

**System studies on 1H-Benzotriazol and Tolyltriazoles in
river water and wastewater: Sources, fate and risks**

by

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Dedication

To my husband, Mate and my family, Dédi, Mama, Anya, Apa and Julika. You are my inspiration; you gave me the strength to carry on. Thank you.

Máténak, Dédinek, Mamikámnak, Anyának, Apának és Julikának. Köszönem nektek, hogy hittetek bennem és erőt adtatok, amikor én már feladtam volna. Nélkületek nem sikerült volna. Szeretlek benneteket.

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Abstract

Benzotriazoles (BTs) such as 1H-benzotriazole (1H-BT), 5-methyl-1H-benzotriazole (5Me-BT) and 4-methyl-1H-benzotriazole (4Me-BT) have a wide range of industrial applications. BTs are present for example in dishwasher detergents, in automotive antifreeze formulations and aircraft de-icing/anti-icing fluids (ADAF) as corrosion inhibitors. BTs belong to the group of “emerging contaminants” that have got in recent years more and more in the focus of environmental scientists, policy makers and the general public. These compounds are ubiquitous and highly mobile in the aquatic environment. It has been already shown that BTs have negative effects on aquatic organisms.

The objective of the present study was among others to monitor 1H-BT, 4Me-BT and 5Me-BT in river- and wastewater. River water samples were taken from five rivers in the Hengstbach/Schwarzbach catchment area, a medium-sized catchment area of about 400 km². River water grab samples were taken during six different sampling. The aim of this monitoring study was to get a seasonal catchment-wide overview on measured concentrations and mass loads of BTs.

BTs concentrations were determined in 24-hours influent composite samples taken on different month from three wastewater influents in Germany. In addition, 2-hours composite influent samples collected during one day in April were analyzed to determine the daily periodic emissions of BTs mass flows.

Moreover, ADAF used at German airports and three dishwasher detergent tablets commonly used in Germany were analyzed for the presence of BTs to study the distribution pattern of those compounds in different products.

An analytical method based on SPE and GC-MS has been developed and optimized for the determination of the presence of the corrosion inhibitors 1H-BT, 4Me-BT and 5Me-BT in environmental samples.

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List of Abbreviations

1H-BT	1H-Benzotriazole
4Me-BT	4-methyl-1H-benzotriazole
5Me-BT	5-methyl-1H-benzotriazole
A	Cross-sectional Area
A	Peak Area
AAF	Aircraft Anti-icing Fluid
ACN	Acetonitril
ADAF	Aircraft De-icing and Anti-icing Fluid
ADF	Aircraft De-icing Fluid
AOC	Airline Operators Committee
b	Width
BTs	Benzotriazoles
bw	Body weight
C	Concentration
CCD	Catalytic Combustion Detector
DCM	Dichloromethane
DFS	German Air-Traffic Control Corporation
DID	Discharge Ionization Detector
DP	Deicing Pad
E₀	Eluotropic Series
ECD	Electron Captured Detector
EI	Electron Impact
EICD	Electrolytic Conductivity Detector
EPA	Environmental Protection Agency
eq	Equation
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
GC	Gas Chromatography
GREAT-ER	Geography-Referenced Regional Exposure Assessment Tool for European Rivers
h	Depth
He	Helium
HID	Helium Ionization Detector
HPLC	High-Performance Liquid Chromatography
HPV	High Production Volume
hr	Hour
IRD	Infrared Detector
IS	Internal Standard
LC	Liquid Chromatography
LD50	Lethal Dose 50%
LOD	Limit of Detection

logK_{ow}	Octanol-Water Partitioning Coefficient
LOQ	Limit of Quantification
m/z	Mass to Charge Ratio
M_{abs.}	Absolute Mass
ME	Matrix Effect
MeOH	Methanol
MLQ	Mean Low Flow
mos	Month Study
MQ	Average Flow rate
MS	Mass Spectrometry
MSD	Mass Selective Detector
n	Number of Samples or Sampling
N₂	Nitrogen
NPD	Nitrogen Phosphorus Detector
P	Sampling Point
pH	(pondus Hydrogenii) a measure of acidity or basicity of an aqueous solution
PID	Photo Ionization Detector
pKa	Acid Dissociation Constant
PN	Fixed Reference Horizon
PTFBA	Perfluorotributylamine
PTV	Programmed Temperature Vaporizing
Q	Discharge
R	Response Factor
RSD	Relative Standard Deviation
SIM	Selected Ion Monitoring
SPE	Solid Phase Extraction
SPME	Solid Phase Micro Extraction
Stdev	Standard Deviation
St-DVB	Styrene-divinylbenzene
SuS	Surrogate Standard
T	Temperature
TCD	Thermal Conductivity Detector
TEA/TCD	Thermal Energy (Conductivity) Analyzer/Detector
TOC	Total Organic Carbon
TTs	Tolyltriazoles
UV	Ultra Violet
v	Velocity
V	Volume
W	Water Level
W%	Recovery
WCSI	Water Cycle Spreading Index
WWTP	Waste Water Treatment Plant

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1. Introduction

1.1 Corrosion Inhibitors

A corrosion inhibitor is a chemical compound that, when added to a liquid or a gas, decreases the corrosion rate of a material, typically a metal or an alloy (Hackerman, 2006; Electrochemistry Encyclopedia). Corrosion in an aqueous environment and in an atmospheric environment (which also involves the aqueous phase) is an electrochemical process because corrosion involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. It results from the overwhelming tendency of metals to react electrochemically with oxygen, water, and other substances in the aqueous environment. Fortunately, most useful metals react with the environment to form more or less protective films of corrosion reaction products that prevent the metals from going into solution as ions (Kruger, 2001; Electrochemistry Encyclopedia). The breakdown and repair of the passivity process just described is involved in many but not all of the various types of corrosion; for example: pitting corrosion, crevice corrosion, stress corrosion cracking, hydrogen damage, corrosion fatigue, intergranular corrosion, uniform corrosion, selective leaching, erosion corrosion, and finally galvanic and thermo galvanic corrosion. (Kruger, 2001; Electrochemistry Encyclopedia).

N-heterocyclic compounds have been widely used as corrosion inhibitors (Riggs, 1974.). Among these, benzotriazole (BTs) is known as one of the best corrosion inhibitors for copper and its alloys in a wide range of environments (Walker, 1973; Fox et al., 1979; da Costa and Agostinho, 1989; Ashour et al., 1995; Laz et al., 1992). BTs are mainly used for anticorrosion in aircraft anti- and de-icing fluids (ADAF) and in dishwasher detergents. BTs are also added to many other formulations that come in direct contact with metals, such as brake fluids, fluids in industrial cooling systems, metal-cutting fluids and solid cooling lubricants to prevent corrosion (EPA, 1997). One can also find BTs in automotive antifreeze formulations (Hart et al., 2004). Manufacturers claim use in the following applications: water treatment, metal working fluids, fuels, inks, lubricants, flooring and cleaners (PMC Specialties Group, 2000). The addition of BTs to aqueous acidic, neutral and alkaline solutions is common and has been proven to significantly reduce corrosion

(Walker, 1975). BTs show metal complex properties, forming a complex polymeric film on the metal surface, which shields the underlying metal molecules from further chemical attack (Chadwick and Haschemi, 1978). In fact, the stability of metal complexes of BTs follows the Irving-Williams order (Venkat Ramana et al., 1991); namely that for a given ligand, the stability of complexes increases from barium (Ba) to copper (Cu) and dropping for zinc (Zn).

1.2 Aircraft de-icing and anti-icing fluids (ADAF)

Airplanes are designed based on the predictable effects of airflow over clean wings. The accumulation of ice, snow or frost on the wings disturbs this airflow and results in increased drag, increased stall speed, and may cause an abnormal pitch characteristic. Ice, snow or frost only as thick and rough as medium sandpaper can significantly reduce aerodynamic performance (Schwitzerbaum et al., 1999).

The purpose of aircraft deicing fluids (ADF) is to remove ice and snow from control surfaces (wings, rudders, and fuselages). Ice and snow are typically removed from aircraft using a heated mixture of Type I ADF and hot water applied under pressure (Fraport, 2007). Type I fluids are primarily used for de-icing and do not offer any significant anti-icing holdover protection. Because of this Type I fluids are commonly used in a two-step de-icing/anti-icing procedure as a first step, after which the final application of Type II or Type IV anti-icing fluids (AAF) provides the required extra protection. Undiluted Type I fluids must contain a minimum of 80% ethylene or propylene glycol by weight, with the balance composed of water, buffers, wetting agents and oxidation inhibitors. Deicing chemicals used in aircraft deicing must also be non-corrosive to prevent damage to aircraft aluminum and sensitive electronic systems (Schwitzerbaum et al., 1999). Airlines typically use a fifty-fifty mixture of Type I ADF/water for deicing purposes (Fraport, 2007). During a normal winter season at a medium size international airport, the estimated need for ADF can vary from 1000–10,000 tons depending on weather conditions and traffic density (Betts, 1999; Cornell et al., 2000).

Aircraft anti-icing may follow deicing as a means to prevent the further accumulation of snow or ice on the deiced surfaces either while an aircraft is waiting for takeoff during

especially severe weather, or during overnight parking. Anti-icing is accomplished by applying Type IV AAF to clean (i.e. ice free) aircraft surfaces. Type IV AAF is also composed of ethylene or propylene glycol, along with thickeners that allow the fluid to cling to the aircraft and provide prolonged protection and longer holdover times. This increased viscosity is lost when Type IV AAF undergoes shear stresses, such as those experienced during takeoff. The unique characteristics of Type IV AAF require the use of special low-shear applicator nozzles. In 1997, the Society of Automotive Engineers (SAE) published standards for AAF (SAE, 1997); Type II and IV fluids contain a minimum of 50% glycol by weight. In general, chemicals other than glycol make up 1 to 5% of ADAF, but the exact formulations currently in use are proprietary (USDOT, 1992).

The ADAF period begins in October and ends in April of the following year at Frankfurt Airport (Fraport, 2007). The procedures are intended to provide safe, orderly and efficient deicing/anti-icing of aircraft at their gate or ramp position and access of aircraft to the designated remote Deicing Pads (DPs). The contents of this plan have been agreed upon between Fraport, as the airport authority, herein referred to as Fraport AG, German Air Traffic Control (DFS), responsible for air traffic control, the Airline Operators Committee (AOC), on behalf of the aircraft operators, and the aircraft deicing/anti-icing provider NICE Aircraft Services & Support GmbH, herein referred to as “the provider” (Aircraft Services and Support). The deicing/anti-icing fluids used currently at Frankfurt Main Airport are SAE Type I (Kilfrost DF PLUS) and SAE Type IV (Kilfrost ABC-S PLUS). 250 L-1200 L of ADF were applied per anti- or deicing operation (depending on aircraft type) (Fraport, 2007).

1.3 Benzotriazoles (BTs)

1H-benzotriazole (1H-BT) and its derivatives are in the chemical category of polar high production-volume chemicals (HPV), which have broad applications in various industrial processes as well as in households (Karpel et al., 2009). As defined by the US-Environmental Protection Agency (EPA) under the HPV Program, a chemical category is “a group of chemicals whose physicochemical and toxicological properties are likely to be similar or follow a regular pattern as a result of structural similarity”. The structure of BTs

was determined as early as 1896 (Grabe and Ulmann, 1896), and synthesis reactions were published as early as 1921 (Charrier and Beretta, 1921). In the 1960s, BTs were identified as a corrosion inhibitor for copper (Cotton and Scholes, 1967). BTs are added to many formulations that get into contact with metals, such as ADAF, antifreeze, cutting fluids, hydraulic brake fluids, dishwasher detergents for silver protection and industrial cooling systems (Pillard et al., 2001; Weiss and Reemtsma, 2005). BTs are heterocyclic compounds with the common formula $C_6H_5N_3$. BTs are derivatives of a benzene ring on which a vicinal pair of carbon atoms form a covalent bond to three nitrogen atoms in a five-member ring (Hart et al., 2004).

The main BTs compounds that are used as corrosion inhibitors are 1H-benzotriazole (1H-BT) (*CAS 95-14-7*), 4-methyl-benzotriazole (4Me-BT) (*CAS 29878-31-7*) and 5-methyl-benzotriazole (5Me-BT) (*CAS 136-85-6*). The latter are also called tolyltriazoles (TTs). 1H-benzotriazole (1H-BT) is also called 1,2,3-benzotriazole, 1,2,3-triazindene, Cobtratec 99, 1,2-aminophenylene, azimidobenzene, benzene azimide, benzisotriazole and benztriazole (University Oxford). The molecular formula is $C_6H_5N_3$. Its molar mass is 119.12 g/mol (Chemical Book). The chemical structure of 1H-BT is shown in Figure 1.

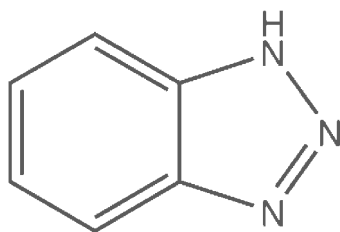


Figure 1. Chemical structure of 1H-benzotriazole (1H-BT).

Their molecular formula of 4Me-BT and 5Me-BT is $C_7H_7N_3$. The chemical structure of 4Me-BT and 5Me-BT is shown in Figure 2.

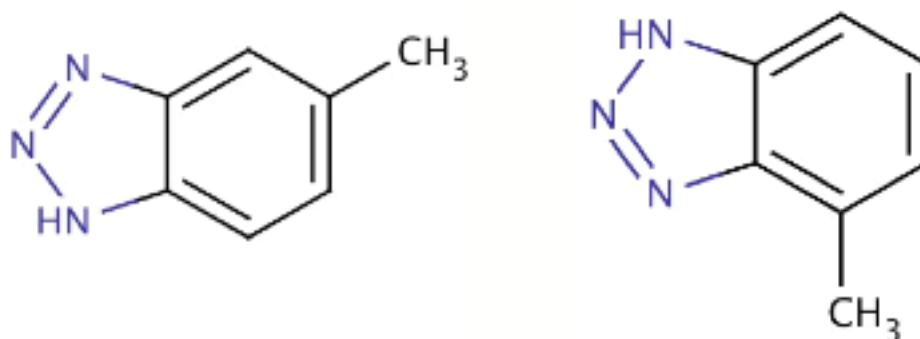


Figure 2. Chemical structures of 4-methyl-benzotriazole and 5-methyl-benzotriazole.

1.3.1 Physicochemical properties of BTs

The physicochemical properties of 1H-BT and 5Me-BT are shown in Table 1. For 4Me-BT gives no information. BTs are relatively polar compounds and dissolve quite well in water. The water solubility is 19.8 g/L for 1H-BT and 1.1 g/L for 5Me-BT. The octanol–water partition coefficients ($\log K_{OW}$) were determined to be 1.23 for BTs and 1.89 for 5M-BT (Hart et al., 2004). According to their relative low values of $\log K_{OW}$ BTs are expected to be highly mobile in surface water, groundwater and soil (Breedveld et al., 2003).

	1H-BT	5Me-BT
pK_a	8.4	-
log K_{OW}	1.4	1.7
Henry's law constant [Pa*m ³ /mol]	0.015	0.016
Water solubility [g/L]	19.8	3.1

Table 1. Physico-chemical properties of 1H-BT and 5Me-BT (adopted from <http://www.syrres.com/escphysdemo.htm>).

Although BTs compounds have been shown to have high affinity for an organic phase, they still have polar character. This property makes these compounds unusual and stems from their strong permanent dipole moments (Hart et al., 2004). 1H-BT was determined through electrochemistry techniques to have a permanent dipole moment of 4.15 Debye (D) (Gaure, 1983). The dipole moment of 5Me-BT was calculated to be 4.19 D using (Hart et al.'s unpublished results) (Hart et al., 2004). These dipole moments are substantial relative to organic alcohols that typically range from 1.5 to 2.5 D (Jones, 1997).

1.3.2 Applications of BTs in the environment

BTs are present in dishwasher detergents as corrosion inhibitors, ultraviolet light stabilizer for plastics, antifoggants in photography, in industrial cooling systems, metal-cutting fluids and in solid cooling lubricants to prevent corrosion (US EPA, 1997). BTs are also added to many other formulations that come in direct contact with metals such as brake fluids, fluids BTs show metal complex properties, they form a multipart film on the metal surface (Chadwick and Haschemi, 1978). Manufacturers claim use for BTs in the following applications: water treatment, metal working fluids, fuels, inks, lubricants, flooring and cleaners (PMC Specialties Group, 2000). Furthermore, BTs are found in automotive antifreeze formulations comprising 0.5-1% by weight (Hart et al., 2004). BTs are added to aircraft de-icing/anti-icing fluids (ADAF) as corrosion inhibitors and also in order to reduce fire hazard. The content of BTs in de-icing products varies between 0.2 and 1.7%, according to the manufacturer (WIPO, 2002). Data on BTs concentrations in ADAF are not available for products that are applied at German airports.

