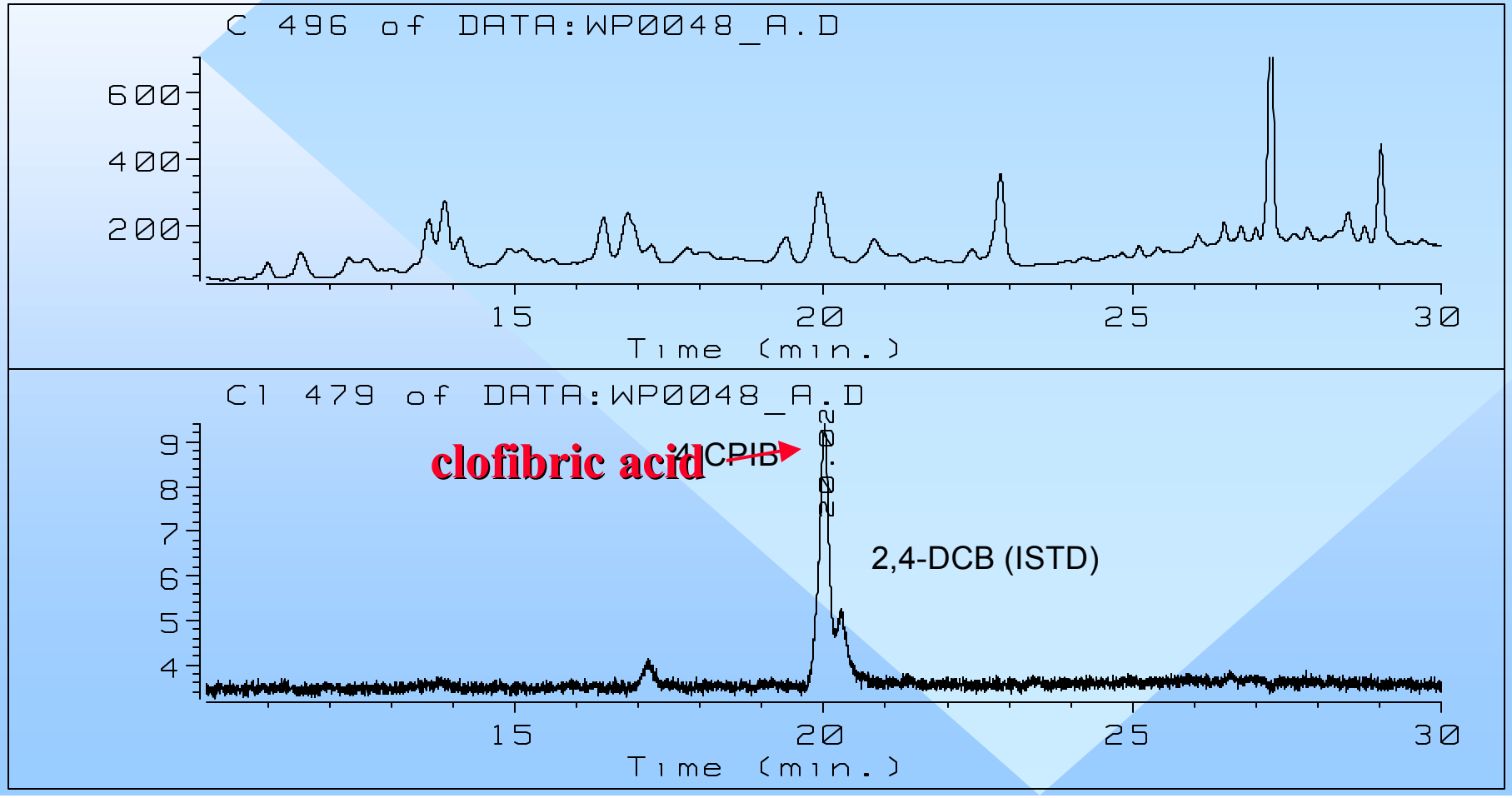
e-mail: thomas.heberer@tu-berlin.de
internet: www.wasseranalytik.de or
www.foodchemistry.de

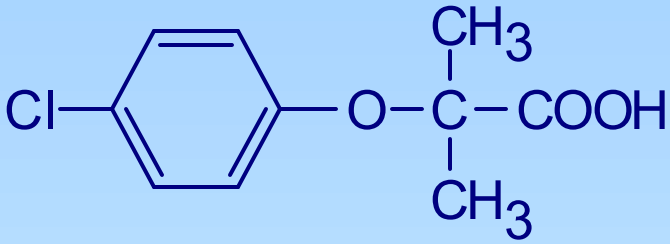
From Municipal Sewage to Drinking Water: Fate and Removal of Pharmaceutical Residues in the Aquatic System of Berlin

Thomas Heberer, K. Reddersen,
Institute of Food Chemistry, Technical University of Berlin, Germany
D. Feldmann, Th. Zimmermann, Central Institute for Public Health, Ministry of Defense, Bonn, Germany

Figure 1:
GC-AED (atomic emission detector) chromatograms of a ground water sample derivatized with pentafluorobenzyl bromide (September 1991).
Element traces for carbon C 496 nm and chlorine Cl 479 nm

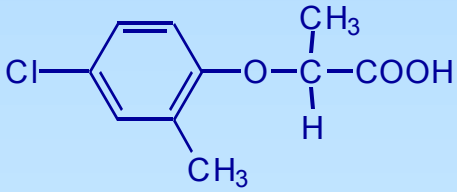


What is clofibric acid ?



Clofibric acid is :

- ✱a phenoxycarboxylic acid
- ✱a structural isomer of the herbicide mecoprop



mecoprop

- ✱the pharmaceutically active metabolite of drugs used as blood lipid regulators in medical care
- ✱ a potential organic indicator for sewage contaminations in sewage farm ground water because it easily leaches through the sewage farm subsoil

