Non target analysis of WWTP effluent water

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Chemical and biological monitoring of sewage effluent water (IVL B1897)

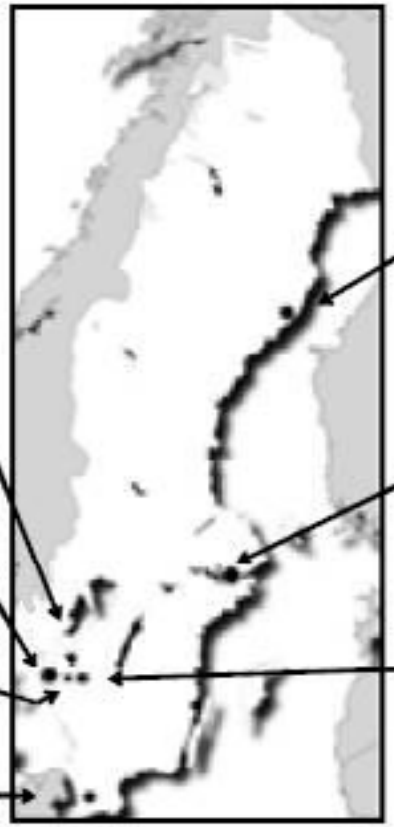
- Aim:
  - generate a frame for development of a national monitoring program of chemicals in WWTP effluents.
  - Chemical characterisation
  - Biological effects (hormones)

Chemical characterisation

– Trace analysis: 12 groups of chemicals (quantification)

– Non target analysis (identification)

The position of the WWTP



Från Haglund & Olofsson 2006

Targeted analytes

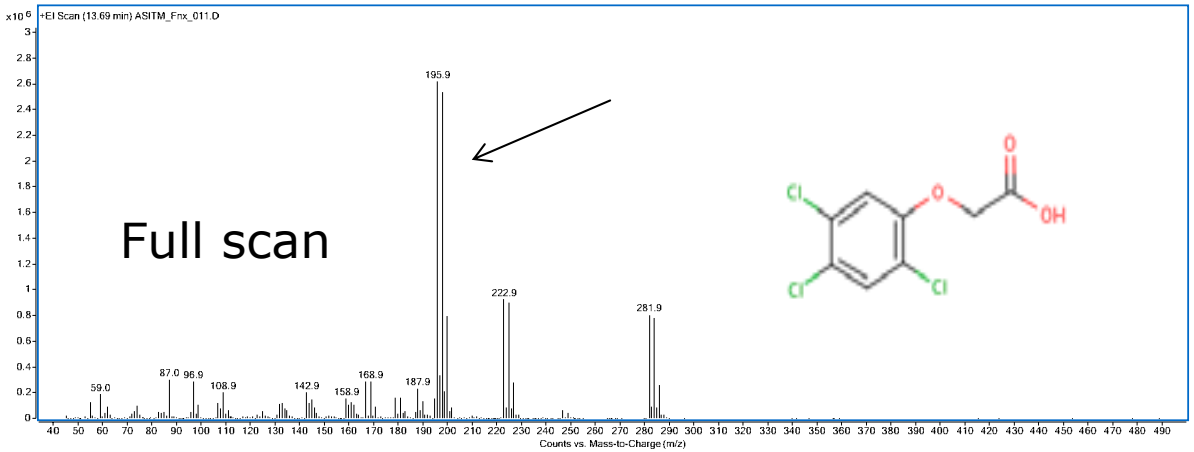
Group of chemicals	Compounds included	Comment
Organdi Sn-compounds	MBT, DBT, TBT, MPhT, DPhT, TPhT	Included in WFD, partial in sludge monitoring program
BFRs	Bromenated diphenylethers, HBCDD	WFD and sludge monitoring program
Phenolic compounds	4-Nonylphenol, 4-t-Oktylphenol, Triclosan, Bisphenol A	Included in WFD, Detected in screening program and sludge monitoring program
Herbicides	Gluphosate, MCPA	Proposal for WFD
Metals	Hg, Cd, Pb, Ag, As, Cu	Partial in WFD, sludge monitoring program
NSAIDs	Ibuprofen, Naproxen, Ketoprofen, Diclofenac	Detected in screening program
PFAS	PFOS, PFOA, PFOSA m.fl.	Proposal for WFD, Detected in screening program and sludge monitoring program
Phthalates	DEHP, DINP, DIDP and others	Partial in WFD, Detected in screening program and sludge monitoring program
Organic phosporus esters	Tris(chloropropyl)phospate, TCPP and others	Sludge monitoring program
VOC	1,1,1-trichloroethan, 1,2-dichloroethan, dichloromethan and others	Partial included in WFD
Chlorobenzenes	1,2,4-trichlorobenzene, pentachlorobensene, HCB	Included in WFD, sludge monitoring program
Siloxaner	D4, D5, D6, MM, MDM, MD2M, MD3M	Detected in screening program
Hormones	Ethinyl estradiol, estradiol, norethindrone	Detected in screening program

