NORMAN Workshop
Stresa, June 19 2006

eawag
aquatic research

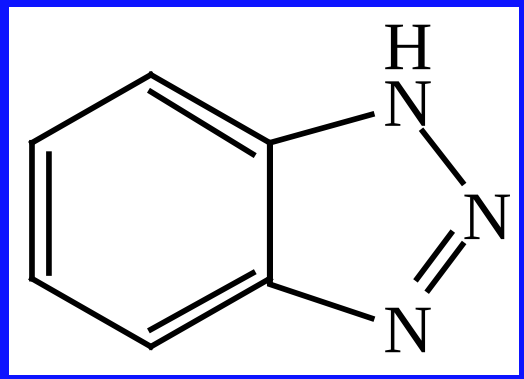
Benzotriazoles anticorrosives in municipal wastewaters and in the aquatic environment

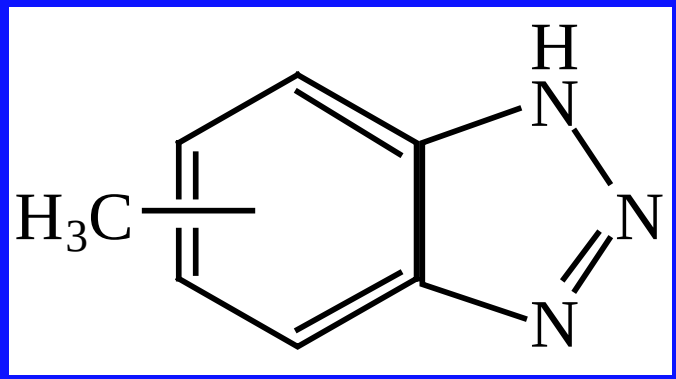
Walter Giger

Swiss Federal Institute of Aquatic Science and Technology

Wasserforschungs-Institut im ETH-Berich

Benzotriazoles



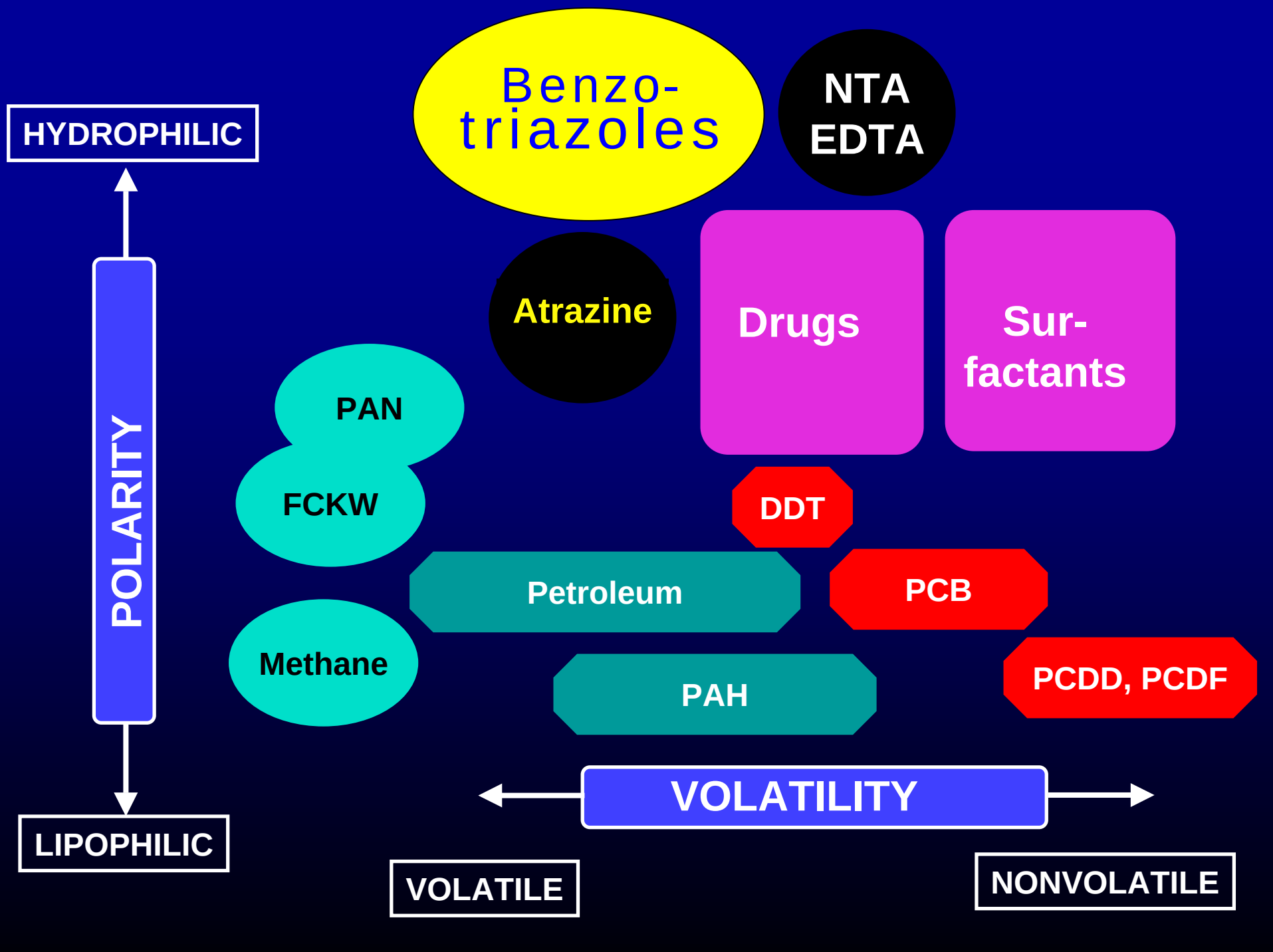


Exposure Measurements Inputs - Chemodynamics

Benzotriazole (BT) and methylbenzotriazoles (MBT, MeBT) (tolyltriazoles, TT)

Christian Schaffner, Dimitra Voutsa, Hans-Peter Kohler, Christa McArdell

- **Definitions, chemical properties, uses**
- **First reports on environmental occurrence**
  - aircraft deicing anti-icing fluid additives (ADAFs)
- **Analytical methods**
  - enrichment, separation, detection, validation
- **Measured exposure assessment**
  - wastewaters, wastewater treatment
  - rivers, bank filtration, groundwater
  - lakes, drinking water treatment
- **Risk assessment**


HYDROPHILIC
POLARITY
LIPOPHILIC
Benzo-
triazoles
NTA
EDTA
Atrazine
Drugs
Sur-
factants
PAN
FCKW
DDT
Petroleum
PCB
Methane
PAH
PCDD, PCDF
VOLATILITY
VOLATILE
NONVOLATILE

Properties of benzotriazoles

- polarized molecules
  - 3 lone-pairs of electrons on 3 nitrogen atoms
  - permanent dipole moment
- well soluble in water (28 / 7 g/L)
- low log K_{ow} : 1.23 / 1.89
- pK_s of BT: 1.6, 8.2
- complexing agent
  - form aqueous-insoluble complexes with copper alloys

