Joint Research Centre

The European Commission's in-house science service

www.jrc.ec.europa.eu

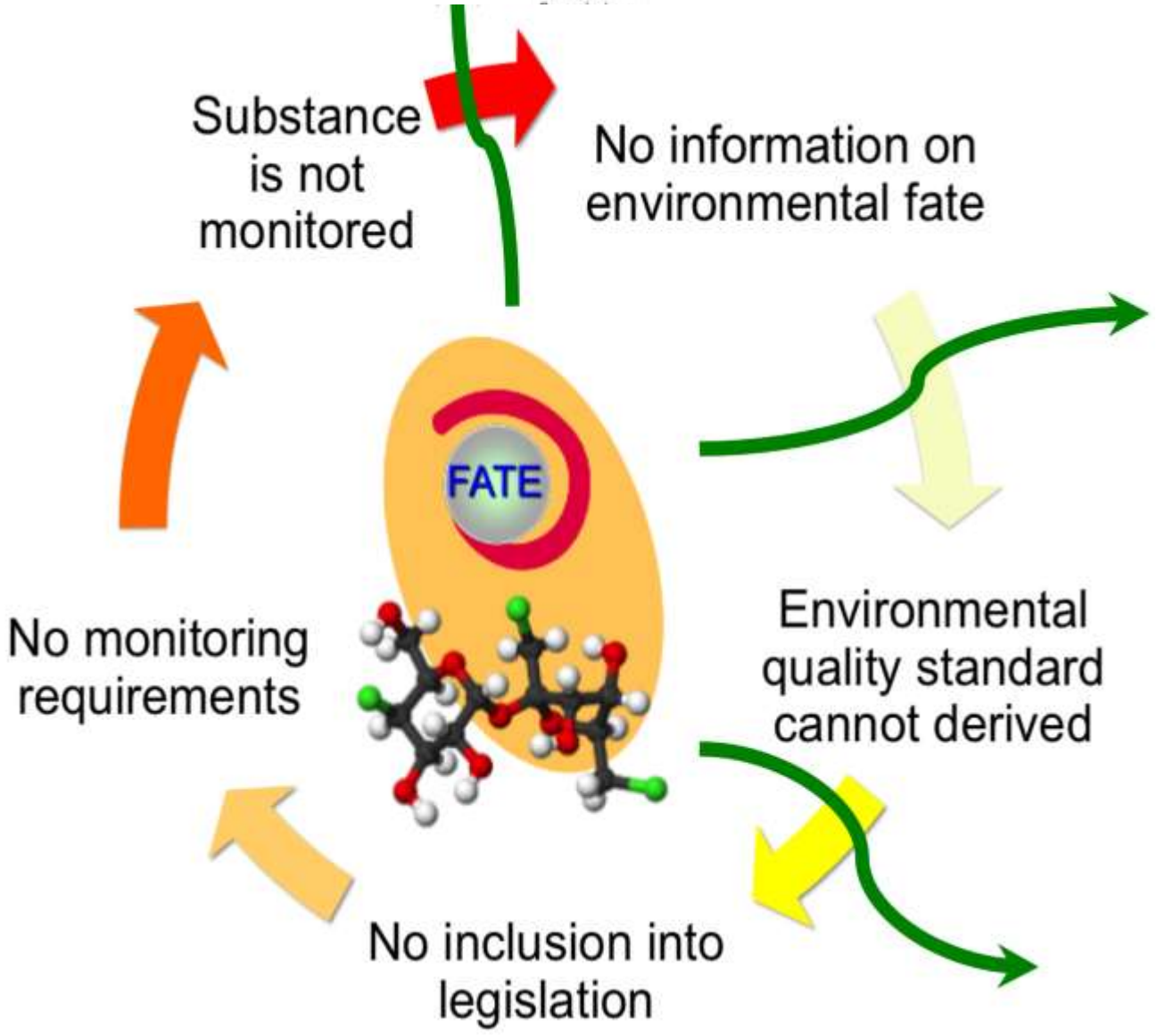
Serving society
Stimulating innovation
Supporting legislation

FATE SEES
Results of a Pan-European Snapshot of randomly taken sewage sludge sample