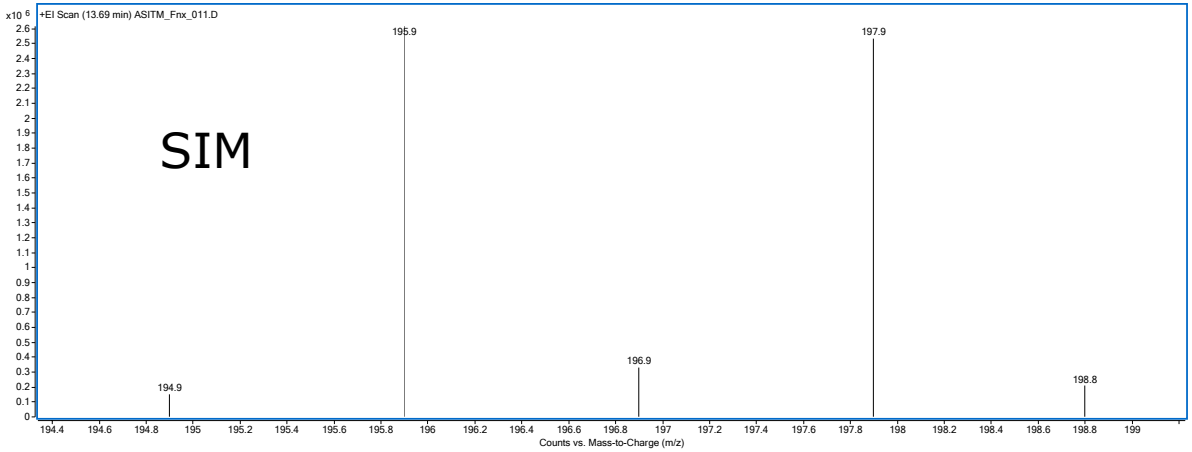
Two ways of using the MS

- "Full Scan" MS: possible to identify compounds, low sensitivity. "Extended characterisation"

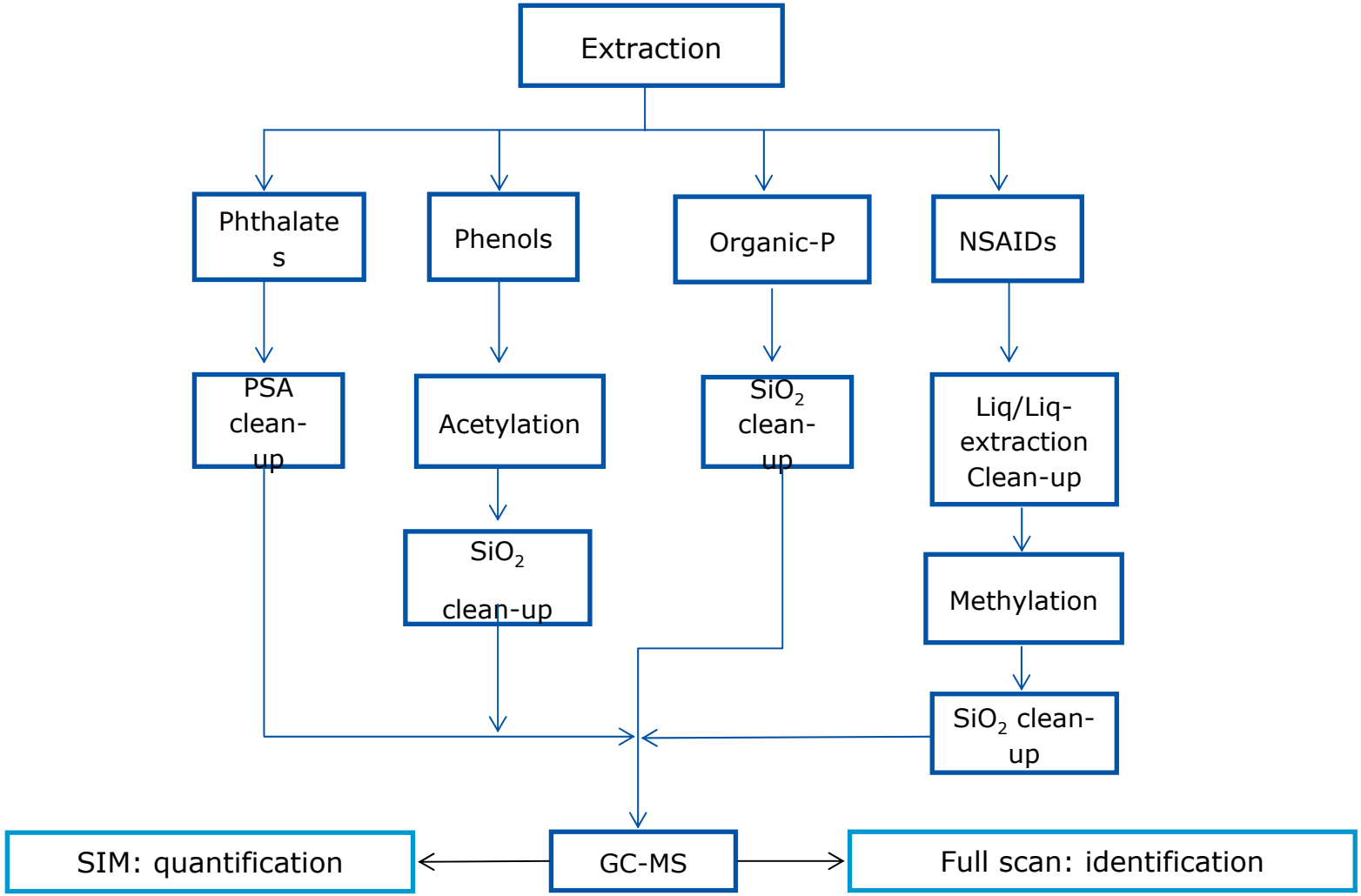
- MS in SIM mode: high selectivity and sensitivity. "Targeted analyses"