The concentrations of 1H-BT and TTs in dishwasher powders and tablets varied between 0.025-1 mg/g (Janna et al., 2010). In a data sheet of the chemical manufacturer Lanxess, a proportion of 0.2 to 0.5% for 1H-BT was recommended in dishwasher detergents. This data sheet contained no information for TTs, but indicated the same contents for other application fields. In the thesis of Stefan Weiss (2007), the content of BTs in dishwasher detergents were 0.04% for 4-MeBT and 0.05% for 5-MeBT, and 0.01% for 1H-BT in dishwasher powders.

However, BTs had not been detected in other types of dishwasher tabs or rinse agents.

Since the data was fluctuated between 0.01% and 0.5% therefore the pro capita usages of 1H-BT in rinse agents was calculated in these intervals. Table 2 shows the annual per capita usage calculated by Pollmeier (2008) for different contents of 1H-BT in rinse agent. 137 tons BTs were used in private households in Germany

Year	Rinse agent	0.010%	0.025%	0.050%	0.100%	0.200%	0.250%	0.500%
1998	0.000707	0.0707	0.177	0.353	0.707	1.41	1.77	3.53
2001	0.000730	0.0730	0.183	0.365	0.730	1.46	1.83	3.65
2006	0.000830	0.0830	0.207	0.415	0.830	1.66	2.07	4.15

Table 2. The annual pro capita usage [t/(cap*a)] for different contents of 1H-BTs in dishwasher detergents (Pollmeier, 2008).

1.3.3 Occurrence of BTs in the environment

Because of different operational areas and high application volumes of ADAF, BTs end up in sewer systems resulting in relatively high loads in wastewater. On account of a low sorption capacity of BTs (Hart et al., 2004) as well as a low biodegradability (Pitter and Chuboda, 1990) the elimination of BTs during wastewater treatment is estimated to be low. Verheyen et al. (2009) found TTs in milk processing industrial effluent in concentrations of 4400 ng/L for 4Me-BT and 730 ng/L of 5Me-BT. Leerdam et al. (2009) detected BTs in maximum concentration of 8 µg/L for 1H-BT and 3sti µg/L for TTs (summed concentration of two isomers). BTs and TTs were quantitatively determined in municipal effluents in Switzerland (Voutsas et al., 2006). The separation of 4Me-BT and 5Me-BT isomers was also not available here. 1H-BT and TTs concentrations in primary and secondary effluents of municipal WWTP varied from below 10 to 100 µg/L. (Reetsma et al., 2009) the effluent concentrations were in range of 7-18 µg/L of 1H-BT, 1-5 µg/L of 4Me-BT and 0.8-0.25 µg/L of 5Me-BT. In Berlin region BTs and TTs isomers were determined in untreated municipal wastewater with mean dissolved concentrations of 12 µg/L of 1H-BT, 2.1 µg/L of 4Me-BT and 1.3 µg/L of 5Me-BT (Weiss et al., 2006). By Jover et al. (2009) was 1H-BT detected in influent in concentration 7.3 µg/L, in effluent 2.4 µg/L and in industrially effluent 8.2 µg/L. 4Me-BT and 5Me-BT were founded just in

industrial effluent in concentration 17 µg/L and 6.9µg/L.

On account of the incomplete removal of BTs during wastewater treatment potential input in rivers must be classified as relatively high. BTs have been detected in the Glatt River, Switzerland, with concentrations of 0.64-3.7 µg/L for 1H-BT and 0.12-0.63 µg/L for TTs. In the Landwehr Canal in Berlin, Germany, the average concentrations were 0.9 µg/L for 1H- BTs, 0.2 µg/L for 4Me-BT and 0.1 µg/L for 5Me-BT (Weiss et al., 2006). 1H-BT and 4Me- BTs were found in the Rhine and Elbe rivers with concentrations increasing from 0.13 µg/L to 0.35 µg/L over 700 km in the Rhine and <0.05 µg/L to 0.48 µg/L over 640 km in the Elbe River; from 0.2 to 0.5 µg/L in the Rhine and from 0.1 µg/L to 0.45 µg/L in the Elbe, respectively (Reemtsma et al., 2009). In river water samples from the Havel River average concentrations of 1H-BT, 4Me-BT and 5Me-BT were measured at 1.6 µg/L, 2.1 µg/L, and 0.34 µg/L, respectively (Reemtsma et al., 2009). 5Me-BT was quantified in two river samples downstream of the city of Hamburg in the Elbe River (Reemtsma et al., 2009). Median concentrations of 1H-BT, 4Me-BT and 5Me-BT in the Main River were 0.13 µg/L, 0.099 µg/L, and 0.063 µg/L (n=7) (Kiss and Fries, 2009). Median concentrations of 1H-BT, 4Me-BT and 5Me-BT in the Hengstbach River were 0.633 ng/L, 0.476 ng/L, and 0.095 ng/L, respectively (Kiss and Fries, 2009). To our knowledge all previous reports on the occurrence of BTs in surface water were limited to isolated samples, which does not allow for comprehensive exposure assessment. It seems necessary to investigate the fate of BTs catchment-wide after their release into river water to evaluate the impact on water quality in a watershed.

1.3.4 Degradability of BTs

BTs are resistant to biodegradation (Castro et al., 2005). A gradual removal has been observed in the presence of peroxidases from horseradish plants and the white rot fungus *Phanerochaete chrysosporium* (Wu et al., 1998). Removal from aqueous phase has also been observed in the presence of several other plants (Castro et al., 2001). The biologically mediated transformation of 5Me-BT under aerobic conditions has recently been observed; it also appeared that 4Me-BT is recalcitrant (Rao et al., 1996; Cornell et al., 2000). Under anaerobic conditions both TTs isomers seem to persist (Grunden, 2001).

Rapid decomposition has been observed by the Fenton reaction and photochemically under the influence of UV irradiation (Wu et al., 1998; Andreozzi et al., 1999). BTs can be degraded photochemically using UV irradiation; however, high radiation doses are required and intermediate products form, which gives a negative response in acute toxicity tests (NGI, 2002). 1H-BT can be degraded by UV irradiation at pH values below 7. 1H-BT is not significantly mineralized by UV irradiation, but transformed into other compounds, of which aniline and phenazine were identified (Helm et al., 2003). Based on photochemical degradation experiments (Andreozzi et al., 1999), the stability of BTs has been shown to increase with pH.

Table 4 shows elimination of BTs in wastewater treatments (WWTPs). Elimination efficiencies for 1H-BT and for the sum of the 5Me-BT and 4Me-BT isomers in water treatment plants (WWTPs) varied from 13 to 62% and from 23 to 74% respectively (Voutsas et al., 2006), with a slightly better removal for the TTs.

However, Weiss et al. (2006) observed a higher removal efficiency in conventional activated sludge wastewater treatment for 1H-BT (37%) than for 5Me-BT (11%). 4Me-BT was not removed at all during the treatment process. These findings are consistent with the observation of Cornell et al. (2000) that 5Me-BT is biodegradable and 4Me-BT is recalcitrant. 5Me-BT is much more aerobically degradable than 4Me-BT (Weiss and Reemtsma, 2005). In bench-scale bioreactor systems 5Me-BT was completely biodegraded after 17 days, but 4Me-BT was only 25% biodegraded after 28 days (Weiss et al., 2006). These findings are consistent with the observations of Cornell et al. (2000) that 5Me-BT is biodegradable and 4Me-BT is recalcitrant. The much higher stability of 4Me-BT as compared to 5Me-BT has also been observed in WWTP and in surface waters (Weiss and Reemtsma, 2005; Weiss et al., 2006). Anaerobic degradation was not observed for 1H-BT and TTs in lab reactor experiments (Tham and Kennedy, 2005). Ozonization appears to be capable of cleaning wastewater and is also able to remove BTs during drinking water treatment where this technology is used (Weiss et al. 2006).

Location	Compound	% Elimination	Stdev	n	References
WWTP, Berlin '06	1H-BT	37	17	39	Weiss et al., 2006
WWTP, Berlin '06	4Me-BT	no elimination	25	25	Weiss et al., 2006
WWTP, Berlin '06	5Me-BT	11	25	25	Weiss et al., 2006
WWTP, Berlin '05	1H-BT	19.3	4.6	6	Weiss and Reemtsma, 2005
WWTP, Berlin '05	4Me-BT	4.5	6.1	6	Weiss and Reemtsma, 2005
WWTP, Berlin '05	5Me-BT	20	40.8	6	Weiss and Reemtsma, 2005
WWTP, Europe	1H-BT	34.5	n/a	20	Reemtsma et al., 2006
WWTP, Europe	TTs	11.3	n/a	18	Reemtsma et al., 2006
WWTP, Switzerland	1H-BT	22.6	31.1	14	Voutsas et al., 2006
WWTP, Switzerland	TTs	44.4	18.8	14	Voutsas et al., 2006
Membrane bioreactor	1H-BT	61	12	39	Weiss et al., 2006
Membrane bioreactor	4Me-BT	14	20	25	Weiss et al., 2006
Membrane bioreactor	5Me-BT	61	26	25	Weiss et al., 2006
Ozonization	BTs	>99	-	-	Weiss et al., 2006
Diverse bacteria	BTs	0	-	-	Rollinson and Calley, 1986
Sludge blanket reactor	TTs	0	-	-	Tham, 2005

Table 4. Elimination of BTs in wastewater treatments (WWTPs).

1.3.5 Toxicity of BTs

In contrast to the well-known environmental fate of BTs, very little data is available on toxicity to aquatic organisms, particularly for primary producers and pelagic invertebrates (Janna et al. 2011). BTs are one of the toxic components in deicers (Castro et al., 2005). Some of the first toxicity data produced regarding BTs and their derivatives was published

by Cancilla et al. (1997), who isolated a number of ADAF fractions to determine which contributed to their microtox activity using the Microtox bioassay (Strategic Diagnostics, Newark, USA). The first active fraction was found to be a mixture of BTs and TTs. Since then, acute toxicity assays have revealed that after 96 h, the median lethal concentration (LC50) was 65 mg/L of 1H-BT for the fathead minnow (*Pimephales promelas*), with a corresponding no-observable-adverse-effect concentration (NOEC) of 46 mg/L. The water flea (*Ceriodaphnia dubia*) was found to be slightly less sensitive to BTs, with a LC50 of 102 mg/L (Pillard et al., 2001).

Acute oral, dermal and inhalation toxicity data (mammal toxicity) for the 1H-BT and TTs are summarized in Table 4. All chemicals have test data; all show moderate toxicity following oral administration and low toxicity following dermal administration (Benzotriazoles coalition, 2001). Dose response studies by the oral route, conducted by Sherwin-Williams Company in 1976, showed that 1H-BT is slightly more toxic than TTs and since the slopes of both dose response curves are similar, it was predicted that mechanism of action is similar for chemicals (NTIS, 1977). Investigations of dermal toxicity at 2000 mg/kg in rabbits resulted in essentially identical results for the 1H-BT and TTs (NTIS, 1977).

A summary of the repeat dose toxicity data for the BTs category is also presented in Table 4. Repeat dose studies (28 d or 18-24 month studies) have been conducted with two of the BTs and demonstrate an apparent reduction in toxicity with increasing molecular weight.

A summary of the mutagenicity information for the BTs category is presented in Table 4. The weight of evidence for the members of this category indicates these chemicals are not mutagenic or clastogenic. Consideration was given to effects on reproductive organs in repeated exposure studies to determine whether reproductive toxicity studies were needed. The 78-week oral study of 1H-BT in Fischer 344 rats did not find any evidence of pathology in the reproductive organs. The 104-week oral study of 1H-BT in B6C3F1 mice did not find any evidence of pathology in the reproductive organs. The reproductive organs examined were: prostate/testis/epididymis of males and uterus/ovaries of females (Benzotriazoles coalition, 2001).

	1H-BT	1H-BT, TTs
<i>Acute toxicity</i>		
Oral LD50	560-909 mg/kg bw (rat)	1470-1830 mg/kg bw (rat)
Dermal LD50	>10.000 mg/kg bw (rabbit)	>4000 mg/kg bw (rabbit)
Inhalation LC50	>1.5 mg/l (4 hr) (rat)	>1.73 mg/l (1 hr) (rat)
Repeated Dose NOAEL=	12.100 ppm (oral-rat-18 mos) 23.500 ppm (oral-mouse-24 mos)	125 mg/kg bw (oral-rat-29 D)
Mutagenicity- gene mutation Mutagenicity- chromosome aberration	Ames-postive HGPRT-negative Micronucleus test (mouse)- negative	Ames-negative DNA damage and repair- Negative Micronucleus test (mouse)- negative
Reproductive toxicity	No pathology of reproductive 12.100 ppm (oral-rat-18 mos) 23.500 ppm (oral-mouse-24 mos)	No data found
Developmental toxicity	No data found	No data found

Table 4. Data on mammalian toxicity for 1H-BT and TTs in 1 or 4 hours (hr) and 18 and 24 months studies (mos) (adopted from Benzotriazoles coalition, 2001).

Thus, the entry of BTs in river water implicates negative effects on aquatic organisms (Pillard, 1995; Cancilla et al., 1997; Novak et al., 2000; Cancilla et al., 2003b; Corsi et al., 2006).

1.4 Problem Statement

Benzotriazoles (BTs) are widely used in many products as corrosion inhibitors. BTs are mainly discharged in high amounts from applications of aircraft anti-icing and de-icing fluids (ADAF) and dishwasher detergents into municipal and industrial wastewater treatment plants (WWTPs), where their elimination is low. These compounds are ubiquitous and highly mobile in the aquatic environment. It has been already shown that BTs have negative effects on aquatic organisms.

BTs belong to the group of “emerging contaminants” that have become the focus of environmental scientists, policy makers and the general public in recent years. However, only a few studies exist in the literature that report on the occurrence of BTs in river water. All previous studies were limited to isolated samples, which does not allow for comprehensive exposure assessment.

There are no prescriptive limits for BTs and TTs in control equipment like the Water Framework Directive (Directive 2000/60/EC), where the occurrence of other substances with eco-toxicological effects is already restricted in surface water. Only the assessment of all sources of BTs and the knowledge on transportation and transformation processes permit estimation for BTs and TTs in rivers and streams. Such predictions are the basis for the risk assessment of these compounds in the aquatic environment as well as for appropriate recommendations of measures like substitution by other corrosion inhibitors. At present this is not possible for BTs and TTs, since the contribution of several application areas to the occurrence of compounds in river catchments is still unknown. There are only two studies in Germany for the occurrence of BTs and TTs in streaming waters (Reemtsma et al., 2006; Kiss and Fries, 2009). Thus, monitoring data is lacking to validate exposure models. In Germany, the Rhine-Main region is estimated to be the most heavily loaded area since the Frankfurt Airport is located here. It is the third biggest airport in Europe and the biggest one in Germany (approx. 500,000 aircraft movements in 2007 with rising tendency). The investigations of river waters in the catchments area Frankfurt Airport and of influent and effluents from wastewater treatment plants (WWTP) that receive surface runoff from the airport provides a good indicator for the evaluation of the BTs -TTs-problem in the catchments areas of other German and European airports.

1.5 Research Objectives and Approach

In the view of issues discussed above, five aims were established within this Thesis.

The *first aim* was the development of an analytical method for the detection of BTs in environmental samples like river water and wastewater, as well as in products. This method should be relatively simple, cheap and quick because of the large quantity of samples, and both TTs isomers should be quantified separately.

The *second aim* was the evaluation of the contribution of BTs-input originating from ADAF and dishwasher detergents into the Hengstbach/Schwarzbach River and its tributaries due to WWTP discharges and other sources.

The *third aim* was the determination of spatial and temporal variability of concentrations and mass flows for BTs in the river water collected from rivers of the Hengstbach/Schwarzbach River. This goal is particularly important to determine the diffuse sources of BTs alongside the punctual sources into rivers, e.g. from infiltration of airport's surface run-off as well as how the discharge regime of the catchment area affects the exposure concentrations

The *fourth aim* was to assess the persistence and eco-toxicological risk potential of BTs in the aquatic environment.

2. Experimental Section

2.1 Study Area and River Water Sampling

The catchment area is located in the south-eastern of Frankfurt am Main and in the south of the international airport of Frankfurt airport. Frankfurt am Main Airport, known in German as Frankfurt Airport or Rhein-Main-Airport is a major international airport located in Frankfurt am Main, Germany, 12 km southwest of the city centre (Europien AIS Database). A map of the study area is shown in Figure 3. The mainstream of the selected catchment area with a total area of approximately 400 km² is the River Hengstbach/Schwarzbach. It has a total length of about 43 km and it is called River Schwarzbach after confluence with the Stream Geraethsbach. The catchment area is located in the south-east of the City Frankfurt am Main and in the south of Frankfurt Airport that is the largest airport in Germany and the third-largest airport in Europe (about 500.000 aircraft movements per year). The Stream Hengstbach serves the admission of three municipal WWTPs and one industrial WWTP (operated by Frankfurt Airport) (see Fig. 1). Periodic discharges of storm water runoff from the Frankfurt Airport occur periodically with low concentrations of total organic carbon (TOC) and of water from overloaded rainwater storage reservoirs and French drains, which serves the collection of the loaded face drain of the airport surfaces in the south area of Frankfurt Airport into the River Hengstbach (Fraport, 2007). At mean low flow (MLQ) and average flow rates (MQ) wastewater contributes about 100 and 50%, respectively, to the Hengstbach River.