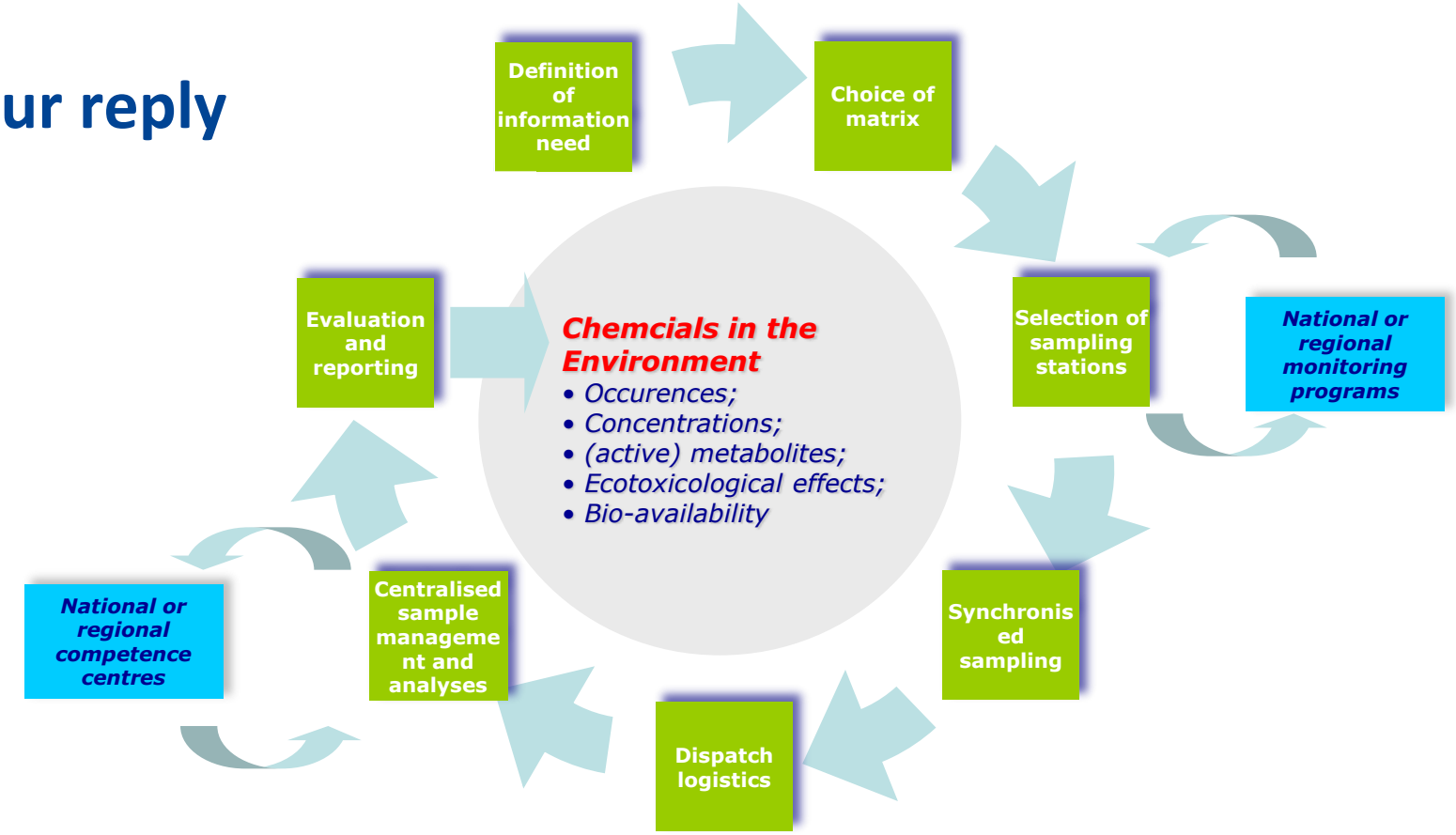
Bernd Gawlik

Contributions of

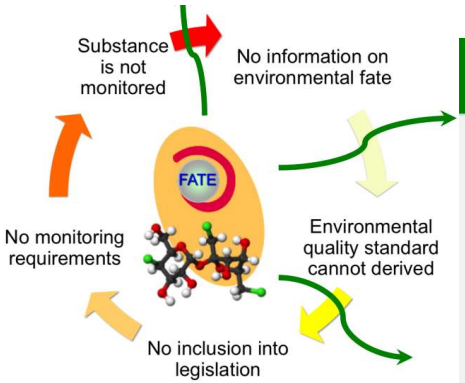
Simona Tavazzi, Oliver Gans (Umweltbundesamt AT), Robert Loos, Gunther, Umlauf, Sara Comero, Giovanni Locoro, Carmen Cristache


Substance is not monitored
No information on environmental fate
FATE
Environmental quality standard cannot derived
No inclusion into legislation
No monitoring requirements

Our reply


Definition of information need
Choice of matrix
Selection of sampling stations
National or regional monitoring programs
Synchronised sampling
Dispatch logistics
Centralised sample management and analyses
National or regional competence centres
Evaluation and reporting
Chemcials in the Environment
• Occurences;
• Concentrations;
• (active) metabolites;
• Ecotoxicological effects;
• Bio-availability

Pan-European Screening



Chemistry-based Assessment

- Pesticides
- Pharmaceuticals
- Personal care products
- Nano-materials
- New Chemicals
- …

Effect-based Assessment

- Target organisms
- Biosensors
- Bioassays
- Transcriptogenomics
- …

Risk-based Assessment

- Effect-direct analyses
- Emission loads
- Fate assessment
- …

Characteristics

- **Concern-driven approach**
- **Integrative assessment**
- **Coordination of existing capacities**
- **Pan-regional assessments**
- **Known data quality**
- **Multi–parameter**
- **Few experts - same samples**






Objective:

To produce independent data on the occurrence of less-investigated and new contaminants in environmental media on a manageable sample set (up to 300) by sharing and synchronising available resources.

Pan-European Screening

FATE COMES

- Compost and treated biowastes
- Link to End-of-Waste activity of JRC IPTS
- Data input to better define EoW Criteria
- Centralised collection of 150 compost and biowaste samples
- Parallel Adhoc sampling
- Included some sludge digestates

FATE SEES

- WWTP Effluents
- Sewage sludge
- Link to Directive 86/278/EEC Discussions
- Invitation to Member States via Environment Attachés
- Centralised collection of 101 effluent samples and 61 sludge samples
- 9 laboratories for effluents
- 3 laboratories for sludges

Per country

Note:

All EU-Countries were officially contacted via the ENV Attaches.