- **Stable and biopersistent**

Uses of benzotriazoles

Anticorrosive agents/additives in:

- airplane deicing and anti-icing fluids (ADAFs)
- engine coolants and oils in automobiles
- industrial cooling systems

- silver protection in dishwasher detergents

- plastic stabilizers
- antifogging in photo processing
- chemical intermediates --> substituted BTs

Enrichment from aqueous samples

Solid-phase enrichment by OASIS HLB

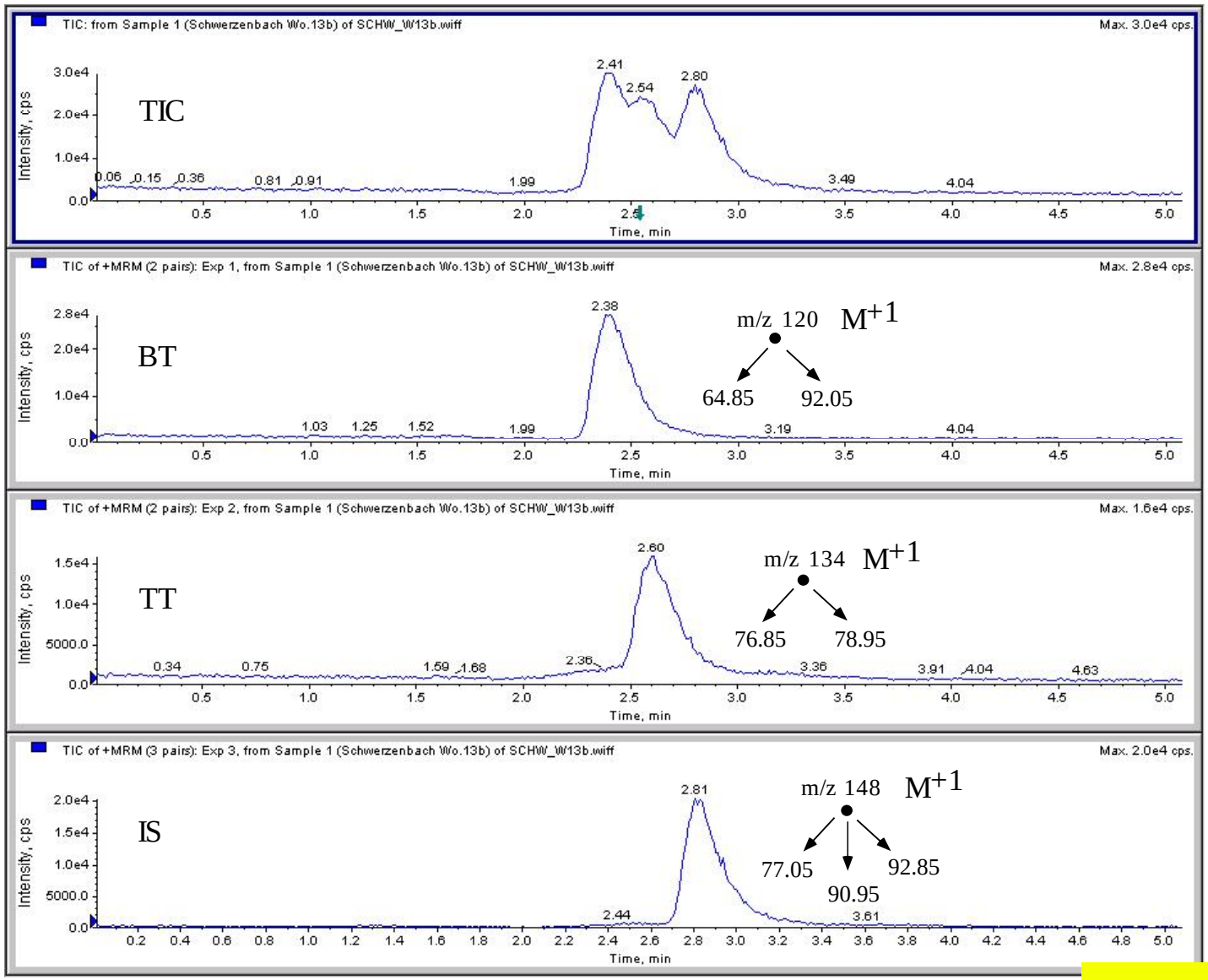
Separation/Detection

LC/MSMS

- Electrospray ionization, positive mode (ESI+)
- Multiple reaction monitoring (MRM)

- LC/UV and LC/MS are not sufficiently selective.
- GC is difficult because of the very polar analytes.