Frankfurt Egelsbach Airport is a small and busy general aviation airport located south of Frankfurt Airport (Fig. 3). The Stream Geraethsbach serves the admission of two municipal WWTPs. The Streams Apfelbach and Muehlbach receive treated wastewater from one and two municipal WWTPs, respectively. The Canal Landgraben receives treated wastewater from five municipal and one industrial WWTP (operated by the Merck Company). The Canal Beinesgraben receives treated wastewater of one municipal WWTP shortly before it confluences with the River Schwarzbach (Fig. 3).

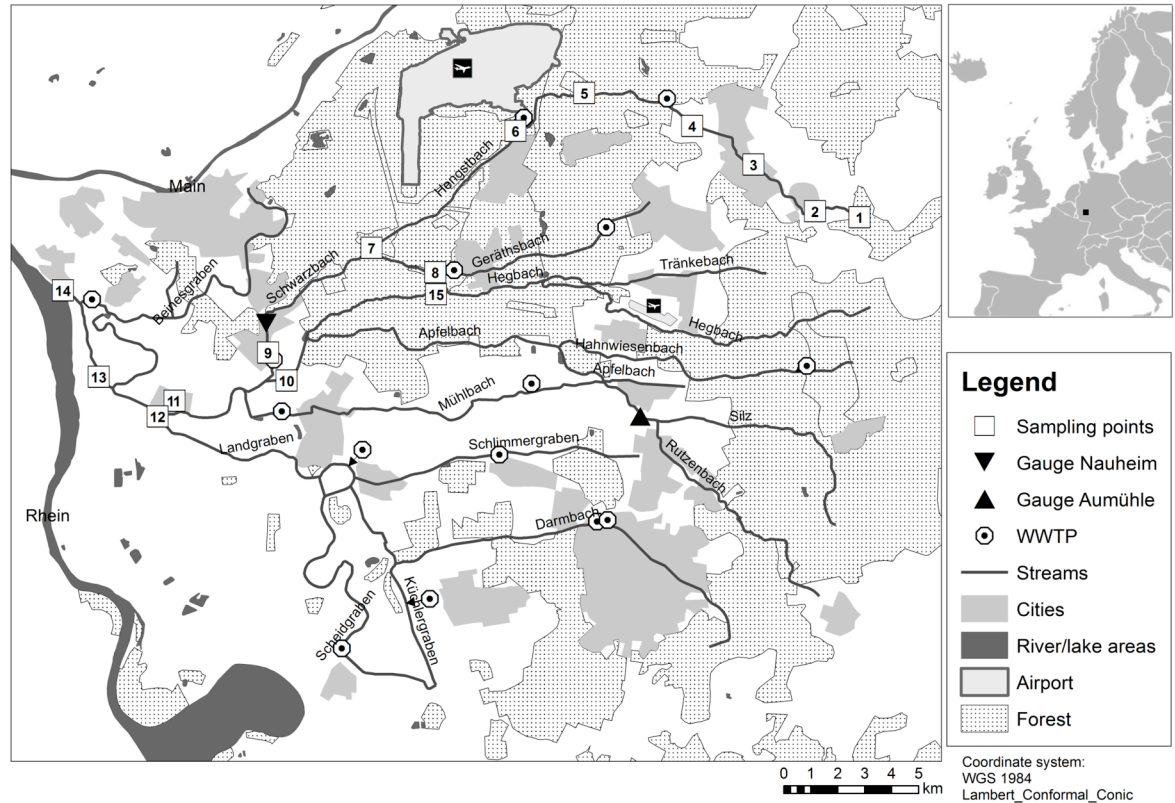


Figure 3. Study area with sampling locations, gauges and WWTPs.

River water grab samples were taken from the mainstream (P1-P7, P9, P11, P13, and P14) and from its tributaries Geraethsbach (P8), Apfelbach (P10), Landgraben (P12), and Hegbach (P15) during six sampling periods, reflecting four winter scenarios (16-17/01/09, 09-13/02/09, 17-20/11/09, 08/02/10) and two summer scenarios (24-25/07/09, 07-09/07/10). Sampling periods result from the fact that it was sometimes impossible to collect all samples on one day. All river water samples were collected in methanol pre-cleaned 2.5 L amber glass bottles and analyzed within one week.

2.2 Wastewater sampling

Influent samples were collected at the WWTPs Niederrad/Griesheim (WWTP-N/G) (about 753.000 inhabitants connected, in 2009; WWTP-G received about 58% of the total amount of wastewater corresponding to about 437.000 inhabitants WWTP-N received 316000 inhabitants) and Sindlingen (WWTP-S) (about 224.000 inhabitants connected). WWTP-N/G is the biggest WWTP in the state Hessen and it ranks thereby among the largest plants in Germany. At this WWTP the influents are mechanical treated in separate parts (Griesheim and Niederrad). The biological treatment follows after mixing. Frankfurt Airport feed its wastewater to WWTP-N and WWTP-S (Institute Fresenius, 2004). This wastewater originates from airport surface runoff, wastewater from rainwater storage reservoirs and household wastewater (Institute Fresenius, 2004). According to our knowledge, WWTP-G does not receive any wastewater from Frankfurt Airport. The mean daily influent discharges during sampling times at WWTP-N, WWTP-G and WWTP-S ranged between 76353 and 173367 m³/day, respectively. The individual influent mass flows were calculated for each WWTP by the individual influent concentrations times the mean daily influent discharges.

12 x 2h flow time proportional composite samples (1.0 L) were collected on 11/02/09, 11/03/09, 04/04/09, 23/04/09 and 14/07/09 from all three influents. The daily mean air temperatures were 2.9 °C on 11/02/09, 5.3 °C on 11/03/09, 15.0 °C on 04/04/09, 12.0 °C on 23/04/11 and 19.6 °C on 14/07/09; the lowest the minimum daily air temperature of -1 °C was measured on 11/02/09 (DWD). For sample collecting automatic samplers were used in a plastic canister. Sampling was carried out under dry weather conditions. At WWTP-G 2-hours composite influent samples (1.0 L) were collected on 23/04/09 (n=10). Sampling was carried out under dry weather conditions and glass bottles were used for sampling. Samples were individual samples, which at intervals of few minutes were taken. Every two hours the sampler switches over into the next sample canister. The bulk sample was then distributed to 2.5 L amber glass bottles and stored frozen at -15°C until analysis. The individual influent mass flows were calculated for each WWTP by the individual influent concentrations times the mean 2-hours influent discharges, which were between 6,185 and 13,781 m³/2h.

Sampling times, names of WWTPs and mean daily influent and effluent discharges are summarized in Table 5.

m³/day	WWTP Niederrad/Griesheim			WWTP Sindlingen	
Sampling time	Influent-N	Influent-G	Effluent	Influent	Effluent
11/02/09	147700	203300	296400	101360	91500
11/03/09	121800	180200	253400	94690	90500
04/04/09	85000	125500	188200	56390	51500
23/04/09	88500	129400	177400	47930	43400
14/07/09	199200	191800	342100	111480	99600

Table 5. Sampling times, names of WWTPs and mean daily influent and effluent discharges.

2.3 Determinations of River Discharge Flows and Water Level

The discharge of surface or underground streams is an important environmental variable to measure for several key reasons. First, one can estimate drought-flows and flood frequency from a time-series of stream discharge. Second, the rate of evapo-transpiration from catchment vegetation can be estimated from the same time-series within a water-balance equation. Thirdly, the multiplication of a concentration of suspended-sediment or a solute with the stream discharge gives the mass of that suspended or dissolved constituent moved over time. Such calculations are important in erosion studies, nutrient budget estimation, and pollution studies (Chappell, 2004; Lancaster University).

Discharge is the volume of water moving down a stream or river per unit of time, commonly expressed in cubic meter per second. Stream discharge can be measured using volumetric gauging, float gauging, current metering, dilution gauging (constant injection or gulp methods), structural methods and slope-area methods. The choice of method depends on the characteristics of the stream and on the application (Chappell, 2004; Lancaster University).

The discharge flow can be determined directly or also indirectly.

The water level W is the perpendicular distance of one point of the water surface from a fixed reference horizon PN (Fig. 4). Water levels can be determined relatively simply using gauges (Dyck and Peschke, 1995). In our case water levels were measured always between

the same point of the bridge and the water surface.

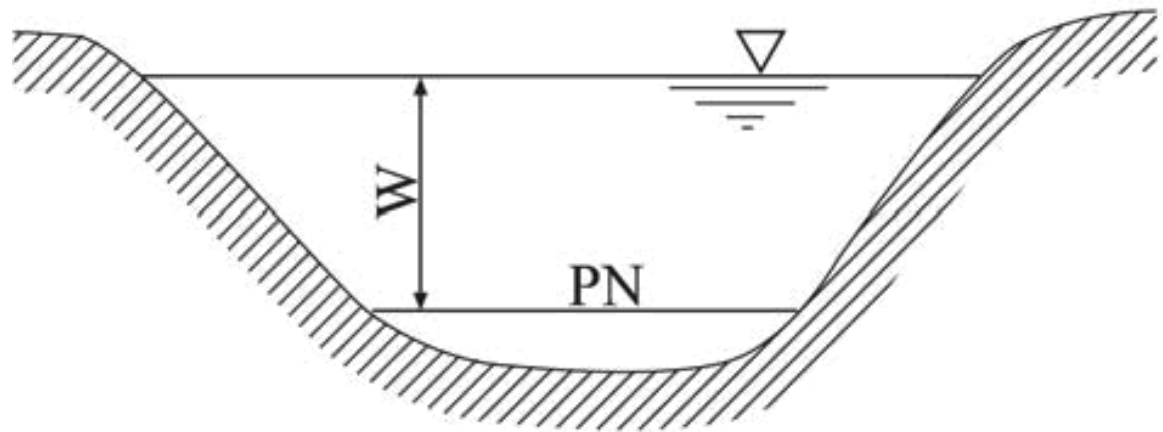


Figure 4. To the explanation of water level (Dyck and Peschke, 1995).



Figure 5. Determination of water level from a bridge at P13.

2.3.1 Direct and Indirect Discharge Measurement

The direct determination can occur by gauging weirs or gauging flume, or rarely also volumetric with a measuring tank. The volumetric method can be used only by small water

quantities (Steiermark).

Gauging weirs are used in small brooks, rivers and artificial canals to approx. $1 \text{ m}^3/\text{s}$ use. In most cases weirs take the form of a barrier across the river that causes water to pool behind the structure (not unlike a dam), but allows water to flow over the top. Weirs are commonly used to alter the flow regime of the river, prevent flooding, measure discharge and to help render a river navigable.



Figure 6. Triangular weir.

Flumes are open-channel flow sections that force flow to accelerate, in the form of a gravity chute that leads water from a diversion dam or weir completely aside a natural flow. These have been extensively used in hydraulic mining and working placer deposits for gold, tin and other heavy minerals. A Venturi Flume is a critical-flow open flume with a constricted flow, which causes a drop in the hydraulic grade line, creating a critical depth.

For volumetric measurement (tank measurement) purpose built measuring tanks, as well as commercial canisters such as buckets, tubs or tons (which have to be calibrated) are used. The measuring tank should be as lightweight as possible. This kind of discharge measurement is relatively exact and simple to handle. A disadvantage of this method of measurement is that the tanks can be used only with a certain downgrade and the necessary

overflow level (German Gauge Regulation: Anlage D, 1998).

To determine the flow indirectly the average current velocity v and corresponding cross-sectional area A are needed. The most frequently applied discharge measurement technique is the velocity measurement using hydraulic metric current meters (Woltmann meter) river in different depths and in different measuring verticals. There are different kinds of hydraulic metric current meters, like water wings (Delphin), current meter with rod. Alternatively the velocity can also be determined with electromagnetic current meter.



Figure 7. Current meter with propeller, range 0.025-10 m/s (adopted from <http://pkd.eijkelkamp.com>).

The velocities were measured using an electromagnetic current meter. The electromagnetic flow meter is based on Faraday's Law that a conductor (water) moving in a magnetic field, produced by a coil in the sensor, produces a voltage. This voltage is perpendicular to the movement of the conductor and perpendicular to the direction of the magnetic field. The voltage is proportional to the velocity of the water. The sampling volume is measured above the surface of the sensor (OTT), around the cylindrical volume of the sensor (Valeport) or above the flat volume of the sensor (Valeport) (De Doncker et al., 2008).

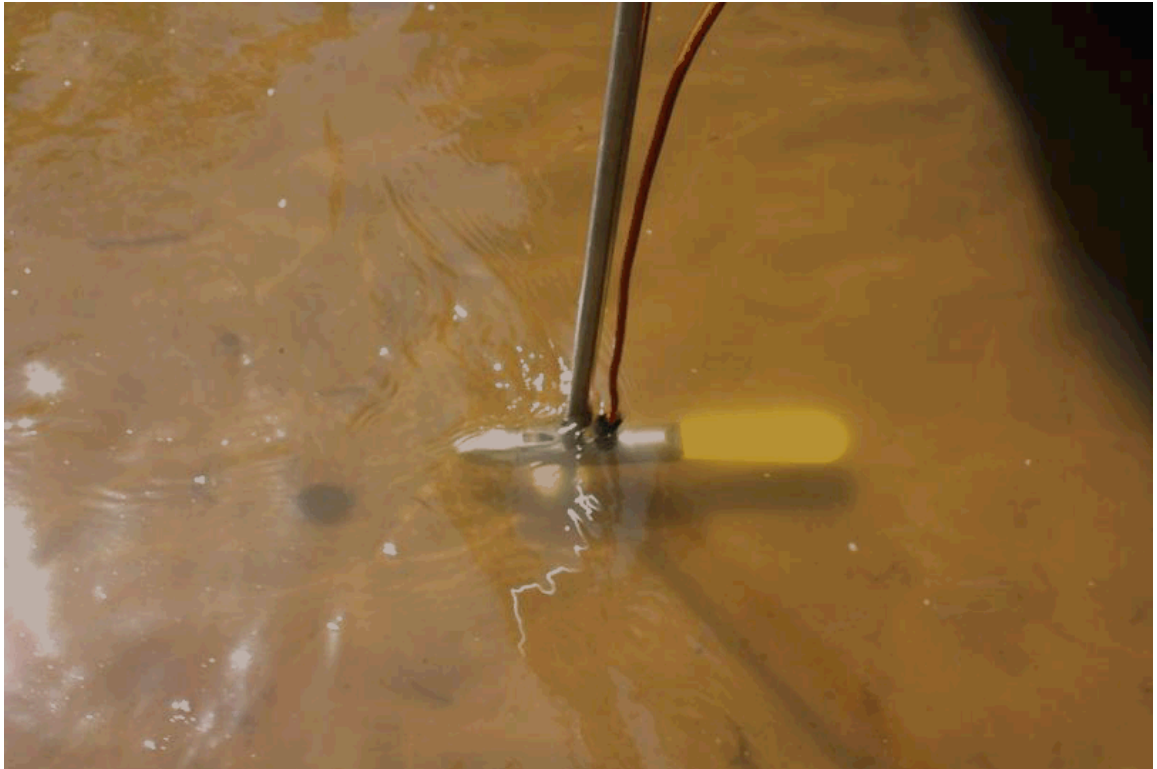


Figure 8. Measurement of flow velocity in the River Hengstbach/Schwarzbach at sampling point P5 with electromagnetic current meter (Nautilus C2000).

2.3.2 Data Evaluations Methods

From the determined flow velocities the discharge flow can be determined analytical using the computation of single segments, or graphically using planimeter of velocity-area and cross sectional area (Dyck and Peschke, 1995).

The graphic evaluation is more descriptive than analytic evaluation (see Fig.9). Nevertheless this type of evaluation is usually used only with complicated flow conditions, e.g. with the irregular geometry of the cross-section profile.

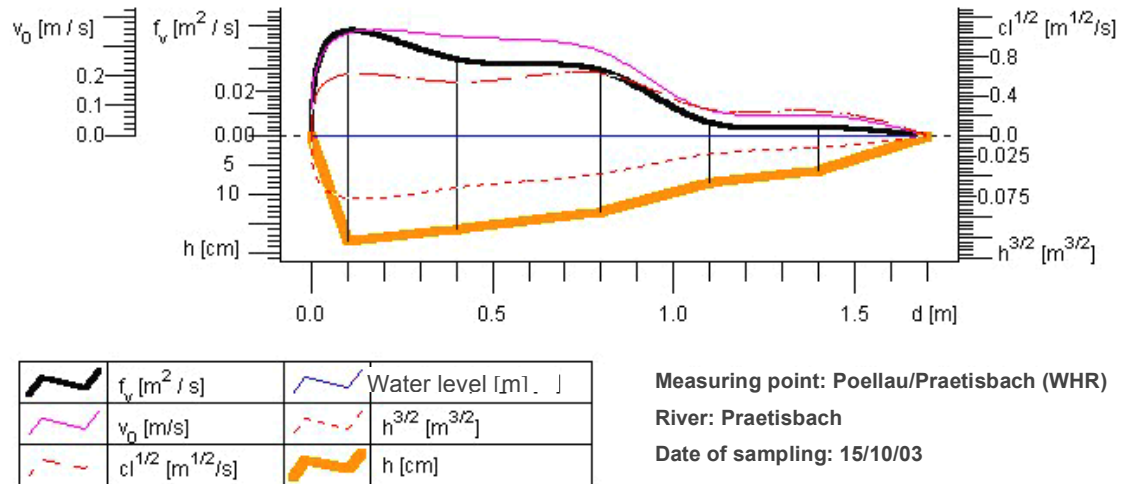


Figure 9. Example for graphic evaluation (adopted from <http://app.hydrographie.steiermark.at>).