MID : Drinking Water Sample

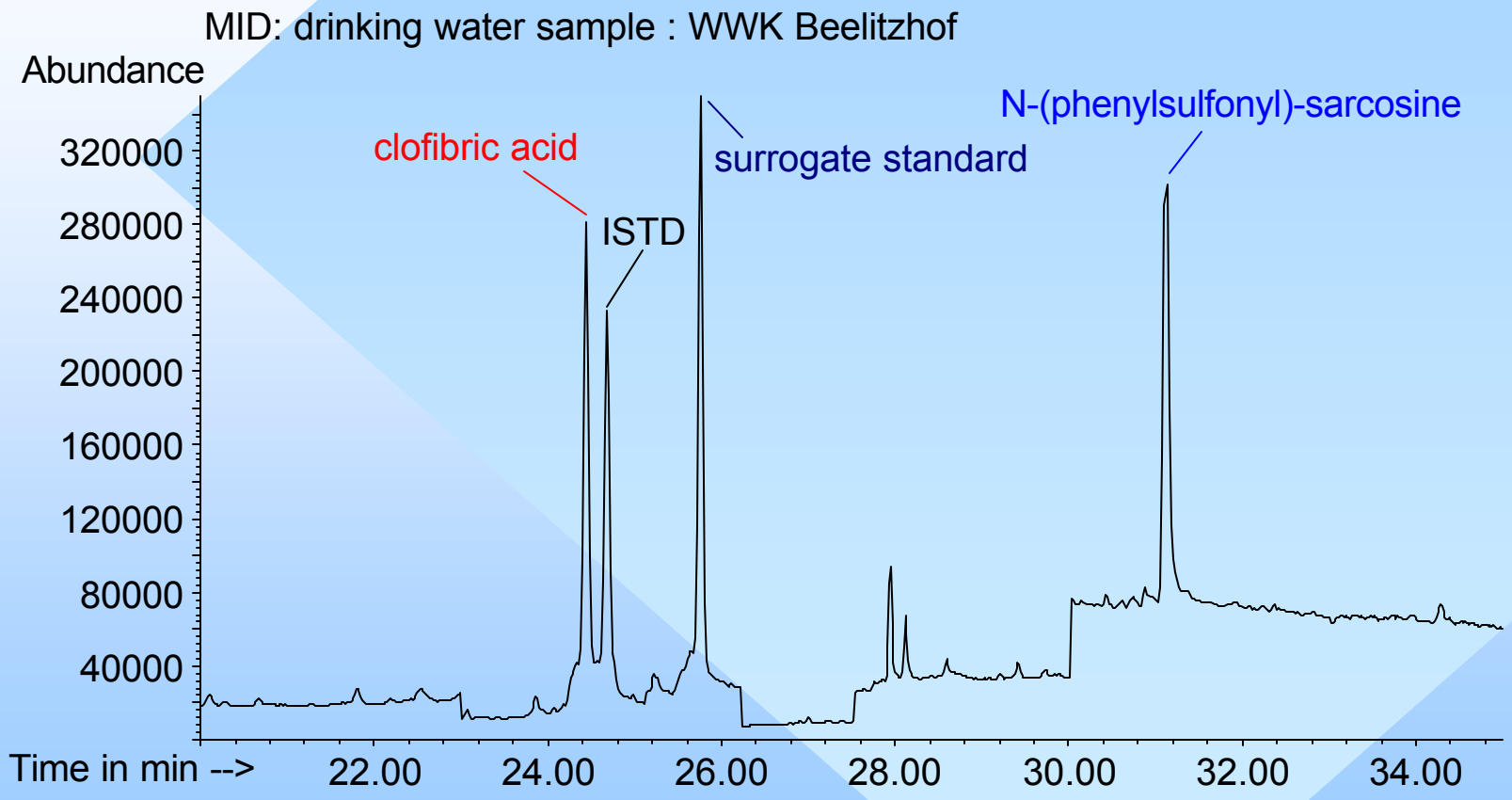


Figure 1. MID-chromatogram of a pentafluorobenzylated extract of a drinking water sample taken from the water works Beelitzhof at August 5th 1994. The sample contained 60 ng/l clofibric acid and 105 ng/l N-(phenylsulfonyl)-sarcosine. Recovery of the surrogate standard : 86 %.

Questions

- Where does it come from? ⇨ Origin?
- What happens to these residues? Where do they go? ⇨ Fate?
- Are there any other drug residues?
- Are there any toxicological or ecotoxigological impacts?

Pharmaceuticals in the environment

- Human Medical Care
  - via discharges of municipal sewage and hospital effluents, sewage sludge‘s (adsorption), landfill leachates (waste disposal), production residues
- Animal Drugs
  - via agriculture (liquid manure), discharges of municipal sewage, sewage sludge‘s (adsorption), landfill leachates (waste disposal), production residues, direct introduction (aquacultures)
- Feed Additives
  - via agriculture (liquid manure), production residues

Pharmaceuticals in the environment

Important prerequisites for the occurrence of pharmaceutical residues from human medical care in the aquatic environment are:

- **the prescribed amounts for the individual drug**
- **the pharmacokinetics in the human organism**
- **the behavior of the drug residues during the sewage treatment process and in the environment** (persistence, sorption, bioaccumulation, metabolism)

Drug residues in effluents from municipal sewage treatment plants in Berlin

Drug residues from various prescription classes (e.g., blood lipid regulators, analgesics, antiepileptic drugs, steroids) were detected up to the low µg/L-level in the effluents of the sewage treatment plants in Berlin.