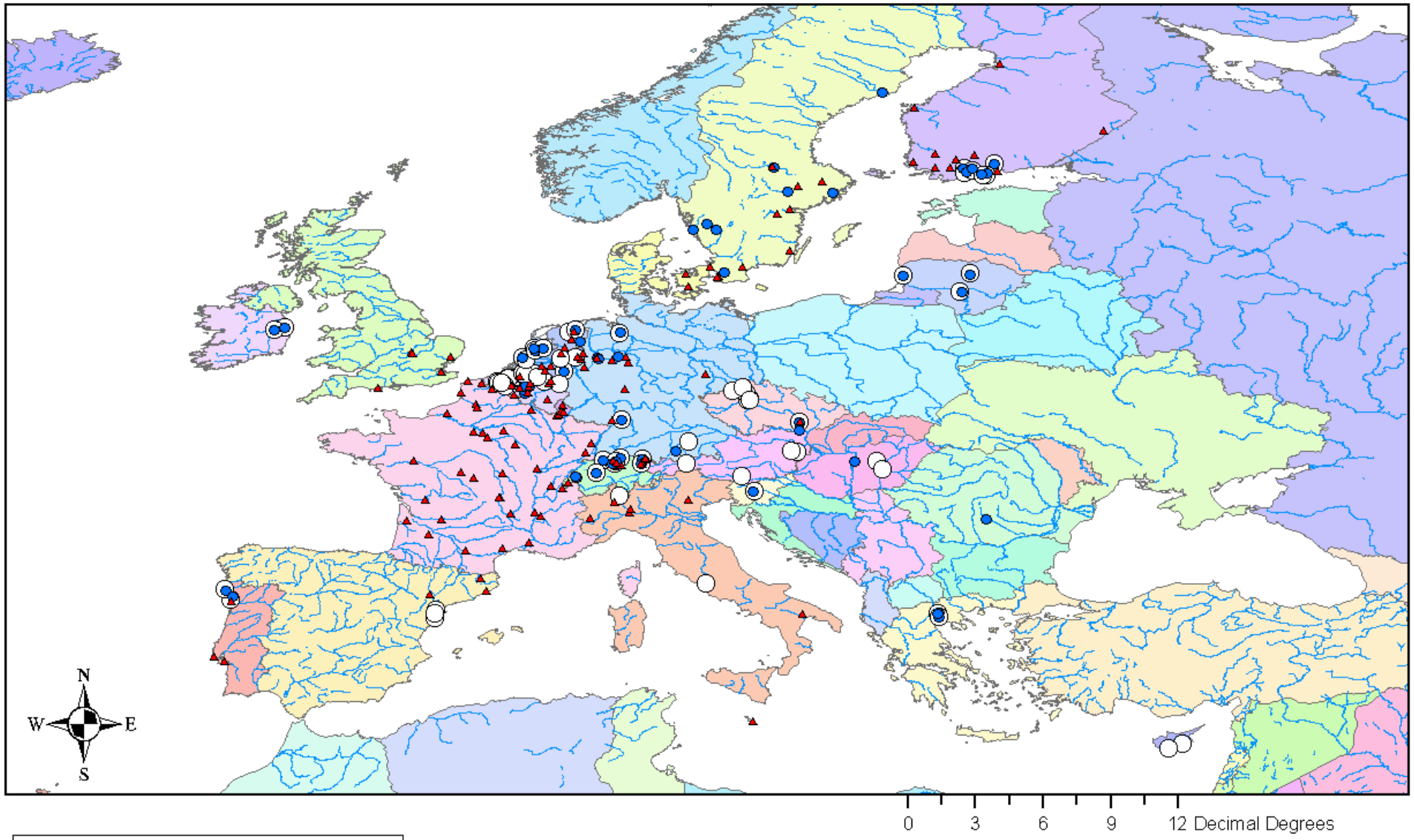
Switzerland based on previous exercises.

In addition, JRC used own contacts.

- Austria: 2
- Belgium: 9
- Czech Republic: 2
- Finland: 6
- Germany: 6
- Greece: 3
- Hungary: 1
- Ireland: 2
- Lithuania: 3
- Portugal: 2
- Romania: 1
- Slovenia: 1
- Sweden: 8
- Switzerland: 9
- The Netherlands: 6

FATE EU-Wide Monitoring - European map

(Status: April 2012)



Sampling sites FATE SEES

JRC asked for:

- Type A (assessment of the pollutants originating from private households): These sites comprise a rural catchment, have no industry and very few craft industry in the catchment and feature a separate sewer system (domestic wastewater only).
- Type B (assessment of the pollutants originating from private households and runoff): These sites comprise a rural catchment, have no industry and very few craft industry in the catchment, and feature a combined sewer system (domestic wastewater and stormwater).
- Type C (assessment of the pollutants originating from private households, urban runoff as well as from industry and craft industry): These sites comprise a predominantly urban catchment, have industry and craft industry in the catchment and feature a combined sewer system (domestic wastewater and stormwater).

Sampling Bill

- Country Address
- River basin receiving effluent
- Geographic coordinates (WGS84)
- Sampling date/time
- Attachments (possible photos, SOPs, or further information you deem useful)
- Contact person for all dispatch issues:
- Sampling operation/Sampling method
- Field observations and weather
- Other observations
- Field analyses
- Relevant information about the plant

Analyses: Material and Methods

Trace elements (without Hg)

- Optima 2100 DV ICP-OES
- Multiwave 3000
- 0.1 g sample intake
- 6 ml Aqua regia
- Horizontal standard was used
- Expanded uncertainties from 0.2% (Cr) to 9.6% (K)

Mercury

- Advanced Mercury Analyser instrument (AMA 254, Altec)

Lyophilsation

- GAMMA 1-16 LSC (Christ)

Validation and QA/QC

- 5 Day validation at intermediate precision
- 8 SI-traceable CRMs used (BCR, NIST)
- 3 in-house materials
- Uncertainty according to GUM
- ISO 17025

PAH in sludges

Phenantrene, Antracene, Fluoranthene, Pyrene, Benzo(a)antracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(e)pyrene, Benzo(a)pyrene, Perylene, Indeno(1,2,3-cd)pyrene, Dibenz(a,h)antracene, Benzo(g,h,i)perylene, Dibenzo(a,l)pyrene, Dibenzo(a,h)pyrene, Dibenzo(a,i)pyrene, Dibenzo(a,e)pyrene, Coronene.

