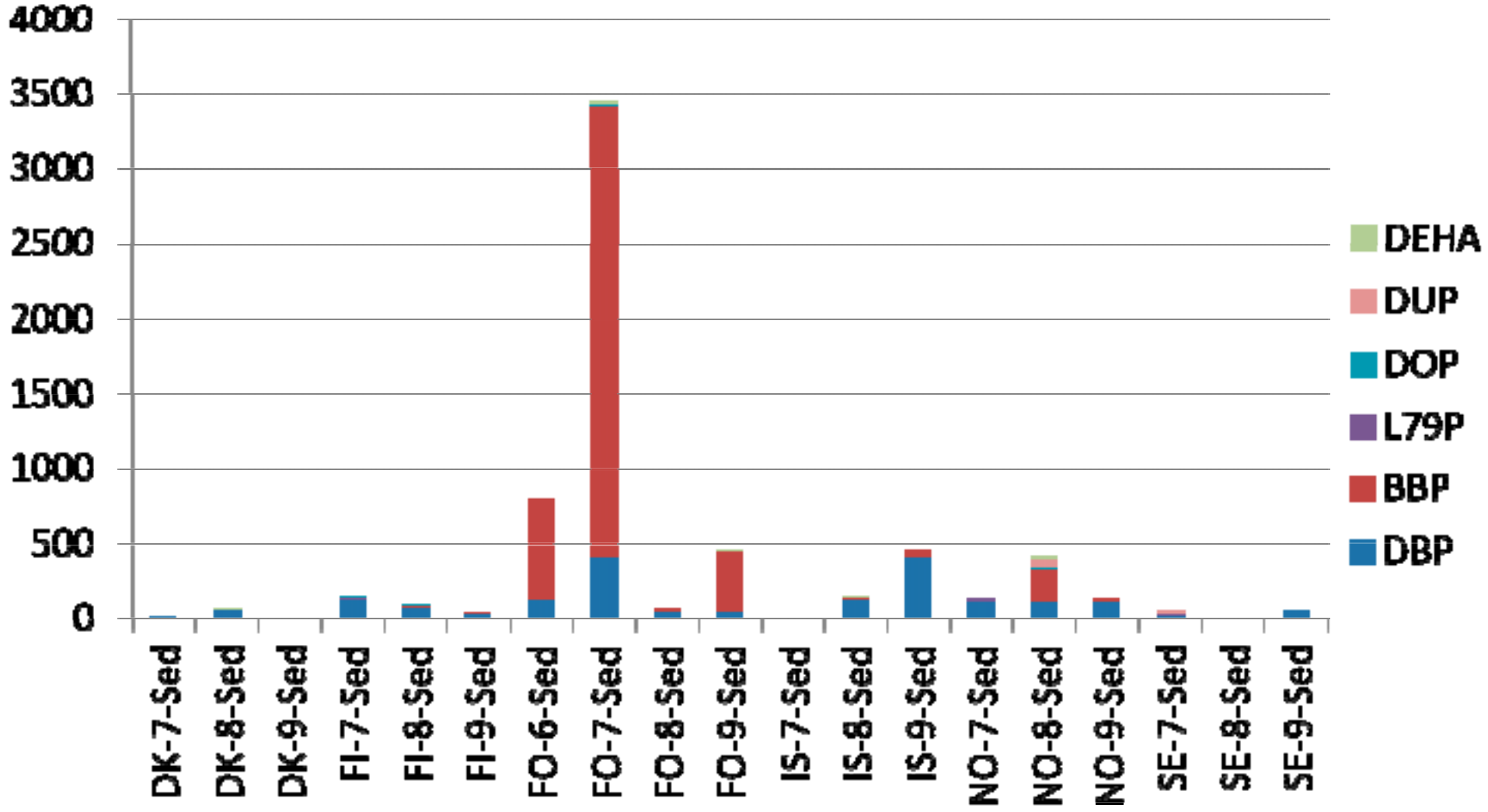


Sediment, µg/kg dw

DEHP, DINP, DIDP only, y-axis expanded



Sediment, µg/kg dw