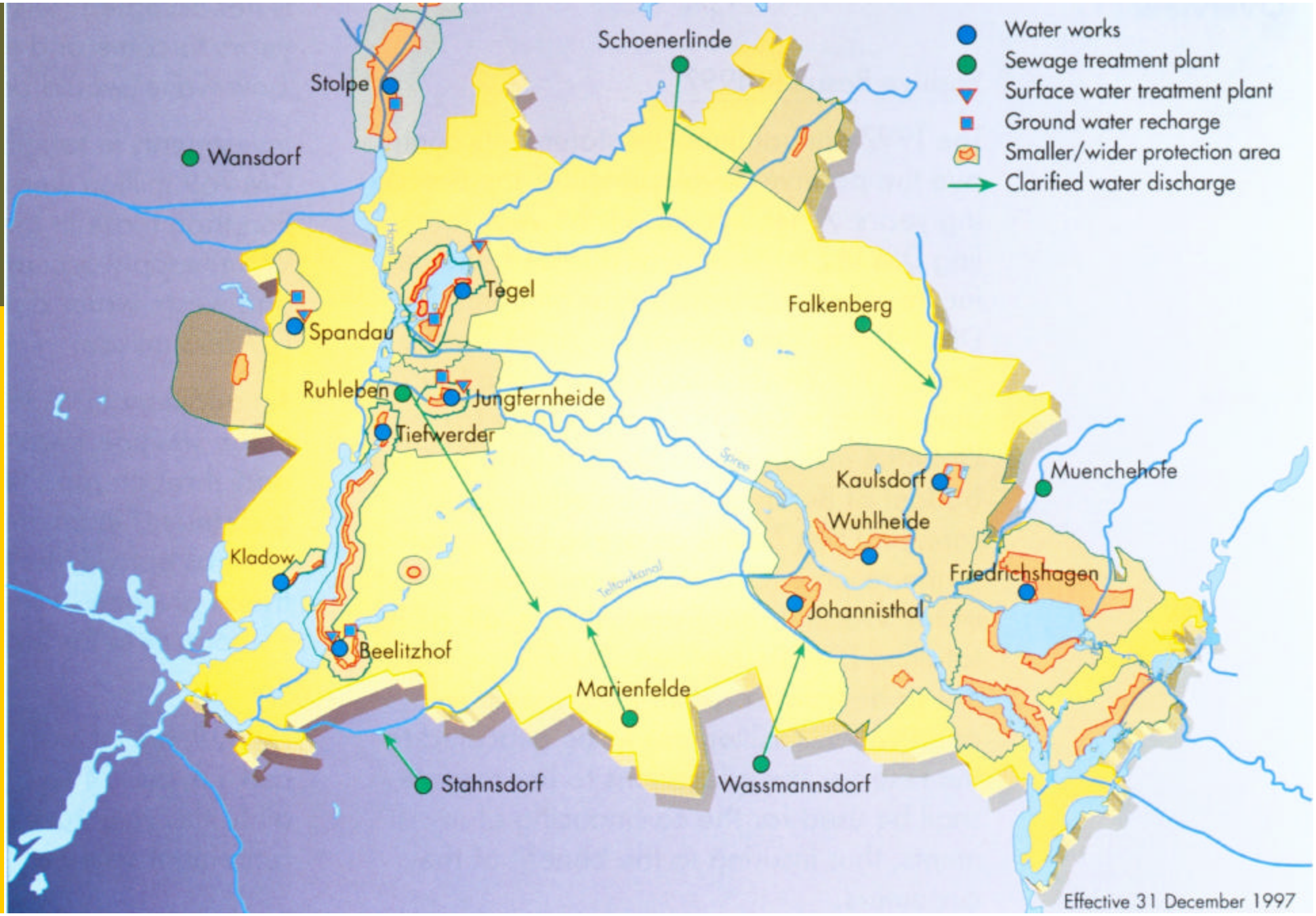
Table 2. Concentrations and removal rates for three drug residues and for caffeine detected in the effluents of sewage treatment works (STWs) in Berlin*.

analyte	maximum effluent concentration	average effluent concentration	removal
	in µg/L	in µg/L	in %
carbamazepine	5.00	2.19	< 5
clofibric acid	0.73	0.47	< 5
diclofenac	4.70	2.76	16
caffeine	3.0	1.63	> 99

* sampling series in May-December 1999 (Heberer et al.; in press); **STWs in Berlin: Ruhleben, Schönerlinde, Waßmannsdorf (mixed samples: 24hours).

The Berlin situation

- High concentrations of municipal sewage contaminants can be expected in the receiving waters resulting from:
  - very low surface water flows,
  - large amounts of raw sewage produced by its population of around 3.5 million people, and
  - a total drinking water consumption of only 127 liters per day and inhabitant (Germany) → concentrated sewage
- High proportions of bank filtrate and artificial ground water enrichment (approximately 75%) used in drinking water production


Water works
Sewage treatment plant
Surface water treatment plant
Ground water recharge
Smaller/wider protection area
Clarified water discharge
Schoenerlinde
Stolpe
Wansdorf
Tegel
Spandau
Falkenberg
Ruhleben
Jungfernheide
Tiefwerder
Kaulsdorf
Muenchehofe
Wuhlheide
Kladow
Friedrichshagen
Johannisthal
Beelitzhof
Marienfelde
Stahnsdorf
Wassmannsdorf
Effective 31 December 1997

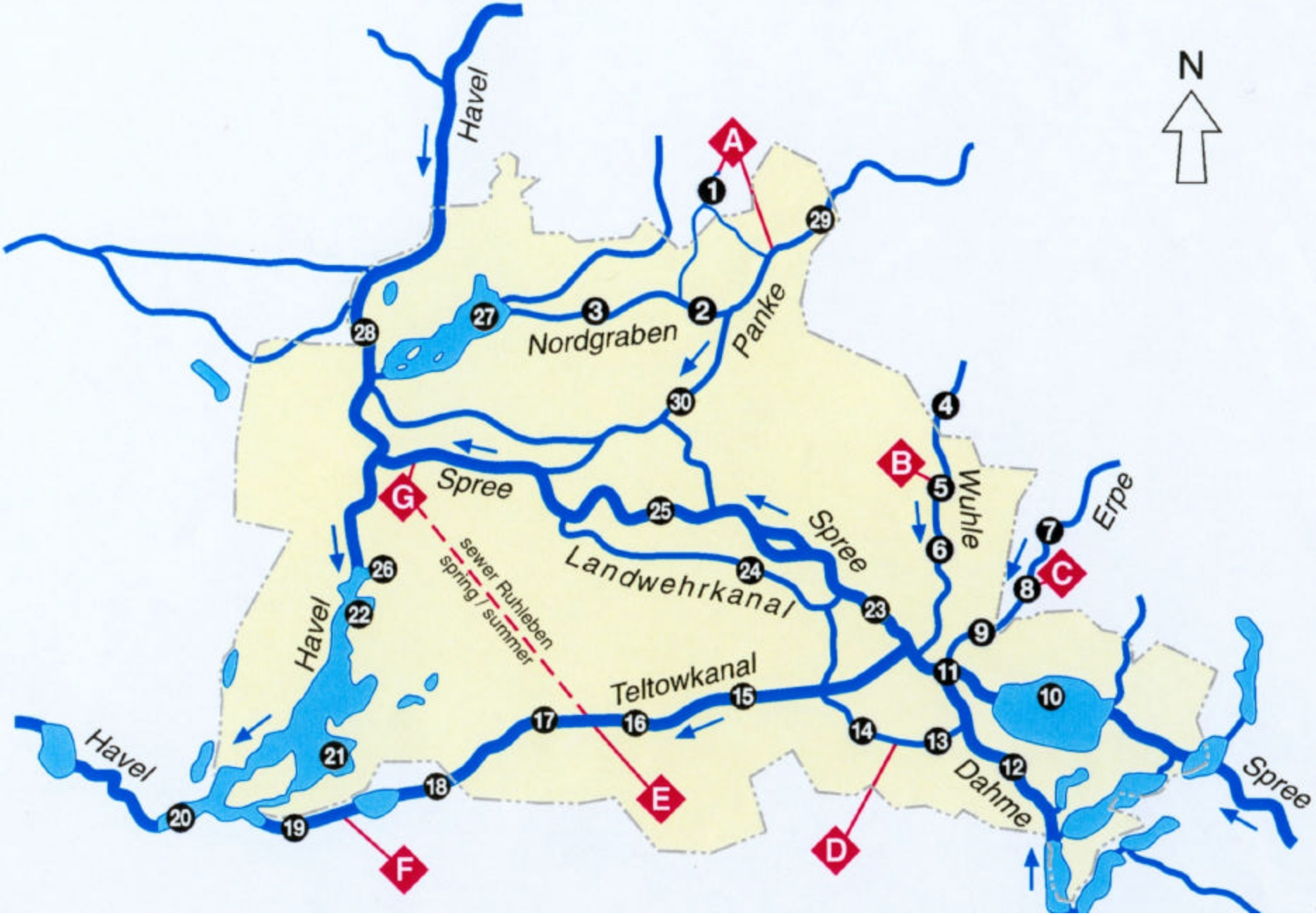
Monitoring of Berlin Surface Waters (1996)