At the analytical evaluation the segment discharge Q_i (m^3/s) was calculated by eq 1:

$$Q_i = A_i \cdot v_i \quad (1)$$

where A_i (m^2) is the cross section surface of the i -segment, v_i is the mean flow velocity (m/s) in the i -segment derived from the weighted arithmetic means of flow velocity measured in different depths.

A_i was calculated by eq 2:

$$A_i = h_i \cdot b_i \quad (2)$$

where h_i (m) is the mean depth by the width of the i -segment and b_i (m) is the width of i -segment.

Although the mean depth (from three measured depths) was calculated from the weighted arithmetic means of the corresponding number of measured depths:

$$h_i = 0.25 \cdot (h_{i1} + h_{i2} + h_{i3}) \quad (3)$$

If less than 6 measuring points for each measuring segments are selected, e.g. with small

depth of water, the mean velocity segment is calculated as a simple arithmetic means from the velocities in the individual measuring points.

Q_i were summed to obtain the total discharge Q (m^3/s):

$$Q = \sum_{i=1}^m Q_i \quad (4).$$

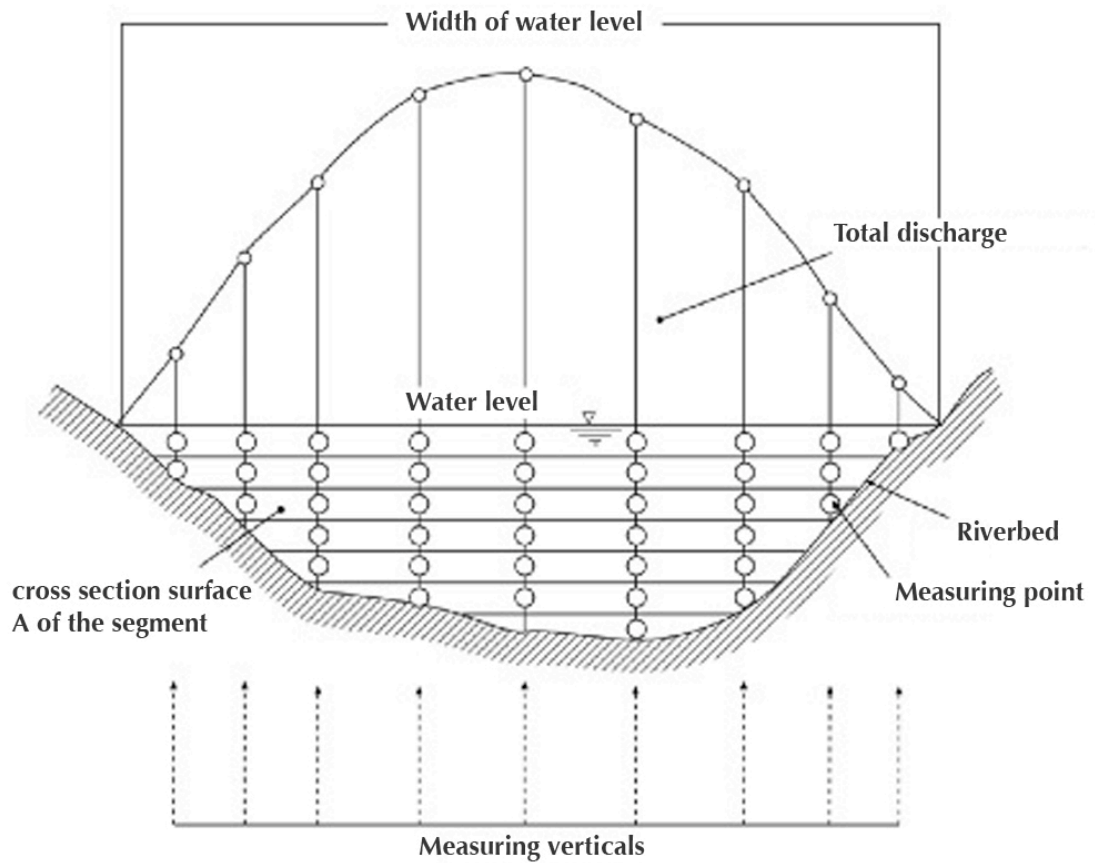


Figure 10. Arithmetic chart of gauging section and discharge water quantity.

The following auxiliary quantities are needed additionally during the evaluation: measuring section A (m^2):

$$A = \sum_{i=1}^m A_i \quad (5),$$

width of water level B (m):

$$B = \sum_{i=1}^m B_i \quad (6),$$

cross-section depth h (m):

$$h = A / B \quad (7),$$

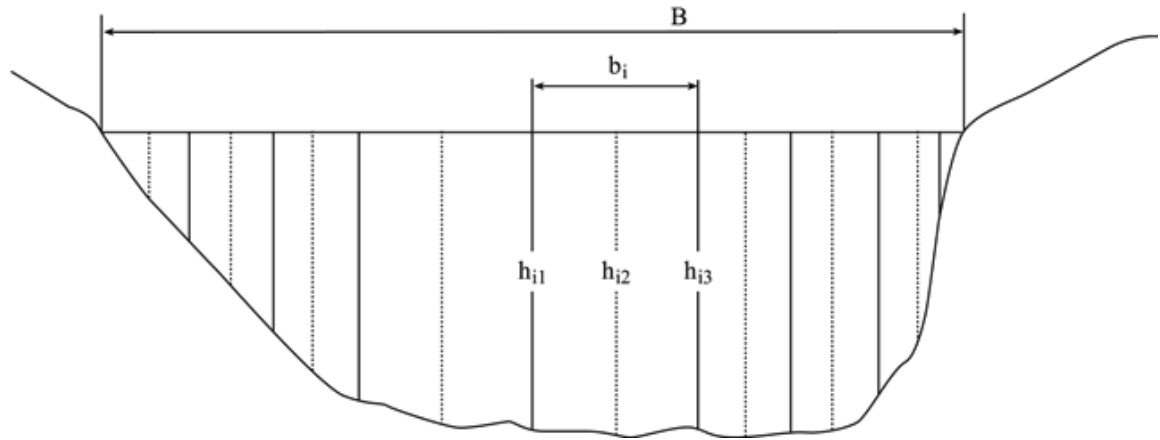


Figure 11. Division of gauging section: width of water level B , width of the i -segment b_i and the mean depth by the width of the i -segment h_i .

the maximum depth h_{\max} , the mean cross-section velocity v (m/s):

$$v = Q / A \quad (8),$$

the mean surface velocity v_0 (m/s):

$$v_0 = 1 / B \sum_{i=1}^m B_i \cdot v_{i0} \quad (9),$$

the maximum surface velocity $v_{0\max}$ from all measured data and the reference water level W (m):

$$W = 1 / Q \sum_{i=1}^m Q_i \cdot W_i \quad (10).$$

The reference water level is needed, if during measurement the water level should be changed (Steiermark).

2.3.3 Measurement Points and Dates

Since only one permanent routinely working discharge measurement level was located in the catchment area (gauge Nauheim maintained by the Hessian Agency for Environment and Geology; R3460790, H5535080; Fig. 1) the values of river discharge (Q) were computed from three periods (17-20/11/09, 25-27/03/10 and 07-09/07/10) by multiplying the area of water in the river cross section by the average velocity of the water in that cross section using the velocity-area mid-section method (De Doncker et al., 2008).

This method is based on the measurement of flow velocity in a river at different depths at different distances across the river to take into account the velocity profile. At P5, P6, P7, P9 and P11 in the mainstream and at P8 and P12 in the tributaries, the mean cross sections of the rivers were measured and divided into single segments with similar widths, ensuring that the different velocities were reflected very well. Between four and seven verticals were selected in the middle of each segment, in which the flow velocities were measured at each depth. For each of these vertical parts, the velocity of the water was measured at different depths with an electromagnetic current meter (Nautilus C2000, OTT, Kempten, Germany) that can measure velocities up to 3 m³/s. Velocity profiles over the entire water depth were obtained from these measurements. The velocity measurements were not influenced by temperature, the concentration of suspended matter, chemicals or salinity. The discharge flows determined and computed with analytical evaluation method.

For calibration, river discharge monitoring data was taken at gauge Nauheim, located next to P9 (Fig. 1) from the database of HLUg (<http://www.hlug.de>). The mean river discharges

during the sampling periods at gauge Nauheim (calculated from the mean daily river discharges) were as follows: 0.294 m³/s (RSD: 6 %) on 16-17/01/09, 0.833 m³/s (RSD: 38 %) on 09-13/02/09, 0.842 m³/s (RSD: 43 %) on 17-20/11/09, 1.18 m³/s on 07/02/10, 0.674 m³/s (RSD: 34 %) on 24-25/07/09 and 0.217 m³/s (RSD: 44 %) on 07-09/07/10 (<http://www.hlug.de>).

Further, it was assumed that Q is directly proportional to the river water level. The distance from the bottom of a bridge to the water surface was measured on each sampling event at each sampling point and plotted against the values of Q, which resulted from the discharge measurements from three periods (17-20/11/09, 25-27/03/10 and 07-09/07/10). For sampling events when Q was not obtained from measurements, it was estimated using these correlations.

For the year 2009, mass flows of 1H-BT, 4-MeBT and 5-MeBT were calculated from the measured river discharge and the concentrations of BTs in three different months: January (16-17/01/09), July (24-25/07/09) and November (17-20/11/09). The monthly mean air temperatures in these months were -0.4, 10.3 and 17.8 °C, respectively (DWD). A relation between the air temperature and BTs mass flows in the Stream Hengstbach/Schwarzbach was investigated by an Analysis of Variance (ANOVA) at a significance level (p) of 0.05 using the months of sampling and corresponding BTs mass flows as different factors levels and observation values, respectively.

2.4 Chemical Analysis

2.4.1 Materials, Chemicals and Standard Solutions

1H-BT ($\geq 99.0\%$), 5Me-BT ($\geq 98.0\%$) and 5.6-dimethyl-1H-benzotriazole-monohydrate (99.0%), used as a surrogate standard (SuS) were purchased from Sigma-Aldrich (Seelze, Germany). A technical mixture of TTs containing 5Me-BT and 4Me-BT (99.5%) was purchased from Dr. Ehrendorfer (Augsburg, Germany). The concentration ratio of 4Me-BT: 5Me-BT in the TTs mixture was determined at 2:1 considering the response of 5Me-BT in the pure 5MeBT standard. Fluoazifop-butyl (98.0%) was purchased from Dr. Ehrendorfer (Augsburg, Germany) and used as an internal standard (IS). HPLC-grade

methanol was obtained from Sigma-Aldrich (Seelze, Germany). Phosphoric acid (85.0%) was purchased from Merck (Darmstadt, Germany). Ultrapure water was taken from an Arium 611VF water purification system (Sartorius, Goettingen, Germany). A mixed standard stock solution containing 1H-BT, TTs and SuS, respectively for determination of response factors and recoveries was prepared in methanol with concentrations of 0.11 g/L for 1H-BT, 0.066 g/L for 4Me-BT, 0.033 g/L for 5Me-BT and 0.1 g/L for SuS, respectively (see Table A3). The stock solution was diluted with methanol if necessary. Individual stock solutions of IS and SuS, respectively were also prepared in methanol with concentrations of 0.105 g/L and 0.101 g/L, respectively.

2.4.2 Sample preparation

Sample preparation is a crucial step in any analytical method, especially in chromatography, where samples have to be homogenous, free of interference and safe for the column. During sample preparation the special compounds are isolated, interferences removed and analytes concentrated. Filtration, homogenization, precipitation, chemical reaction, solvent exchange, concentration, matrix removal, solubilization - these are just a few of the available tools that may be used individually or in combination to get the sample into a form compatible with the analytical instrument required for analysis.

Solid phase extraction (SPE) is a separation process by which compounds that are dissolved or suspended in a liquid mixture are separated from other compounds in the mixture according to their physical and chemical properties. For high sensitivity analyses, such as GC/MS, proper sample preparation can be critical for minimizing matrix effects and concentrating analytes of interest. Analytical laboratories use solid phase extraction to concentrate and purify samples for analysis; it is an increasingly useful sample preparation technique (Supelco, 1998). With SPE, many of the problems associated with liquid/liquid extraction can be prevented, such as incomplete phase separations, less-than-quantitative recoveries, use of expensive, fragile specialty glassware, and disposal of large quantities of organic solvents. SPE is more efficient than liquid/liquid extraction, yields quantitative extractions that are easy to perform, is rapid, and can be automated. Solvent use and lab time are reduced (Supelco, 1998).

2.4.2.1 River Water

All river water samples were collected in 2.5 L amber glass bottles and analyzed within one week. River water samples and also blank samples (ultrapure water) were first filtered through 0.45 μm membrane cellulose nitrate filters (Sartorius, Goettingen, Germany). After filtration the samples were spiked with with 20 μL of SuS (addition level: 0.808 $\mu\text{g/L}$) and stored over night at 5°C. On the next day samples were adjusted to pH 2.5 by adding phosphoric acid.

2.4.2.2 Wastewater

Wastewater samples were collected with automatic samplers each in a plastic canister and then the bulk samples were distributed to 2.5 L amber glass bottles and stored frozen at -15°C until analysis. Influent samples (1.0 L) and effluent (2.5 L) were first filtered through Whatmann prefolded filter paper, Grade 597 $\frac{1}{2}$ (Sigma Aldrich, Seelze, Germany), then through 0.5 μm cellulose membrane filters, Grade 389 F (Sartorius, Goettingen, Germany) and finally through 0.45 μm membrane cellulose nitrate filters (Sartorius, Goettingen, Germany). After filtration samples were spiked with 20 μL of SuS (addition level: 2.02 $\mu\text{g/mL}$) and stored over night at 5°C. Then, samples were adjusted to pH 2.5 by adding phosphoric acid.

2.4.2.3 Products

20 g of each dishwasher detergent tablet were pulverised in a mortar. The powder was dissolved in 1 L of ultrapure water. The pH values of solutions of the dishwasher detergent varied between 9.49 and 10.74 \pm 0.03.

A de-icing fluid (Type I, density 1.045 g/cm^3) and an anti-icing fluid (Type IV, density 1.038 g/cm^3) were analysed. In addition, a surface de-icing fluid (SDF, density 1.354 g/cm^3) on a potassium format basis was also analysed (all densities were taken from the product data sheets). Each fluid (20 g) was dissolved in 1 L of ultrapure water. The pH values of the ADAF solutions were 8.15 \pm 0.03 (Type I), 7.93 \pm 0.03 (Type IV) and 8.47

± 0.03 (SDF). 50 mL of ADAF, SDF and dishwasher detergent solutions were spiked with 20 μL of SuS (addition level: 40.4 $\mu\text{g/L}$).

2.4.3 Solid phase extraction (SPE)

Solid-phase extraction refers to the non-equilibrium exhaustive removal of chemical constituents from a flowing liquid sample via retention on a contained solid sorbent, and subsequent recovery of selected constituents by elution from the sorbent (Wells et al., 2000). The SPE is a five steps process. The first step is the selection of the SPE cartridge for the analyte of interest; the second is the cleaning and conditioning of the cartridge; the third is sample loading; the fourth washing; and the last is elution. The process is called retention if the analyte is completely adsorbed on the solid surface. The compounds must be removed from the solid surface and collected. In a typical solid phase extraction the best way to remove and collect the compounds is liquid. When a liquid provides a more desirable environment for the analyte than the solid phase does, then the compound of interest is desorbed and can be collected in the liquid as it exits the SPE device. This is called elution.

There are some reasons why the extraction could be pointless. The most common reason is the interference with another compound, which should be removed before the extraction. The sorbent material has to be cleaned up, a process that is a very important part of the extraction.

The optimization of a SPE procedure implies the selection of the most appropriate sorbent, the design of the SPE bed, the determination of the volume of sample to load, and of the nature and volumes of solvents to wash the column first and further elute the analyte (Werkhown-Goevie et al., 1981; Thurmann and Mills, 1998; Hennion, 1999 and Poole et al., 2000). In order to optimize each process, we need to know more about the capacity of a solid-phase sorbent and how that relates to sample type, sample pH, ionic strength, and so on. It is also important, how the properties of different sorbent materials affect retention and elution steps for the analyzed compounds (Simson and Wells, 2000).