DEHP, DINP, DIDP excluded

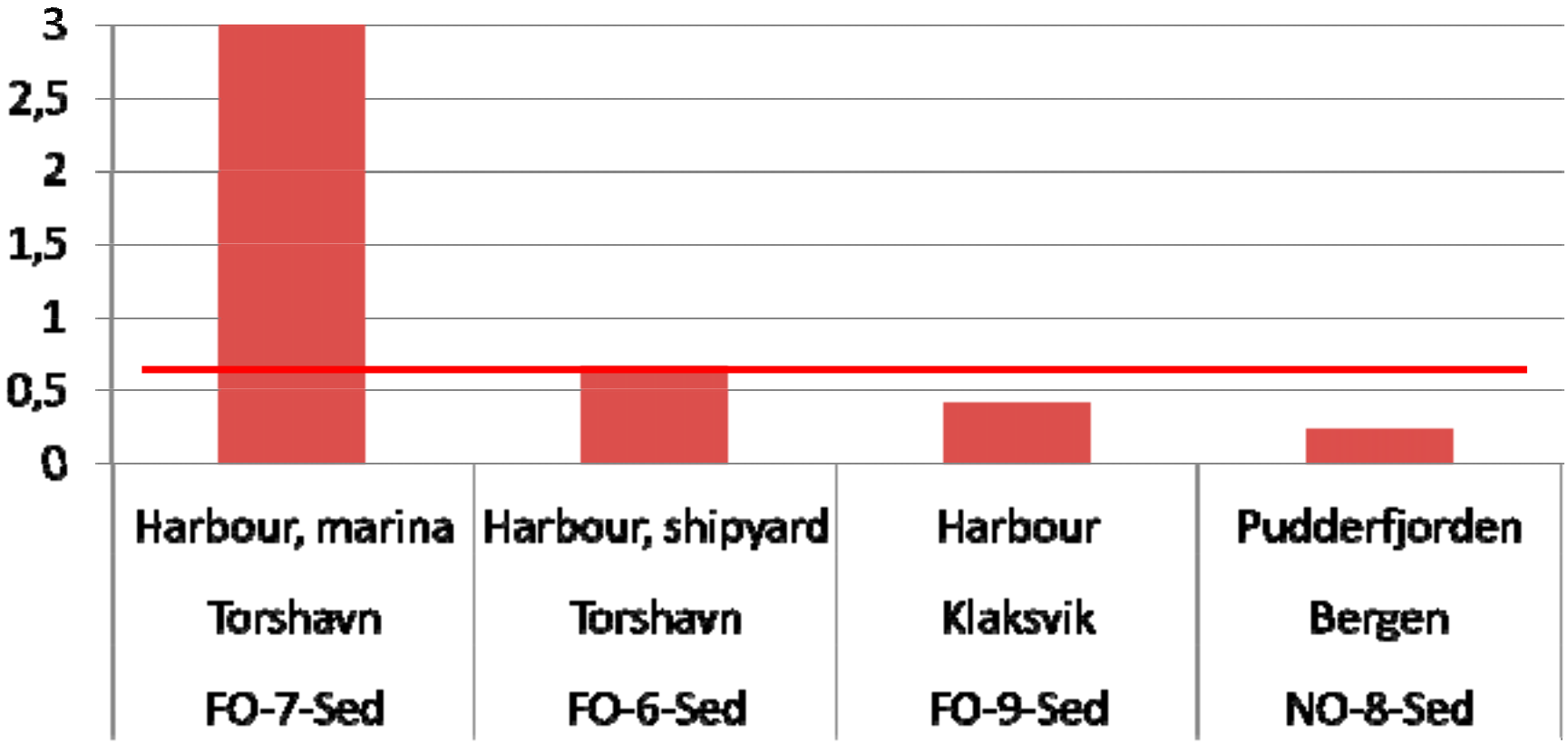


Toxicity, sediments

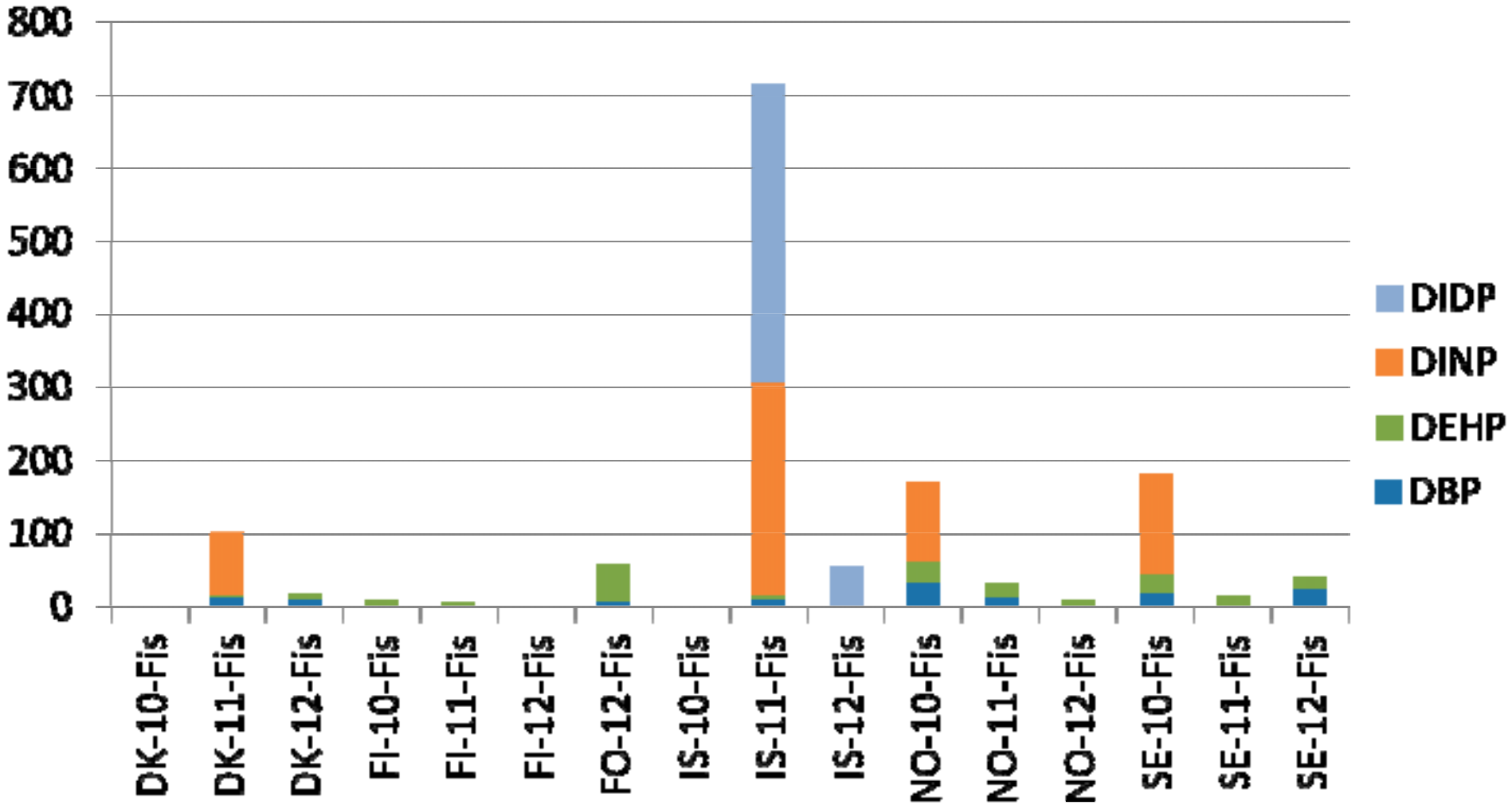
		PNEC	Sediment, max
DBP	mg/kg dw	3.1	0.4
BBP	mg/kg ww	1.7 (0.17)	1
DEHP	mg/kg dw	>100	9.5
DUP est	mg/kg dw	5000	0.06
DEHA est	mg/kg dw	0.7	0.027