Analysis for :

- pesticides, polar contaminants (e.g. DDA, NPS)
- **pharmaceutical residues**
- phenols
- synthetic musks *(polycyclic musks and nitro musks)*

further parameters:

- physical and chemical parameters (e.g. pH, conductivity, DOC, COD, phenolic index, NO_3, NO_2, ammonia, phosphate, boron)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Nordgraben
Panke
Spree
Landwehrkanal
Wuhle
Erpe
Teltowkanal
Dahme
Havel
Havel
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sewer Ruhleben
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GC-MS-MS: surface water sample

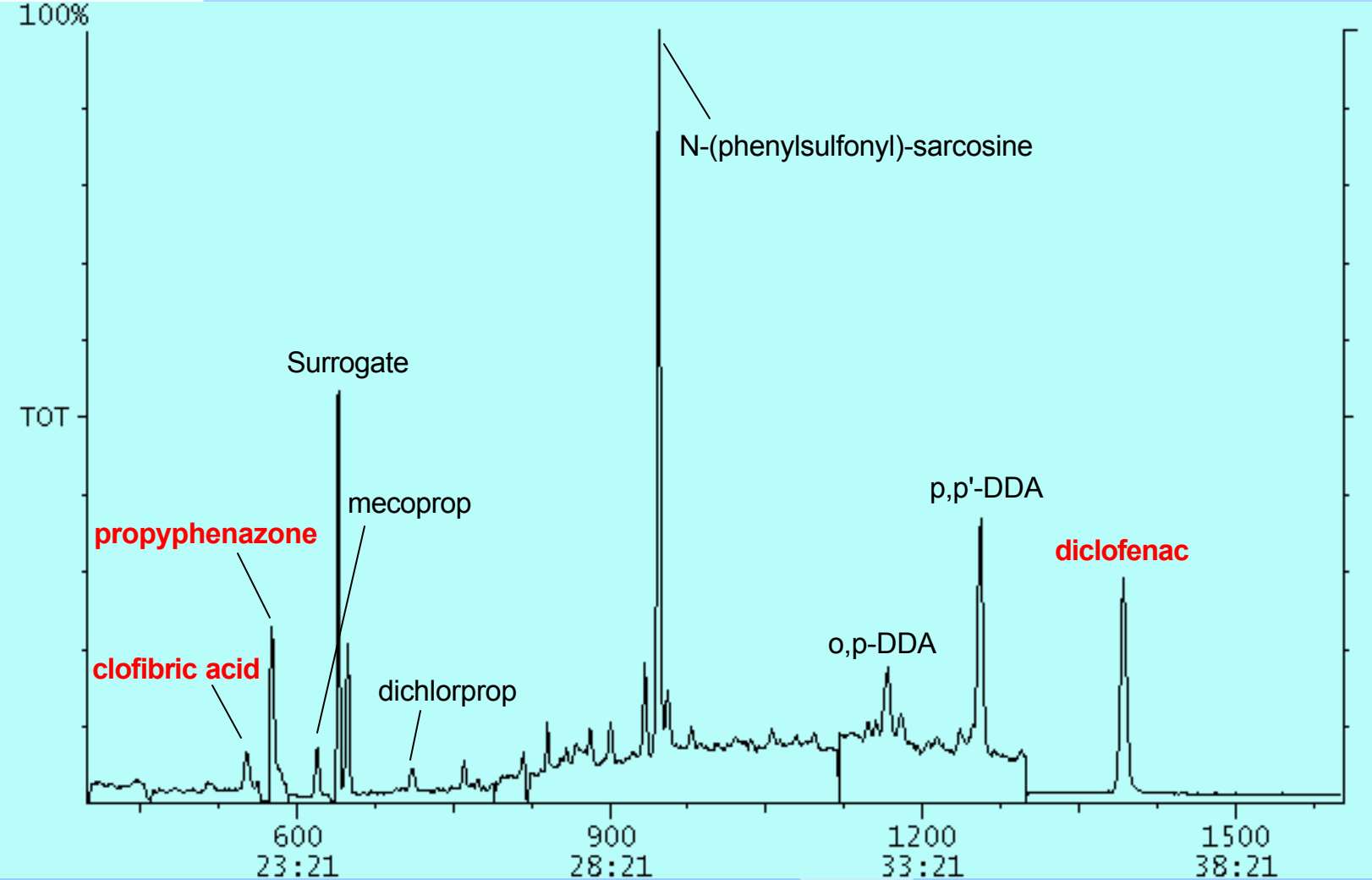


Figure 5. GC-MS-MS daughter ion chromato-gram of a pentafluoro-benzylated extract of a surface water sample

