Analysis of Polar Organic Chemicals in European River and Ground Waters by SPE-LC-MS-MS

Robert Loos[a], Giovanni Locoro[a], Serafino Contini[a], Sara Comero[a], Alberto Pistocchi, Bernd M. Gawlik[a]

with contributions by: David Schwesig[b], Friedrich Werres[b], Peter Balsaa[b], Oliver Gans[c], Stefan Weiss[c], Ludek Blaha[d]

a: European Commission, Joint Research Centre (JRC), Institute for Environment and Sustainability (IES), Via Enrico Fermi, 21020 Ispra, Italy
b: IWW Water Centre, Moritzstr. 26, 45476 Muelheim an der Ruhr, Germany
c: Umweltbundesamt GmbH, Spittelauer Lände 5, 1090 Vienna, Austria
d: Masaryk University, RECETOX , Kamenice 3, 62500 Brno, Czech Republic

Norman workshop: Mixtures and metabolites of chemicals of emerging concern
18-19 November 2009
VU University, Amsterdam

Organized by RIVM and IVM

Policy Background

- The increasing contamination of freshwater systems with industrial chemical compounds which are released deliberately into the environment, is one of the key environmental problems we are facing today.
- **Water Framework Directive** (WFD) **2000/60/EC** to achieve "good water status" for all European waters by 2015.
- Groundwater is the most sensitive and the largest body of freshwater in the European Union (EU) and, in particular, also a main source of public drinking water supplies in many regions.
- EU **Groundwater Directive** (GWD) **2006/118/EC** on the protection of groundwater against chemical pollution and deterioration sets out criteria for the assessment of the chemical status of groundwater.

DIRECTIVE 2006/118/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 12 December 2006

on the protection of groundwater against pollution and deterioration

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 175(1) thereof,

Having regard to the proposal from the Commission,

Having regard to the Opinion of the European Economic and Social Committee [1],

Having regard to the Opinion of the Committee of the Regions [2],

Acting in accordance with the procedure laid down in Article 251 of the Treaty [3], in the light of the joint text approved by the Conciliation Committee on 28 November 2006,

Whereas:

(1) Groundwater is a valuable natural resource and as such should be protected from deterioration and chemical pollution. This is particularly important for groundwater-dependent ecosystems and for the use of groundwater in water supply for human consumption.

(2) Groundwater is the most sensitive and the largest body of freshwater in the European Union and, in particular, also a main source of public drinking water supplies in many regions.

(3) Groundwater in bodies of water used for the abstraction of drinking water or intended for such future use must be protected in such a way that deterioration in the quality of such bodies of water is avoided in order to reduce the level of purification treatment required in the production of drinking water, in accordance with Article 7(2) and (3) of Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy [4].

(4) Decision No 1600/2002/EC of the European Parliament and of the Council of 22 July 2002 laying down the Sixth Community Environment Action Programme [5] includes the objective to achieve water quality levels that do not give rise to significant impacts on, and risks to, human health and the environment.

(5) In order to protect the environment as a whole, and human health in particular, detrimental concentrations of harmful pollutants in groundwater must be avoided, prevented or reduced.

(6) Directive 2000/60/EC sets out general provisions for the protection and conservation of groundwater. As provided for in Article 17 of that Directive, measures to prevent and control groundwater pollution should be adopted, including criteria for assessing good groundwater chemical status and criteria for the identification of significant and sustained upward trends and for the definition of starting points for trend reversals.

(7) Having regard to the need to achieve consistent levels of protection for groundwater, quality standards and threshold values should be established, and methodologies based on a common approach developed, in order to provide criteria for the assessment of the chemical status of bodies of groundwater.

(8) Quality standards for nitrates, plant protection products and biocides should be set as Community criteria for the assessment of the chemical status of bodies of groundwater, and consistency should be ensured with Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources [6], Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market [7], and Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market [8], respectively.

(9) The protection of groundwater may in some areas require a change in farming or forestry practices, which could entail a loss of income. The Common Agricultural Policy provides for funding mechanisms to implement measures to comply with Community standards, namely through Council Regulation (EC) No 1698/2005 of 20 September 2005 on support for rural development by the European Agricultural Fund for Rural Development (EAFRD) [9].

[1] OJ C 112, 30.4.2004, p. 40.
[2] OJ C 109, 30.4.2004, p. 29.
[3] Opinion of the European Parliament of 28 April 2005 (OJ C 45 E, 23.2.2006, p. 15), Council Common Position of 23 January 2006 (OJ C 126 E, 30.5.2006, p. 1) and Position of the European Parliament of 13 June 2006 (not yet published in the Official Journal). European Parliament Legislative Resolution of 12 December 2006 (not yet published in the Official Journal) and Council Decision of 11 December 2006.
[4] OJ L 327, 22.12.2000, p. 1. Directive as amended by Decision No 2455/2001/EC (OJ L 331, 15.12.2001, p. 1).
[5] OJ L 242, 10.9.2002, p. 1.
[6] OJ L 375, 31.12.1991, p. 1. Directive as amended by Regulation (EC) No 1882/2003 of the European Parliament and of the Council (OJ L 284, 31.10.2003, p. 1).
[7] OJ L 230, 19.8.1991, p. 1. Directive as last amended by Commission Directive 2006/85/EC (OJ L 293, 24.10.2006, p. 3).
[8] OJ L 123, 24.4.1998, p. 1. Directive as last amended by Commission Directive 2006/50/EC (OJ L 142, 30.5.2006, p. 6).
[9] OJ L 277, 21.10.2005, p. 1. Regulation as amended by Regulation (EC) No 1463/2006 (OJ L 277, 9.10.2006, p. 1).

(23) Directive 2000/60/EC includes in Article 11(2) and Part B of Annex VI on the programme of measures a non-exclusive list of supplementary measures which Member States may choose to adopt as part of the programme of measures, *inter alia*:

— legislative instruments,

— administrative instruments, and

— negotiated agreements for the protection of the environment.

(24) The measures necessary for the implementation of this Directive should be adopted in accordance with Council Decision 1999/468/EC of 28 June 1999 laying down the procedures for the exercise of implementing powers conferred on the Commission [1].

(25) In particular, it is necessary to follow the regulatory procedure with scrutiny as regards measures of general scope designed to amend non-essential elements of this Directive, inter alia by deleting some of those elements or by supplementing this Directive by adding new non-essential elements to it,

HAVE ADOPTED THIS DIRECTIVE:

Article 1

Purpose

1. This Directive establishes specific measures as provided for in Article 17(1) and (2) of Directive 2000/60/EC in order to prevent and control groundwater pollution. These measures include in particular:

(a) criteria for the assessment of good groundwater chemical status; and

(b) criteria for the identification and reversal of significant and sustained upward trends and for the definition of starting points for trend reversals.

2. This Directive also complements the provisions preventing or limiting inputs of pollutants into groundwater already contained in Directive 2000/60/EC, and aims to prevent the deterioration of the status of all bodies of groundwater.

Article 2

Definitions

For the purposes of this Directive, the following definitions shall apply in addition to those laid down in Article 2 of Directive 2000/60/EC:

1) 'groundwater quality standard' means an environmental quality standard expressed as the concentration of a particular pollutant, group of pollutants or indicator of pollution in groundwater, which should not be exceeded in order to protect human health and the environment;

2) 'threshold value' means a groundwater quality standard set by Member States in accordance with Article 3;

3) 'significant and sustained upward trend' means any statistically and environmentally significant increase of concentration of a pollutant, group of pollutants, or indicator of pollution in groundwater for which trend reversal is identified as being necessary in accordance with Article 5;

4) 'input of pollutants into groundwater' means the direct or indirect introduction of pollutants into groundwater as a result of human activity;

5) 'background level' means the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions;

6) 'baseline level' means the average value measured at least during the reference years 2007 and 2008 on the basis of monitoring programmes implemented under Article 8 of Directive 2000/60/EC or, in the case of substances identified after these reference years, during the first period for which a representative period of monitoring data is available.

Article 3

Criteria for assessing groundwater chemical status

1. For the purposes of the assessment of the chemical status of a body or a group of bodies of groundwater pursuant to Section 2.3 of Annex V to Directive 2000/60/EC, Member States shall use the following criteria:

(a) groundwater quality standards as referred to in Annex I;

(b) threshold values to be established by Member States in accordance with the procedure set out in Part A of Annex II for the pollutants, groups of pollutants and indicators of pollution which, within the territory of a Member State, have been identified as contributing to the characterisation of bodies or groups of bodies of groundwater as being at risk, taking into account at least the list contained in Part B of Annex II.

The threshold values applicable to good chemical status shall be based on the protection of the body of groundwater in accordance with Part A, points 1, 2 and 3 of Annex II, having particular regard to its impact on, and interrelationship with, associated surface waters and directly dependent terrestrial ecosystems and wetlands and shall *inter alia* take into account human toxicology and ecotoxicology knowledge.

[1] OJ L 184, 17.7.1999, p. 23. Decision as amended by Decision 2006/512/EC (OJ L 200, 22.7.2006, p. 11).