Identification or sensitivity mode





Analytical scheme



Target analysis of phenols and NSAID

Compound	Concentration (µg/l)	Frequense
4-nonylphenol	<0.087-0.27	(4/7)
4-*t*-octylphenol	<0.019-0.067	(2/7)
Triclosan	0.016-0.110	(7/7)
Bisphenol A	<0.120-1.300	(5/7)
Ibuprofen	0.008-5.0	(7/7)
Naproxen	0.081-3.0	(7/7)
Ketoprofen	0.068-1.4	(7/7)
Diclofenac	0.071-0.620	(7/7)

Target analysis of phthalates and Org-P

Compound	Concentration (µg/l)	Frequense
DEHP	<0.1-0.49	(6/7)
DEP	0.030-1.47	(7/7)
DIBP	0.046-0.21	(7/7)
DBP	0.081-0.28	(7/7)
BBzP	<0.01-0.050	(4/7)
DOP	<0.01	(0/7)
DINP	<0.1	(0/7)
DIDP	<0.1	(0/7)
TIBP	0.029-2.8	(7/7)
TBP	0.019-0.39	(7/7)
TCEP	0.19-1.8	(7/7)
TDCP	<0.008-0.82	(6/7)
TBEP	0.24-16	(7/7)
TPhP	0.015-0.12	(7/7)
EHDPP	0.0092-0.069	(7/7)

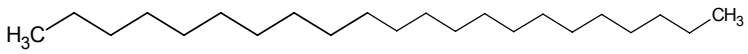
Identification

- Identification on unfractionated extract: very complex chromatograms
- Identification on fractionated and derivatised extract

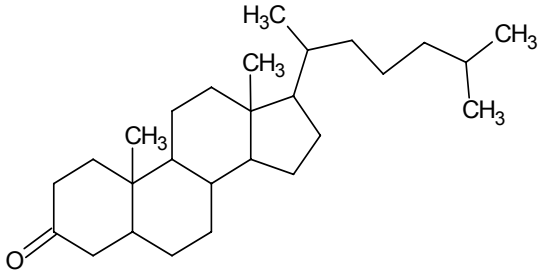
Identification

- **Identification support**:
- Reference library in the MS
- Published spectra
- Manuel interpretation of MS-spectrum
- Comparison of unknown with reference compounds