Concentration profiles for clofibric acid and diclofenac in the Teltowkanal

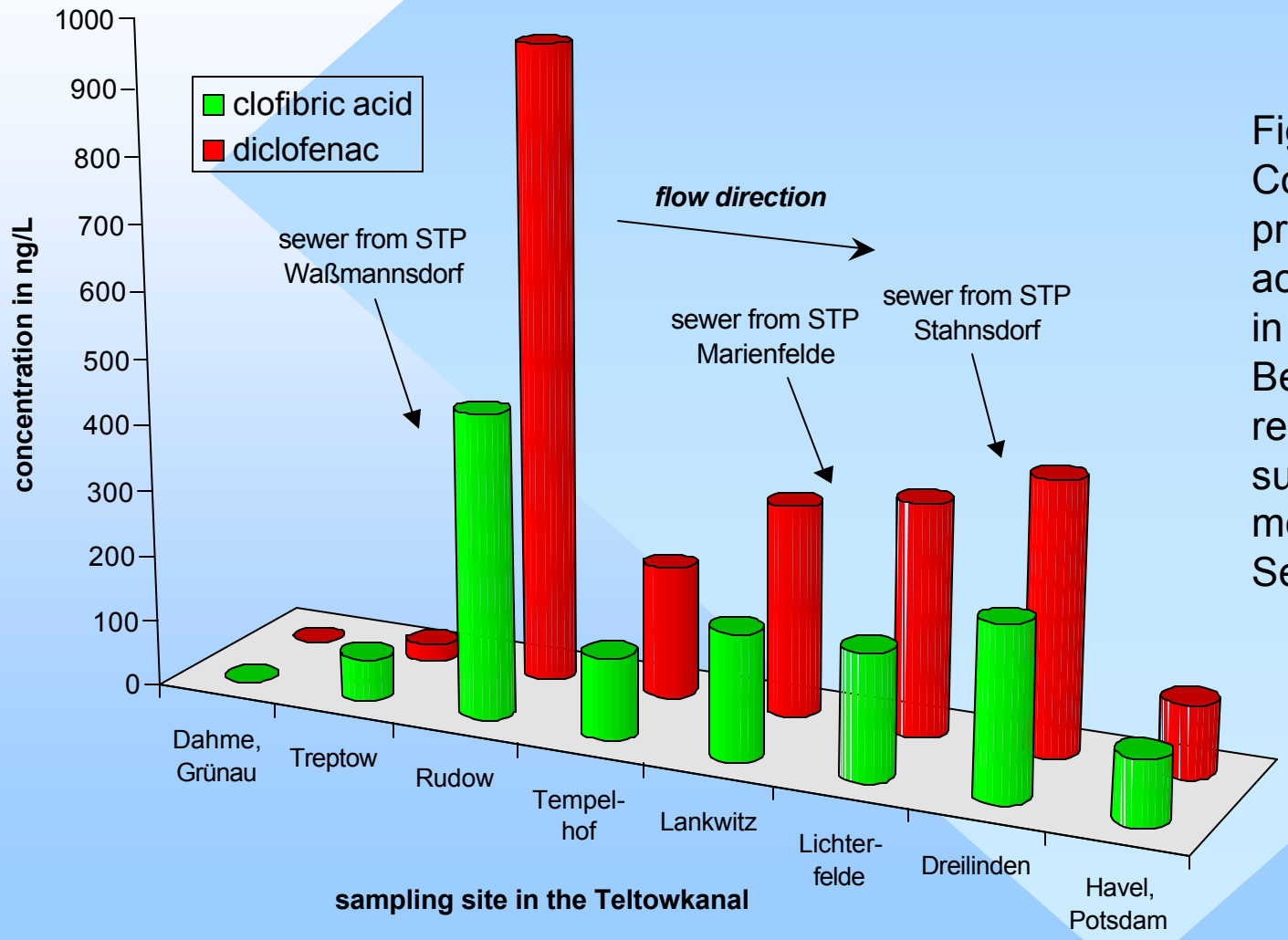


Figure 2. Concentration profiles for clofibric acid and diclofenac in the Teltowkanal in Berlin. Selected results from a surface water monitoring in September 1996.

Concentration profiles for several drug residues found in the Teltowkanal (1999)

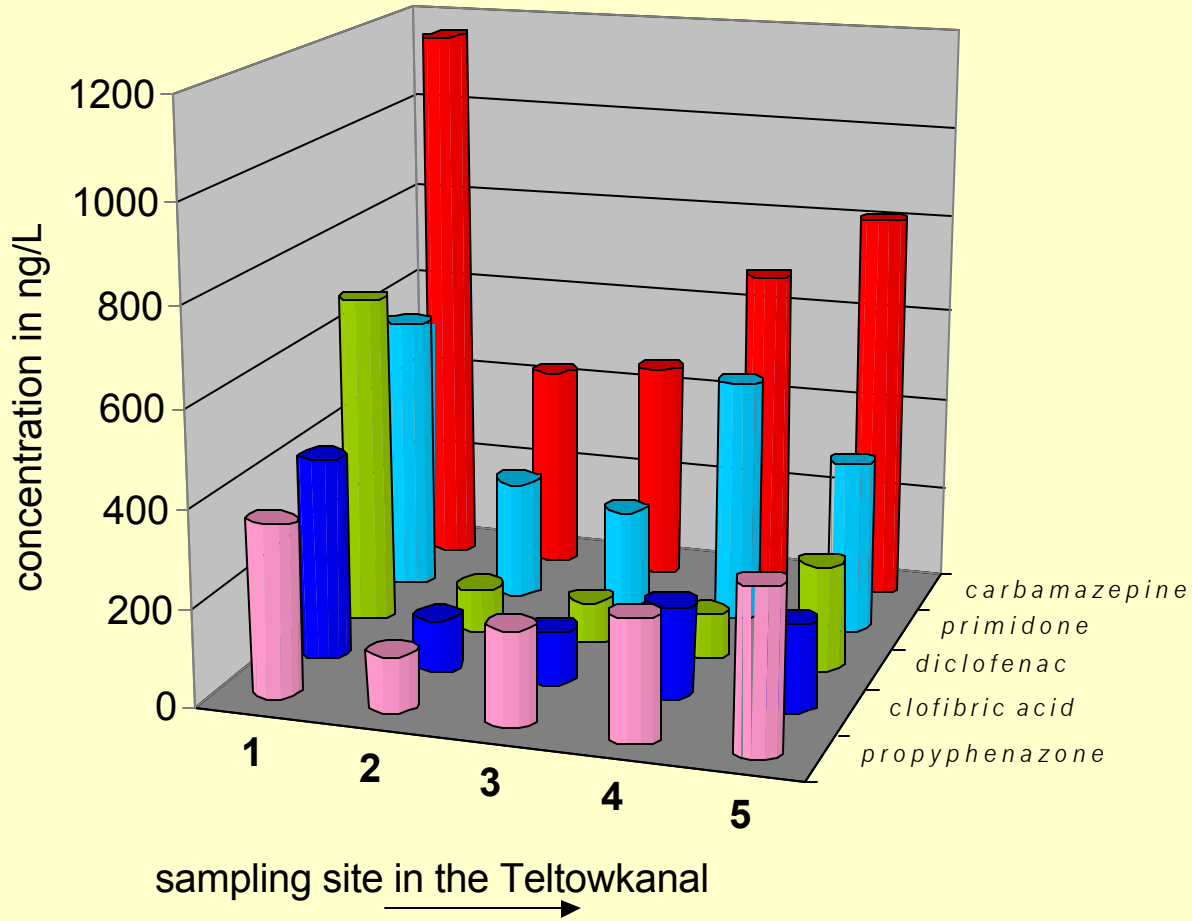


Figure 3. Concentration profiles for carbamazepine, clofibric acid, diclofenac, primidone and propyphenazone in the Teltowkanal in Berlin. Selected results from investigations in July 1999. Sampling locations (1-5) at the downstream of the STWs of Wassmanns-dorf (1), Marienfelde and Ruhleben (4), and Stahnsdorf (5).