Sample preparation

- 0.1 g of lyophilized sample
- Triple SLE with Hexane:Acetone 80:20, %v/v
- GC-MS analysis

Validation

- Linearity (5-1500 ng/g)
- LOD (4.6-7.6 ng/g)
- LOQ (5.3-13.6 ng/g)
- Trueness: z-score: -0.5-2.0
- Repeatability* and Intermediate precision: 1-15%
- Recovery (56-74%)
- Uncertainty Estimation: 24%

*Repeatability, intermediate precision and day-to-day variation

Perfluorinated Surfactants (PFCs)

PFOA, PFNA, PFOS

Sample preparation

- 1 g of lyophilized sample
- SLE with MeOH
- ENVI-Carb Clean-up
- UHPLC-MS/MS analysis

Method characterization

- IS quantitation method (PFNA $^{13}C_5$, PFOS $^{13}C_4$, PFOA $^{13}C_4$)
- Extraction Efficiency: 67-87%
- Accuracy 1-20%
- LOQ (0.2-0.5 ng/g)*

*** LOQs are matrix and run dependant**

Polycyclic Musks

Cashmerane, Celestolide, Phantolide, Traesolide, Galaxolide, Tonalide

Siloxanes

Decamethylcyclopentasiloxane, Decamethyltetrasiloxane, Dodecamethylcyclohexasiloxane, Dodecamethylpentasiloxane, Octamethlycyclotetrasiloxane, Octamethlytrisiloxane

Sample preparation

- 1 g of lyophilized sample
- Sequential Extraction with EtOH and complexing agent, n-Hexane
- Clean-up with aluminium oxide
- GC-MS

Method characterization

- IS quantitation method (^{13}C-marked surrogate standards)
- GC-MS (EI+ Mode, single ion recording) and recovery correction by surrogate standard
- DM Correction according to EN 12880
- LOD: 10-20 ng/g (PCM) 5-60 ng/g (Siloxanes)
- LOQ: 5.0-10 ng/g (PCM) 10-120 ng/g (Siloxanes)

Non-target screening analysis

(individual checks for 64 compounds)

Sample preparation

- 1 g of lyophilized sample
- SLE with MeOH
- ENVI-Carb Clean-up
- UHPLC-MS/MS analysis

Criteria followed for detection of analytes:

- ✓ 4 IP according to EU Commisssion Decision 2002/657/EC
- ✓ RT in the sample within ± 20% the RT of the compound in the analytical standard
- ✓ The relative abundance of the two selected MRM transitions in the samples must be within ± 20% of the two MRM ratios in the analytical standard

Non-target screening analysis

Pesticides

Atrazine	**216 > 174; 104**
Atrazine-desethyl	**188 > 146; 104**
Atrazine-desisopropyl	**174 > 104; 79**
Terbutylazine	**230 > 174; 132**
Terbutylazine-desethyl	**203 > 78**
Terbutryn	**242 > 186; 91**
Simazine	**202 > 104; 132**
Propazine	**230 > 146; 188**
Diuron	**233 > 72; 133**
Isoproturon	**207 > 72; 165**
Chlortoluron	**336 > 235; 219**
Linuron	**249 > 160; 133**
Alachlor	**270 > 238; 162**
Metolachlor	**284 > 252; 176**
Diazinon	**305 > 169; 97**
Molinate	**188 > 126; 98**
Metoxuron	**229 > 72; 156**
Hexazinone	**253 > 171; 85**
Carbaryl	**202 > 145; 127**
Carbendazim	**192 > 160; 105**
Carbofuran	**222 > 123; 165**
Chloridazon	**222 > 77; 65**
Chloridazon-desphenyl	**213 > 72; 140**
Chloridazon-methyl-desphenyl	**160 > 88; 101**
Fenarimol	**332 > 81; 190**
Fenitrothion	**278 > 109; 79**
Flusilazole	**316 > 165; 247**
Iprodion	**331 > 246**
Ioxynil	**370 > 127; 215**
Imidacloprid	**254 > 153; 86**
Methabenzthiazuron	**222 > 165; 150**
Tolylfluanid	**347 > 137; 238**
Vinclozolin	**316 > 284; 75**
2,4-D	**219 > 161; 125**
2,4,5-T	**255 > 197; 161**
Mecoprop	**213 > 141; 105**
Bentazone	**239 > 132; 197**
MCPA	**199 > 141; 105**
Dichlorprop	**233 > 161; 125**

Non-target screening analysis

Phenols	
Nitrophenol	138 > 108; 92
2,4-Dinitrophenol	183 > 109; 123
Sweeteners	
Acesulfame K	162 > 78; 82
Sucralose	395 > 359
Saccharin	182 > 42; 106
Pharmaceuticals	
Acetylsalicylic acid	137 > 93
Carbamazepine	237 > 194; 165
Ibuprofen	205 > 161; 159
Diclofenac	294 > 250; 214
Ketoprofen	253 > 209; 197
Naproxen	229 > 169; 185
Gemfibrozil	249 > 121; 106
Clofibric acid	213 > 127; 85
Bezafibrate	360 > 274; 154
Atenolol	267 > 145; 190
Metopropol	268 > 116; 103
Propanolol	260 > 255; 237
Sotalol	273 > 133; 255
Tamoxifen	372 > 72; 129
Personal Care Products	
Triclosan	287 > 35
Caffeine	195 > 138; 110
DEET	192 > 91; 119
Benzotriazoles	
1H-Benzotriazole	120 > 65; 92
1-Methyl-benzotriazole	134 > 77; 106
Benzothiazole	136 > 109; 65

Results – Some Limits

Description	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn (%	PAH
EU Limit (86/278/EEC)		20-40		na	1000-1750	16-25		300-400	750-1200		0.25-0.40	
Austria (Steiermark)	20	10	100	500	500	10	20	100	500		0.2	
Belgium (Flanders)	150	6		250	125	5		100	300		0.09	
Belgium (Walloon)		10		500	600	10		100	500		0.2	
Denmark	25**	0.8		100	1000	0.8		30	120		0.4	3
Finland		1.5		300	600	2		100	150		0.15	
France												
Germany		10		900	800	8		200	900		0.25	
Greece		20-40		500	1000-1750	16-25		300-400	750-1200		0.25-0.4	
Ireland		20		1000	1000	16		300	750		0.25	
Italy		20		1000		10		300	750		0.25	
Luxembourg		20-40		1000-1750	1000-1750	16-25		300-400	750-1200		0.25-0.4	
Netherlands		1.25		75	75	0.75		30	100			
Portugal		20		1000	1000	16		300	750		0.25	
Spain***		20-40		1000-1750	1000-1750	25		400	1200		0.4	
Sweden		2		100	600	2.5		50	100		0.08	3
Estonia*		15		1200	800	16		400	900		0.29	
Latvia*		20		2000	1000	16		300	750		0.25	
Poland*		10		500	800	5		100	500		0.25	
USA	75	85			4300	57	75	420	840	100	0.75	
EU proposal												6