Phthalate extract

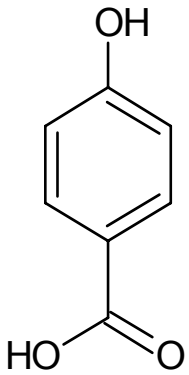


Aliphatic hydrocarbones



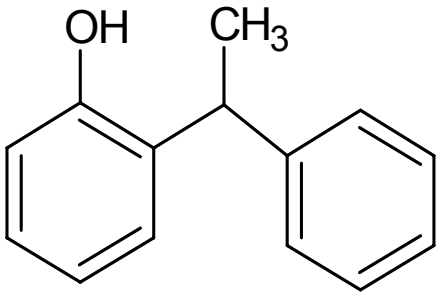
Cholestan-3-on

Phenolic fraction



4-hydroxy benzoic acid

CAS 99-96-7

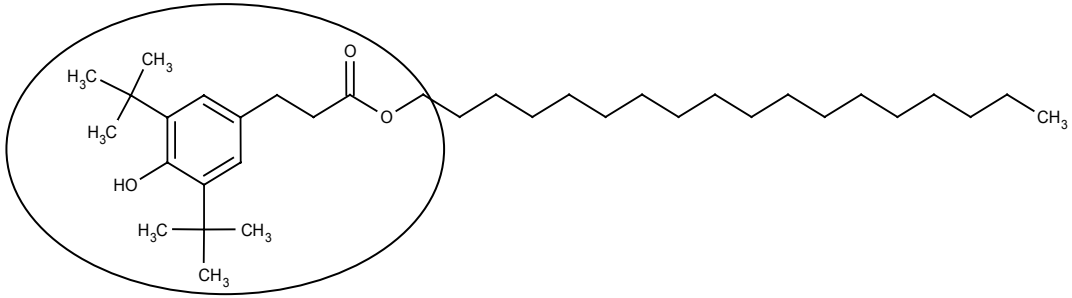


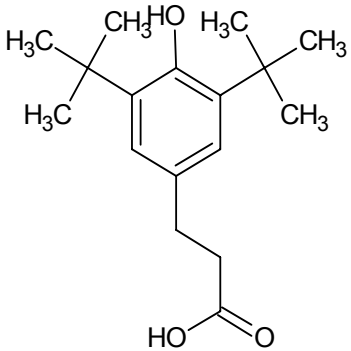
2(1-phenylethyl)phenol

CAS 4237-44-9

alkoholes, aldehydes

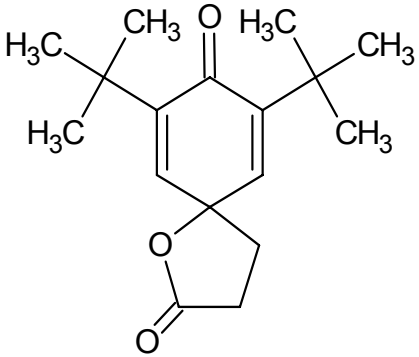
NSAID-extract: antioxidante





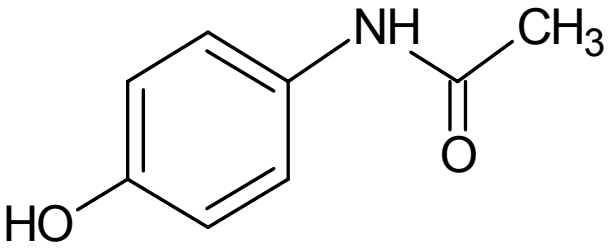
3,5-di-tert-buthyl-4-hydroxyphenylpropionic acid