Temporal fluctuations of the input of drug residues into the Teltowkanal (2000)

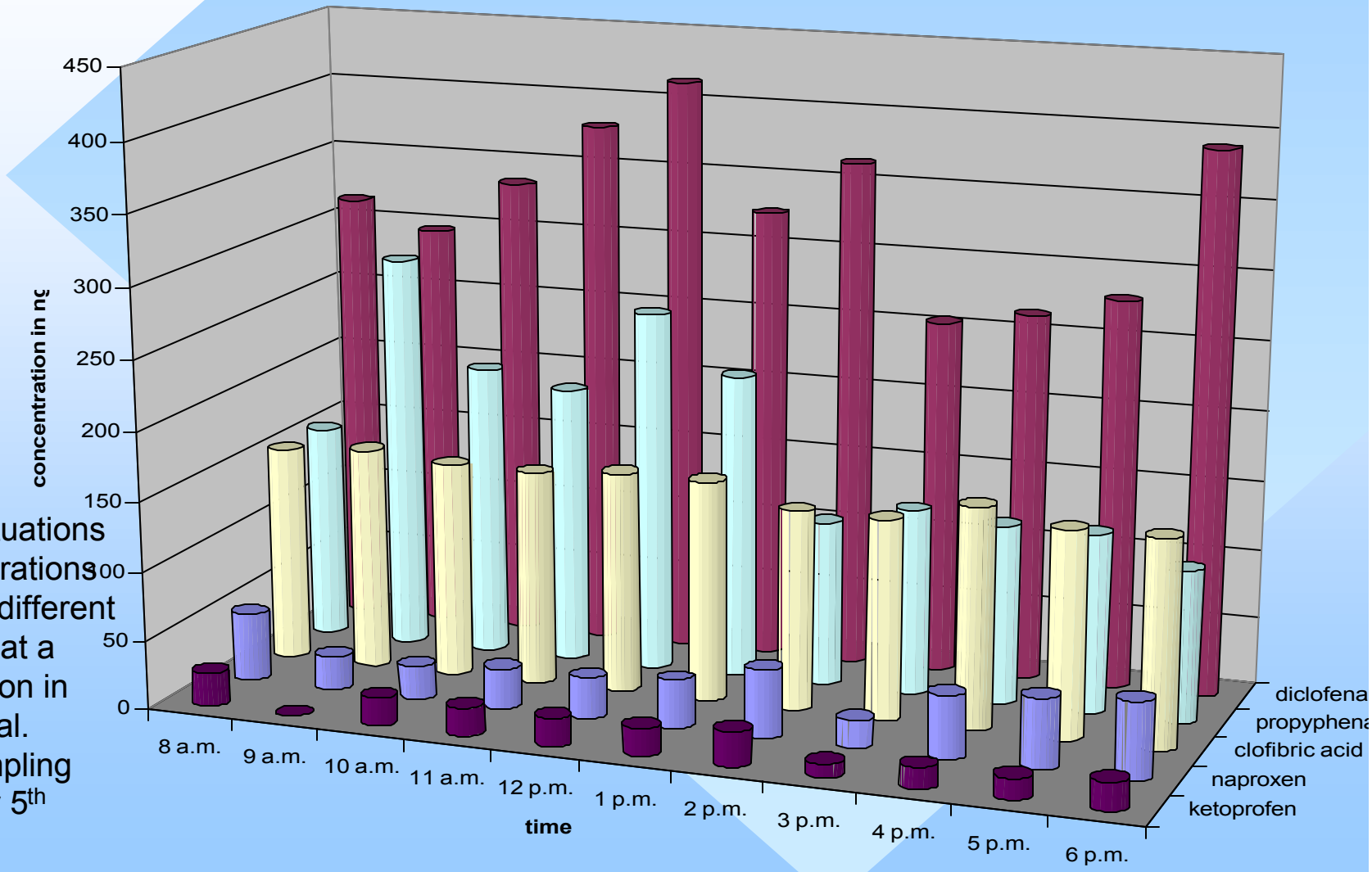
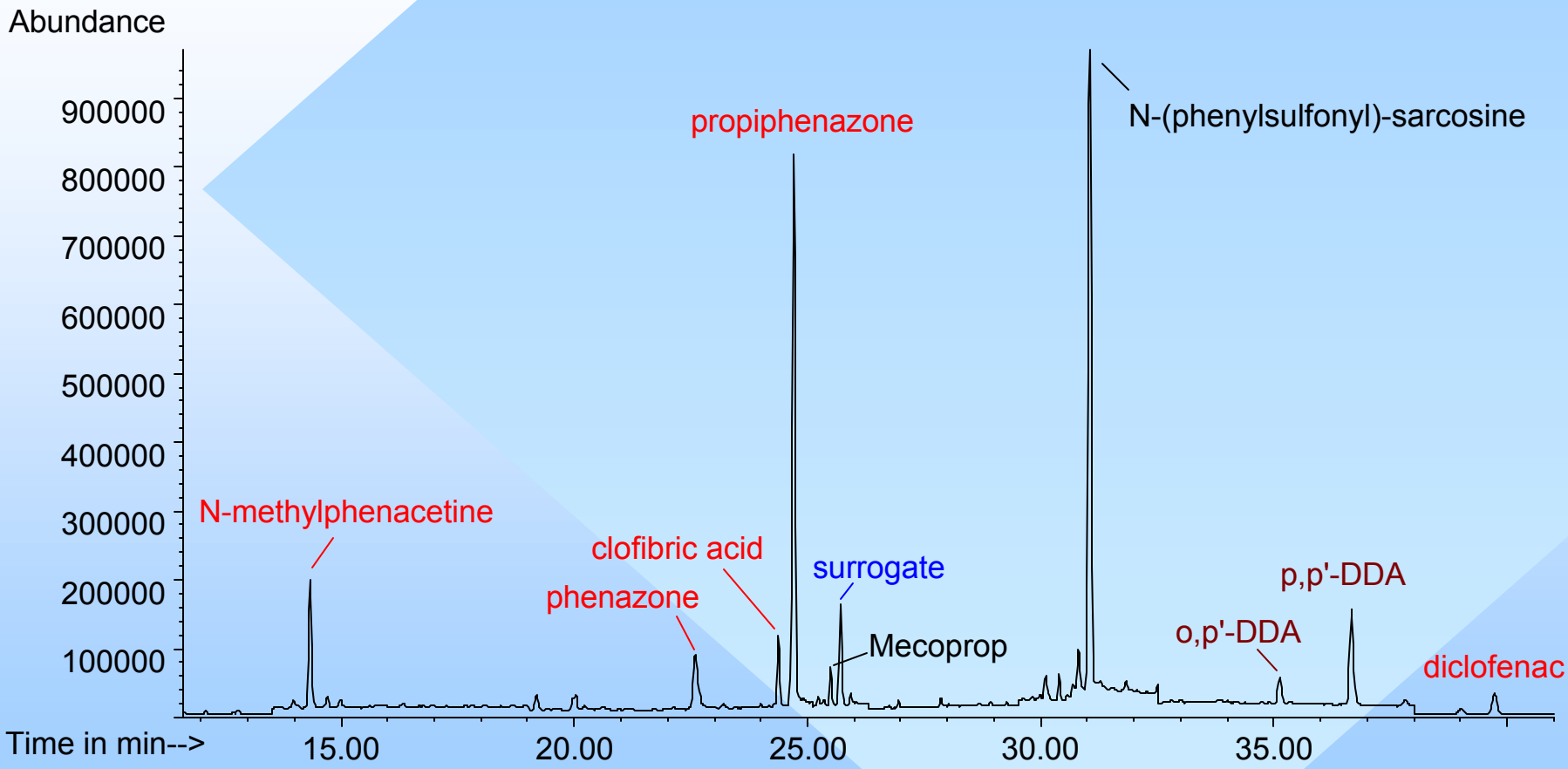