PCDD/F and dioxin-like PCB profiles in soils amended with sewage sludge, compost, farmyard manure, and mineral fertilizer since 1962

Umlauf et al. (Environ Sci Pollut Res (2011) 18:461–470))

PCDD/F and dioxin-like PCB profiles in soils amended with sewage sludge, compost, farmyard manure, and mineral fertilizer since 1962 (Umlauf et al. 2009)

- Long-term field experiment
- Influence of sewage sludge (SSL), compost (COM), and farmyard manure (FYM) to a luvisol derived from loess on the contents of PCDD/Fs and DL-PCBs.
- Control plots with mineral fertilizer
- Compare the biowaste-amended soils with soils affected only by atmospheric deposition
- Depth of 90 cm
- PCDD/Fs and dioxin-like PCBs
- 39 SSL and COM applications exceeding 4times the German limit
- Doubling of the international toxicity equivalent (I-TEQ) budget for PCDD/Fs
- Threefold increase for DL-PCBs
- FYM had no effect on the PCDD/F and PCB content
- Average contribution of the DL-PCBs to the WHO-TEQ was 19% in the MIN and FYM plots and somewhat higher in the COM (23%) and in the SSL (27%) plots.

Conclusion of study

- Soils treated with SSL and COM were still a factor of 4 below the German guideline value of PCDD/Fs for arable land.
- No enhancement of translocation of PCDD/ Fs and PCBs into subsoils
- Similarity of congener patterns in all soils points towards atmospheric deposition of PCDD/Fs and DL-PCBs as the main intake route in the soils.
- The higher levels in the SSL- and COM- amended soils can be explained by the fact that both biowastes are subject to atmospheric deposition occurring at their origin.
- COM: accumulation in the foliage
- SSL: atmospheric particulate from wet and dry deposition is collected in the wastewater treatment system via urban runoff.

Results – SSD Metals 1 (mg/kg dw)

Description	Cd	Cu	Hg	Ni	Pb	Zn (%)
Average	1.0	256.9	0.4	29.0	47.6	0.1
Median	0.9	240.1	0.4	20.1	30.4	0.1
Min	0.3	27.3	0.1	8.6	4.0	0.0
Max	5.1	578.1	1.1	310.4	429.8	0.1
N	61	61	61	61	61	61
Positive detection	57	61	61	61	61	61
in %	93	100	100	100	100	100
Exceedence	36	59	6	10	5	21
Min of selected	0.8	75	0.75	30	100	0.08
	DK	NL	NL	BE/LX	NL/SE	SE
EU Limit (86/278/EEC)	20-40	1000-1750	16-25	300-400	750-1200	0.25-0.40

Results – SSD Metals 2 (mg/kg dw)

Description	As	Co	Cr	Mo	Se
Average	12.5	6.3	79.8	4.9	8.1
Median	8.9	5.6	37.9	5.0	5.8
Min	5.6	1.5	10.8	1.7	3.4
Max	56.1	16.7	1542.2	12.5	53.6
N	61	61	61	61	61
Positive detection	21	61	61	61	40
in %	34	100	100	100	66
Exceedence	3	0	8	0	0
Min of selected	20	100	75	20	100
	AT	AT	NL	AT	US

Results – SSD Metals 3 (mg/kg dw)

Description	Ag	Ba	Mn	Ti	V
Average	3.5	224.8	328.5	439.7	25.0
Median	2.5	197.1	281.1	349.7	21.5
Min	0.1	41.5	75.2	65.2	2.3
Max	14.7	579.9	959.7	1070.9	135.4
N	61	61	61	61	61
Positive detection	58	61	61	61	61
in %	95	100	100	100	100

Results – SSD Metals 4 (mg/kg dw)

Description	Al (%)	Fe (%)	Mg (%)	K (%)	P (%)
Average	1.7	3.8	0.4	0.4	3.1
Median	1.3	2.5	0.4	0.3	2.9
Min	0.1	0.2	0.0	0.1	1.0
Max	6.0	14.9	2.2	2.6	5.6
N	61	61	61	61	61
Positive detection	61	61	61	54	54
in %	100	100	100	89	89
Compost				1.01	0.72

PAHs (ng/g)

Description	Fluoranthene	Pyrene	Benzo(b)fluoranthene	Benzo(a)pyrene
Average	814.1	698.1	662.4	369.9
Median	499.4	501.9	632.7	254.9
Min	34.5	47.2	25.1	17.9
Max	3216.8	2637.0	1919.4	1475.5
N	32	32	32	32
Positive detection	32	32	29	32
in %	100	100	91	100
Exceedence	0	3	0	0
Min of selected	4000	1654	2500	1500
	FR	EPA Study	FR	FR

Description	Phenantrene	Antracene	Benzo(a)antracene	Chrysene	Benzo(k)fluoranthene	Benzo(e)pyrene	Perylene
Average	644.4	112.8	452.4	537.0	260.3	338.7	192.7
Median	264.5	57.9	315.5	398.2	176.5	260.8	149.9
Min	29.9	15.3	9.1	21.0	9.9	18.9	18.5
Max	5552.2	724.0	1832.6	2020.5	1048.0	1477.0	543.8
N	32	32	32	32	32	32	32
Positive detection	32	27	31	30	32	32	19
in %	100	84	97	94	100	100	59