Multi-Residue Analysis

- Multi-compound analysis for **polar organic water pollutants**
- Solid phase extraction **SPE**
- Triple-quadrupole **LC-MS-MS**

SPE
(Autotrace®; Caliper)

LC-MS-MS
(Quattro micro Waters)

Polar Compounds / LC-MS²

Alkylphenolics

Nonylphenol (NP)	219 > 133
4n-NP	219 > 106
4n-NP (d8)	227 > 112
tert-Octylphenol (OP)	205 > 133
4n-OP	205 > 106
Bisphenol A	227 > 133
NPE_1C	277 > 219
NPE_2C	321 > 219
NPE_3C	365 > 219
NPE_nOs (n=2-17)	

Phenols

1-Nitrophenol	138 > 108
2,4-Dinitrophenol	183 > 109

Sucralose

395 > 359

Perfluorinated Surfactants

PFOS	499 > 80
PFHxS	399 > 80
PFOS ($^{13}C_4$)	503 > 80
PFHpA	363 >319
PFOA	413 > 369
PFOA ($^{13}C_4$)	417 > 372
PFNA	463 > 419
PFDA	513 > 469
PFUnA	563 > 519
PFBS	299 > 80
PFHxS	399 > 80

Pesticides

Atrazine	216 > 174
Atrazine ($^{13}C_3$)	219 > 177
Terbutylazine	230 > 174
Atrazine-desethyl	188 > 146
Terbutylazine-desethyl	202 > 146
Simazine	202 > 132
Simazine ($^{13}C_3$)	205 > 135
Propazine	230 > 146
Diuron	233 > 72
Isoproturon	207 > 72
Linuron	249 > 160
Alachlor	270 > 238
Metolachlor	284 > 252
Diazinon	305 > 169
Molinate	188 > 126
Metoxuron	229 > 71.6
Hexazinone	253 > 171
Carbaryl	202 > 145
2,4-D	219 > 161
Mecoprop	213 > 141
Bentazone	239 > 132
MCPA	199 > 141
MCPA d3	222 > 144
Dichlorprop	233 > 161
Propanil	216 > 160
Atrazine-OH	198 > 156
Terbutylazine-OH	212 > 156
Fenarimol	329 > 217

Pharmaceuticals

Carbamazepine	237 > 194
Carbamazepine (d10)	247 > 204
Ibuprofen	205 > 161
Ibuprofen ($^{13}C_3$)	208 > 163.4
Diclofenac	294 > 250
Diclofenac (d4)	298 > 254
Ketoprofen	253 > 209
Naproxen	229 > 185
Gemfibrozil	249 > 121
Benzafibrate	360 > 274

Steroid Estrogens

17β-Estradiol	271 > 145
Estriol	287 > 145
Estrone	269 > 145
Diethylstilbestrol	267 > 222
17a-Ethinylestradiol	295 > 145

Personal Care Products

Triclosan	287 > 35
Caffeine	195 > 138
DEET	192 > 119

Antibiotics

Sulfomethoxazole	254 > 156

Benzotriazoles

1H-Benzotriazole	120 > 64.6
1-Methyl-1H-benzotriazole	134 > 78.6

Solid-Phase Extraction (SPE)

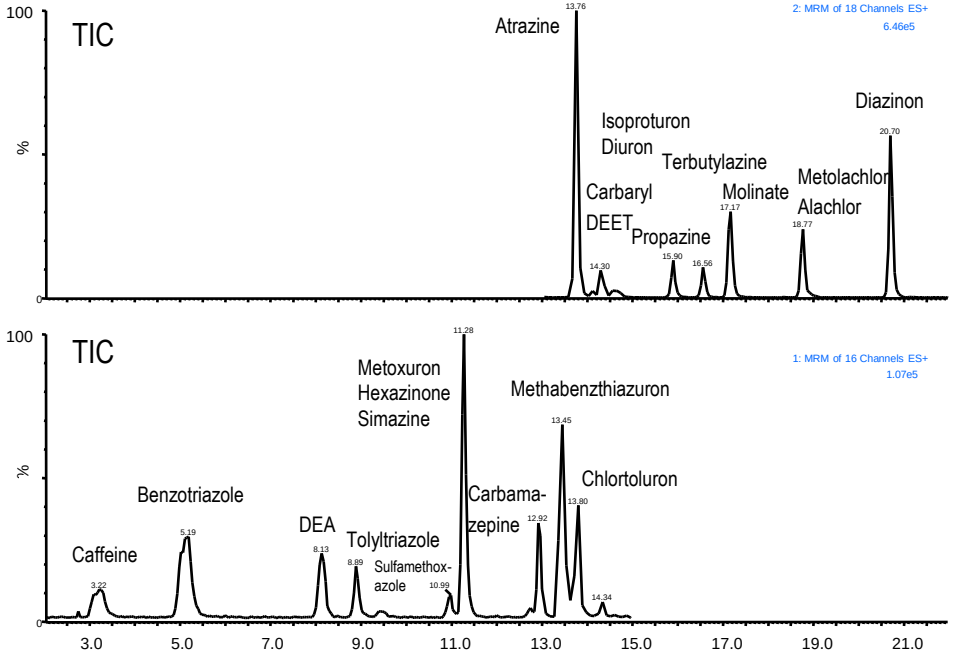
- Analysis of the liquid water phase (decanting)
- Oasis HLB (200 mg; 6 mL)
- 500 ml water (1L)
- Internal standard: Concentration 10 – 100 ng/L
- PFOA $^{13}C_4$; PFOS $^{13}C_4$; 4n-NP d_8; NP/OP $^{13}C_6$; Bisphenol A $^{13}C_{12}$; Carbamazepine d_{10}; Ibuprofen $^{13}C_3$; 2,4-D d3; MCPA d3; Atrazine $^{13}C_3$; Simazine $^{13}C_3$; Triclosan d10; Sucralose d6
- Extraction of 400 ml water (950 mL)
- Elution with methanol
- Concentration to 250 µl (or 500 µl)
- Injection volume 5 µL

Oasis HLB
(200 mg)

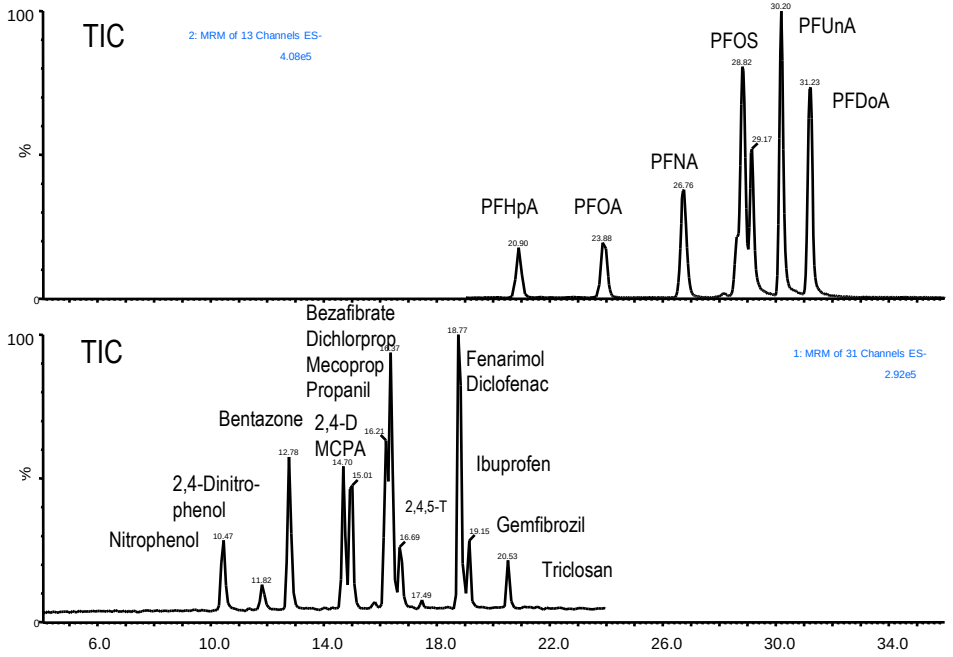
Loos et al., Anal. Bioanal. Chem. 387 (2007) 1469–1478

Multi-residue LC-MS-MS

Positive



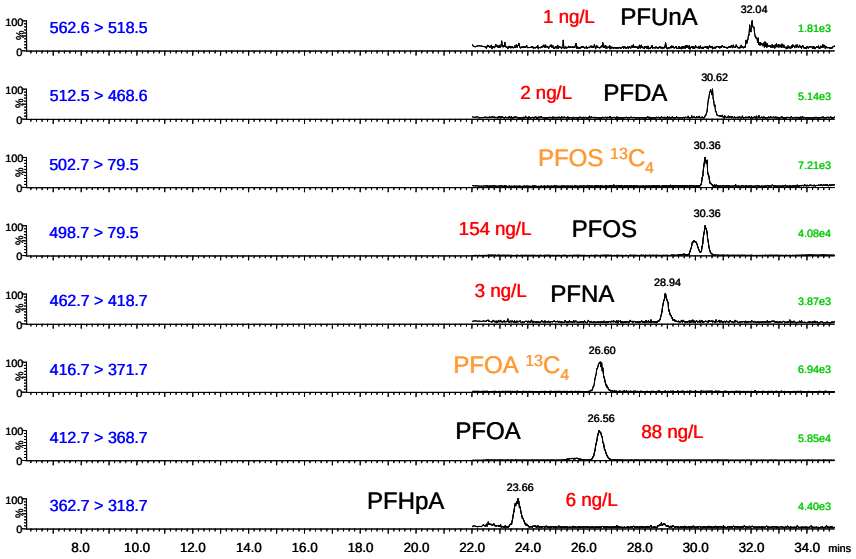
Negative

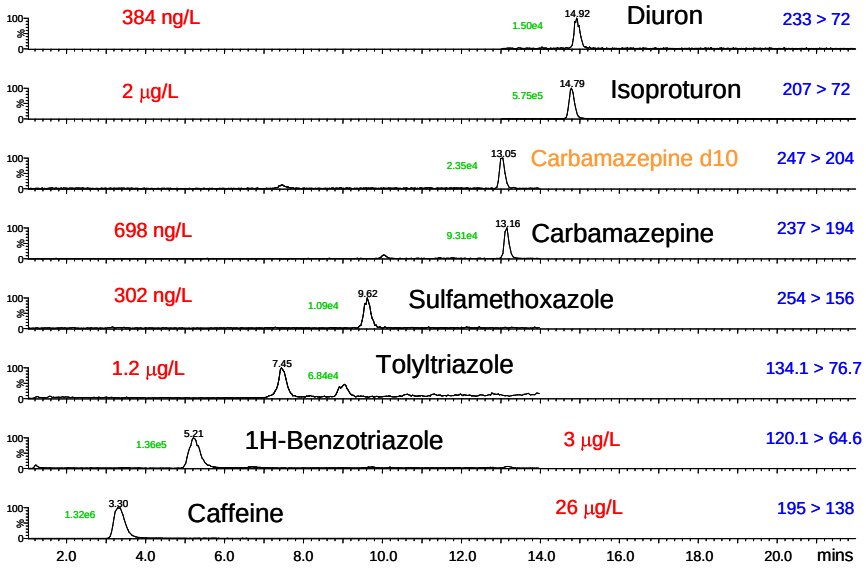


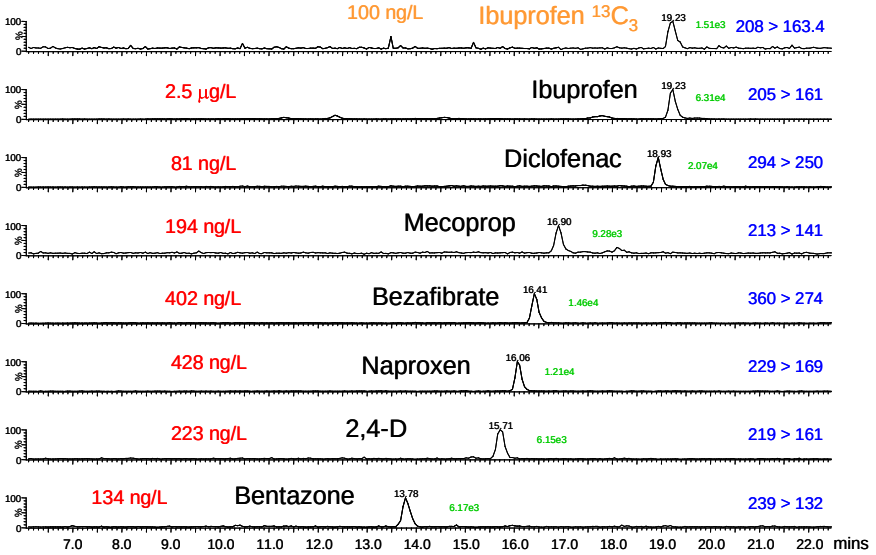
Conditions:

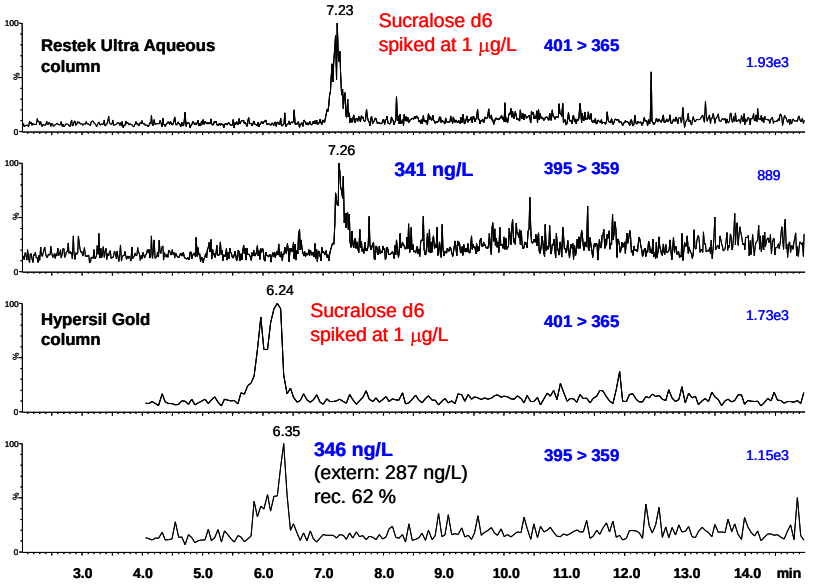
Hypersil gold column, 100 × 2.1 mm, water (0.1 % acetic acid) – acetonirile, gradient start with 90 % water, up to 90 % acetonitrile

LC-MS² chromatograms of river waters



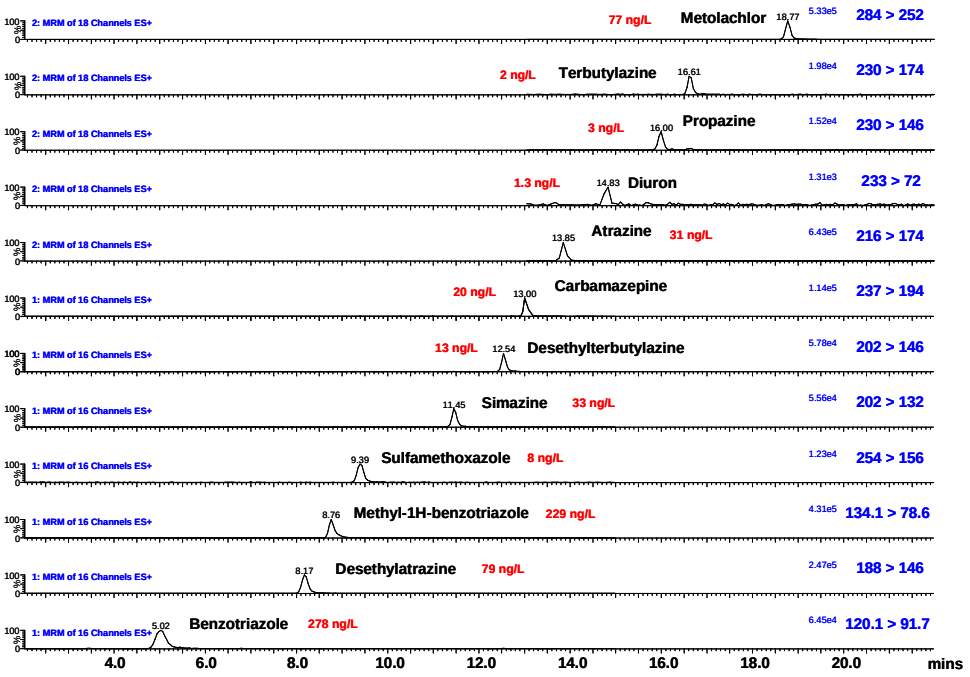




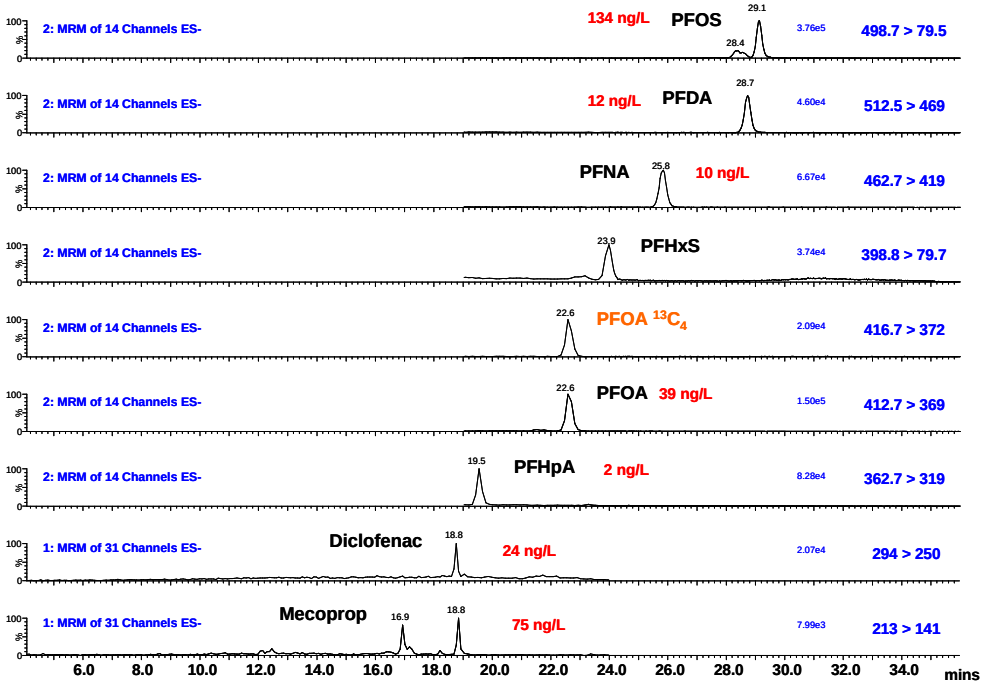


LC-MS² chromatograms of ground waters

Positive ionization



Negative ionization



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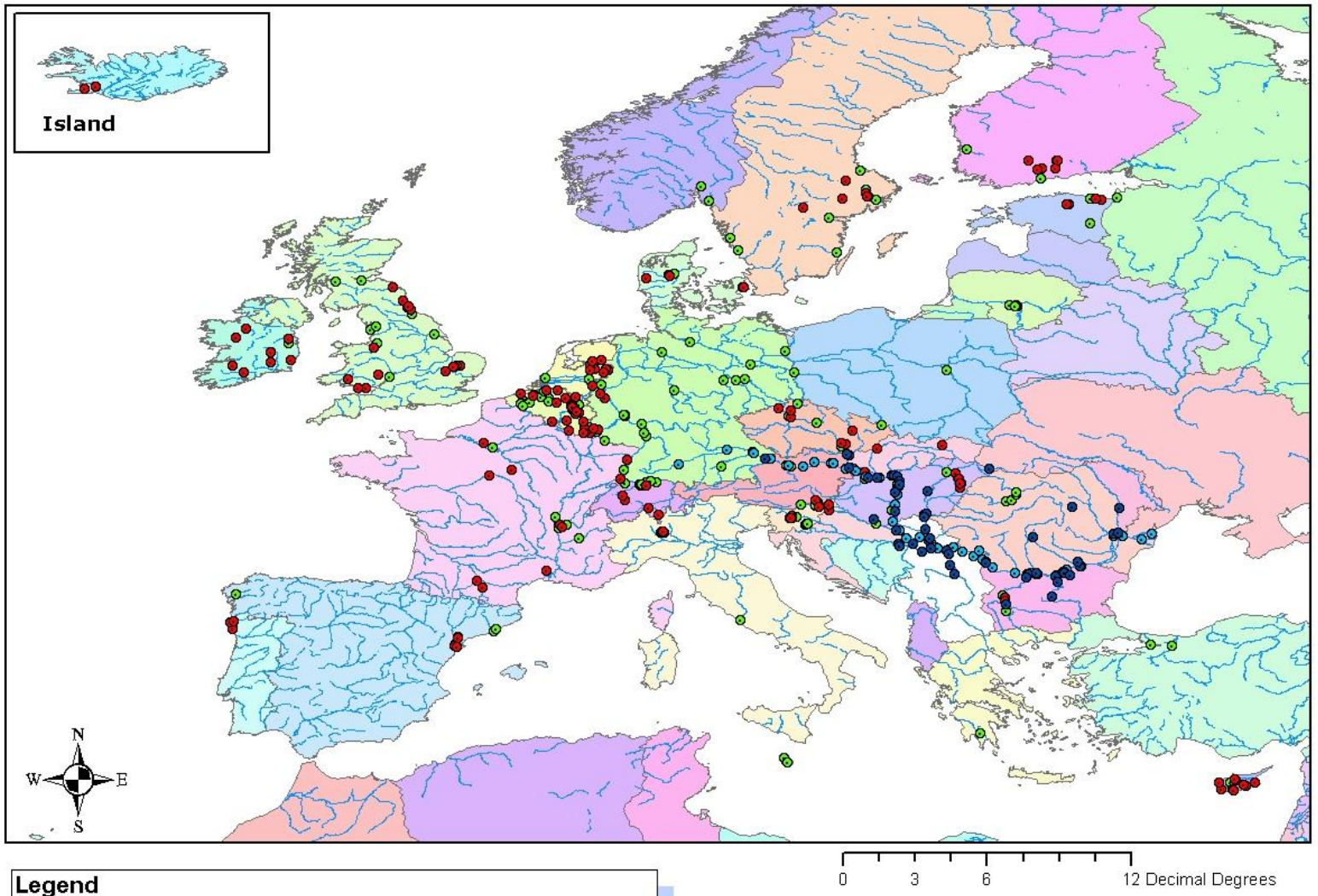
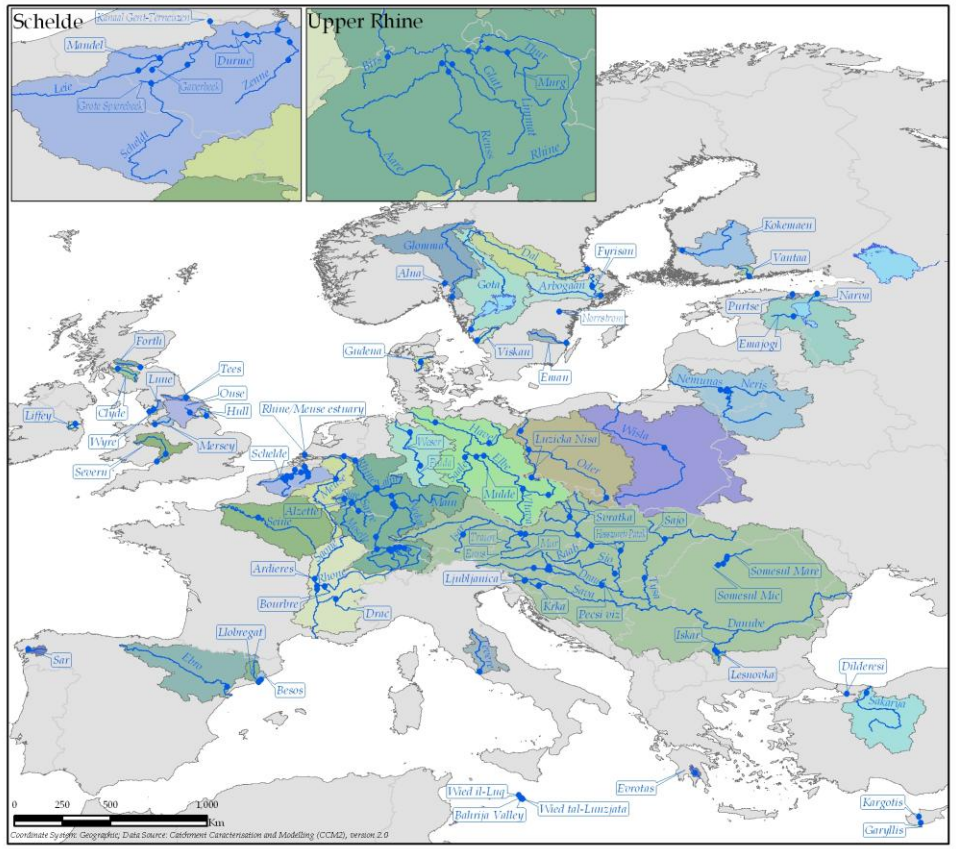