2.4.3.1 Selection of optimum elution solvent

There is a need to determine the optimum elution solvent; and secondly the appropriate volumes and flow rates. An eluotropic series (E_0) arranges solvents in order of decreasing elution strength for solutes from a particular adsorbent (Zwir-Ferenc and Biziuk, 2006). For example, acetonitrile (E_0 0.65) and methanol (E_0 0.95) are commonly used eluting solvents in SPE. The larger value of E for methanol in the series means greater eluting power. In addition the solvent viscosity is also important factor: the more viscous the sample or solvent, the slower the process. The solvents chosen must have appropriate eluting powers, which mean the ability to desorb compounds and also to dissolve them (SPE principles, techniques and applications, Chapter 5). Volatility, chromophoric nature, purity, reactivity and toxicity are also important properties of solvents that are used in SPE. Choice of solvent will strongly influence the crucial results of recovery, selectivity, speed, and simplicity (SPE principles, techniques and applications, Chapter 5). To determine elution solvent three different polar liquid were tried: dichloromethane (DCM), acetonitril-methanol mixture (ACN:MeOH) (50-50%) and methanol (MeOH).

Which eluting solvent volume is used is also important. Using SPE, the initial sample volume (V_i) divided by the final, or eluting, solvent volume (V_f) indicates the degree of concentration expected on 100% recovery.

2.4.3.2 Selection of Sorbent Materials

During the optimized method several SPE parameters were calibrated prior to real sample analysis. The first step for the development of SPE method is selection of sorbent materials best suited for analysis of water sample.

To select sorbent materials 2.5 L of deionized water was spiked with 100 μ l of mix standard solution. For our compounds and solvent material the best way was Bond Elut ppl cartridges (Varian, USA). Bond Elut PPL is St-DVB polymer that has been modified with a proprietary non-polar surface. PPL will retain even the most polar classes of analytes, including phenols. The large particle size allows ease of flow for viscous or particulate rich water samples, while the high surface area and strong hydrophobic ensure reproducible extractions with high recoveries upon elution (Agilent). This type was studied in two

different sizes and with three different bed weights, like PPL 200 mg sorbent mass with 3 ml cartridge volume, C18 200 mg sorbent mass with 3 ml cartridge volume and PPL 100 mg sorbent mass with 1 ml cartridge volume.

2.4.3.3 Determination of Breakthrough Volume

The most important parameter controlling the SPE process is the breakthrough volume, which is the volume that can be loaded onto a SPE bed providing a given ratio of outlet to inlet analyte concentration (Ortega et al., 2001). Other authors use a definition based on mass instead of concentration (Loevkvist and Joensson, 1987; Van der Straeten et al., 1985 and Senum, 1981). The breakthrough volume represents the maximum sample volume, which can be applied with the best recovery. This explains why it has received much attention for measurements and prediction. Bidlingmeyer (1984) reported that recovery is dependent on flow rate through the SPE device because breakthrough volume is decreased due to band-broadening at higher flow rates. Mayer and Poole (1994) found that the recovery of analytes by SPE shows significant flow-rate dependence when the sample volume exceeds the breakthrough volume of the analyte.

The influence of SPE breakthrough volume was determined from 6 x 1.0 L, 6 x 2.0 L and 6 x 2.5 L deionized and waste water, all spiked with mixed standard stock solution. BTs and SuS were extracted from different volumes by SPE and analyzed as reported in section 6.2.3. Peak area ratios of compound specific quantification ions to the quantification ion of IS were taken to identify of the best breakthrough volume.

For determination of breakthrough volume in river water deionized water were used in three different volume like 6 x 1.0 L, 6 x 2.0 L and 6 x 2.5 L. Peak area ratios of compound specific quantification ions to the quantification ion of IS were taken to identify of the best breakthrough volume.

For determination of breakthrough volume in wastewater samples two sorbent cartridges were used (see Fig. 12).

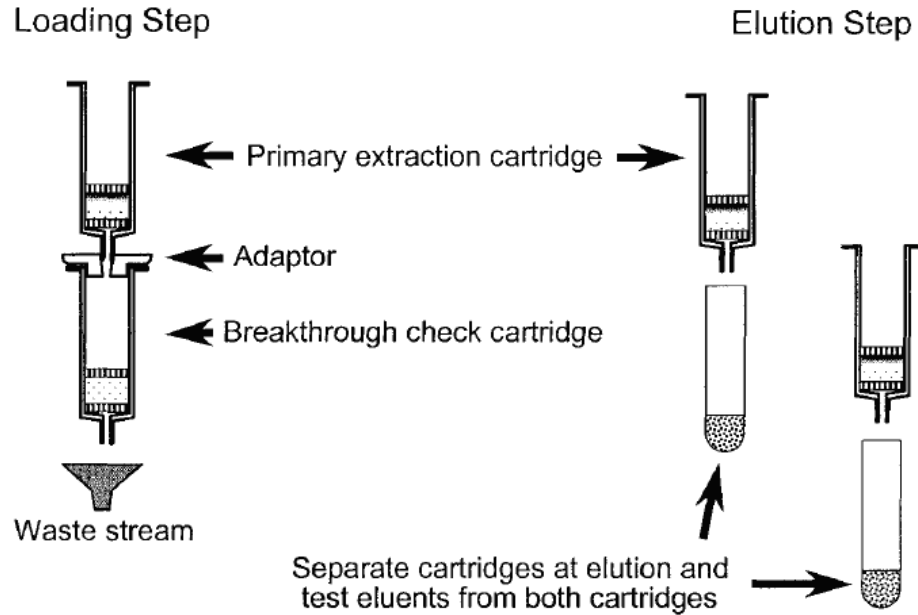


Figure 12. Determination of breakthrough volume for waste water samples (Wells, 2000).

If any of the analyte appears in the eluent of the second cartridge after sample loading and separate elution of each cartridge, then the sorbent capacity of the first cartridge has clearly been exceeded. For products the breakthrough volume of river water were used.

2.4.3.4 Determination of the Optimum pH-Value

Solutions used in SPE procedures have a very broad pH range (Zwir-Ferenc and Biziuk, 2006). The meaning of pH in SPE is very important. If a compound is ionizable, the extraction will be pH dependent. The pKa values of analytes can be used to guide us in selecting an appropriate pH. 1H-BT and 5Me-BT have acid dissociation constants (pKa) of 8.76 and 8.50, respectively (Hart et al., 2004) and it is very important to determine an optimum pH-value of the water samples to achieve interactions with the specific sorbents material. Weak acids with higher pKa values dissociate in neutral or basic solutions and interactions of ions with the ppl sorbents are impossible.

The influence of pH on the extraction efficiency was studied by analyzing 2.5 L of deionised water spiked with the mixed standard stock solution (addition levels: 1.3-4.4

ng/mL) at pH values of 5.8 (equilibrated with the atmosphere and without any addition of acid) and 2.5 (with addition of phosphoric acid), respectively (n=3). The ratios of each BTs to IS were compared to evaluate the influence of pH on extraction efficiency.

2.4.4 Optimization of GC/MS Parameters

There are several analytical literature reported to analyze BTs with GC/MS. Corsi et al. (2003) reported the analytic of BTs with SPE- GC/MS. We took this method as base. The aim of our work was a more sensitive and rapider method for BTs.

SPE extracts were analyzed using GC/MS (GC: 6890N System, MS: MS5973 Inert mass selective detector, both Agilent Technologies, Santa Clara, USA) in the selected ion monitoring (SIM) mode. The GC was equipped with an MPS-XL auto sampler (Gerstel, Mülheim an der Ruhr, Germany). It is very important to choose a good column for the analysis. The selection of column diameter, film thickness of stationary phase, and length of column is also important part of prepare of analysis. The column for analysis BTs in river water, waste water and product was chosen a DB-5ms 30 m length capillary column with 0.25 mm diameter and 0.25 μm film thicknesses (Agilent Technologies, Santa Clara, USA). The column material is Phenyl Arylene polymer virtually equivalent to a (5%-Phenyl)-methylpolysiloxane. Helium (purity 5.0) was used as carrier gas. The column was operated in the constant pressure mode at 70 kPa in split less mode. The injector temperature was set to 280°C. The oven was maintained at 80 °C to heat up afterwards with a heating up rate of 15 °C/min to 300 °C.

For MS calibration Autotune was taken. As calibration compound perfluorotributylamine (PTFBA) was used and automatically adjusts the MS parameters to meet predefined criteria for operation in EI mode (Agilent). Autotune adjusts all MSD parameters to predetermined target values. ATUNE.U is an autotune, which maximizes instrument sensitivity over the mass range, using PFTBA masses 69, 219, and 502. Use this tune for applications requiring maximum sensitivity that do not require the traditional abundance ratios of 100% m/z 69, 35 - 85% m/z 219, and 1 - 5% m/z 502. For data reprocessing and analysis Chemstation Software (Agilent Technologies, Santa Clara, USA) was used. For identification of compounds Wiley Mass Spectral Library was used.

2.4.5 Response factors

The response factor is the ratio of the signal-to-sample size, and is used for more accurate quantitative analysis with a gas chromatographic detector (Grob, 2004).

$$R_{IS/BTs} = \frac{A_{IS} \cdot mass_{BTs}}{A_{BTs} \cdot mass_{IS}} \quad (12)$$

$$R_{IS/SuS} = \frac{A_{IS} \cdot mass_{SuS}}{A_{SuS} \cdot mass_{IS}} \quad (13)$$

$$R_{SuS/BTs} = \frac{A_{SuS} \cdot mass_{BTs}}{A_{BTs} \cdot mass_{SuS}} \quad (14)$$

, where $R_{IS/BTs}$ and $R_{IS/SuS}$ are the response factors for recoveries, $R_{SuS/BTs}$ is the response factor for the determination of concentration. A_{IS} , A_{BTs} and A_{SuS} are the peak areas of quantitation ions and $mass_{IS}$, $mass_{BTs}$, and $mass_{SuS}$ are the absolute masses.

In our first report (Kiss and Fries, 2009) 4Me-BT was quantified in river water samples by the method of 5Me-BT. 4Me-BT concentrations were estimated based on the response of 5Me-BT standard, because the pure standard of 4Me-BT was still not available. Although, both isomers are very similar, it is very important to quantify both isomers separately, they behave differently in the environment. There is no available for the analyses of 4Me-BT the response factor of 5Me-BT to use (Corsi et al., 2003; Kiss and Fries, 2009; Cancilla et al., 2003).

Response factors between IS and BTs ($R_{IS/BTs}$) and IS and SuS ($R_{IS/SuS}$) were determined by directly injecting 1 μ L of mixed standard solutions containing 1H-BT, 5Me-BT, 4Me-BT and SuS at seven concentration levels between 7.5 and 112.7 μ g/mL (triplicates were performed for each concentration level). All solutions were spiked with 4 μ L of the IS stock solution. Response factors were calculated by relating the peak area of IS to the peak areas of BTs and SuS, respectively. Previously, peak areas were corrected by the weight of each compound. $R_{IS/BTs}$ and $R_{IS/SuS}$ were used for determination of recoveries of BTs and SuS in river water, wastewater, products and ultrapure water (see Table A2, Fig. A1-A2).

For quantification of BTs mean values of $R_{SuS/BTs}$ were used. Mean response factors and relative standard deviation (RSD) are shown in Table 6.

Compound name	Mean response factor $R_{IS/BTs}$ (n=6) (RSD, %)	Mean response factor $R_{SuS/BTs}$ (n=6) (RSD, %)	Mean recovery [%] (RSD, %)	LOD [ng L ⁻¹]	ME [%]
River Water					
1H-BT	4.84 (4)	0.51 (4)	25 (3)	5	-
4Me-BT	4.05 (24)	0.42 (24)	66 (6)	2	-
5Me-BT	2.09 (12)	0.22 (12)	55 (10)	4	-
SuS	9.55 (20)	-	100 (5)	-	-
Waste Water					
1H-BT	2.76	0.52	37 (11)	4	107
4Me-BT	2.00	0.45	205 (18)	1	227
5Me-BT	1.16	0.23	166 (0.1)	2	128
SuS	2.11	-	109 (3)	-	146
Anti-icing fluid/ultrapure water					
1H-BT	4.84 (4)	0.51 (4)	41 (19)	-	-
4Me-BT	4.05 (24)	0.42 (24)	36 (20)	-	-
5Me-BT	2.09 (12)	0.22 (12)	40 (21)	-	-
SuS	9.55 (20)	-	63 (14)	-	-

Table 6. Mean response factors, recoveries [%], limit of detections [ng/L] and matrix effects (ME) [%] for river water, waste waster and products.

2.4.6 Recoveries

Recovery (W%) is a measure for reproducibility of an analyse method. Recovery from spiked samples is calculated by measuring the amount of analyte eluted from the sorbent and comparing the original concentration to the concentration remaining after SPE (Mitra, 2004). W% were calculated by eq:

$$M_{abs.BTs} [ng] = \left(M_{abs.IS} \cdot R_{IS/BTs} \cdot \frac{A_{BTs}}{A_{IS}} \right) \quad (15)$$

$$M_{abs.SuS} [ng] = \left(M_{abs.IS} \cdot R_{IS/SuS} \cdot \frac{A_{SuS}}{A_{IS}} \right) \quad (16)$$

, where $M_{abs,IS}$ is the mass of IS, that was added to SPE-extract. $M_{abs,BTs}$, and $M_{abs,SuS}$ are the absolute mass, that were to the samples before SPE

$$W\%_{BTs} = \frac{100 \cdot M_{abs,BTs}}{M_{abs,BTs,added}} \quad (17)$$

$$W\%_{SuS} = \frac{100 \cdot M_{abs,SuS}}{M_{abs,SuS,added}} \quad (18)$$

, where $W\%_{BTs}$ and $W\%_{SuS}$ are the recoveries of the compounds and the SuS.

The recoveries for 1H-BT, 5Me-BT, 4Me-BT and SuS in river water were determined by analyzing 2.5 L of river water (n=3) using SPE-GC/MS spiked with 20 μ L of the mixed standard stock solution (addition levels were 0.26-0.88 μ g/L). The recoveries for the quantification of BTs in the anti-icing fluid were determined by analyzing 50 mL of ultrapure water (n=3) spiked with 20 μ L of the mixed standard stock solution (addition levels: 13.2-44 μ g/L). Three non-spiked samples of river water were also analyzed and signals of BTs were subtracted from signals obtained for spiked samples. The ratios between the mean recoveries of SuS and individual BTs were used for quantification of BTs in river water and in the anti-icing fluid solution.

The recoveries were determined for 1H-BT, 5Me-BT, 4Me-BT and SuS by analysing 1.0 L of wastewater influent samples (n=2) spiked with 100 μ L of the mixed standard stock solution (addition levels were 3.3 - 11 μ g/L) and non-spiked samples of wastewater influent (n=3, 100 μ L of methanol was added to those samples). Signals for each BTs were subtracted from signals obtained for spiked samples. Recoveries were calculated by relating the weighted masses to the masses detected in the extracts after SPE.

The recoveries for the detection of BTs in ADAF and detergent tabs were determined by analyzing 50 mL of ultrapure water (n=3) spiked with 20 μ L of the mixed standard stock solution (addition levels were 13.2-44 μ g/L). Recoveries were calculated by relating the weighted masses to the masses detected in the extracts after SPE. Previously, peak areas were corrected by the weight of each compound.

The results of determination of recoveries for river water, wastewater and products were shown in Table 6.

2.4.7 Concentration of BTs

The concentrations of BTs in samples (C_{TC}) were calculated by the following eq:

$$C_{BTs} [ng / l] = \left[M_{abs.SuS} \cdot R_{SuS/BTs} \cdot \frac{A_{BTs}}{A_{SuS}} \cdot F \right] / V \quad (19)$$

where C_{TC} is the concentration of compound $M_{abs,SuS}$ is the mass of SuS, that was added to SPE-extract, $R_{SuS/TC}$ is the response factor, A_{TC} and A_{SuS} are the peak areas of quantitation ions, that were to the samples before SPE, F is the the ratio of the $W\%_{SuS}$ -to- $W\%_{BTs}$, because the concentration must be corrected with the recovery and V (L) is the sample volume.

3. Results and Discussion

3.1 Method development

Samples and also blank samples (ultrapure water) were first filtered through Whatmann prefolded filter paper, Grade 597 ½ (Sigma Aldrich, Seelze, Germany), then through 0.5 µm cellulose membrane filters, Grade 389 F (Sartorius, Goettingen, Germany) (both pre-cleaned with methanol) and finally through 0.45 µm membrane cellulose nitrate filters (Sartorius, Goettingen, Germany) using vacuum pump filtration. After filtration samples were spiked with 20 µL of Su.S (addition level: 2.02 ng/mL) and stored over night at 5°C. Then, samples were adjusted to pH 2.5 by adding phosphoric acid. Bond Elut ppl cartridges were used (100 mg/L, Varian, USA) to enrich the BTs and SuS. Cartridges were conditioned with 1 mL methanol at atmospheric pressure, cleaned with 1 mL methanol under vacuum (850 mbar) and conditioned again with 1 mL methanol at atmospheric pressure. Water samples were percolated through the SPE-cartridges under vacuum with a flow rate of approximately 10 mL/min. Sorbents were dried under vacuum for approximately 20 min and eluted three times with 333 µL of methanol. Subsequently, extracts were evaporated to dryness under a gentle stream of nitrogen. Dry residues were dissolved again in 100 µL methanol, spiked with 4 µL of the IS stock solution (addition level: 4.2 µg/mL) and transferred to 2 mL glass vials equipped with inlets (0.25 mL) (both were purchased from Wicom, Heppenheim, Germany).