Description	Indeno(1,2,3-cd)pyrene	Dibenz(a,h)antracene	Benzo(g,h,i)perylene	Dibenzo(a,l)pyrene	Dibenzo(a,h)pyrene	Dibenzo(a,i)pyrene	Dibenzo(a,e)pyrene	Coronene
Average	342.2	138.2	355.9	52.7	148.6	na	71.8	197.1
Median	241.1	102.4	276.2	59.0	109.0	na	71.8	166.9
Min	24.2	7.1	29.7	39.4	14.1	na	70.2	18.6
Max	1401.5	547.7	1334.9	59.6	432.6	na	73.4	549.8
N	32	32	32	32	32	32	32	32
Positive detection	32	31	32	3	22	0	2	27
in %	100	97	100	9	69	0	6	84

Polycyclic musks

(ng/g)	Cashmeran	Celestolide	Phantolide	Traesolide	Galaxolide	Tonalide
Average	102.6	44.0	22.6	204.0	10801.8	1026.4
Median	70.0	37.0	18.0	140.0	8600.0	890.0
Min	11.0	15.0	10.0	18.0	1100.0	210.0
Max	560.0	120.0	65.0	1300.0	51000.0	4000.0
N	56	57	58	59	60	61
Positive detection	49	48	27	55	56	56
in %	87.5	84.2	46.6	93.2	93.3	91.8

25
10000

0
15000

Germany
Galaxolide: 10000 ng/g
Tonalide: 15000 ng/g

Siloxanes

ng/g	Octamethyltrisiloxane	Octamethylcyclotetrasiloxane	Decamethyltetrasiloxane	Decamethylcyclopentasiloxane	Dodecamethylpentasiloxane	Dodecamethylcyclohexasiloxane
Average	16.0	730.4	21.2	10825.0	129.1	2824.2
Median	14.0	370.0	22.0	6750.0	115.0	2500.0
Min	10.0	90.0	11.0	2100.0	30.0	810.0
Max	24.0	2200.0	31.0	28000.0	250.0	5900.0
N	12	13	14	15	16	17
Positive detection	3	8	6	11	11	11
in %	25.0	61.5	42.9	73.3	68.8	64.7

Perfluorinated surfactants

(ng)g)	PFOA	PFNA	PFOS
Average	6.8	4.8	71.5
Median	3.8	2.7	46.5
Min	1.2	0.0	1.7
Max	47.5	68.1	438.4
N	63	63	63
Positive detection	63	63	61
in %	100.0	100.0	96.8

Screening 1

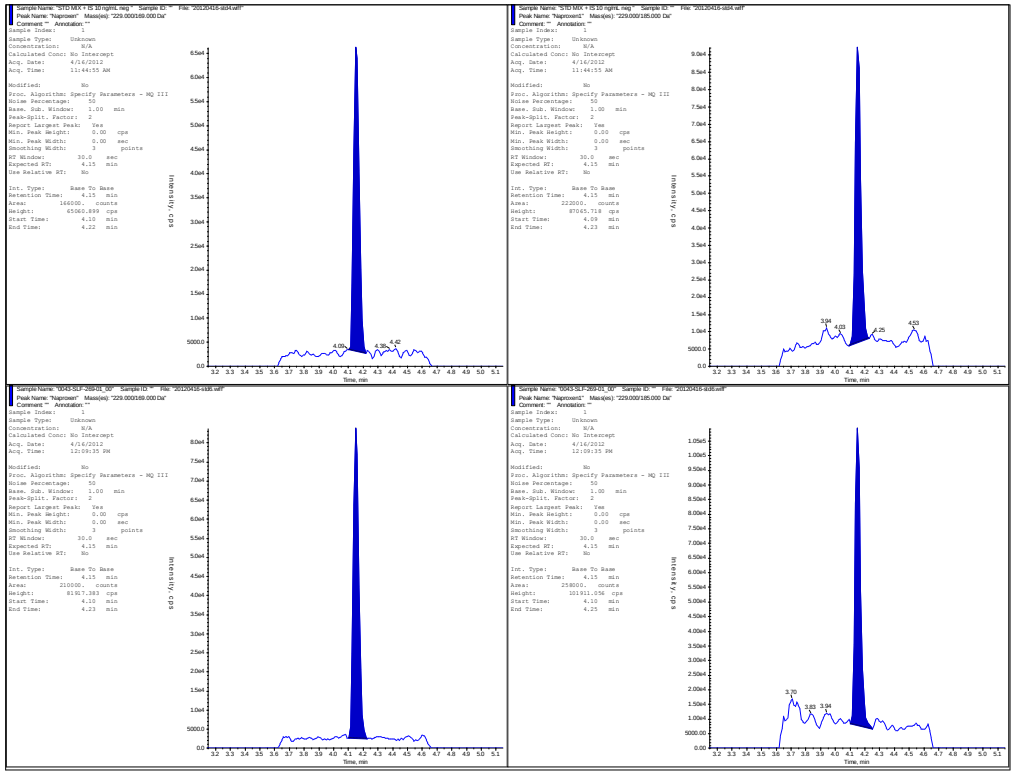
(ng/g)	Average	Median	Min	Max	N	Positive detection	in %
2,4-Dinitrophenol	0.9	0.5	0.1	4.0	58	38	65.5
Acesulfame K	14.7	4.6	0.1	156.7	58	53	91.4
Acetylsalicylic acid	63.9	32.0	0.6	563.0	58	57	98.3
Bezafibrate	0.7	0.2	0.0	6.8	58	41	70.7
Chloramphenicol	1.7	0.3	0.0	7.6	58	5	8.6
Clofibric acid	1.7	1.0	0.1	10.5	58	17	29.3
Dichlorprop	0.1	0.1	0.0	0.5	58	9	15.5
Diclofenac	43.6	29.2	1.3	429.1	58	47	81.0
Gemfibrozil	2.9	1.8	0.3	9.4	58	6	10.3
Ibuprofen	18.2	10.8	0.2	108.2	58	42	72.4
Imidacloprid	0.8	0.8	0.8	0.8	58	1	1.7
Ketoprofen	2.6	1.1	0.3	8.6	58	8	13.8
MCPA	0.9	0.3	0.3	2.2	58	3	5.2
Mecoprop	0.8	0.8	0.4	1.2	58	2	3.4
Naproxen	2.6	1.4	0.2	9.0	58	34	58.6
Nitrophenol	3.7	2.1	0.2	22.2	58	50	86.2
PFDA	10.7	5.2	0.0	69.2	58	33	56.9
PFHpA	1.9	0.5	0.1	23.3	58	46	79.3
Saccharin	8.9	3.5	0.6	72.8	58	37	63.8
Sucralose	2.0	0.8	0.0	19.2	58	36	62.1