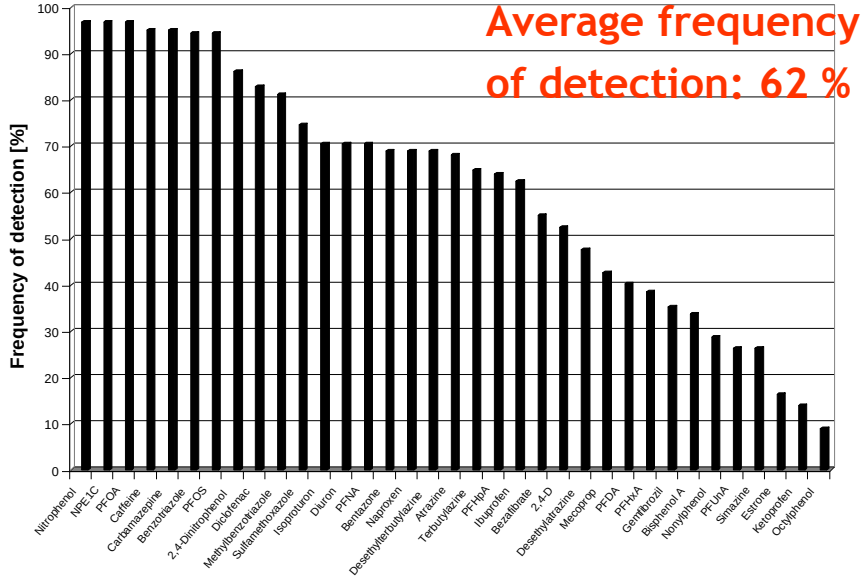
Surface water: 122 samples

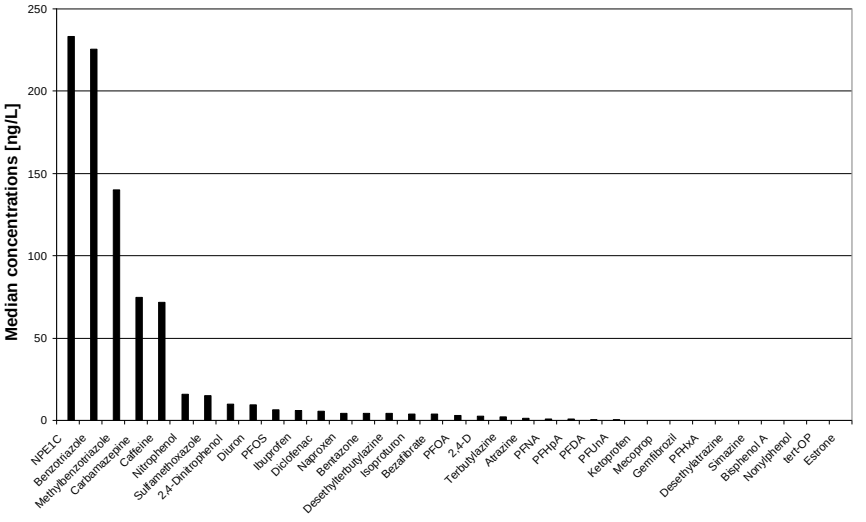
Ground water: 164 samples

Danube and tributaries: 103 samples

EU-wide survey of polar pollutants in rivers







The **most frequently detected compounds** were 1-nitrophenol (freq 97%), NPE_1C (97%), PFOA (97%), caffeine (95%), carbamazepine (95%), PFOS (94%), benzotriazole (94%), 2,4-dinitrophenol (86%), diclofenac (83%), and tolyltriazole (81%).

The **highest median concentrations** were measured for NPE_1C (233 ng/L), benzotriazole (226 ng/L), tolyltriazole (140 ng/L), carbamazepine (75 ng/L), and caffeine (72 ng/L).

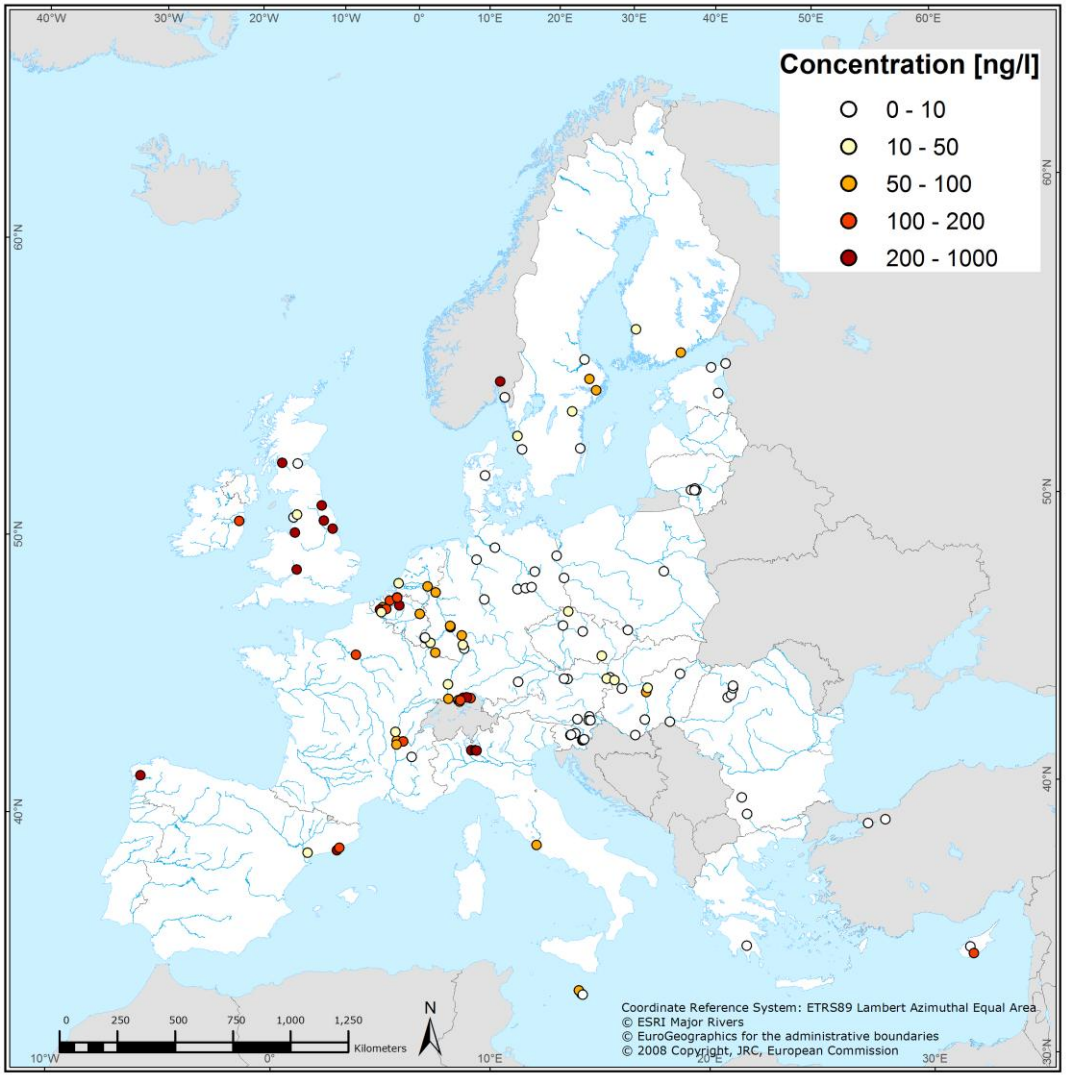
Loos et al., Environ. Poll. 157 (2009) 561

EU Rivers

- Pesticides were in general found in relatively low concentration ranges, most likely because the survey was conducted in autumn.
- Among the 122 river water samples analysed, there were 11 samples, which contained only few chemical substances at very low concentrations.
- The compounds detected at low concentrations (<50 ng/L) in these "clean" water samples were benzotriazole, tolyltriazole, caffeine, and NPE_1C, which shows their ubiquitous occurrence in even remote areas.
- The most pristine water samples came from water bodies in Estonia, Lithuania, and Sweden, which might be explained by the low population density in these sampling areas.