In Corsi et al. (Corsi et al., 2003) decafluorobiphenyl was suggested as an IS for the analysis of BTs in water because no isotopically labeled standards exist. The peak for decafluorobiphenyl in split less mode resulted in peak splitting and a strong peak tailing due to a very short retention time of 4 min (Kiss and Fries, 2009). Because a better sensitivity can be achieved by analyzing in split less mode fluoazifop-butyl was tested as suggested by Ternes (Ternes et al., 1998) for the analysis of neutral drugs as well as beta-blockers in aqueous matrices. Since the retention time of the min-butyl fluoazifop of 13.0 min was much longer peak tailing or peak splitting was not observed during analysis during analysis in split less mode. Thus, fluoazifop-butyl was chosen as an IS for all further analysis.

There are several analytical literature reported to analyze BTs with GC/MS. Corsi et al. (2003) reported the analytic of BTs with SPE- GC/MS. We took this method as base. The aim of our work was a more sensitive and rapider method for BTs.

SPE extracts were analyzed using a GC-MS system (GC: 6890N System, MS: MS5973 Inert mass selective detector, both Agilent Technologies, Santa Clara, USA). The GC was equipped with an MPS-XL auto sampler (Gerstel, Mülheim an der Ruhr, Germany) in the selected ion monitoring (SIM) mode. The column was a DB-5ms (30 m x 0.25 mm x 0.25 μm , Agilent Technologies, Santa Clara, USA). Helium (purity 5.0) was used as carrier gas. The column was operated in the constant pressure mode at 70 kPa in split less mode. The injector temperature was set to 280°C. The oven was maintained at 80°C to heat up afterwards with a heating up rate of 15°C/min to 300°C.

3.1.1 Identification and Quantification of BTs

The quantification ions were m/z 119 for 1H-BT, m/z 104 for 4Me-BT and 5Me-BT, m/z 118 for SuS and m/z 282 for IS. Qualifier ions were m/z 91 and m/z 64 for 1H-BT, m/z 133 and m/z 78 for 5Me-BT and 4Me-BT, respectively, m/z 147 and m/z 91 for SuS and m/z 283 for IS. Identification of 1H-BT, 5Me-BT and 4Me-BT in environmental samples was done by comparing mass spectra and retention times resulting from analyses of analytical standards. Chromatographic separation of the isomers 4Me-BT and 5Me-BT was successful and retention times were different of the both TTs.

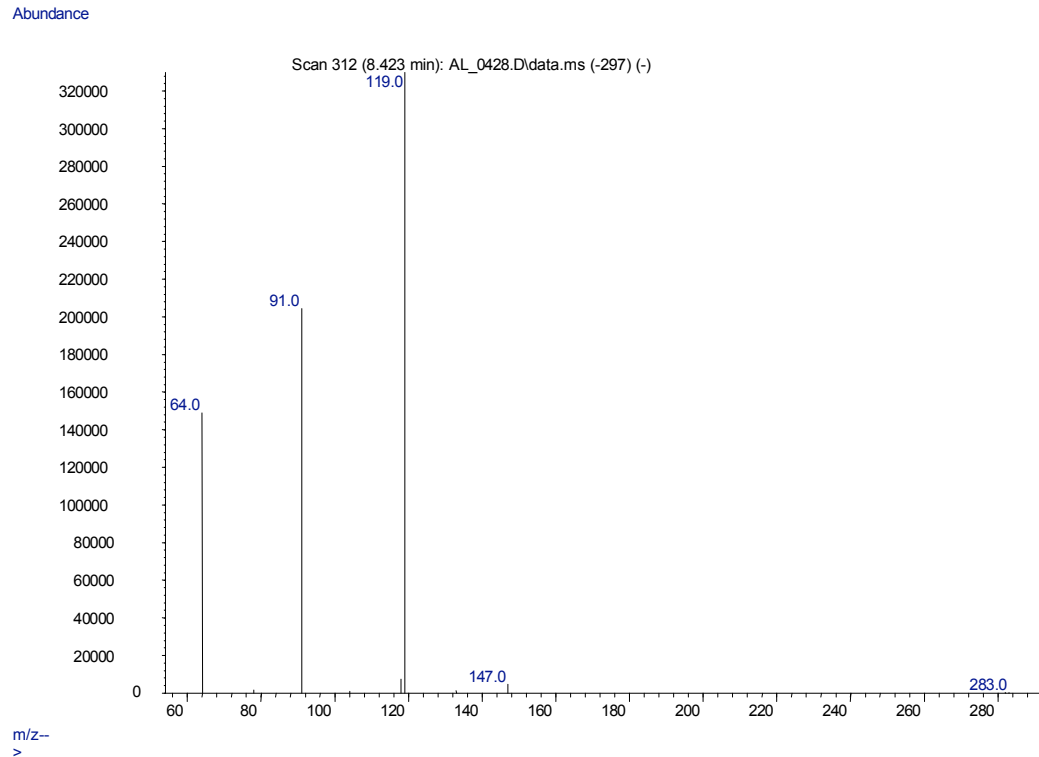


Figure 13. Mass spectra of 1H-BT in SIM mode.

3.1.2 Problems in Analytic of BTs with GC/MS

There are many causes of column performance degradation, like thermal degradation (overheating), column breakage, oxygen damage, chemical damage (acid and bases) and column contamination (non-volatile and semi-volatile). By analysis of BTs the most common problem was a column contamination, or chemical damages. These problems originate from complex matrix samples, in our case from extracted river- and wastewater samples. Mostly wastewater samples contain such non-volatile or semi-volatile compounds, which may cause peak tailing, column bleed, loss of efficiency, peak size or baseline problems (noise, drift, humps, blobs and peaks) and retention time shifts.

3.1.2.1 Matrix Effects

Untreated wastewater samples have relatively high matrix content. Interfering matrix components can affect the reproducibility of the developed procedure, leading to erroneous

results in quantification (Gonzalez et al., 2002). In our case the RSD for the recovery samples (n=3) were all below 18% demonstrating a good reproducibility. Quantitation can be also affected by signal enhancement or signal suppression in the mass spectrometer due to the co-extracted and co-eluted matrix. For the assessment of matrix effects the procedure suggested by Matuszewski et al. (Matuszewski et al., 2003) was applied. Two aliquots of untreated wastewater (1.0 L each) were extracted with SPE for the assessment of the matrix effect. One extract was spiked with 100 μ L of the BTs standard solution (addition levels: 16.5-55.0 μ g/mL) and with 4 μ L of the IS stock solution. For the control, 100 μ L methanol was taken and spiked with 100 μ L of the BTs standard solutions (addition levels: 16.5-55.0 μ g/mL) and with 4 μ L of the IS stock solution. The matrix effect (ME) was calculated using the following eq. 1:

$$\text{ME (\%)} = \text{B/A} \times 100 \quad (11)$$

,where A is the peak area of the compound resulting from the analysis of the standard solution and B is the corresponding peak area of the compound resulting from the analysis of the spiked wastewater extract (the peak area ratio of BTs to IS resulted from the analysis of the non-spiked extract was subtracted). If ME is higher than 100% it means that signal enhancement occurs in the MS due to the co-extracted and co-eluted matrix. ME values are lower than 100% means if signal suppression occurs in the MS (Matuszewski et al., 2003). Values of ME were 107% (1H-BT), 227% (4Me-BT), 128% (5Me-BT) and 146% (SuS). Signal enhancement from matrix effects was observed for both TTs and for SuS whereas for 1H-BT no matrix effect was observed. Matrix effects could be the reason that recoveries exceed 100% for both TTs isomers and for SuS. For quantitation of BTs in untreated wastewater recoveries determined for untreated wastewater water were used to compensate matrix effects.

3.1.2.2 Retention Gap or Guard Column

First we have to clear what is the different between a retention gap and a guard column. A guard column is used to provide a surface for non-volatile residues to deposit so that they do not accumulate in the analytical column (Rood, 2007). The non-volatile residues accumulate in guard column. But guard column do not prevent semi-volatile residues. A

retention gap is used to improve peak shapes in specific situations (Rood, 2007). It is necessary in specific situation like cool on-column injection, splitless and megabore direct injection or non-bonded stationary phase with splitless or on-column injection. A retention gap also acts in the same way as a guard column; thus it may protect the column against non-volatile residue accumulation situations (Rood, 2007). Also, a guard column and retention gap is the same thing, but they serve different purposes.

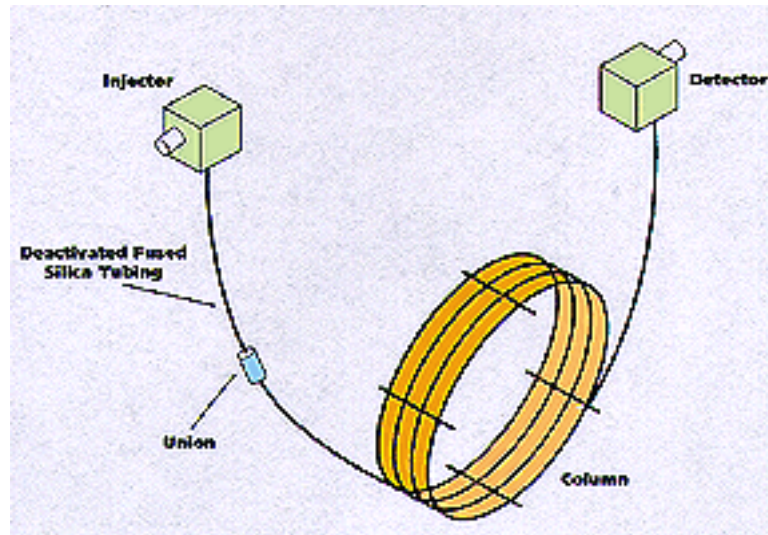


Figure 14. Retention gap or guard column (adopted from <http://www.chem.agilent.com>).

The influence of consecutive analyses of SPE extracts containing a complex matrix on the performance of separation and on the method sensitivity was studied. Since BTs are rather polar compounds special attention has to be paid on the performance of the chromatographic system. Usually the use of a retention gap is recommended for the analysis of complex matrix samples e.g. wastewater samples (Grob and Schilling, 1987) to retain non-volatile residues that may contaminate a column. To optimize chromatographic conditions two column configurations were tested in order to obtain the best separation between BTs and the matrix compounds and symmetric peak shapes. A guard column is often a 3-5 meter or retention gap is a 5–10 meter piece of deactivated fused silica tubing attached to the front of the analytical column using some type of union. It is normal capillary tubing, but it contains no stationary phase. It is deactivated to prevent any interaction between the column and the analyzed compounds. The diameter is usually the

same as an analytical column. In Figure 15, the mass trace m/z 104 with signals for 4Me-BT and 5Me-BT obtained from the analysis without and with the retention gap is shown.

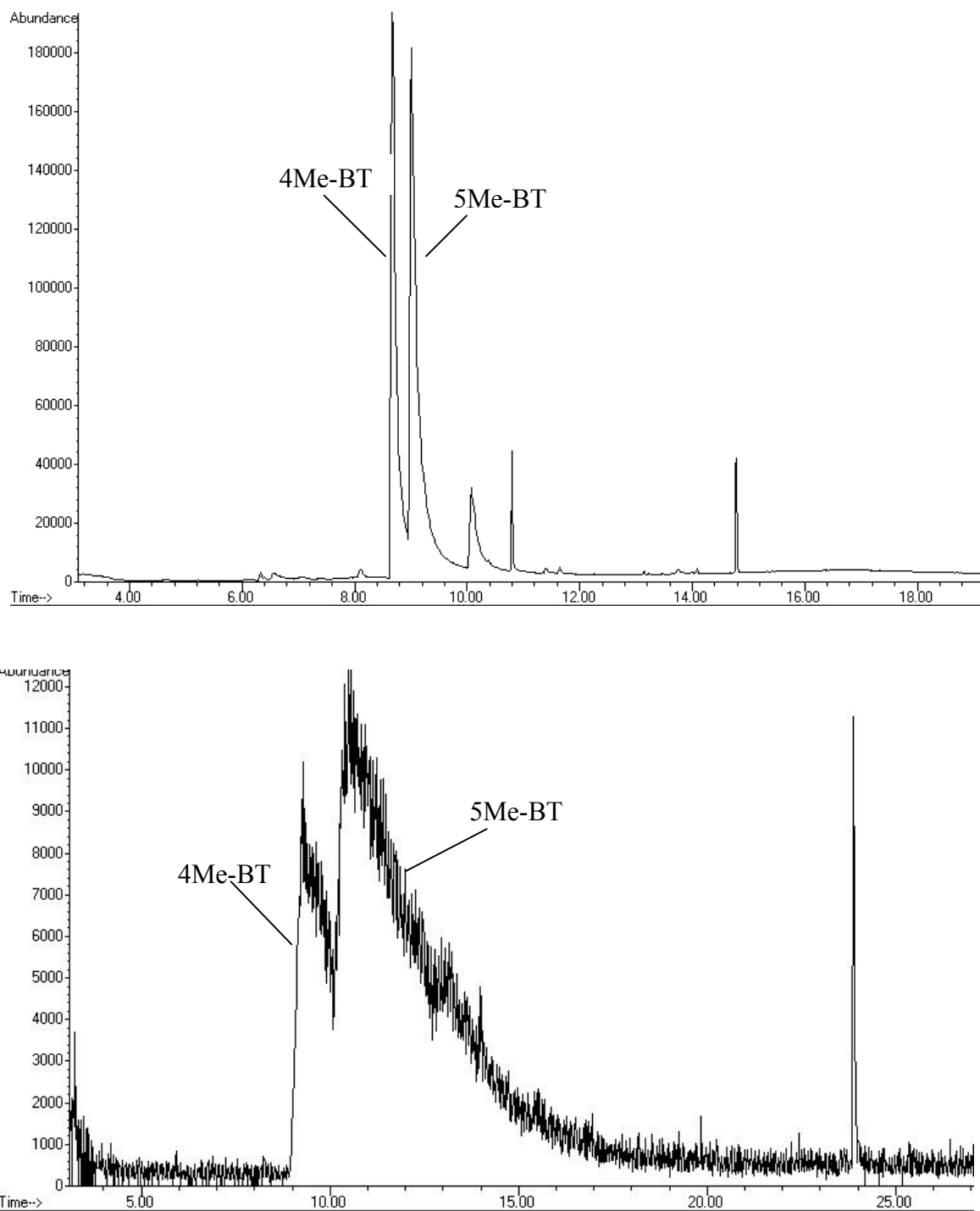


Figure 15. Mass trace m/z 104 and signals of 4Me-BT and 5Me-BT, respectively obtained from GC-MS analysis of the BTs stock solution after analysis of three wastewater extracts without (top) and with (bottom) a retention gap.

A fused silica tube column (5 m x 0.25 mm x 0.25 μm , Agilent Technologies, Santa Clara, USA) was installed as guard column in front of the DB-5ms. The fused silica tube column and DB-5ms column were connected with each other with a Union connector (Agilent Technologies, Santa Clara, USA). After analyzing three untreated wastewater extracts, the most complex sample in our analysis, with both column sets, and 1 μL of the BTs -standard stock solution was injected and analyzed. The use of guard column resulted in smaller peaks and increased peak tailing for 4Me-BT and 5Me-BT according to enhanced matrix effects. As it was expected the non-volatile residues were deposited in the guard column. Unfortunately, this strongly affected peak size and shape. One can conclude that GC-MS is appropriate to analyze BTs in wastewater samples but special attention has to be paid on keeping the system clean e.g. glass injection liner and first few meters of the column. The use of guard column is not recommended.

3.1.2.3 Column Wash

The column contamination was a big problem in GC/MS analysis. It could be non-volatile or semi-volatile. Non-volatile contaminants accumulate in the column and they do not elute, it can give interacts and adsorption problems. Semi-volatiles also accumulate but they can elute, it may take hours to days, before they leave the column. They cause baseline problems peak shape problems. Solvent rinsing is the best method to remove contaminants from the column. Solvents flush trough the column and wash out the contaminants. Column rinse kit was used for washing of column (see Fig. 16). The rinse kit was attached to a pressurized gas source (nitrogen (N_2) or helium (He), in our case N_2), and the column was inserted into the rinse kit. Solvent was added to the vial, and from the vial was pressurized using the gas source trough the column. Residues dissolved into the solvent and leaved the column with the solvent. The solvent was then purged from the column, and the column is properly conditioned. The material of contaminants is usually unknown. For this reason, there are no exact guidelines to which rinse solvents to use for a particular situation. In our case Methanol and Hexane were used.