CAS 123173-45-5

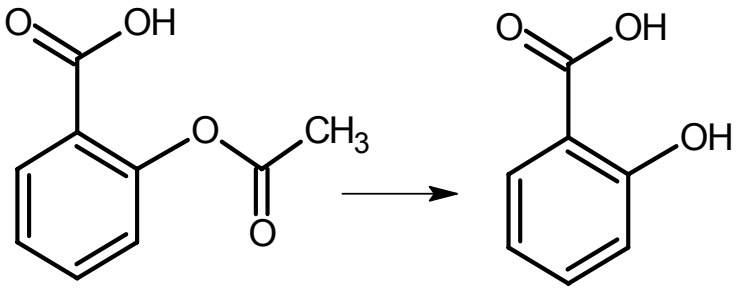


CAS 82304-66-3

NSAID-extract: pharmaceuticals

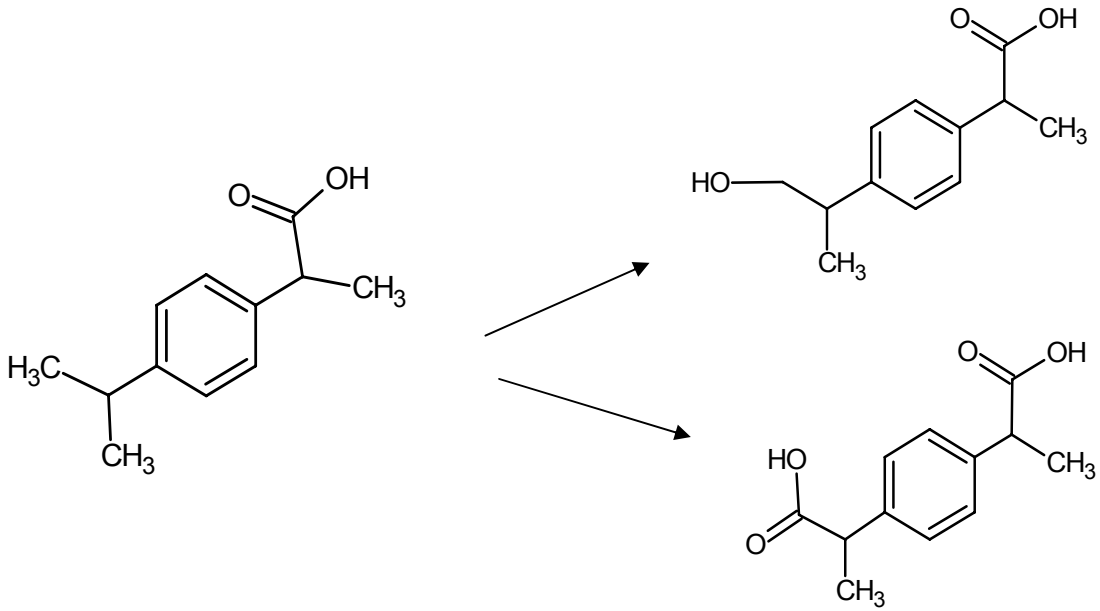


Paracetamol



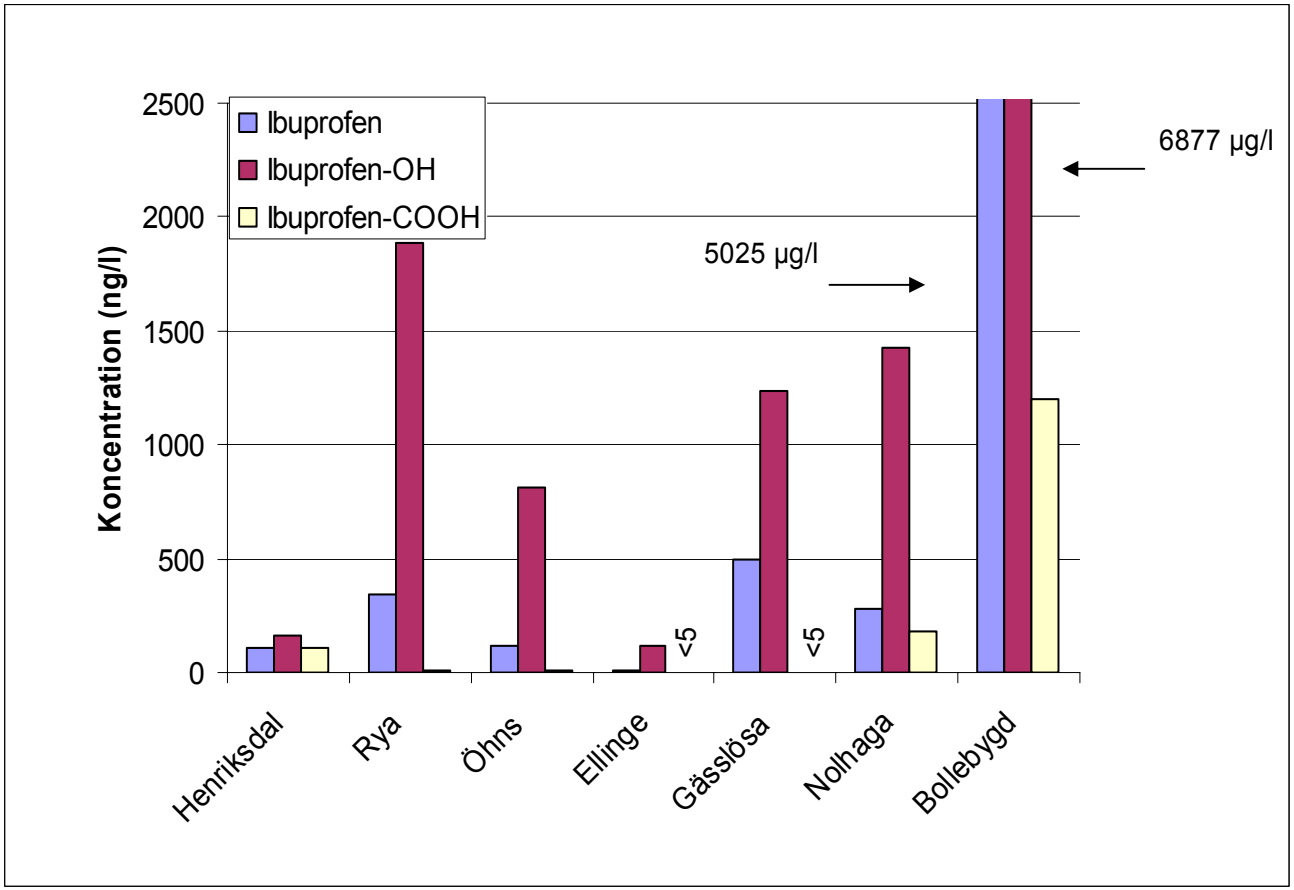
Acetylsalicylic acid & Salicylic acid

NSAID-extracts: pharamaceuticals

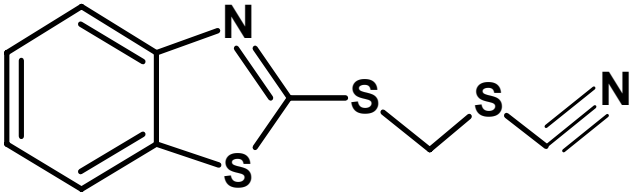


Ibuprofen metabolism

NSAID-extracts: metabolites

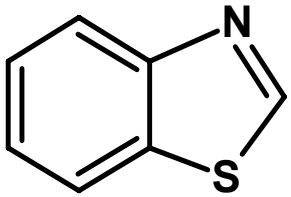


NSAID-extract: rubber related

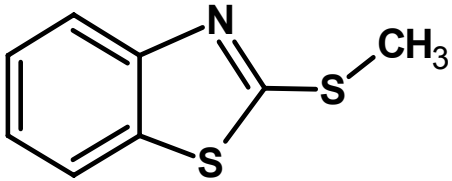


2-(thiocyanomethylthio)benzothiazole

CAS 21564-17-0



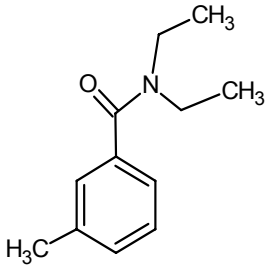
Benzotiasol CAS 95-16-9



2-(methylthio)benzotiasol

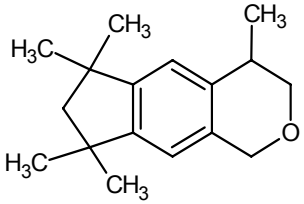