Figure 4. Temporal fluctuations of the concentrations measured for different drug residues at a selected location in the Teltowkanal. Repeated sampling on September 5th 2000.

MID: bank filtrate



MID chromatogram recorded applying GC-MS with SIM of a bank filtrate sample collected from a water works. The sample contains diclofenac* (100 ng/l), N-(phenylsulfonyl)-sarcosine* (1440 ng/l), phenazone (1250 ng/l), propiphenazone (1465 ng/l), clofibric acid* (100 ng/l) und N-methylphenacetine. * PFB-ester

Pharmaceutical residues in Berlin ground water aquifers

drug residue	concentration range in ng/l*
clofibric acid	n.d. – 7300
diclofenac	n.d. – 380
fenofibrate	n.d. – 45
gentisinic acid	n.d. – 540
gemfibrozil	n.d. – 340
ibuprofen	n.d. – 200
ketoprofen	n.d. – 30
phenazone	n.d. – 1250
primidone	n.d. – 690
propiphenazone	n.d. – 1465
salicylic acid	n.d. – 1225
clofibric acid derivative	(n.d. - 2900)**
N-methylphenacetin	(n.d. - 470)**

Table 3. Concentrations of drug residues found in Berlin ground water wells located near contaminated surface waters. Results of investigations carried out in 1996 and 1999.

** n.d.: not detected; ** concentrations were only estimated, standards not being commercially available.*

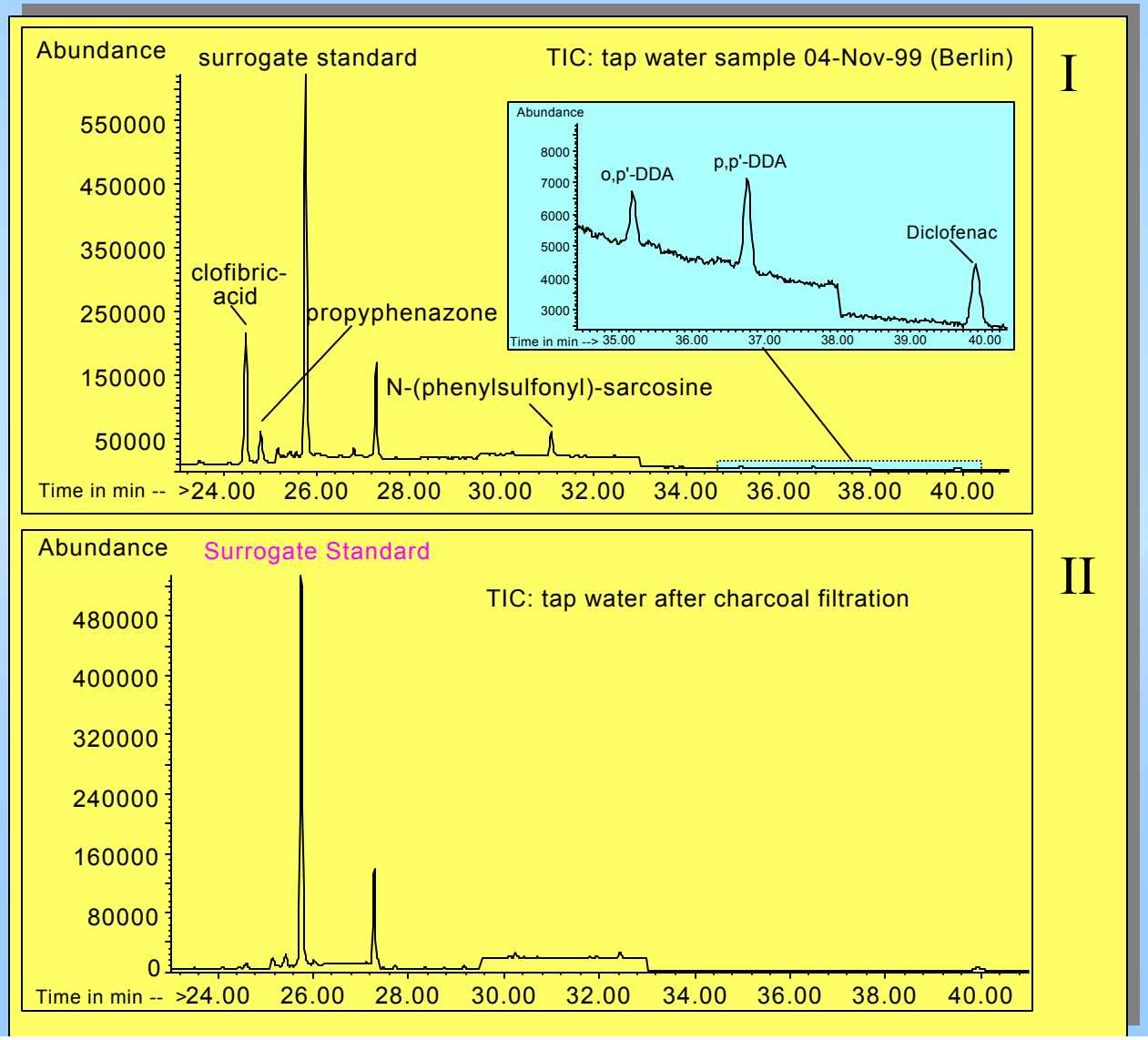
Clofibric Acid in Berlin Drinking Water Samples - 1994 -