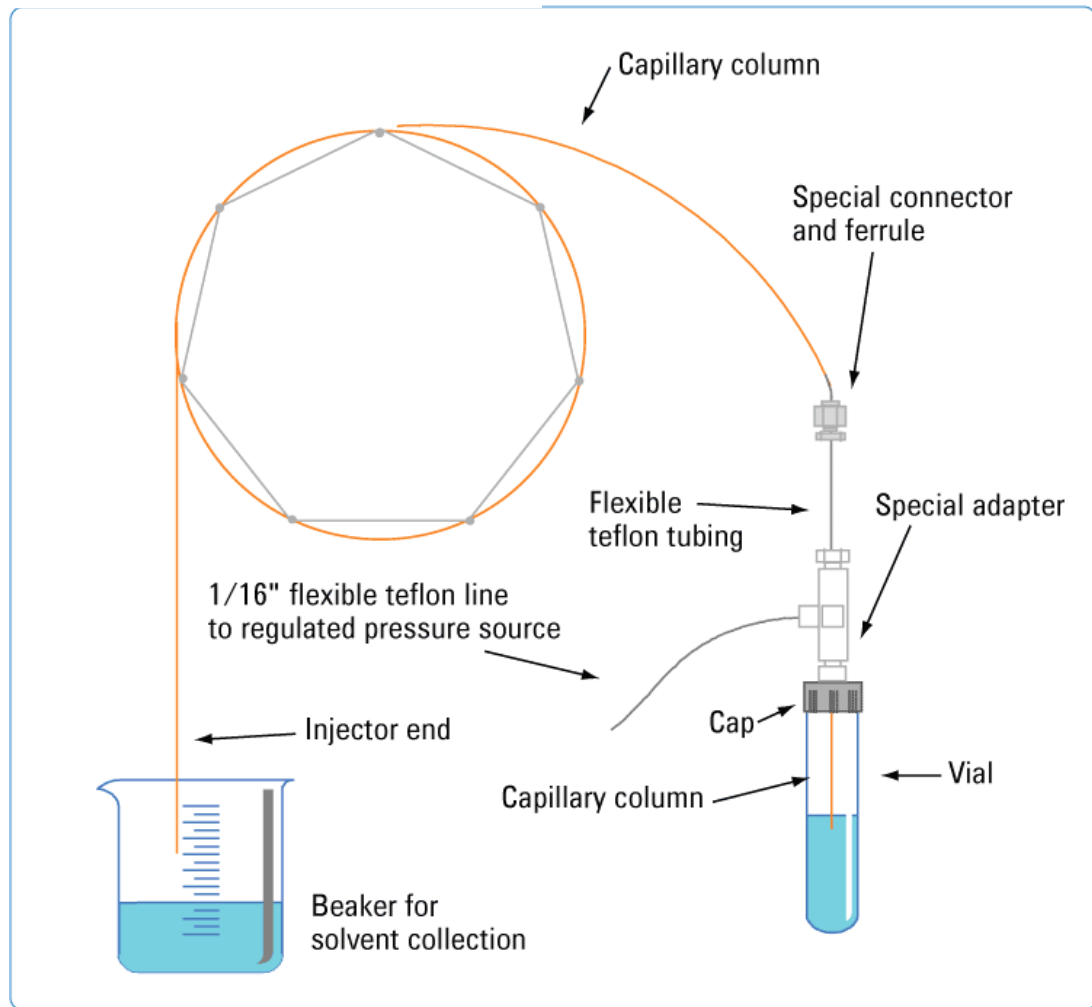


Figure 16. Typical rinsing set-up (adopted from <http://www.chem.agilent.com>).

The steps of solvent rising process are shown in the following:

1. cut 0.5-1 m from injection end of the column
2. insert the detector end of the column into the rinse kit
3. add and pressurize 4-5 ml Methanol with < 20 psi (< 1ml/min) solvent flow rate
4. add and pressurize 4-5 ml Hexane with < 20 psi (< 1ml/min) solvent flow rate
5. 1 hour just with N₂ with < 20 psi (< 1ml/min) solvent flow rate
6. build the column into the GC/MS
7. oven program: from 40 °C with 2-3 °C/min to the maximum column temperature and hold it 2 min.

3.1.3 Retention Times

The retention time of the analyzed compound loom large, with it very high confidence identification is possible. Retention time shifts are very common for any number of reasons. The small retention time shift means usually no problem. If just the retention time shifts, but the sensitivity and the response factor remain the same, the reason may be change of the column length, change of the carrier gas pressure or different oven temperature program. The retention time shift with peak and sensitivity problem are caused by contamination, change of column activity or difference of column diameter or thickness. After several environmental samples (river or waste water) retention time shift were observed (see Fig. 17).

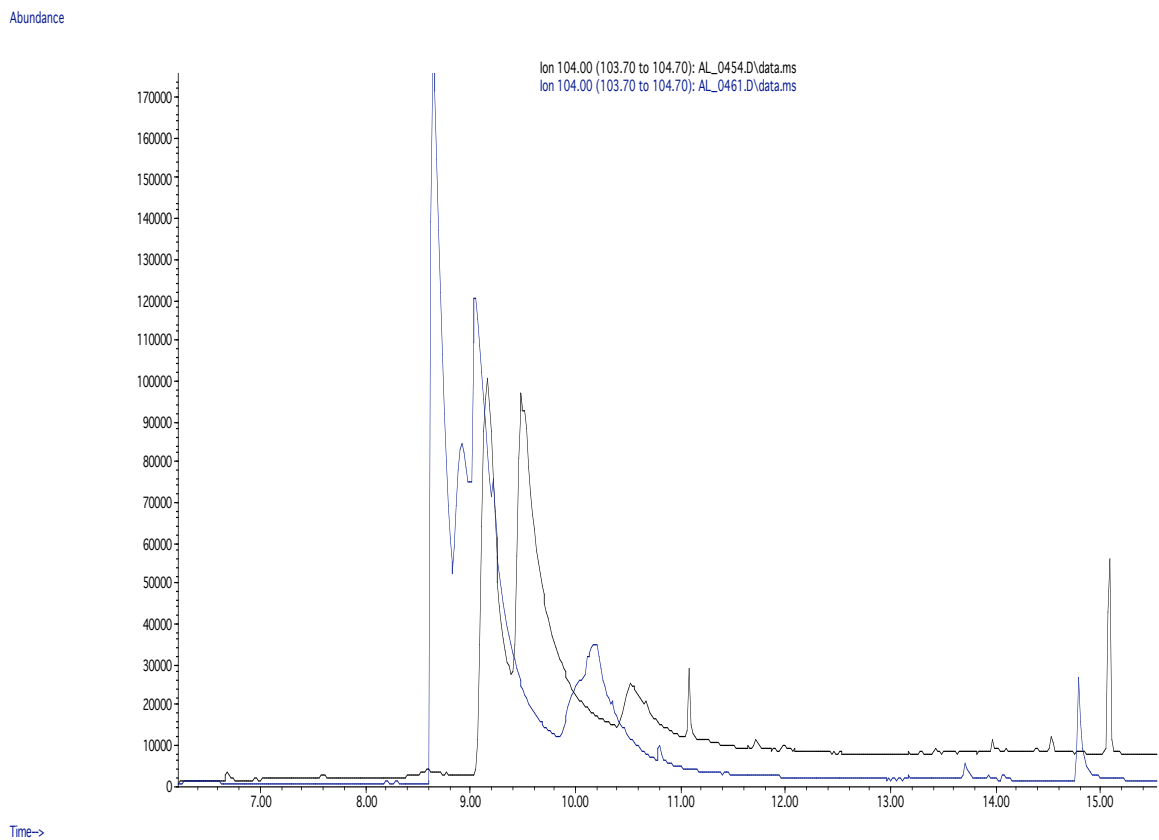


Figure 17. Retention time shift of signal m/z 104 in river water.

3.1.6 Limits of Detection (LOD) and Limit of Quantification (LOQ)

Procedural blanks of 1H-BT, 5Me-BT and 4Me-BT were studied by analyzing 2.5 L deionized water with 20 μ L of the SuS stock solution (six replicates were analyzed). The limits of detection (LOD) were calculated for river water according to DIN 32645 (2008-11). Limits of quantifications (LOQ) were set at three times the LOD. Mean recoveries, LODs and LOQs for river water, wastewater and products are shown in Table 10. The LODs were 5 ng/L for 1H-BT, 2 ng/L for 4Me-BT, 4 ng/L for 5Me-BT for river water; and 4 ng/L for 1H-BT, 1 ng/L for 4Me-BT, 2 ng/L for 5Me-BT for wastewater. The LOD and LOQ values were relative low still, much more better than by LC-MS/MS. Corsi et al (2003) used the response factor of 5Me-BT for the quantification of 4Me-BT, the LOD was for both isomers 0.08 mg/L. In our case, with different, separated analytical parameters were the LODs different. Although, both isomers are very similar, it is very important to quantify both isomers separately.

3.2 River Discharge Flow

The values of the Pearson's correlation coefficient (r) for the correlation of the distance between the bottom of a bridge and the water surface of the stream and the measured values of Q ranged between -0.41 and -0.999 (see Table A1). In Figure 18 the values of Q at P9 ($Q_{\text{this study}}$) are plotted against the mean daily values of Q monitored at gauge Nauheim (Q_{HLUG}) (<http://www.hlug.de>). A good correlation between Q_{HLUG} and $Q_{\text{this study}}$ was observed ($r=0.81$) at values of $Q_{\text{HLUG}} \leq 0.731 \text{ m}^3 \text{ s}^{-1}$. Up to this value, the methodology for determining Q in river water was validated. However, at a greater value of Q_{HLUG} of $1.18 \text{ m}^3 \text{ s}^{-1}$, the value of $Q_{\text{this study}}$ was about two times lower. This would result in an underestimation of mass flows at higher river discharges using the velocity-area mid-section method applied here. Thus, only sampling events where the value of $Q_{\text{this study}}$ was equal to or below the threshold of $0.651 \text{ m}^3/\text{s}$ (16-17/01/09, 17-20/11/09, 24-25/07/09, 07-09/07/10) were used.

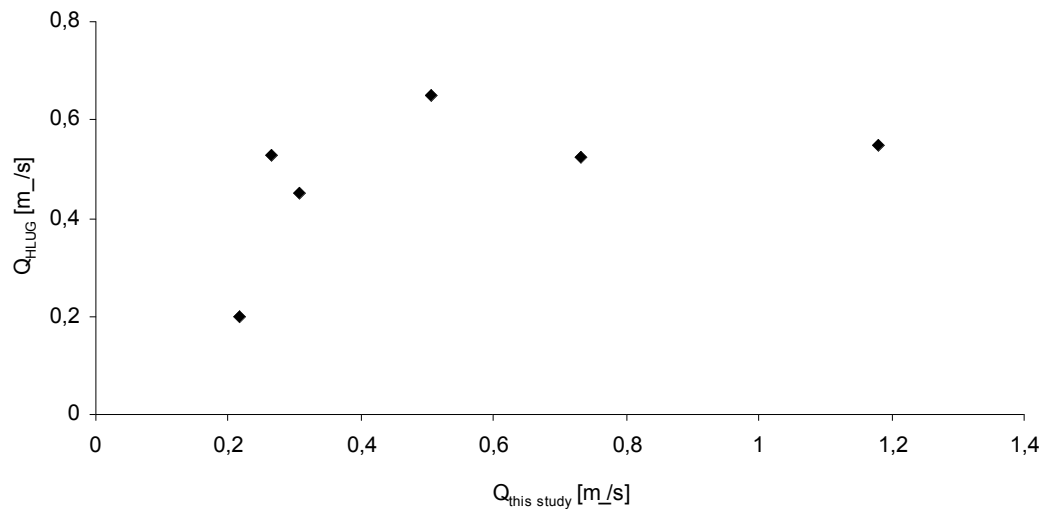


Figure 18. Temporal variations of river discharge (Q) measured at P9 in this study ($Q_{\text{this study}}$) and monitored at gauge Nauheim (Q_{HLUG}) (<http://www.hlug.de>).

3.3 Occurrence of BTs in river water

3.3.1 Concentrations of BTs

In most of the studied rivers, 1H-BT, 4Me-BT and 5Me-BT were detected with great temporal and spatial concentration variations (see Table A4, A5, A6). Mean BTs concentrations in the Stream Hengstbach/Schwarzbach (P5-P14) in winter ($n=4$) and in summer ($n=2$) downstream from the source are shown in Figure 19 (error bars reflect min/max values for different sampling times, $n \leq 6$). In winter (16-17/01/09, 09-13/02/09, 17-20/11/09, 07/02/10), mean concentrations were between 177 and 4521 ng/L (1H-BT), 270 and 4345 ng/L (4Me-BT) and 24 and 1766 ng/L (5Me-BT). In summer (24-25/07/09, 07-09/07/10), concentrations were lower at between 137 and 1183 ng L⁻¹ (1H-BT), 171 and 2538 ng L⁻¹ (4Me-BT), and 27 and 566 ng L⁻¹ (5Me-BT). According to the usage of corrosion inhibitors and their incomplete removal in WWTPs, the occurrence of BTs in river water must be directly related to the discharge of wastewater effluents into the mainstream. 4Me-BT showed the highest concentrations, followed by 1H-BT and 5Me-BT. In winter, the mean concentrations of all BTs increased continuously up to sampling point P6 and then decreased due to dilution, with the exception of sampling points P9 and P14

(according to low removal efficiencies during wastewater treatment, in-stream removal processes are estimated to be negligible). Spatial and temporal concentration variations were much higher in winter than in summer. The highest concentrations of all compounds were measured during 16-17/01/09. The results of concentrations of BTs in the tributaries of the Stream Hengstbach/Schwarzbach are shown in Table 7.

Concentrations (ng/L)	16-17/01/09			09-13/02/09			24-25/07/09			17-20/11/09			08/02/10			07-09/07/10		
	1HBT/	4Me-BT/	5Me-BT	1HBT/	4Me-BT/	5Me-BT	1HBT/	4Me-BT/	5Me-BT	1HBT/	4Me-BT/	5Me-BT	1HBT/	4Me-BT/	5Me-BT	1HBT/	4Me-BT/	5Me-BT
<i>Geraethsbach</i>																		
P8	6013	5054	694	1850	1428	262	206	240	107	1160	1123	343	1881	2441	684	900	649	127
<i>Apfelbach</i>																		
P10	<LOD	26	<LOD	123	38	10	<LOD	<LOD	<LOD	<LOD	94	6	<LOD	<LOD	<LOD	<LOD	64	11
<i>Landgraben</i>																		
P12	<LOD	<LOD	<LOD	2564	1279	183	110	418	73	884	1447	191	1231	2040	222	333	392	46
<i>Hegbach</i>																		
P15	<LOD	<LOD	<LOD	131	29	17	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Mass loads (g/day)																		
<i>Geraethsbach</i>																		
P8	161	131	19.6				3	3	1.31	18	23	5.28						
<i>Apfelbach</i>																		
P10	-	0.27	-				-	-	-	-	0.75	0.04						
<i>Landgraben</i>																		
P12	-	-	-				15.4	58.5	10.2	135	221	29.2						
<i>Hegbach</i>																		
P15	-	-	-				-	-	-	-	-	-						

Table 7. Concentrations and mass flows of 1H-BT, 4Me-BT and 5Me-BT in tributaries during different sampling times.

Again, in winter the concentrations of all three compounds were higher than in summer, especially in the Stream Geräthsbach. To assess a seasonal source influence BTs mass loads were calculated and evaluated.