DEHP: 1 mg/kg dw may affect microbial processes

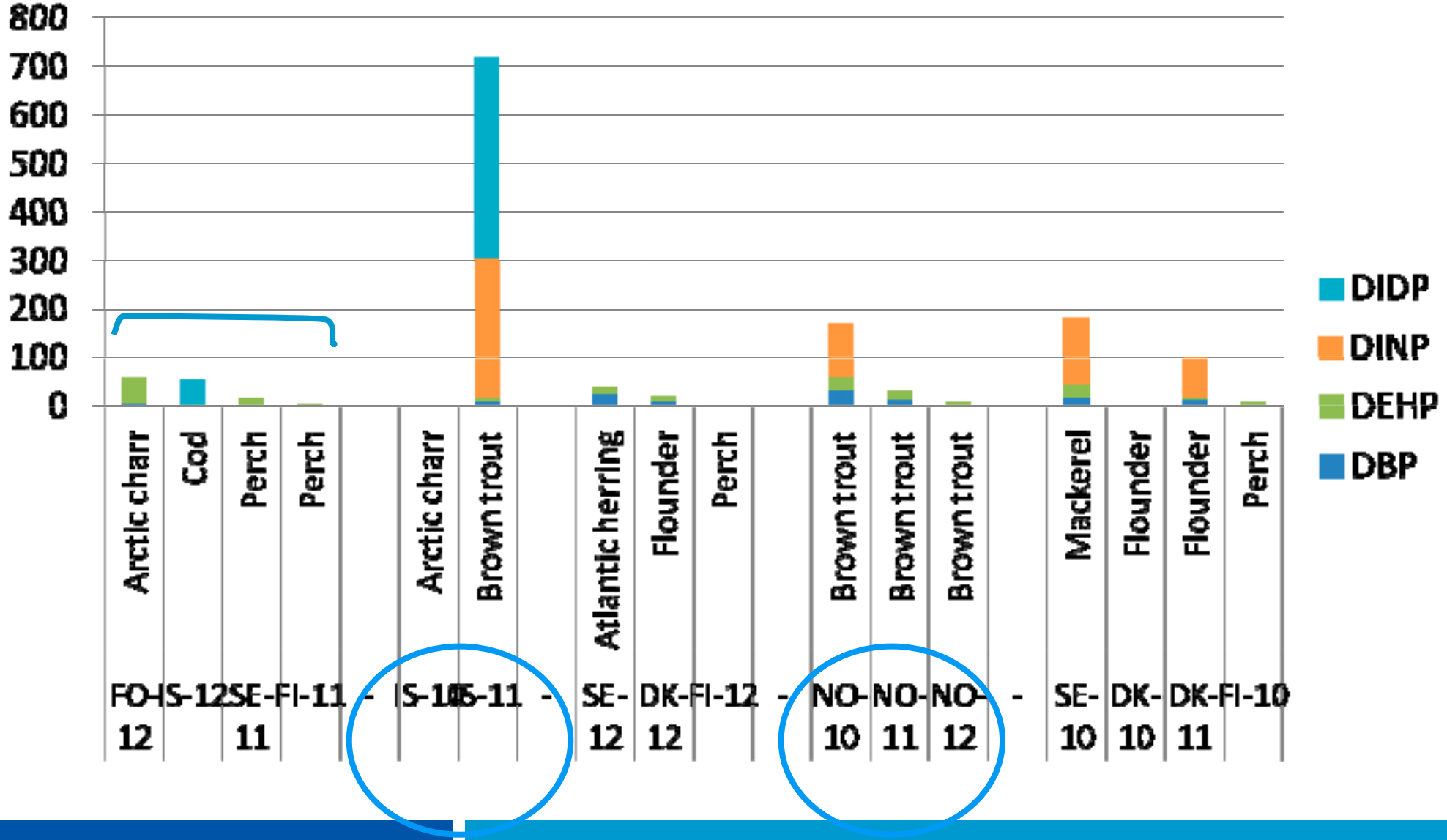
Sediment, BBP, mg/kg dw



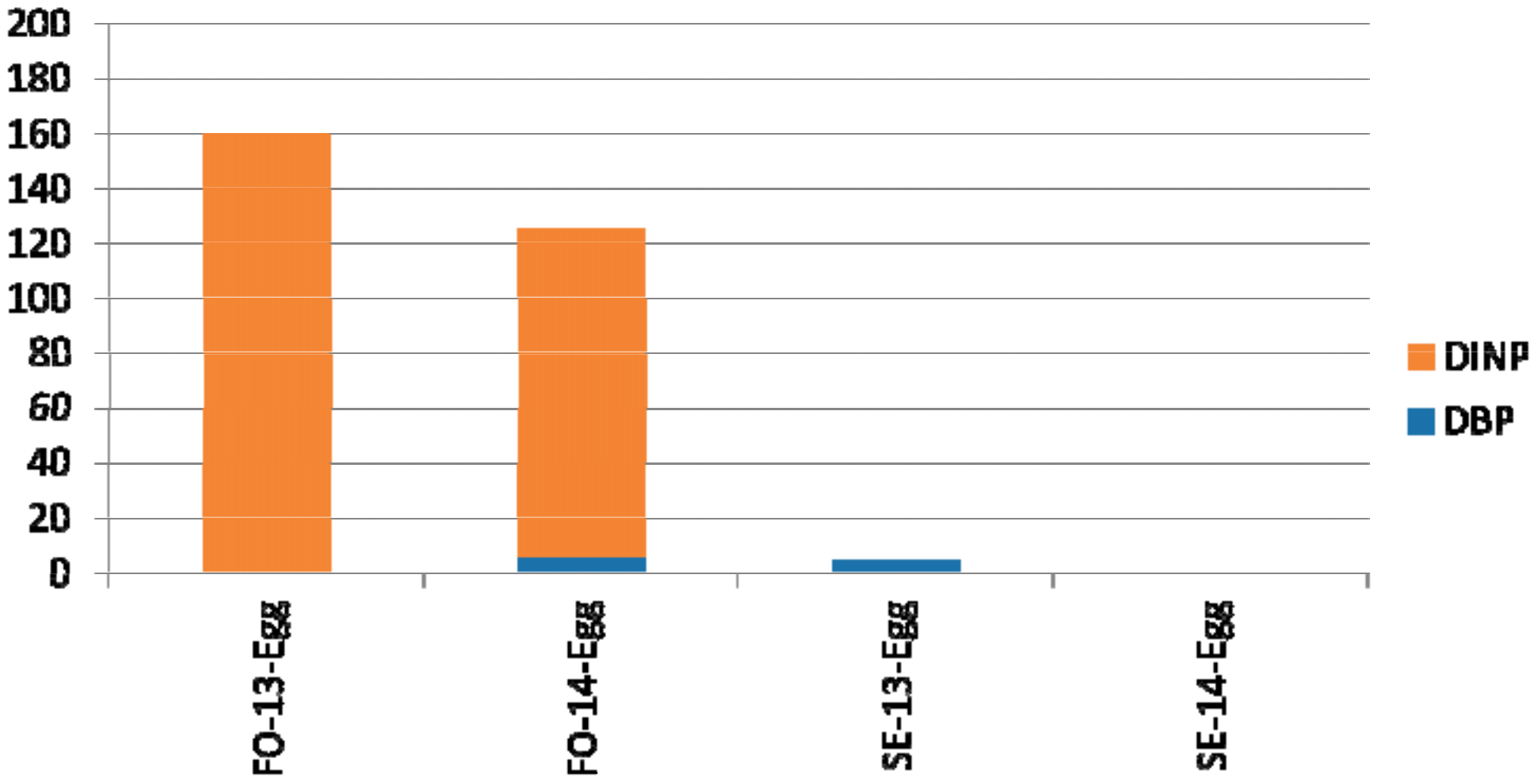
Fish muscle, µg/kg fw



Fish muscle, µg/kg fw



Eggs, Guillemot, µg/kg fw



Sweeteners

- Aspartam
- Cyclamate
- Sucralose

- Effluents
- Sludges (selection of)