LC/MSMS results



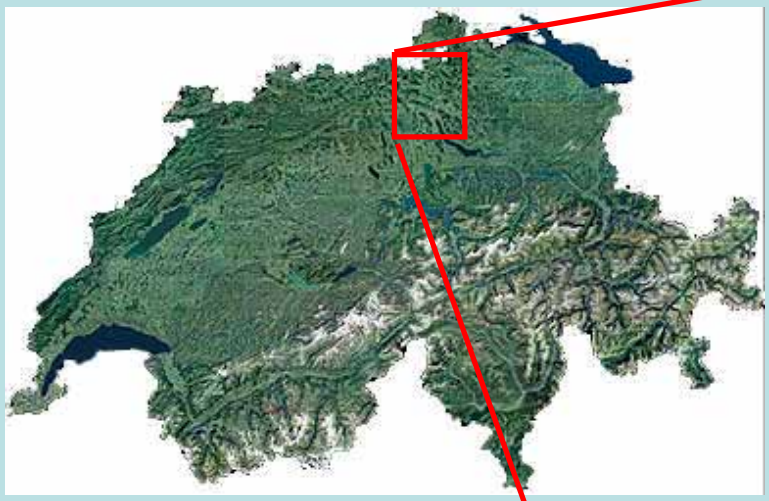
5 min

Validation

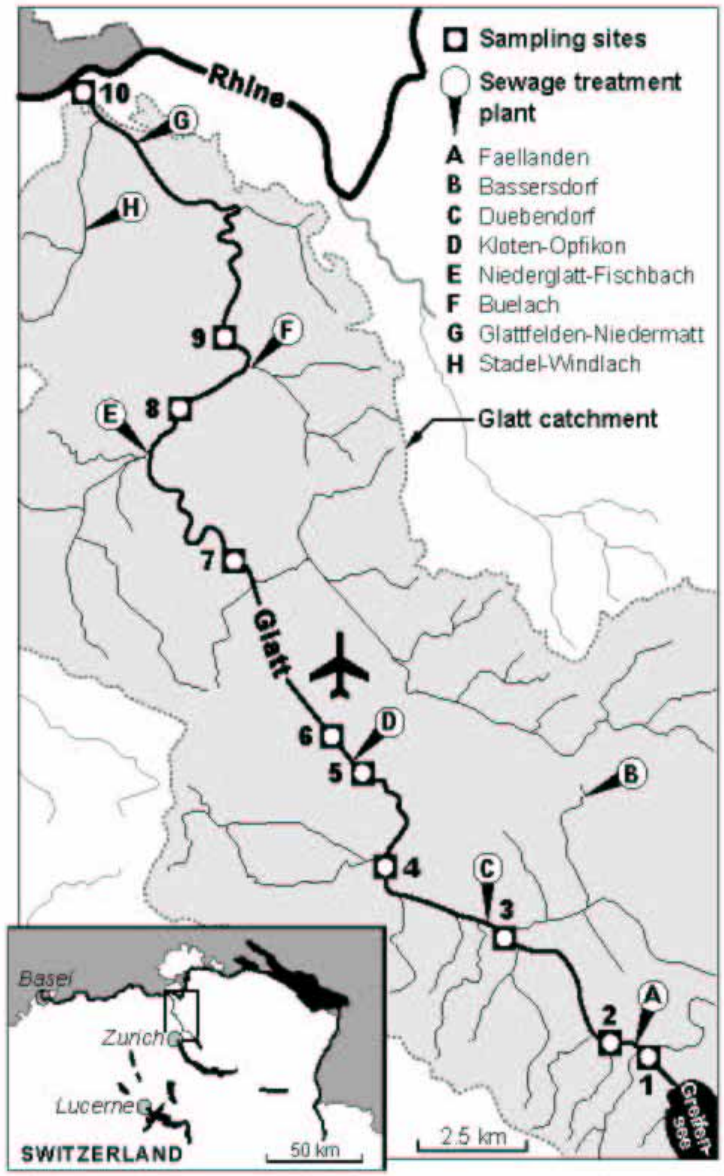
	BT	µg/L ± SD	TT	
Reproducibility River water, 100 mL, n=10	0.46 ± 0.011	(2.4%)	0.11 ± 0.006	(6.0%)
Instrumental reproducibility n=7	0.50 ± 0.005	(1.0%)	0.11 ± 0.003	(2.7%)
Recovery (%) 0.5 - 8 µg/L added	99 ± 8		97 ± 10	
Linearity	10 -1000 ng absolute, corr. coeff. = 0.998			
Limit of detection (µg/L) 3 x SD	0.03		0.02	
Limit of quantification (µg/L) 10 x SD	0.11		0.06	

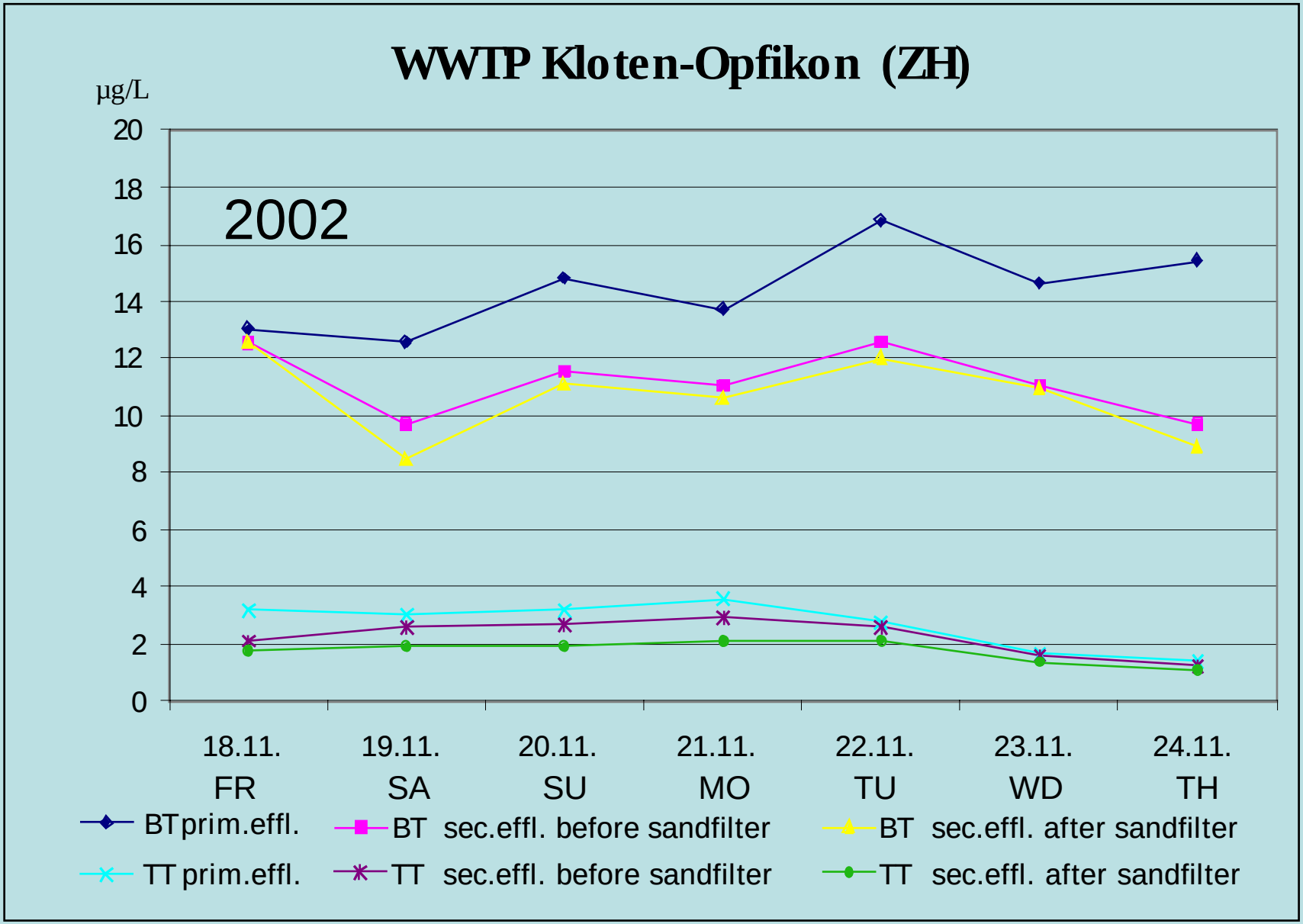
Ground and drinking water, 1L LOQ : 7 ng/L 3 ng/L