Loos et al., Environ. Poll. 157 (2009) 561

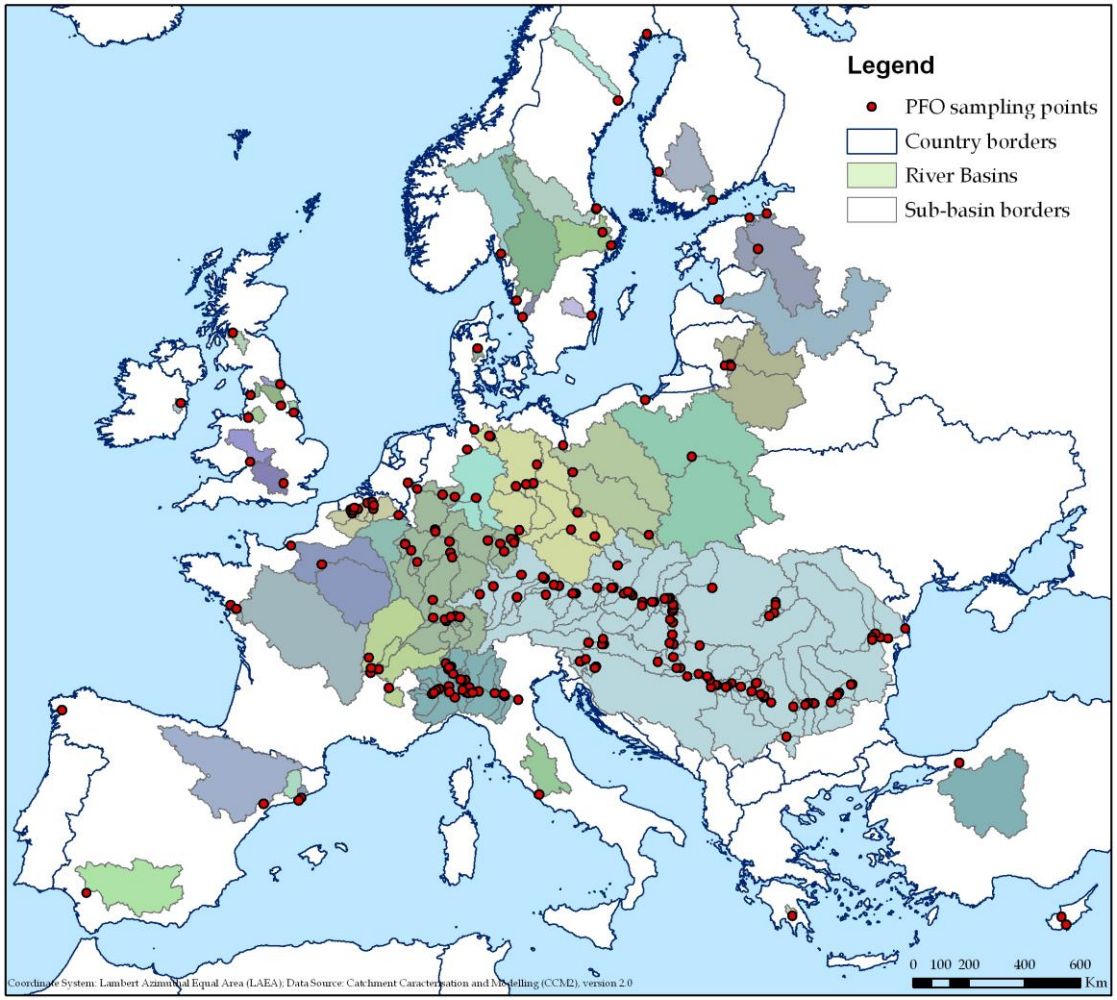
Sucralose: Artificial Sweetener

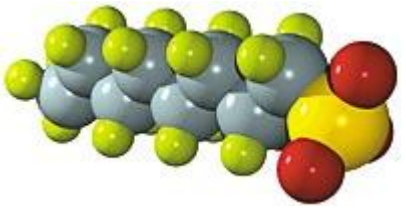


- Sucralose presence was confirmed in about **50 % of all samples** investigated with a maximum concentration of 924 ng/L in one sample.
- Sucralose was predominately found in samples from the UK, Belgium, the Netherlands, France, Switzerland, Spain, Italy, Norway, and Sweden.
- In samples from Germany and Eastern Europe minor concentration levels were detected, suggesting a lower use of sucralose as artificial sweetener in food products.
- This clearly shows an EU-wide spread of sucralose in surface waters.

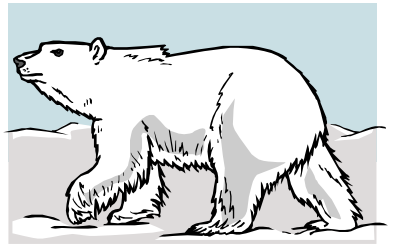
Loos et al., J. Chromatogr. A 1216 (2009) 1126

EU emission estimates for PFOA/S



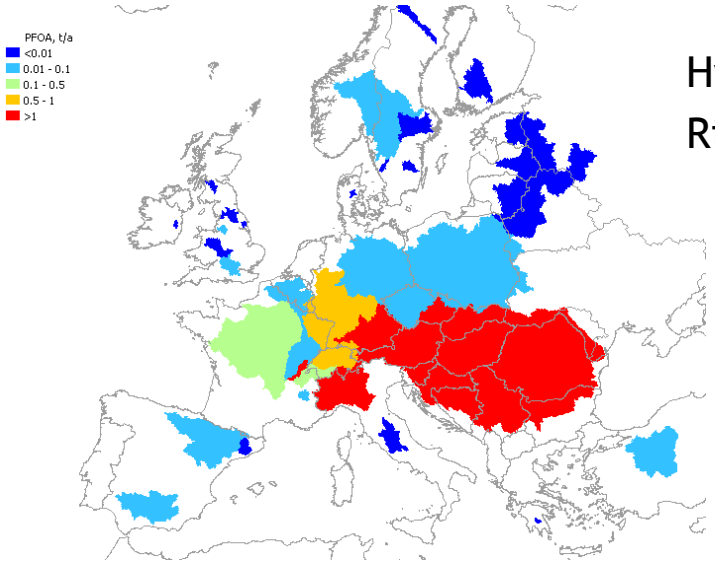


- 46 river monitoring points for rivers which "discharge" into the seas
- Around the same number of relevant rivers / streams (~50) is missing

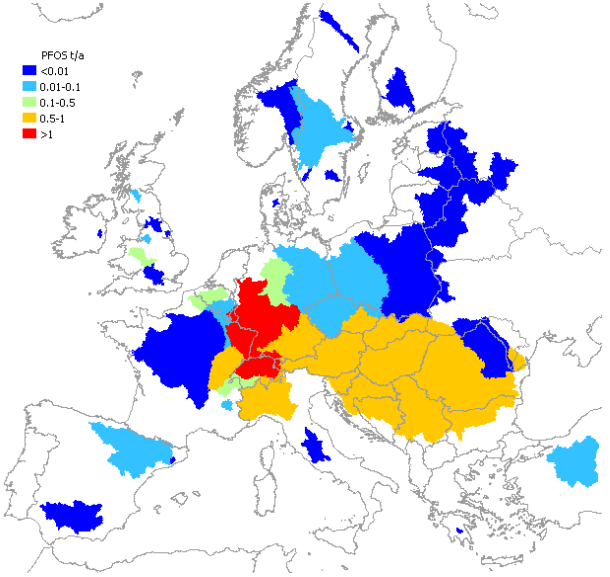


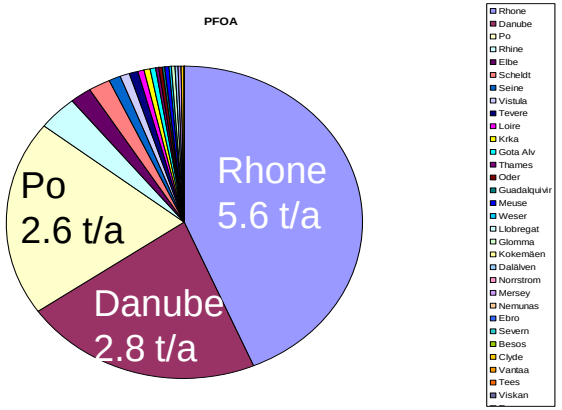
EU emission estimates for PFOA/S

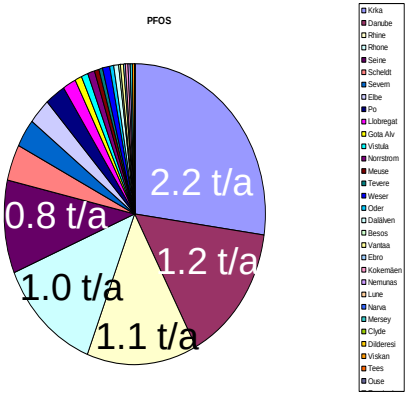
Maps of PFOA and PFOS emissions (t/a) for monitored catchments in Europe



Hydrological
River Flow Data







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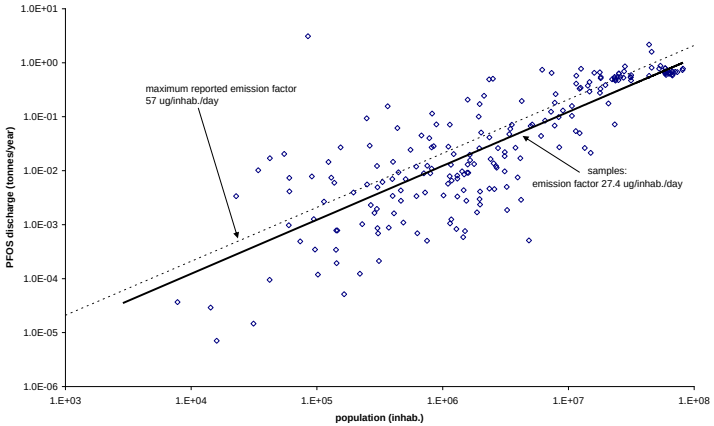
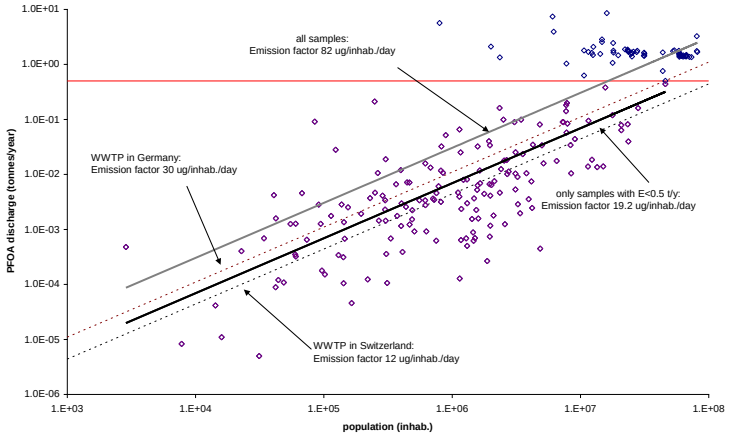
Correlation of PFOA/S with population

Linear scatter plots of observed PFOS/A discharges in European rivers with population in the catchments upstream

PFOS



PFOA



Estimation for the year 2007:

PFOS and PFOA discharges along the whole European river network to coastal areas in Europe: ~ **20 t/a PFOS** and **30 t/a PFOA**.