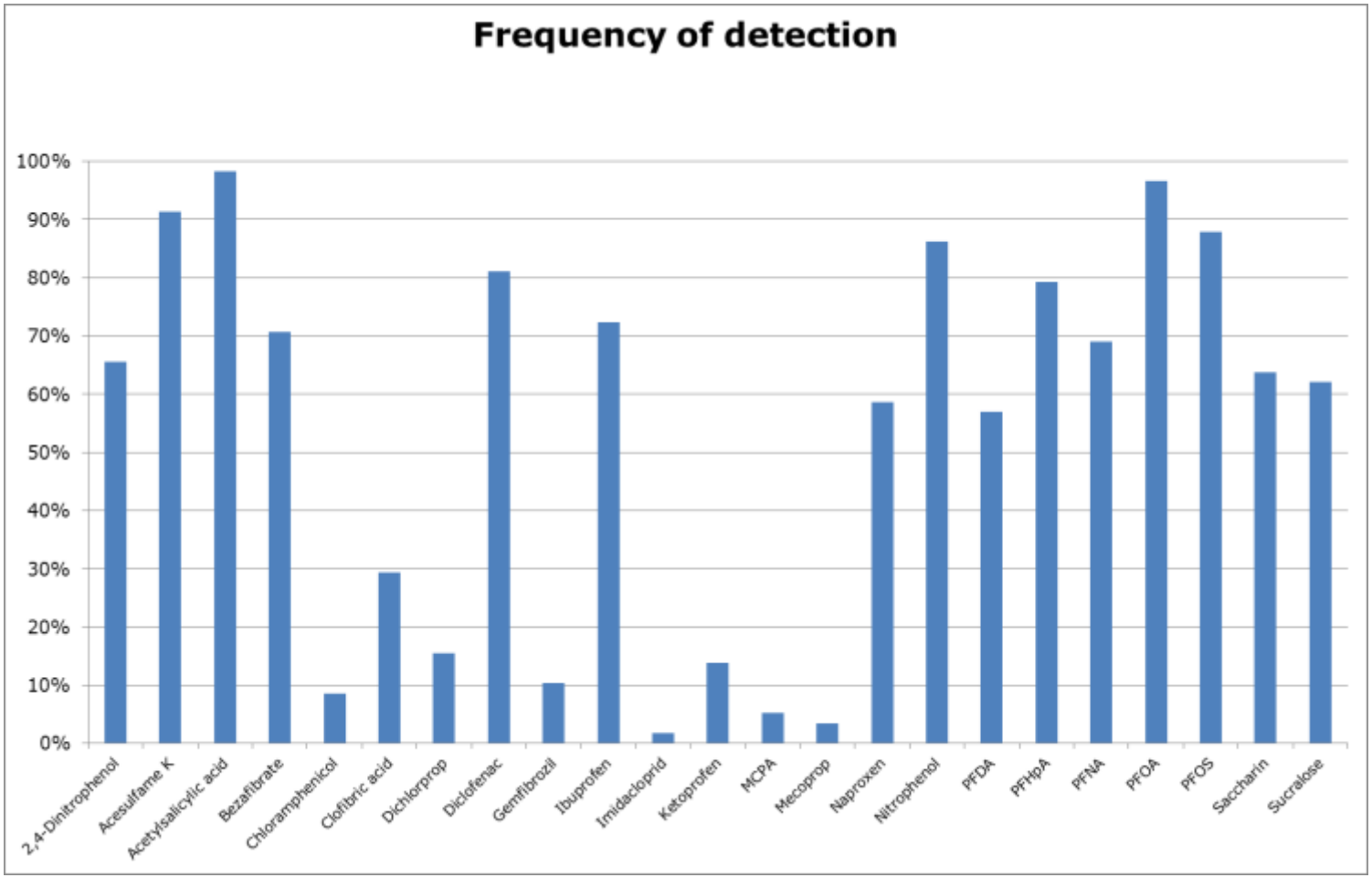
Screening 2

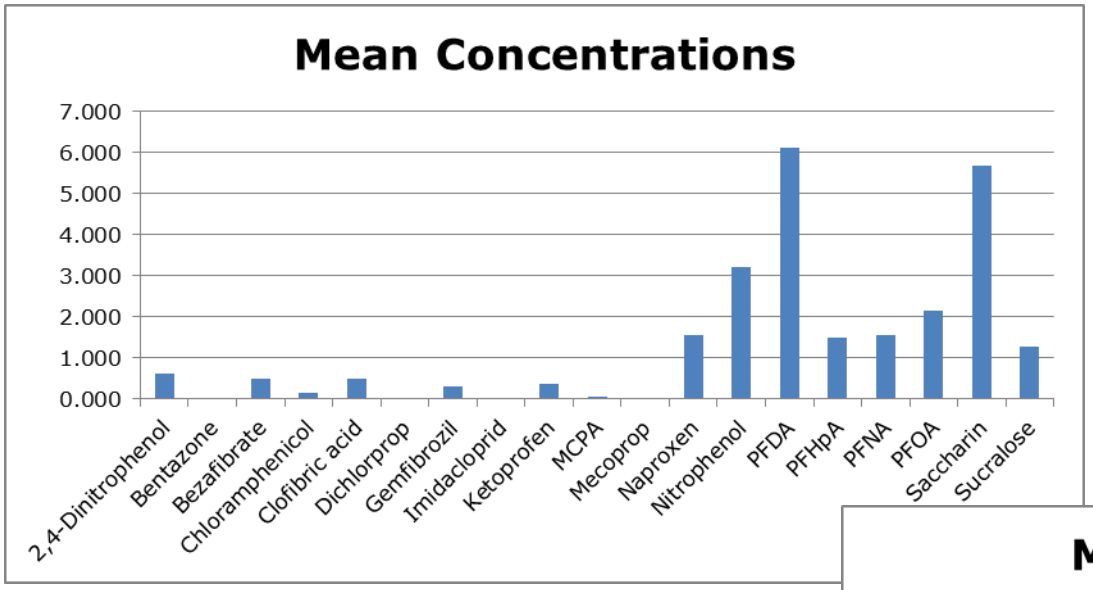
(ng/g)	Average	Median	Min	Max	N	Positive detectio	in %
1-Methyl-1H-benzotriazole	12.2	11.4	3.6	25.3	9	8	88.9
1H-Benzotriazole	7.4	7.4	4.0	10.8	9	2	22.2
Caffeine	25.7	16.8	5.6	93.6	9	8	88.9
Carbamazepine	4.8	4.8	4.8	4.8	9	1	11.1
Carbendazim	1.3	1.1	0.5	2.5	9	6	66.7
Clarithromycin	1.5	1.5	0.0	3.1	9	2	22.2
Diuron	1.3	1.6	0.1	2.7	9	5	55.6
Metopropol	9.6	9.6	6.3	12.9	9	2	22.2
Roxithromycin	1.4	1.4	1.4	1.4	9	1	11.1
Trimethoprim	0.3	0.1	0.0	1.0	9	6	66.7

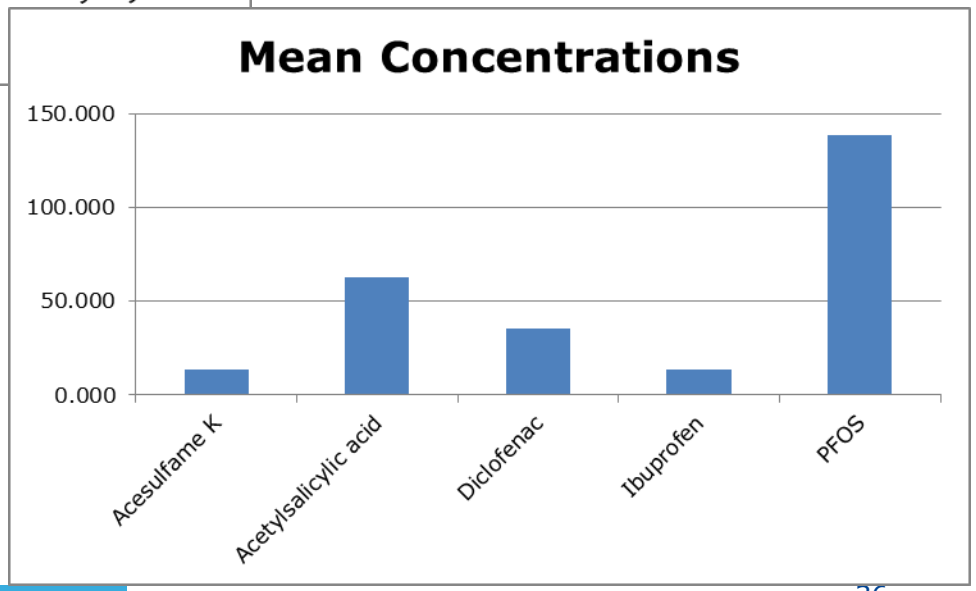
0043-SLF-269-01-00

0043-SLF-269-1-00		STD 10 ng/mL
	Area counts	Area counts
Naproxen (MRM1)	210000	166000
Naproxen1 (MRM2)	258000	222000
Ratio MRM1/MRM2	0.814	0.748
% Diff	8.9	
RT	4.15	4.15
Calc. Conc (ng/g)	12.6	




Frequency of detection
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2,4-Dinitrophenol
Acesulfame K
Acetylsalicylic acid
Bezafibrate
Chloramphenicol
Clofibric acid
Dichlorprop
Diclofenac
Gemfibrozil
Ibuprofen
Imidacloprid
Ketoprofen
MCPA
Mecoprop
Naproxen
Nitrophenol
PFDA
PFHpA
PFNA
PFOA
PFOS
Saccharin
Sucralose


Mean Concentrations
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
2,4-Dinitrophenol
Bentazone
Bezafibrate
Chloramphenicol
Clofibric acid
Dichlorprop
Gemfibrozil
Imidacloprid
Ketoprofen
MCPA
Mecoprop
Naproxen
Nitrophenol
PFDA
PFHpA
PFNA
PFOA
Saccharin
Sucralose


Mean Concentrations
150.000
100.000
50.000
0.000
Acesulfame K
Acetylsalicylic acid
Diclofenac
Ibuprofen
PFOS

Conclusions

- Results of HM show that there is room to lower current limits
- Benefit in terms of P and K to be considered, too. → link to limit?
- No indication that PCB and PCDD/F under current practice are justifying introduction of limits
- Data for PAH seem to confirm this, too.
- PFC: to be discussed further
- Results on PCM and Siloxane indicate that there is need to shift the attention towards a more risk oriented approach → bioassays/sensors?
- Emerging pollutants: rather an issue for effluent than for sludge
- A more systematic approach (targeted studies) seems desirable to monitor the evolution.

…