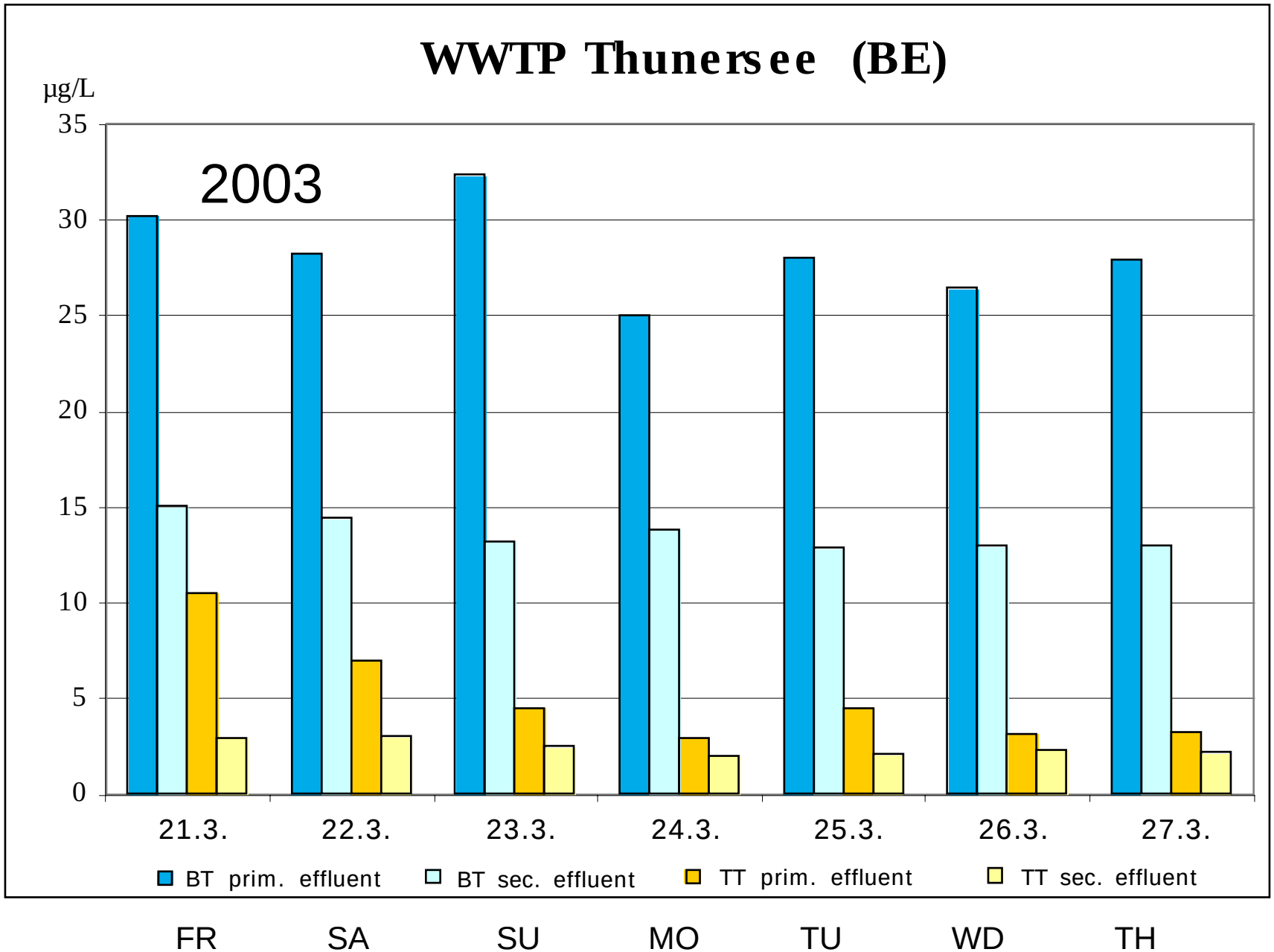
The Glatt River Catchment

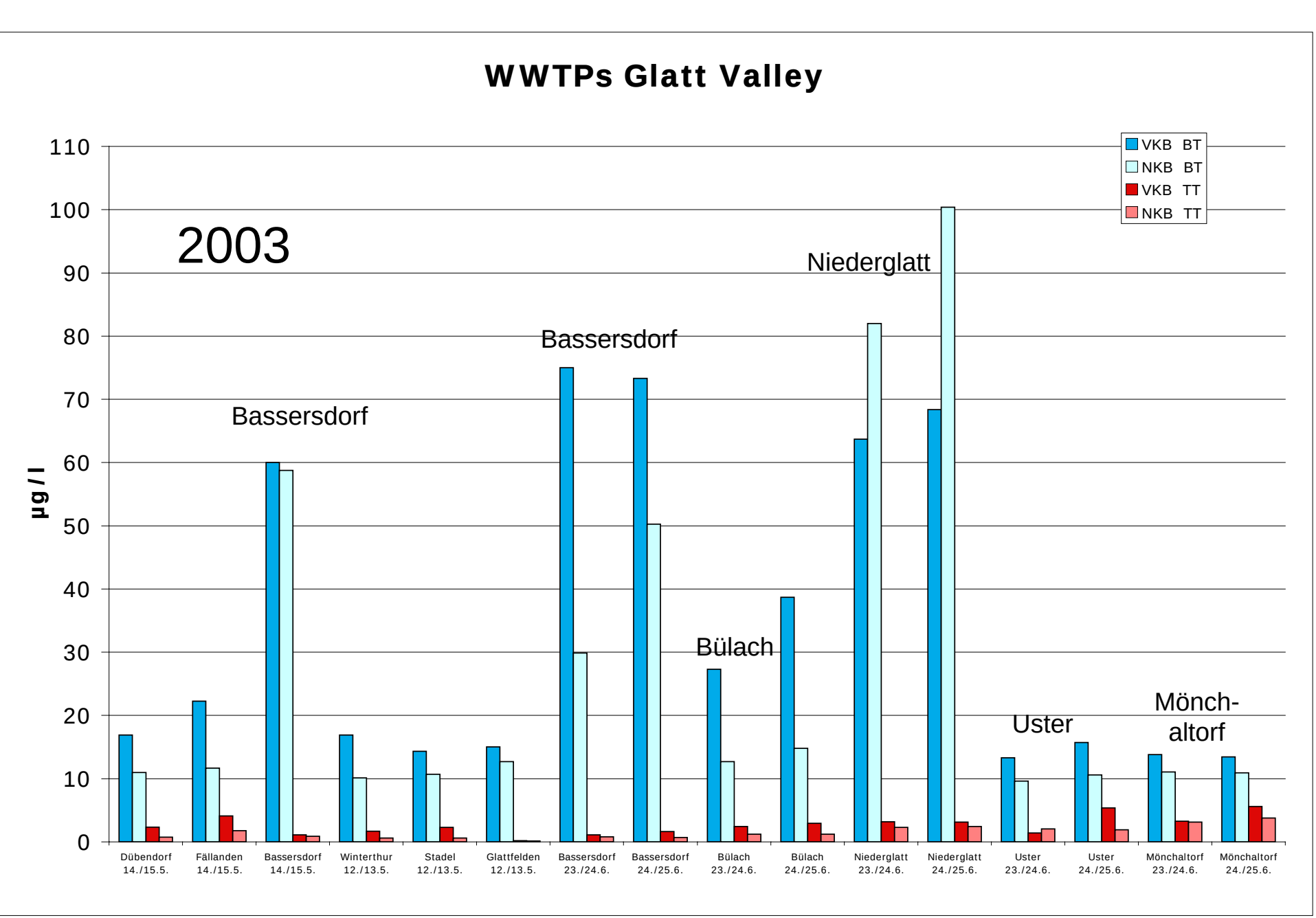


The Glatt River Catchment

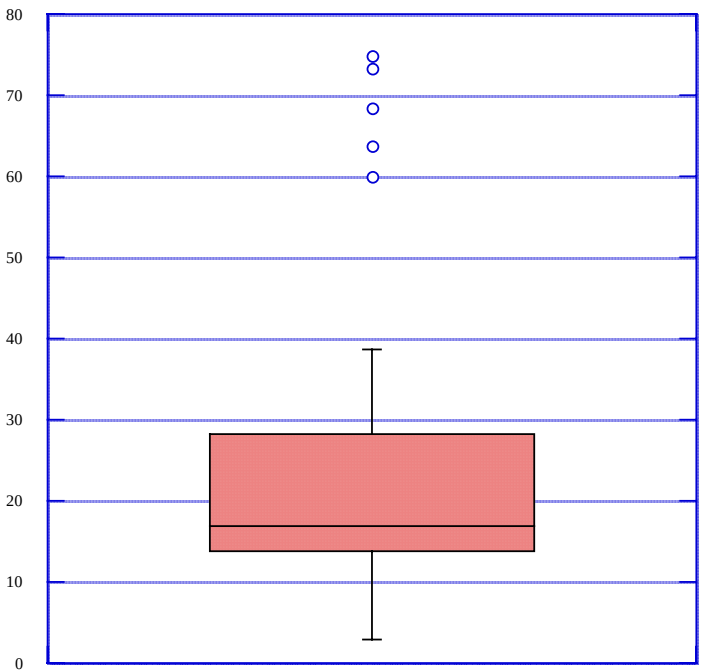



WWTP Kloten-Opfikon (ZH)
µg/L
20
18
16
14
12
10
8
6
4
2
0
2002
18.11.
FR
19.11.
SA
20.11.
SU
21.11.
MO
22.11.
TU
23.11.
WD
24.11.
TH
BT prim.effl.
BT sec.effl. before sandfilter
BT sec.effl. after sandfilter
TT prim.effl.
TT sec.effl. before sandfilter
TT sec.effl. after sandfilter

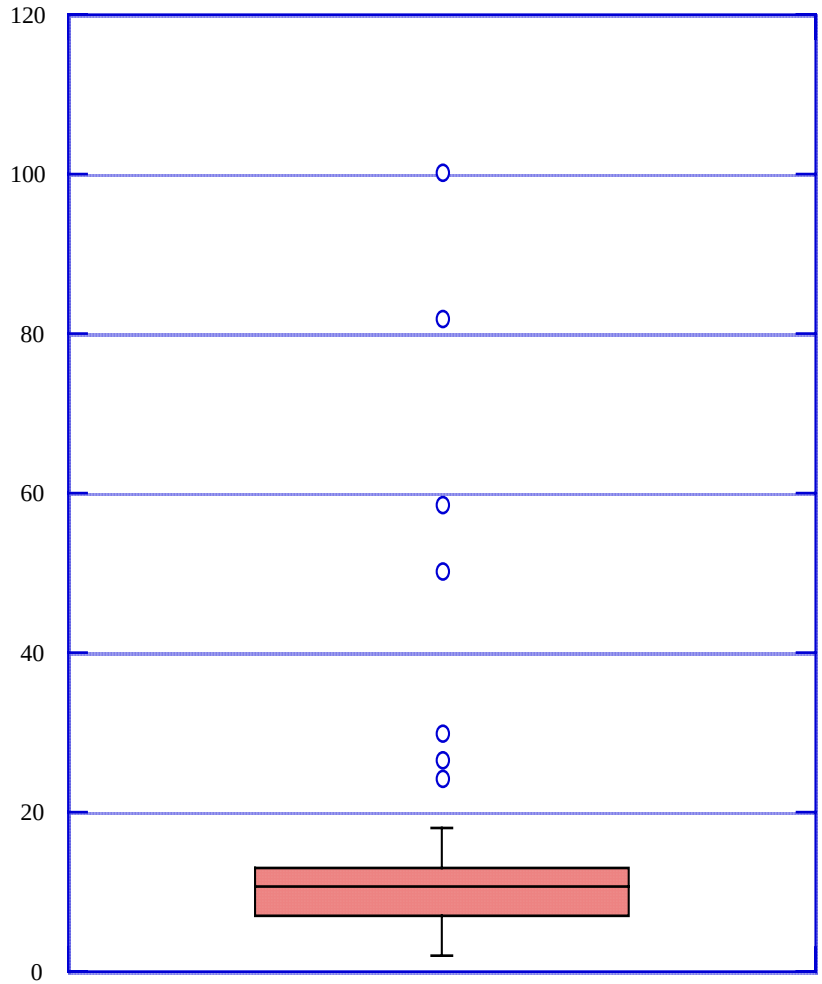

WWTP Thunersee (BE)
µg/L
35
30
25
20
15
10
5
0
2003
21.3.
22.3.
23.3.
24.3.
25.3.
26.3.
27.3.
BT prim. effluent
BT sec. effluent
TT prim. effluent
TT sec. effluent
FR
SA
SU
MO
TU
WD
TH


WWTPs Glatt Valley
2003
µg / l
VKB BT
NKB BT
VKB TT
NKB TT
110
100
90
80
70
60
50
40
30
20
10
0
Bassersdorf
Bassersdorf
Bülach
Niederglatt
Uster
Mönch-
altorf
Dübendorf 14./15.5.
Fällanden 14./15.5.
Bassersdorf 14./15.5.
Winterthur 12./13.5.
Stadel 12./13.5.
Glattfelden 12./13.5.
Bassersdorf 23./24.6.
Bassersdorf 24./25.6.
Bülach 23./24.6.
Bülach 24./25.6.
Niederglatt 23./24.6.
Niederglatt 24./25.6.
Uster 23./24.6.
Uster 24./25.6.
Mönchaltorf 23./24.6.
Mönchaltorf 24./25.6.