Emission factor: 27 μg/day/person PFOS, and 82 μg/day/person PFOA.

A. Pistocchi, R. Loos, ES&T, ASAP

Environ. Sci. Technol. **2009**, *43*, 386–392

A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate

ALEXANDER G. PAUL, KEVIN C. JONES, AND ANDREW J. SWEETMAN*

Centre for Chemicals Management, Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom

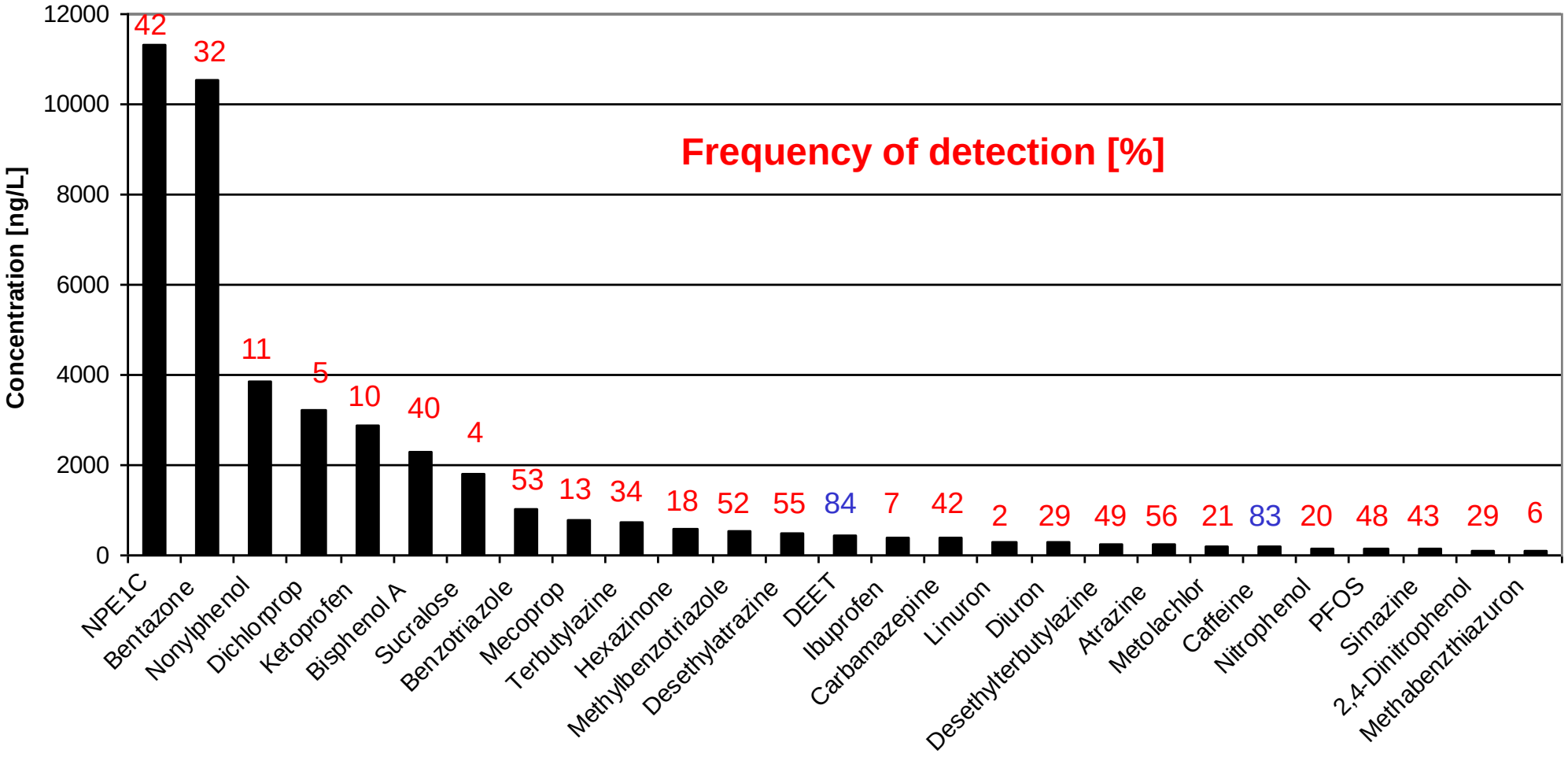
Received August 7, 2008. Revised manuscript received October 17, 2008. Accepted November 3, 2008.

LANCASTER UNIVERSITY

Max. Concentrations and Frequency of Detection in Groundwater

Institute for Environment and Sustainability

Average frequency of detection for all compounds: 25%

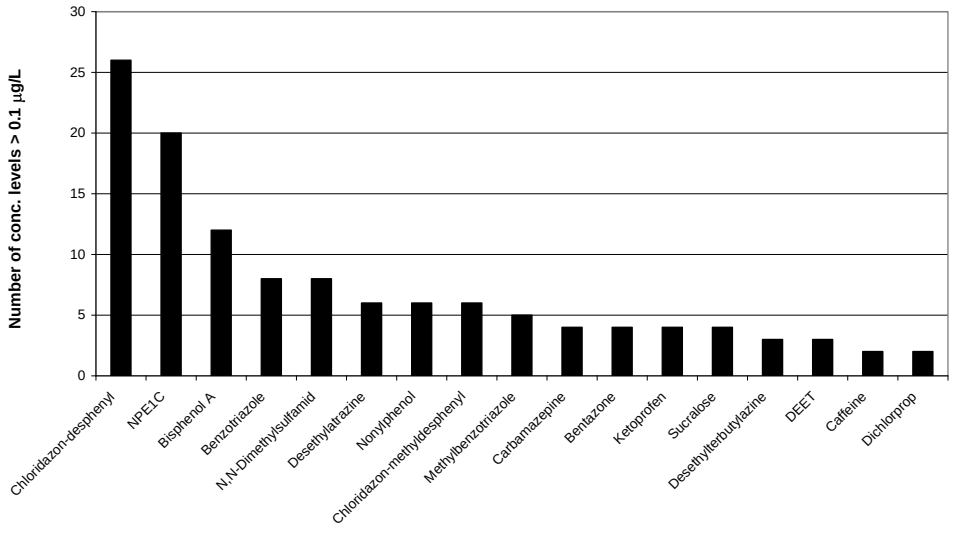


Not included:

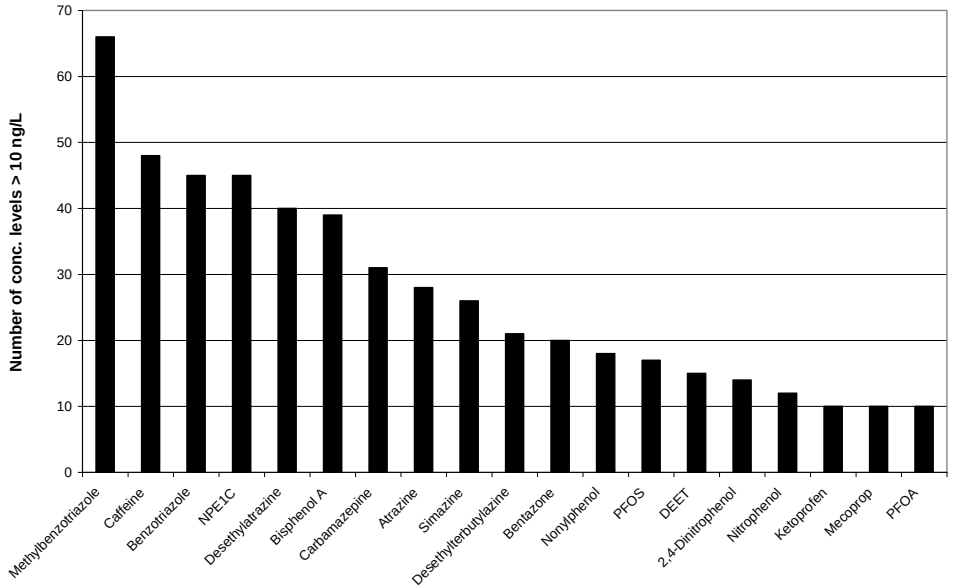
Dimethylsulfamid (max. **52** µg/L in one sample; freq. 12%), Chloridazon-desphenyl (max. **13** µg/L; freq. 17%), Chloridazon-methyldesphenyl (max. 1.2 µg/L; freq. 6%), PFOA (max. 39 ng/L; freq. **66 %**).