CAS 615-55-5

NSAID-extract

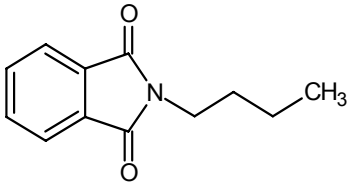


DEET, diethyltolylamide

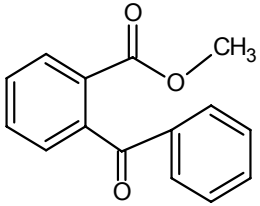
CAS 134-62-3



Galaxolid CAS 1222-05-5

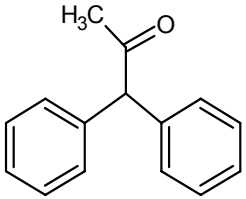


N-buthylphtalamid CAS 1515-72-6



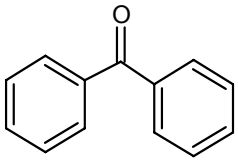
2-benzoyl-benzoic acid methylester

CAS 606-28-0



1,1-diphenylaceton

CAS 781-35-1



Bensophenon

CAS 119-61-9

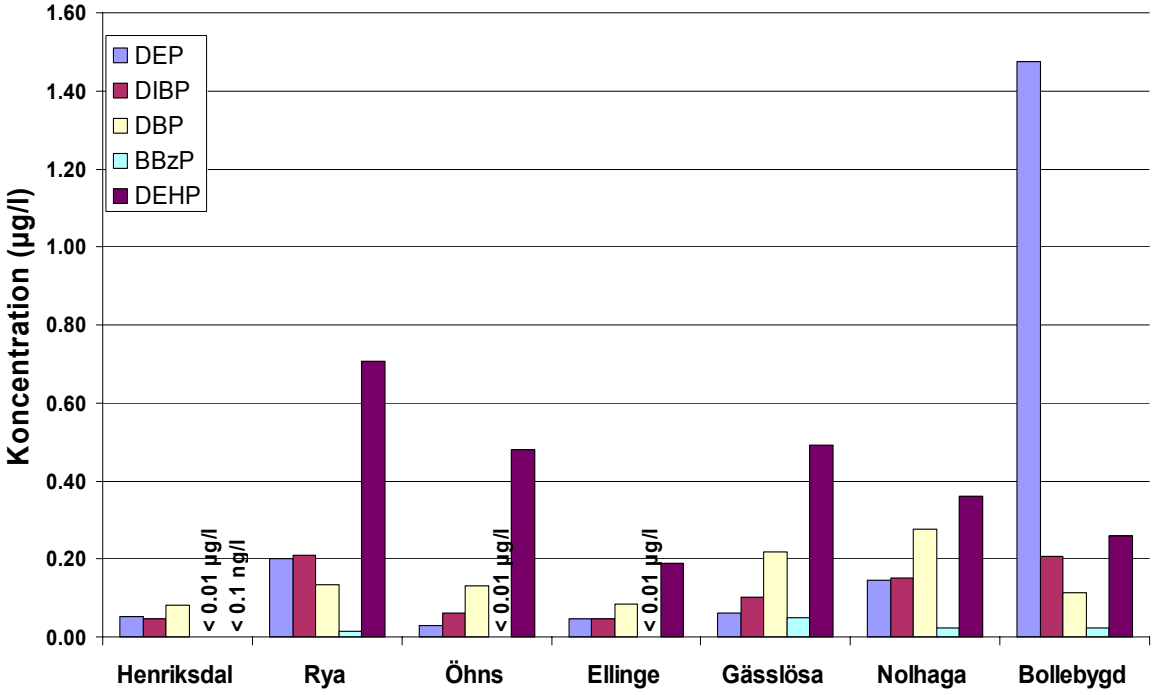
Limitations

- Discriminate of compounds: sampling, extraction, fractionation derivatization
- Compounds that needs special treatment may escape detection. *e.g* quinones
- Unknown spectra (not in library; *e.g.* metabolites)

Conclusions:

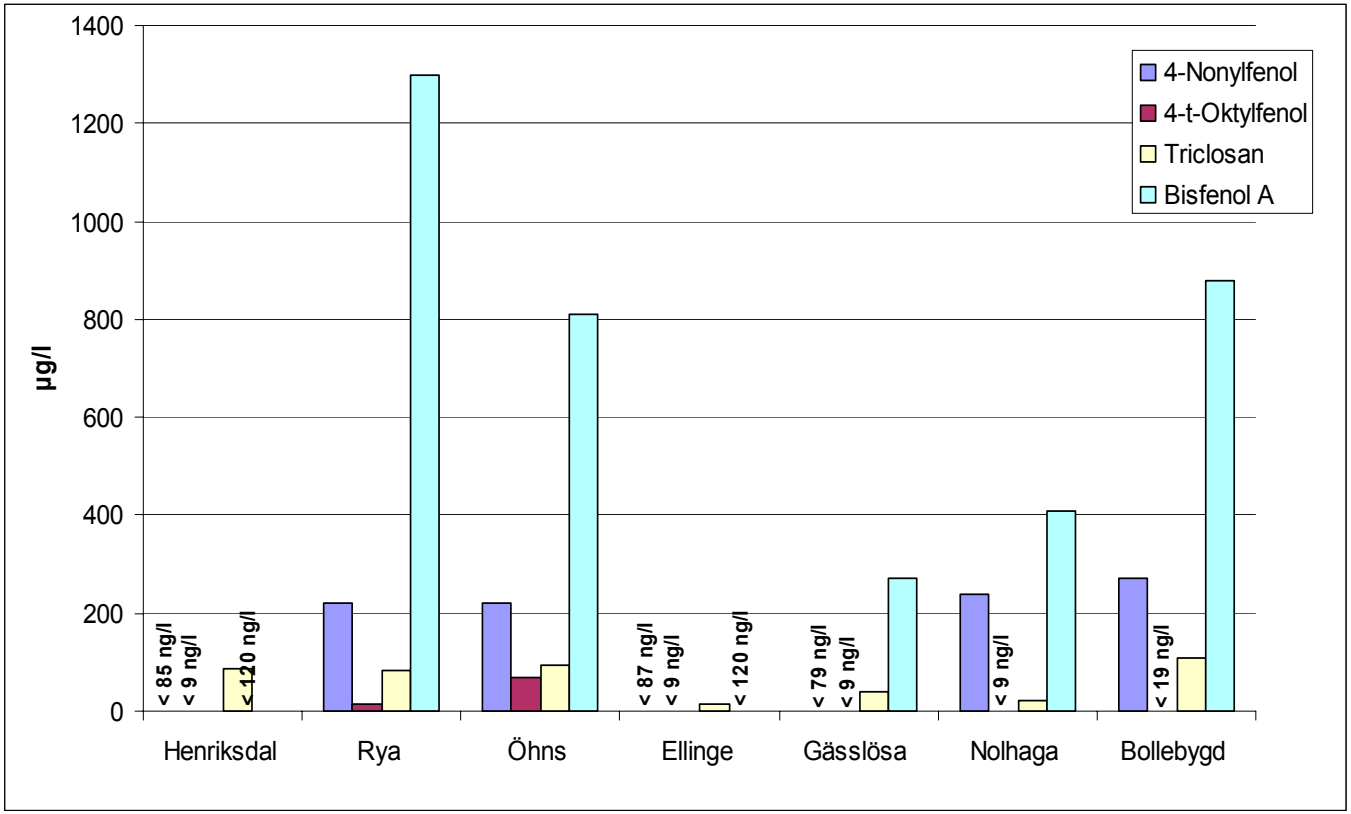
- The methodology was successful: a number of "new" compounds were detected
- Possible to detect "new" pollutant early (monitoring)
- Metabolites can be used as tracers for their precursors
- Sound basis for further development of the method