Benzotriazole in wastewaters, µg/L



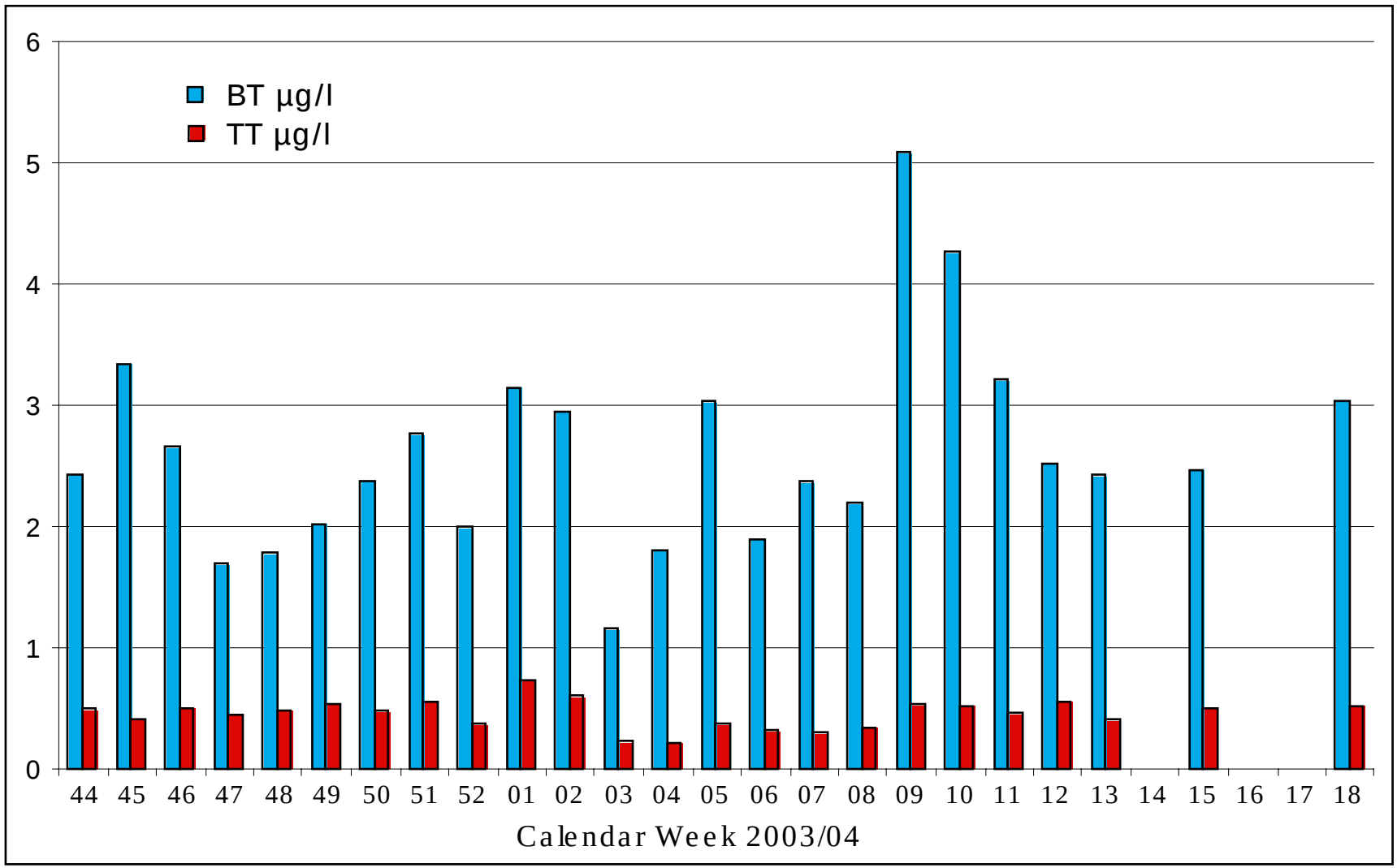
Primary effluents, n = 33

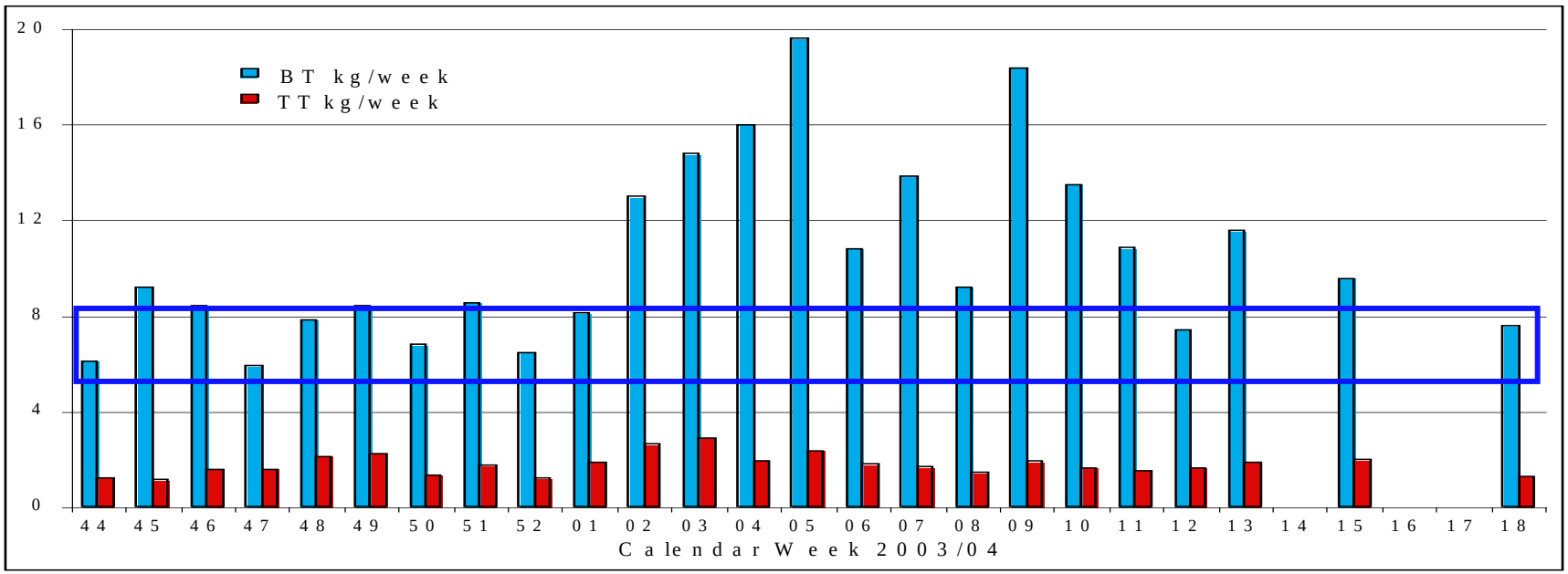


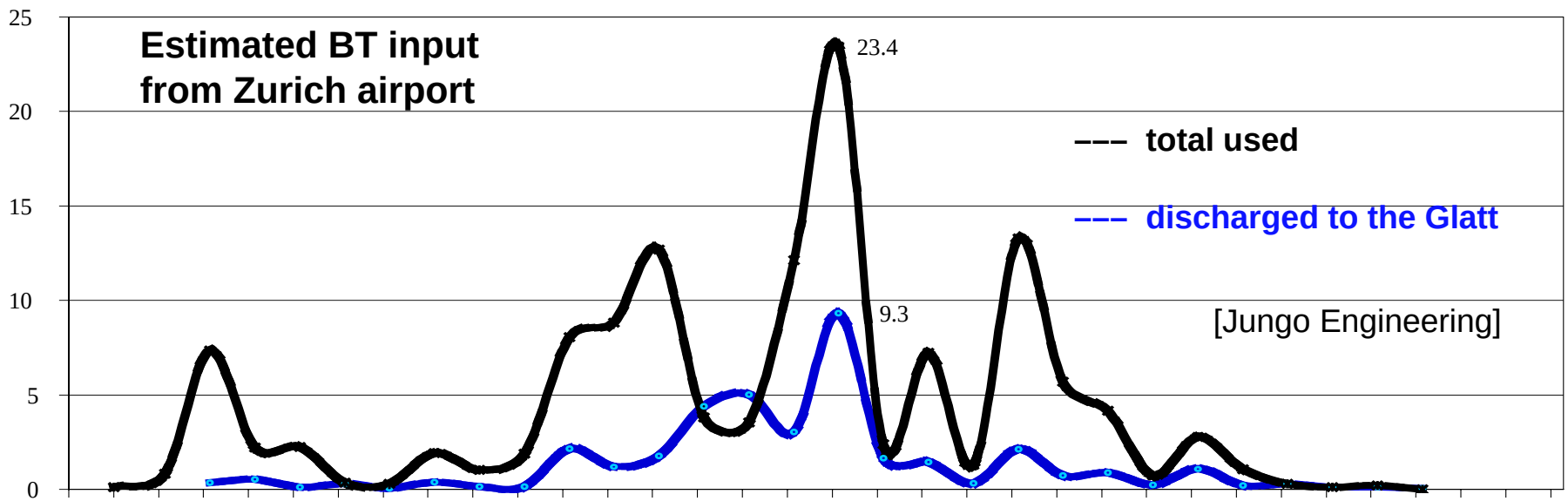
secondary effluents, n = 61

24 wastewater treatment plants

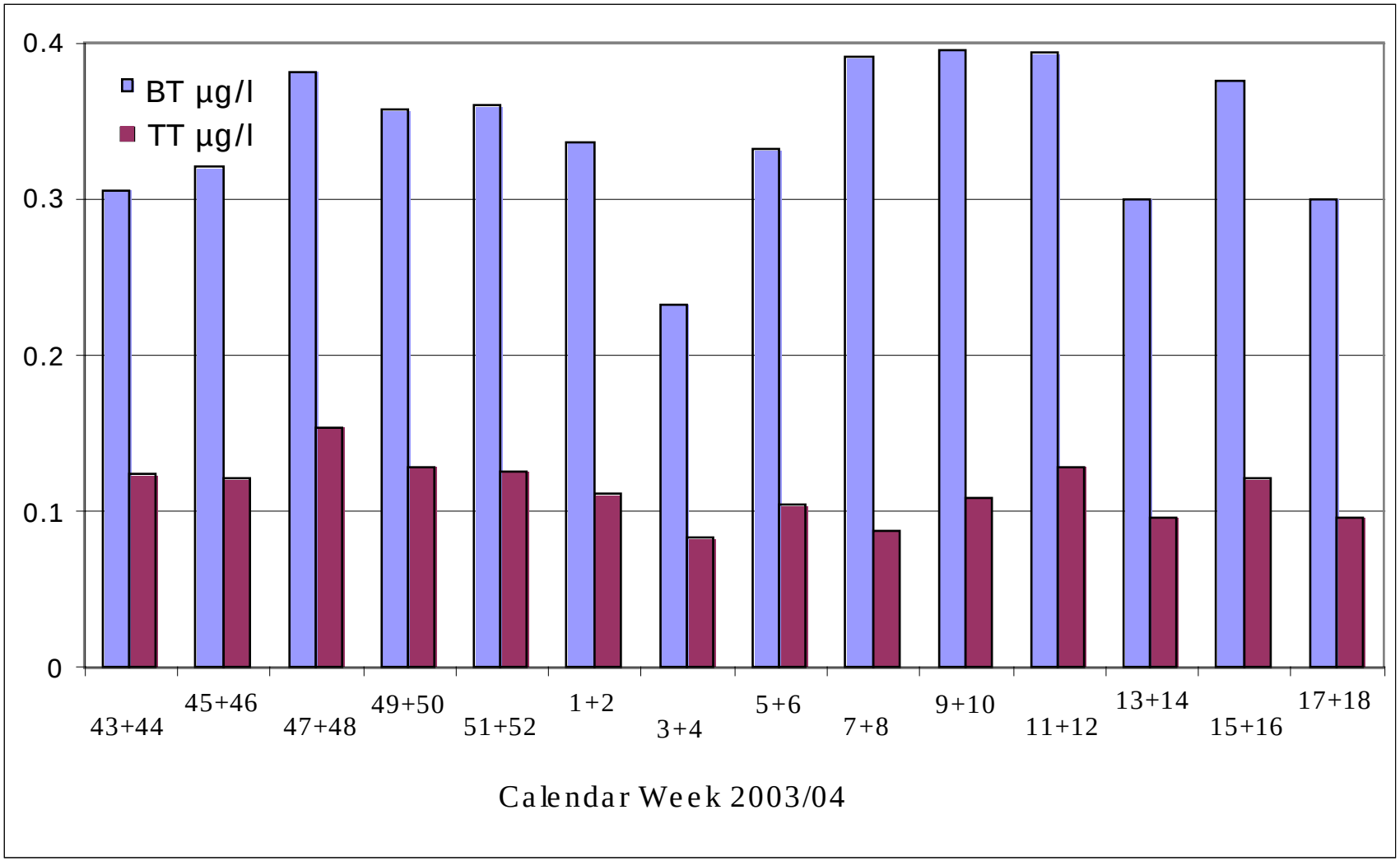
Glatt at Rheinsfelden 2003/4



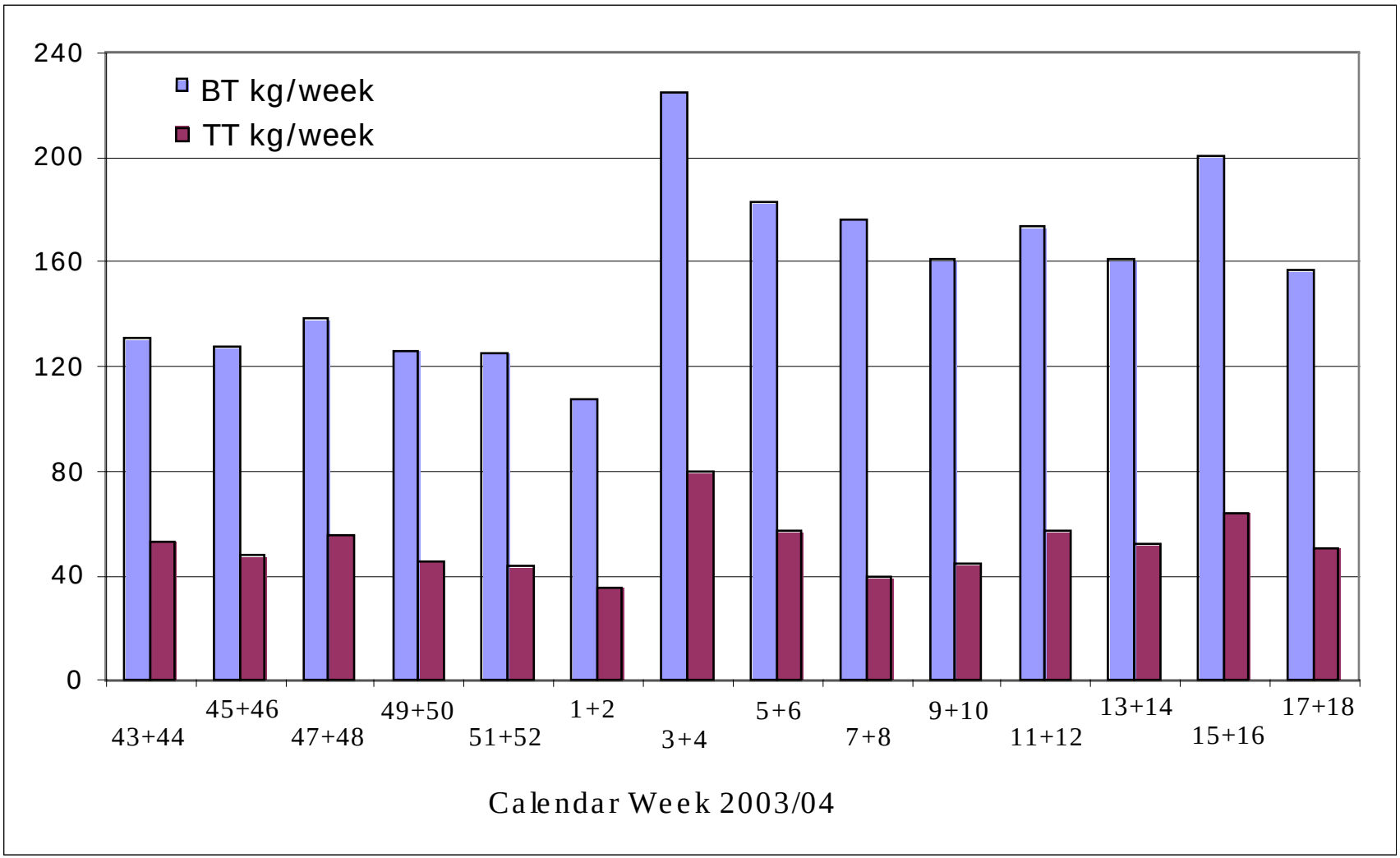

Glatt at Rheinsfelden Loads 2003/04
BT kg/week
TT kg/week
20
16
12
8
4
0
44 45 46 47 48 49 50 51 52 01 02 03 04 05 06 07 08 09 10 11 12 13 14 15 16 17 18
Calendar Week 2003/04


Estimated BT input
from Zurich airport
23.4
9.3
total used
discharged to the Glatt
[Jungo Engineering]