Ground water results

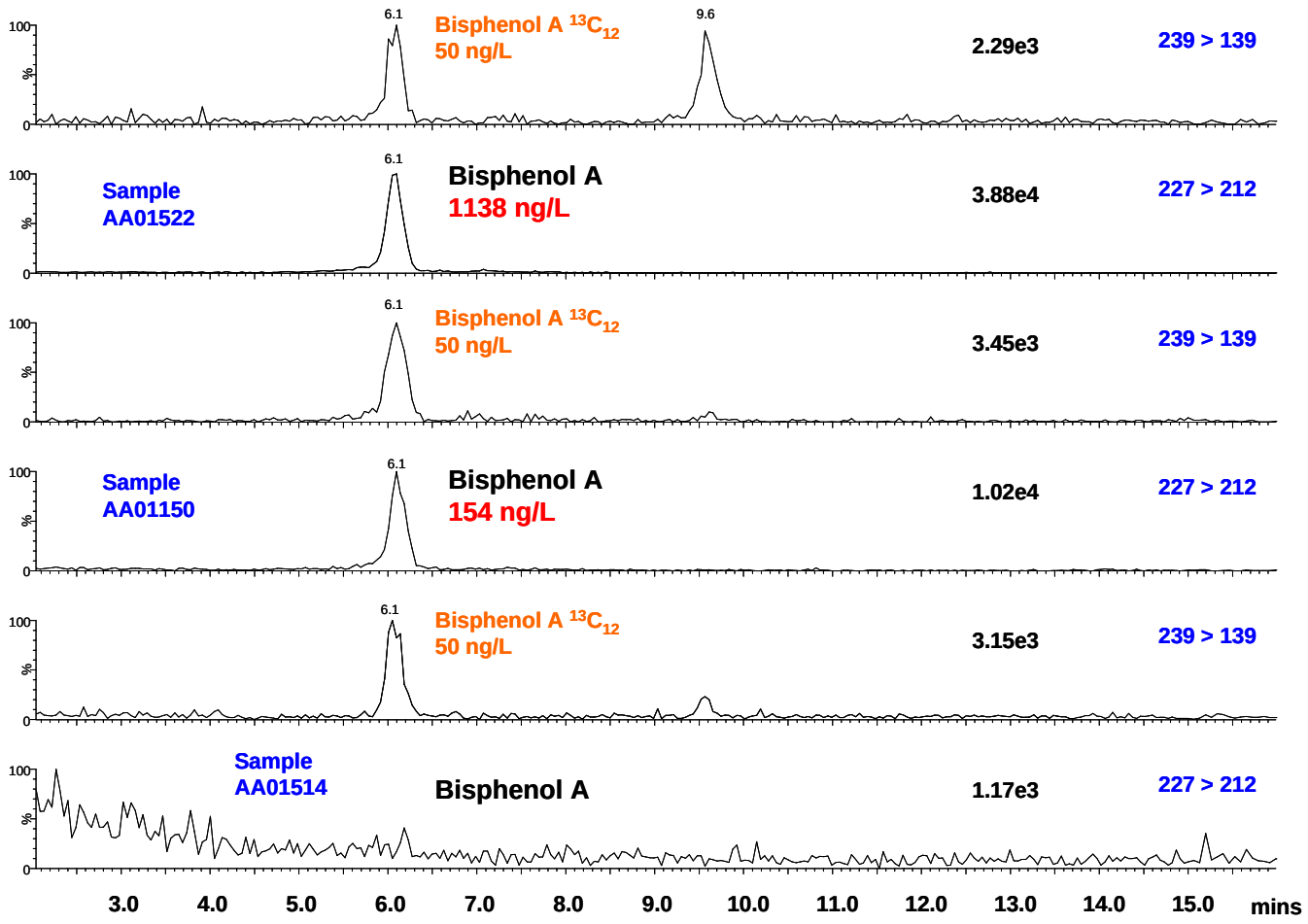
Number of detections > 0.1 µg/L



Number of detections > 10 ng/L



Bisphenol A in ground water



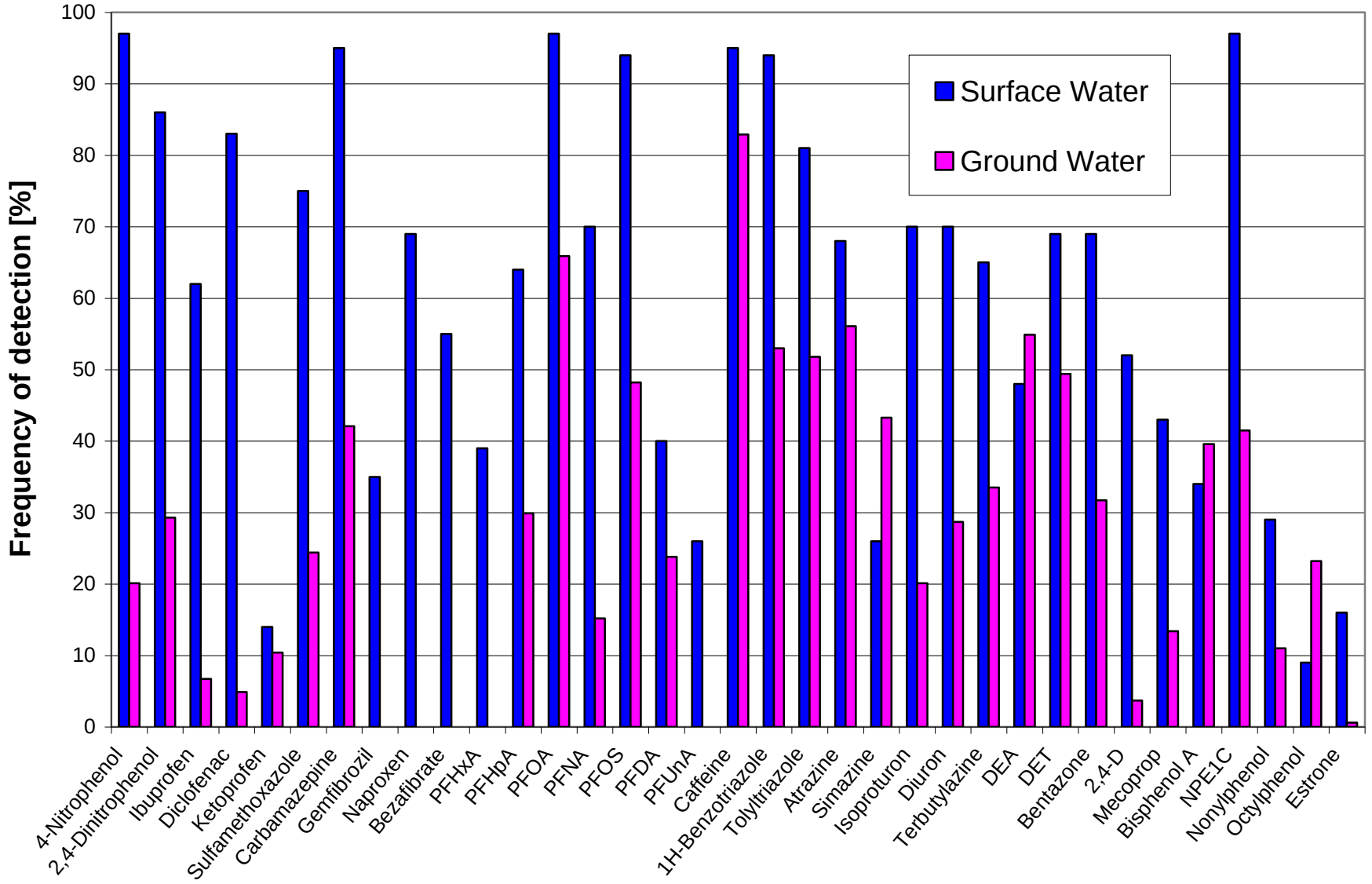
Frequency 40%

Max. 2.3 µg/L

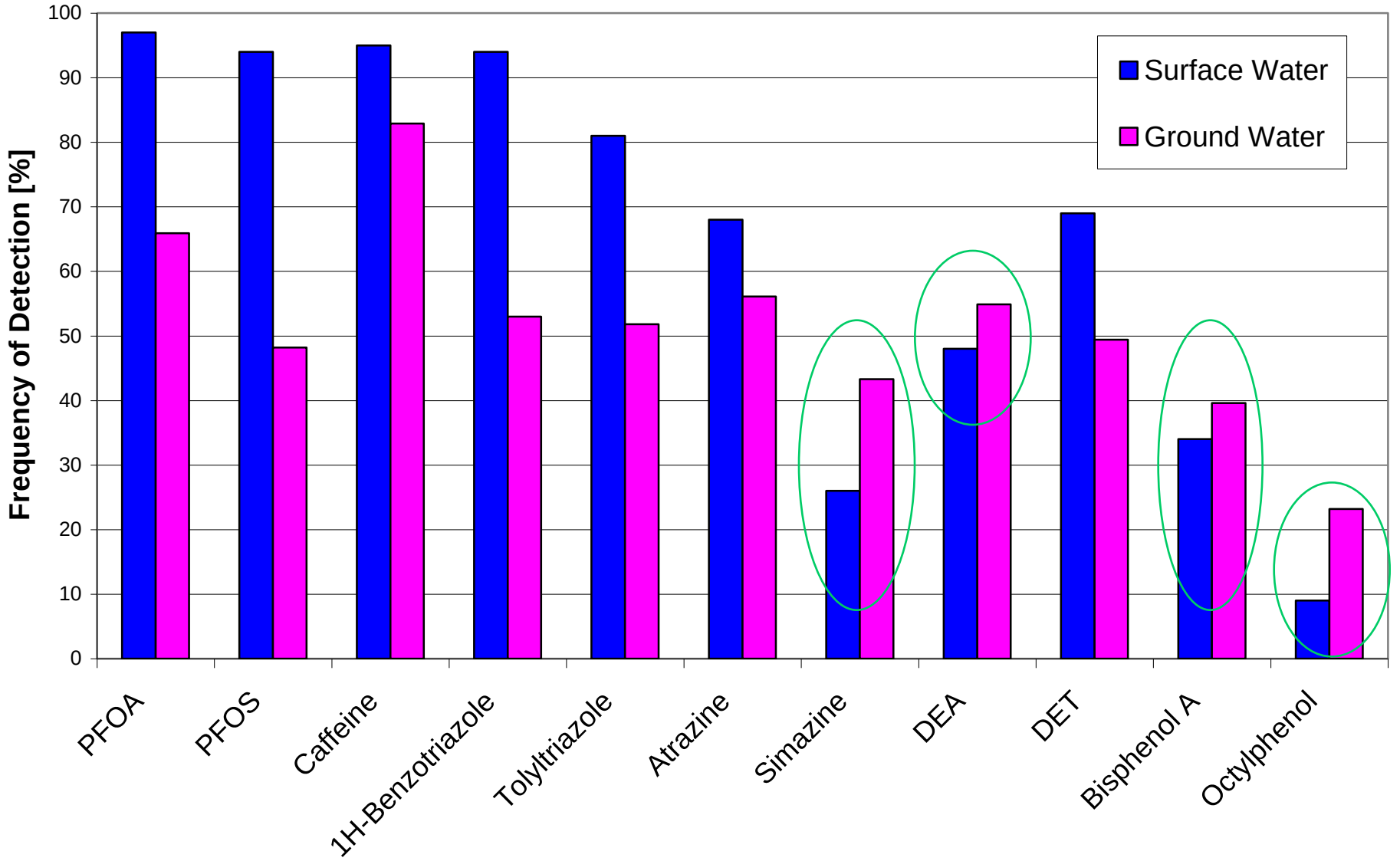
Hohenblum, P., Gans, O., Moche, W., Scharf, S., Lorbeer, G., **2004**. Monitoring of selected estrogenic hormones and industrial chemicals in groundwaters and surface waters in Austria. Sci. Total Environ. 333, 185–93.