Water works	BF [1] in %	GWE [2] in %	clofibric acid in ng/L [5]	NPS [3] in ng/L [5]	SWC [4]
Beelitzhof	**66**	**7**	**60**	**105**	**+**
Buch	0	0	< 5	-	o
Friedrichshagen	82	0	10	25	o
Johannisthal	**62**	**0**	**170**	**105**	**++**
Jungfernheide	52	43	45	-	+
Kaulsdorf	0	0	-	-	+
Kladow	68	0	6	17	+
Köpenick	74	0	6	8	o
Riemeisterfenn	17	0	11	70	+
Spandau	30	48	-	-	-
Stolpe	unbek.	+	13	-	(-)
Tegel	54	27	25	-	+
Tiefwerder	61	0	55	35	+
Wuhlheide	58	0	75	-	+

1: Clofibric acid ; 2: N-(phenylsulfonyl)-sarcosine ; 3: bank filtration ;
4: ground water enrichment ; 5: surface water contamination ; n.d. : not detected

Removal of drug residues from drinking water applying commercial charcoal filters

Figure 10.
MID-chromatograms of the derivatized extracts of two tap water samples from Berlin (4.11.1999) before (I) and after (II) charcoal filtration.



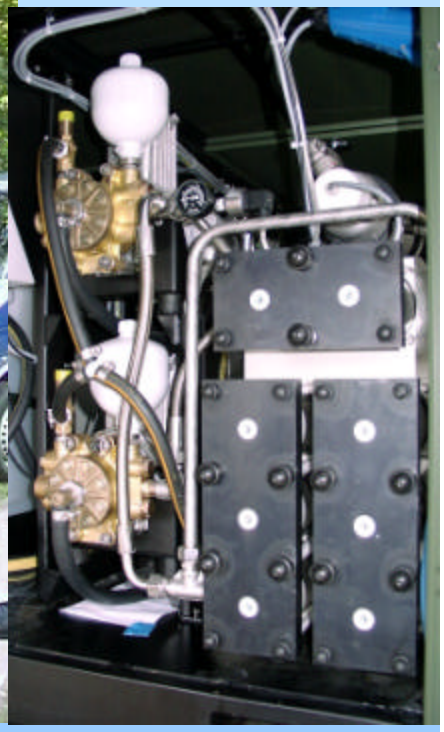
Removal of drug residues from drinking water applying commercial charcoal filters

Analyte	tap water sample (before filtration)	tap water sample (after filtration)
clofibric acid	40 ng/L	not detectable*
propiphenazone	80 ng/L	not detectable*
diclofenac	<10 ng/L	not detectable*
N-(phenylsulfonyl)-sarcosine	120 ng/L	not detectable*
o,p'-DDA	<5 ng/L	not detectable*
p,p'-DDA	<10 ng/L	not detectable*

* detection limits: < 1-5 ng/L

Use of mobile water purification units for the removal of drug residues from surface water applying membrane filtration

Membrane filtration:
Water Clean 1600

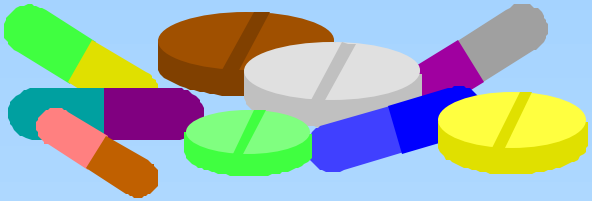


Mobile water purification units for the removal of drug residues and other contaminants from surface water

parameter	SW / DW	time					
		8.00 am	10.00 am	12.00 pm	2.00 pm	4.00 pm	6.00 pm
clofibric acid *ng/l*	surface water	160	160	160	150	120	120
	drinking water	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
diclofenac *ng/l*	surface water	160	380	420	260	210	120
	drinking water	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
mecoprop *ng/l*	surface water	70	90	90	90	100	90
	drinking water	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
aluminium *mg/l*	surface water	0,16	0,65	0,21	0,25	0,18	0,66
	drinking water	0,01	0,01	0,11	0,02	0,02	0,04
iron *mg/l*	surface water	0,96	0,73	0,93	0,95	0,92	0,61
	drinking water	<0,05	<0,05	0,06	<0,05	<0,05	<0,05
nitrite *mg/l*	surface water	0,46	0,42	0,43	0,36	0,35	0,37
	drinking water	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01

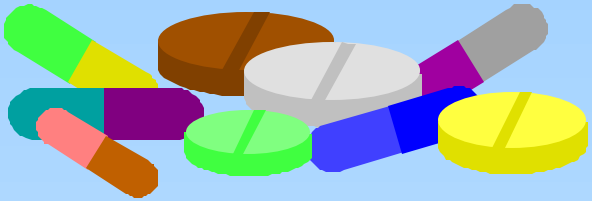
n.d.: not detectable (<1 ng/L)

Conclusions



- Persistent pharmaceuticals are discharged into the aquatic environment from municipal sewage treatment plants which act as point sources.
- Due to their polarity and their relatively high water solubility these residues are not significantly adsorbed in the subsoil and can leach into the ground water.

Conclusions



- Especially in urban areas such as Berlin with high municipal sewage water outputs, there is a potential risk of drinking water contamination when bank filtration or artificial ground water recharge is used in drinking water production.
- Charcoal filtration or membrane filtration may remove these residues from the water.

Acknowledgments

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