25
20
15
10
5
0

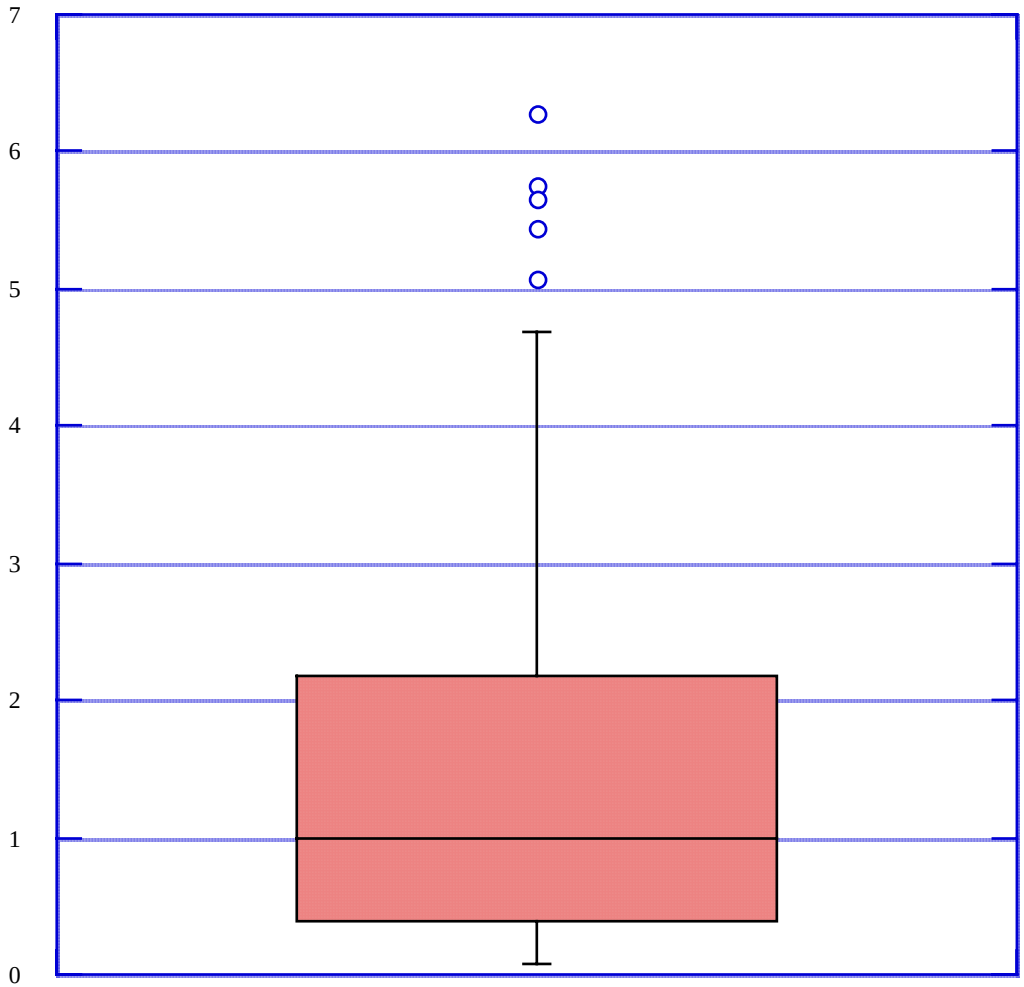
Rhine at Weil Concentrations 2003/04



Rhine at Weil Loads 2003/04



Benzotriazole in rivers, µg/L



n = 351; Glatt, Limmat, Rhine

Bottom lines

- BT and TT are ubiquitous **polar POPs.**
- BT is the forth most abundant individual aquatic contaminant (after EDTA, NTA and LAS carboxylates).
- All municipal wastewaters contain BT and TT.
- The input of TT is unknown.
- In wastewater treatment BT and TT are only partly removed.
- The impact of ADAFs used on Zurich Airport is clearly detectable in the Glatt River.
- Trace levels of BT and TT occur in lake and ground water used for drinking water supplies.
- Ozonation removes BT and TT.

What's next?

- Additional data interpretation regarding the behaviour in wastewater treatment, in rivers and in drinking water treatment

- *Holger Lutze, Andreas Peter, Urs von Gunten*
  Ozonation kinetics, intermediate products

- *Christa McArdell, Hans-Peter Kohler*
  Sorption, biodegradation

Toxic effects of benzotriazoles

- Inhibition of nitrification
- $PNEC_{water}$ = 30 µg/L
  [Steber & Hater, Henkel, 1998]
- Suspect carcinogen
  [Dutch Health Committee, 2000]
  (inadequate data base)
- Anti-estrogenic effect in *in-vitro* studies
  [Routledge, Sumpter, 2004, unpublished]