Osenbrück, K., Gläser, H.-R., Knöller, K., Weise, S.M., Möder, M., Wennrich, R., Schirmer, M., Reinstorf, F., Busch, W., Strauch, G., **2007**. Sources and transport of selected organic micropollutants in urban groundwater underlying the city of Halle (Saale), Germany. Water Res. 41, 3259–3270.

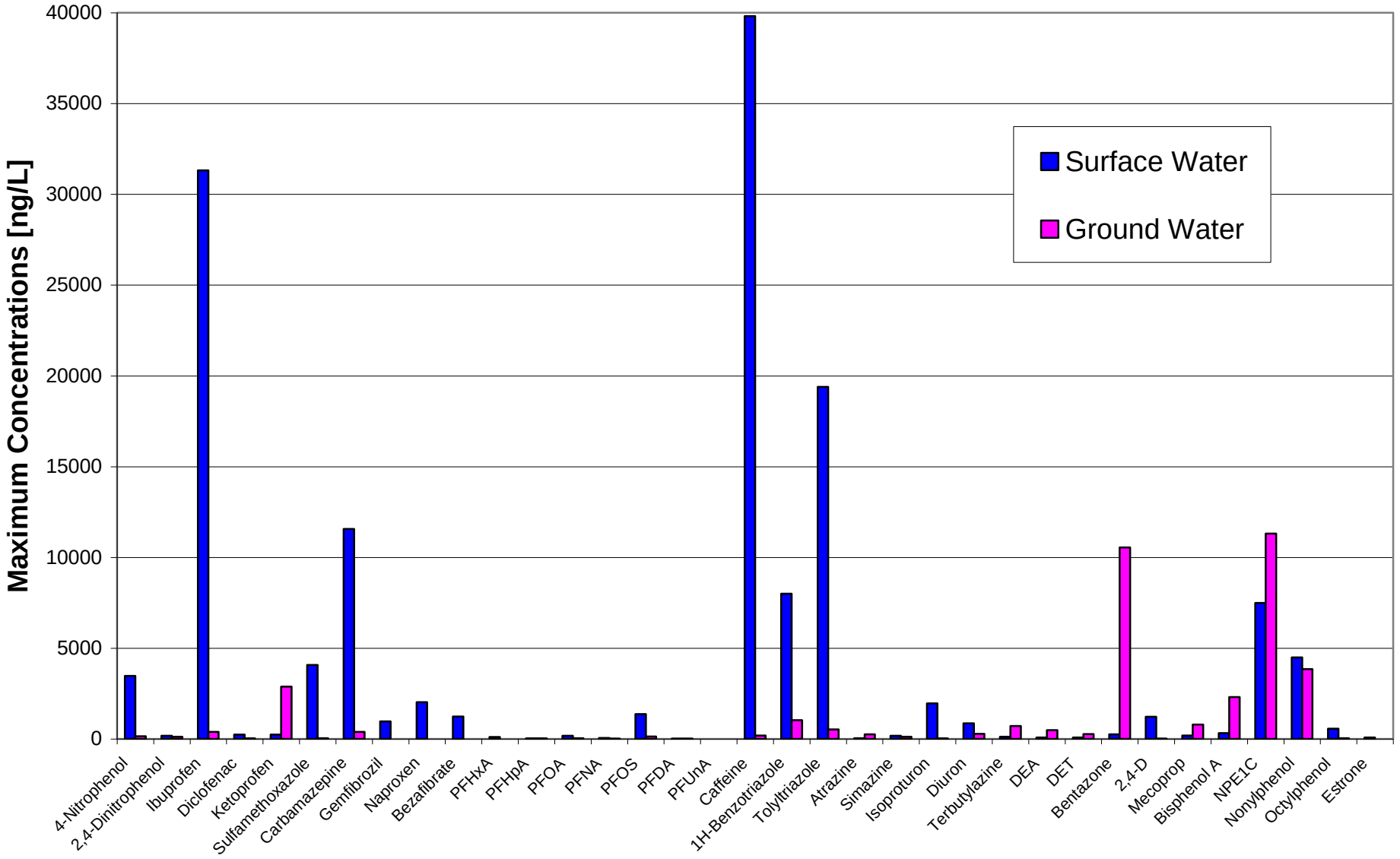
Comparison / Frequency



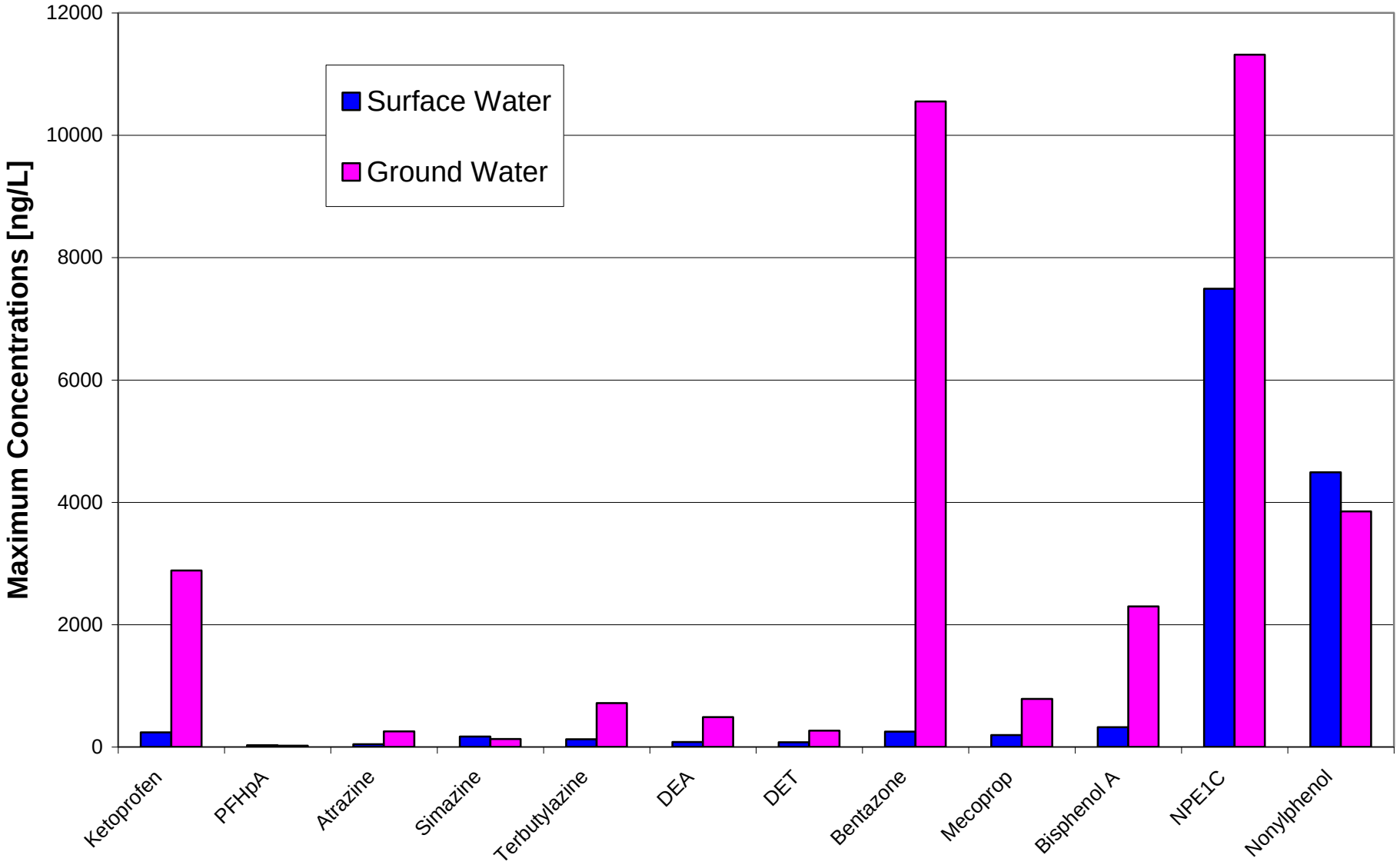
Comparison / Frequency



Comparison / Max. Concentrations



Comparison / Max. Concentrations



Surface River Water

Desethyl-Atrazine (DEA)

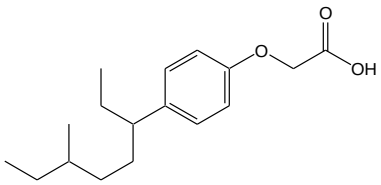
Desethyl-Terbutylazine (DET)

NPE_1C (nonylphenoxy acetic acid)

Frequency 97 %

Max.: 7.5 μg/L

Medium: 233 ng/L



Highest medium concentration of all compounds!

Ground Water

Some metabolites or degradation products of environmental concern where identified.

Chloridazon-desphenyl, Chloridazon-methyldesphenyl, N,N'-Dimethylsulfamid (DMSA), DEA, DET.

NPE_1C is a recalcitrant degradation product of NPEO surfactants; it was among the most relevant compounds detected in ground waters, with a frequency of detection of 42%, and a maximum concentration level of 11.3 μg/L.

Interestingly, this compound is degraded in surface water, but stable in anoxic ground water.

Swartz et al., 2006. Steroid Estrogens, Nonylphenol Ethoxylate Metabolites, and Other Wastewater Contaminants in Groundwater Affected by a Residential Septic System on Cape Cod, MA. Environ. Sci. Technol. 40, 4894-4902.

Chemical Mixtures

- Our results show the importance of multi-residue analytical methods for analyzing chemical mixtures.
- In total, 77 different organic chemical compounds were analyzed in the ground water samples.
- The maximum number of compounds detected at any site was 29, and the median number of detections per site was 12. There was no sample free of organic chemicals; in five samples only 3 compounds were found.
- Moreover, multi-compound analysis is mandatory for compliance with the European groundwater quality standard of 0.5 μg/L for the sum of pesticides (and degradation products).

Conclusions

- Frequency of detection: In surface water higher than in ground water, but some exemptions:

  Simazine, DEA, Bisphenol A, Octylphenol
- For most of the chemicals analysed no environmental limit values or guidance do exist.
- The European WFD however introduces environmental quality standards for 41 (groups of) chemicals.
- Analysis of metabolites is very important.