Targeted analysis - Phthalates

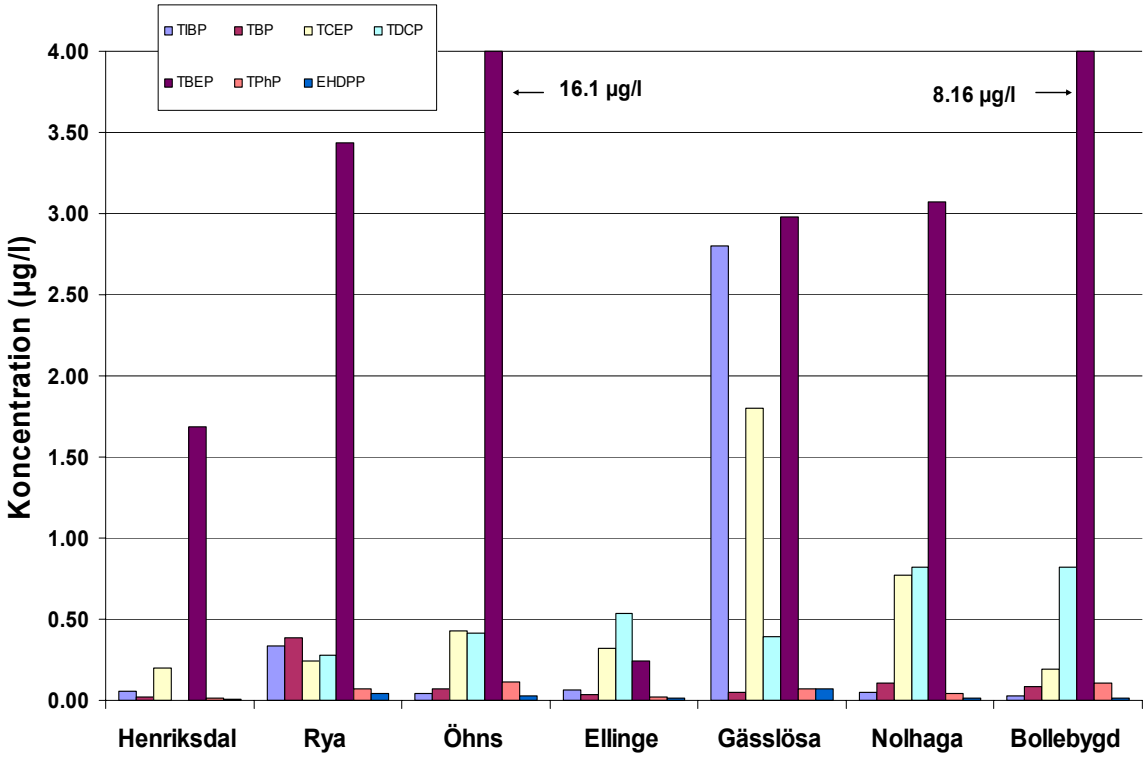
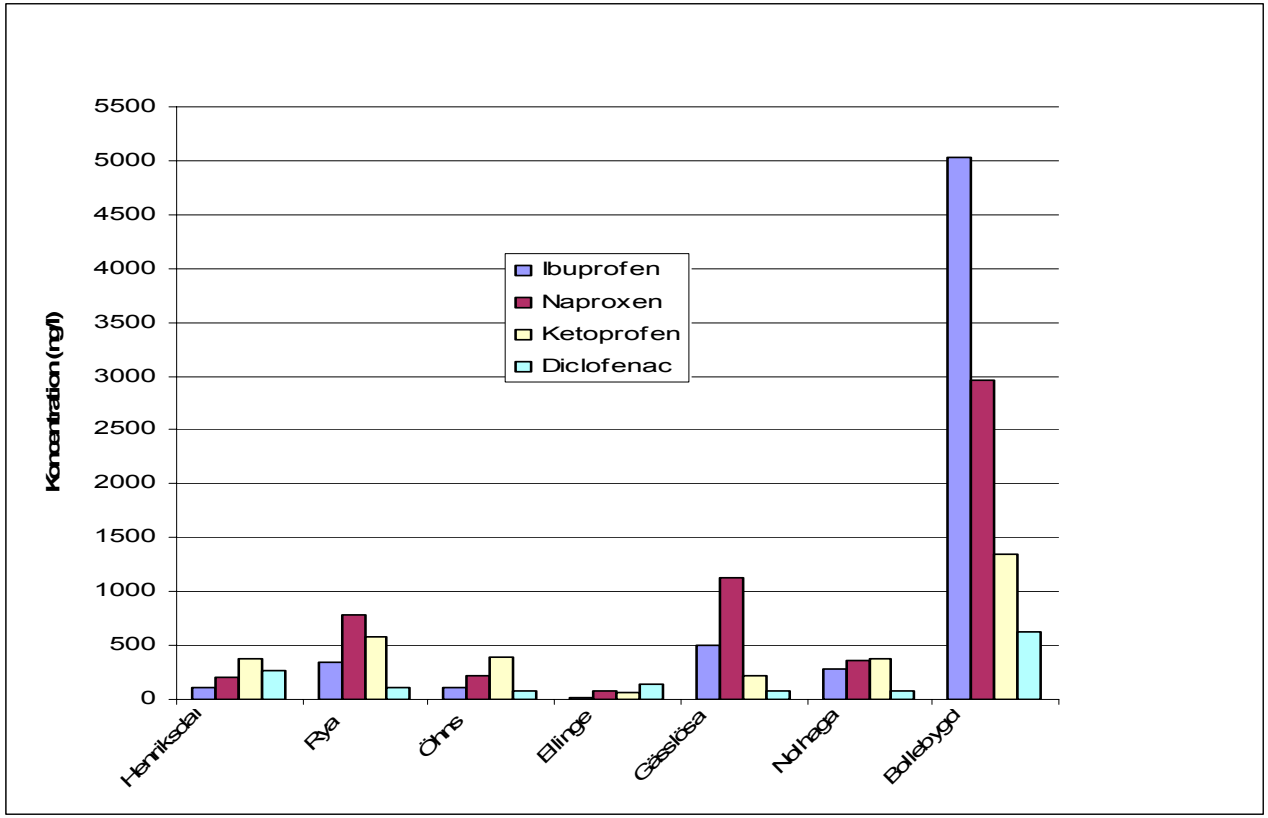


DINP & DIDP <10 µg/l

Targeted analysis – Phenols



Targeted analysis – Organo phosphorus esters



Targeted analysis - NSAID