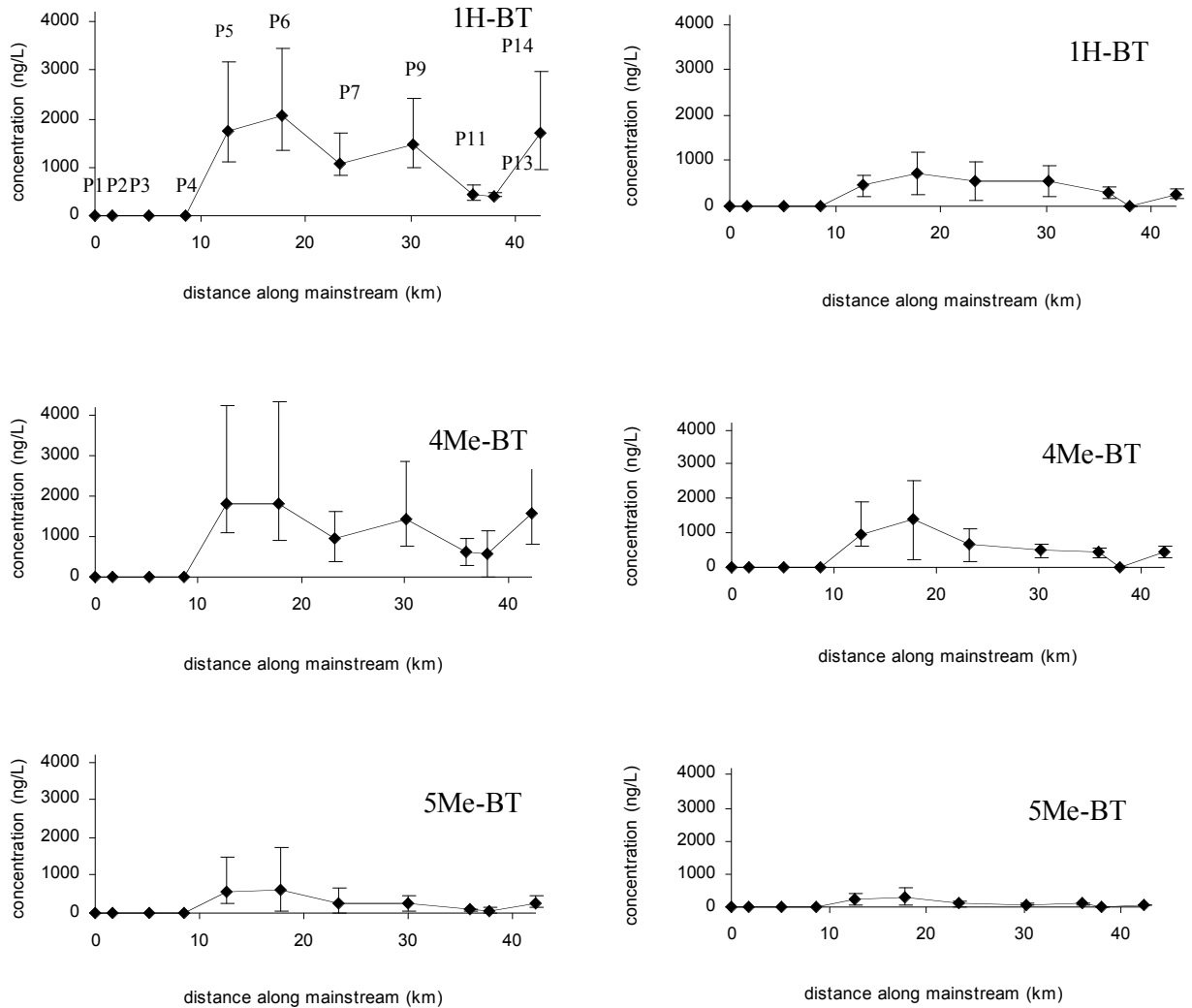


Figure 19. Mean concentrations of 1H-BT, 4Me-BT and 5Me-BT in the mainstream Hengstbach/Schwarzbach measured during winter (n=4) (left column) and summer (n=2) (right column) sampling periods (error bars reflect min./max.).

P1-P4 were located upstream of all effluent discharge points as well as outside of a possible influence of any airport surfaces (Fig. 3). At these sampling points BTs concentrations in river water were all below LOD. This indicates that no influence of surface runoff loaded with BTs from additional sources e.g. applications of antifreezes in motorcar radiators and windscreen wiper systems. In general river discharges and BTs concentrations were higher in winter than in summer. This indicates already a seasonal source influence on BTs concentrations in river water. The highest concentrations of all compounds were measured during 16-17/01/09. Since BTs were detected in the anti-icing fluid used at German airports

an influence of anti-icing operations during winter season might be possible. At P6, which was located immediately downstream the discharge point of the industrial WWTP operated by Frankfurt Airport, relative high concentrations of BTs were detected in winter. Unfortunately no information on treatment of surface runoff contaminated with anti-icing fluids during the de-icing season was available from the Airport holding Fraport AG. Thus, an influence of anti-icing operations on the BTs concentrations river water can only be assumed.

The results of BTs concentrations in the tributaries of the River Hengstbach/Schwarzbach are shown in Table 7. Again, in winter the concentrations of all three compounds were higher than in the summer especially in the Stream Geraethsbach, whereas values of Q were generally higher in winter. The Q values were 0.065 and 0.120 m³/s in summer, and ranged between 0.275-0.638 m³/s in winter. These results indicate an influence of seasonal source on the BTs concentrations in the Geraethsbach tributary as well. An influence of Frankfurt Egelsbach Airport on the concentrations of BTs in river water can only be assumed since detailed information on treatment of surface runoff was not available.

3.3.2 Mass Flows of BTs

To assess a seasonal source influence on BTs mass flows in the studied rivers and to create a database for comparing BTs pollution in different catchments, mass flows of BTs were calculated for selected sampling locations in the mainstream and its tributaries. In Figure 20, the mean mass flows of 1H-BT, 4Me-BT and 5Me-BT in the mainstream at sampling points P5, P6 and P9, respectively, in 2009 are shown. Mass flows were differentiated by the months of sampling: January, July and November. The maximum mass flows were calculated for all three substances in January 2009 when the mean monthly air temperature was lowest, at -0.4 °C (DWD). In July 2009, when the mean monthly air temperature was highest, at 17.8 °C, the mass flows of all three substances were much lower. Results of ANOVA demonstrated a significant source related to temperature influence for all BTs (empirical F-factors were: $F_{2,6} = 16.62$ for 1H-BT, $F_{2,6} = 7.76$ for 4Me-BT and $F_{2,6} = 19.26$ for 5Me-BT). One possible reason for this is the greater use of anti-icing fluids at colder weather. According to their locations, sampling points P6 and P9 could possibly be influenced by airport surface runoff. Since BTs were detected in the anti-icing fluid used at

German airports, anti-icing operations during the winter season may make an impact. At sampling point P6, located next to downstream from the discharge point of the industrial WWTP operated by Frankfurt Airport, BTs mass loads were relatively high in winter. Unfortunately, no information on the treatment of surface runoff contaminated with anti-icing fluids was available from the Airport Holding Fraport AG. Thus, the influence of anti-icing operations on the concentrations of BTs in river water can only be assumed. An influence of surface runoff from the airport was excluded for sampling point P5. Since a significant seasonal source influence on BTs mass flows in river water was observed for all three monitoring stations, the input of BTs into river water from other temperature-dependent application fields than airport anti-icing operations must be considered. In the anti-icing fluid, the concentration of 4Me-BT was highest, followed by 1H-BT and 5Me-BT. In winter, the distribution pattern of BTs in river water differed. In January 2009, the highest mass flows at P6 and P9 were observed for 1H-BT, followed by 4Me-BT and 5Me-BT. The different distribution pattern of BTs in the anti-icing fluid and in river water also suggests other seasonally dependent input sources of BTs.

The latter applications may result in BTs loads in surface runoff that ends up in municipal WWTPs through combined sewer systems. The direct influence of surface runoff on the occurrence of BTs in river water was not observed since the concentration of BTs at sampling points P1-P4, located upstream of all effluent discharge points and outside any possible influence by airport surfaces (Fig. 3), were below the LODs.

Table 11 shows the calculated BTs mass loads in the tributaries. They ranged between 18 and 161 g/day for 1H-BT, 0.27 and 221 g/day for 4Me-BT and 0.04 and 29.2 g/day in winter. Although the highest concentrations were detected in the Stream Geräthsbach, the mass flows were the highest in the Canal Landgraben, according to higher river discharge. In the Stream Geräthsbach, the mass flows of all three substances were much lower in summer compared to in winter. Here, the negative influence of air temperature on BTs mass flows might be attributed to airport operations as well. One explanation could be the abrasion of anti-icing fluids during takes offs from the South runway of Frankfurt Airport.

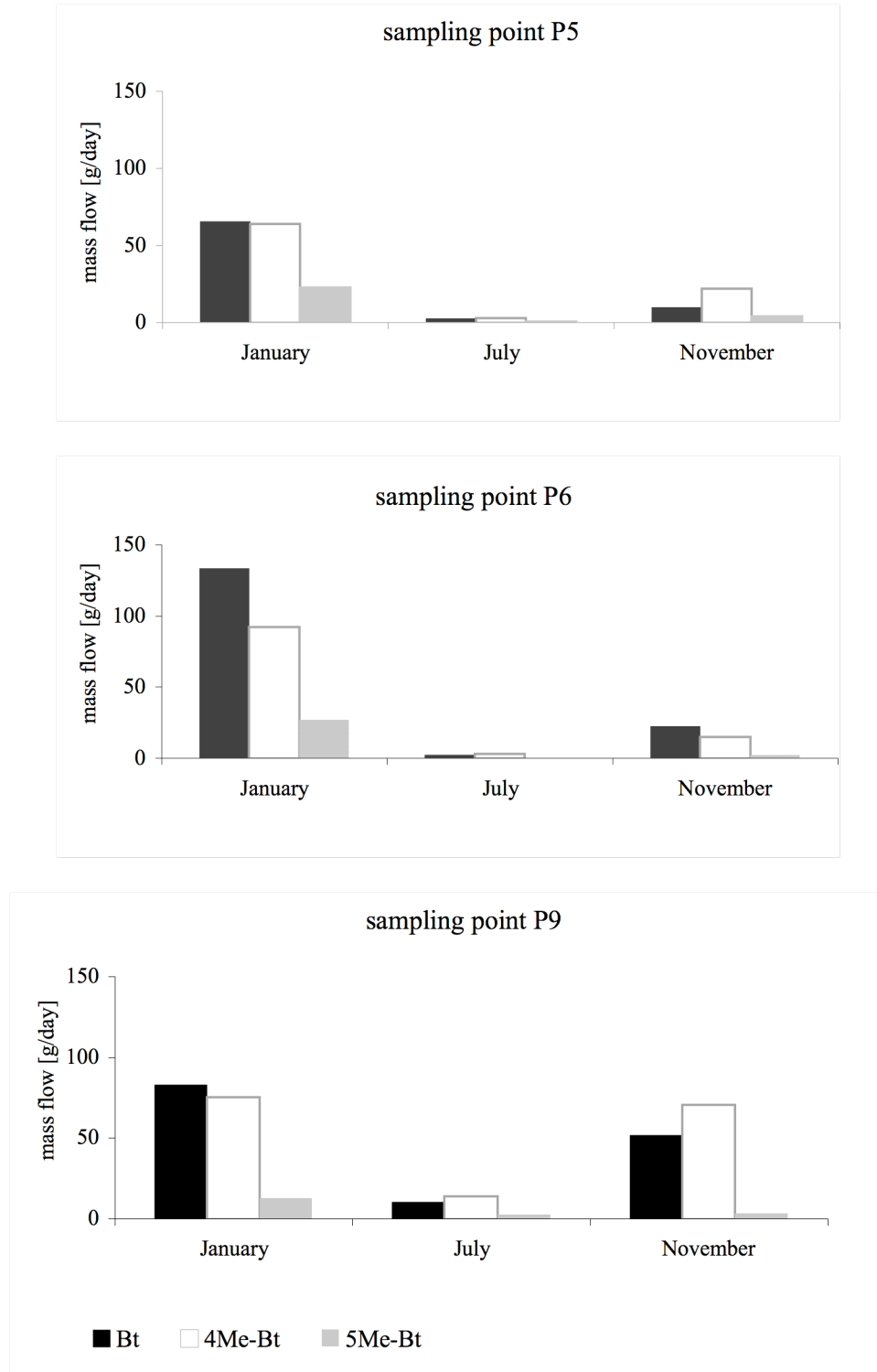


Figure 20. Mean mass flows of 1H-BT, 4Me-BT and 5Me-BT in the mainstream Hengstbach/Schwarzbach at P5, P6 and P9 in January, July and November 2009.

BTs were also detected in the Stream Hegbach in winter, although no WWTP discharges into it. In this case, the influence of Frankfurt Egelsbach Airport can only be assumed since no detailed information on treatment of surface runoff was available. On the other hand, other seasonal source influences on BTs mass flows cannot be ruled out.

3.3.3 Ratio of 1H-BT/TTs

The 1H-BT/TTs ratios of mass flows in the mainstream and its tributaries in July differed to those in January. The 1H-BT/TTs ratios ranged between 0.75 and 1.12 in January and between 0.65 and 0.83 in July. In July, the mass flows of 4Me-BT were higher than the mass flows of 1H-BT (Fig. 4). In January, 1H-BT had the highest mass flows, followed by 4Me-BT; the 5Me-BT had the lowest mass flow. Since in this study no TTs were detected in three commonly used dishwasher detergent tablets and only in dishwasher detergent tablets and powder from one brand out of six in the work of Janna et al. (2011), it turns out that the ratio of 1H-BT/TTs may be poorly suited for identifying the source of these compounds in river water. The absence of TTs from dishwasher detergents indicates additional sources for those compounds. This was also indicated by the detection of a seasonal source influence on BTs mass flows (and the usage of dishwasher detergents must be seasonally independent) at monitoring stations where an influence from anti-icing operations could be ruled out. Moreover, TTs are not indicators of anti-icing agents only because they were also present in river water in July when no ADAF were applied.

3.3.4 Validation of GREAT-ER Model

GREAT-ER is a GIS-assisted computer model for risk assessment and management of chemicals in river basins. A software system that combines a GIS (Geographic Information System) with fate models to produce a simple and clear visualization of predicted chemical concentrations and water quality along a river (GREAT-ER).

In the publication of Pollmeier (2008) a model WATER for BTs in the catchment area of Hengstbach/Schwarzbach was demonstrated. In this study the concentrations for the model were computed with GREAT-ER system usually from domestic use (treated or direct

discharge) and from industrial point sources. For concentration computation the per capita usage, number of the inhabitants, the elimination of the compound in WWTPs and the rivers were considered. The model was applied to demonstrate the behavior of BTs in the single segments of river system. Since there was no information of emission from Frankfurt Airport and industrial WWTPs, BTs -input only from household wastewater could be used for the simulation. The pro capita usages in 2006 and the eliminations of WWTP Berlin were used, like 37% for 1H-BT, 0% for 4Me-BT (instead of -6%) and 11% for 5Me-BT to this simulation. On the GREAT-ER simulation's map the concentrations of BTs were increased after every WWTPs and then, due to the dilution, decreased again. In this simulation the in-stream removal processes were disregarded.

The simulation was compared to measurements in the mainstream. For validation of the simulation the average concentrations from the summer scenario were taken. BTs concentrations determined in the summer scenario might reflect emissions due to their use as corrosion inhibitors in dishwasher detergents or in other temperature independent applications. Emissions of BTs from dishwasher detergents are constant, without any seasonal variations.

At P1-P4 (between 0 and 8 km) points BTs concentrations in river water and in simulation were all below LOD. This indicates no influence of surface runoff loaded with BTs from additional sources *e.g.* applications of antifreezes in motorcar radiators and windscreen wiper systems.

At 1H-BT the measured average concentrations in the mainstream indicate underestimated simulated concentrations, being almost 5 times higher in reality (see Fig. 21a and 21b). The reason could be the different per capita usage of dishwasher detergents (1H-BT was detected in two tab solutions used in Germany) or the higher elimination in WWTP and other BTs sources. The WWTP-Ruhleben (Berlin) receives mainly household wastewater with an industrial input of about 30% (Weiss, 2006). Dishwasher detergents might not have been the only source of BTs.

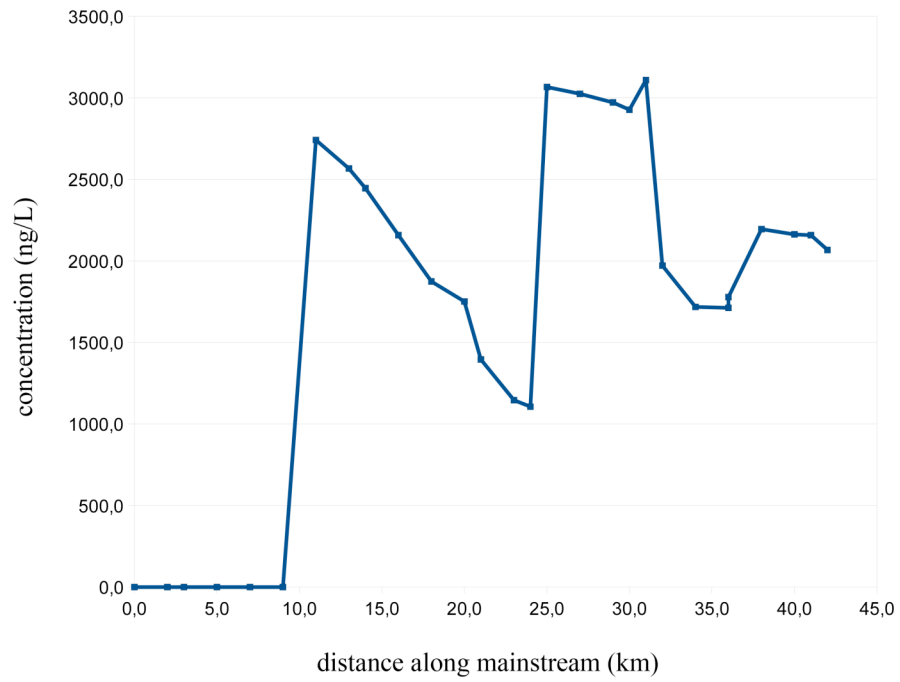


Figure 21a. Concentration profile of 1H-BT in the mainstream, simulation (Pollmeier, 2008).

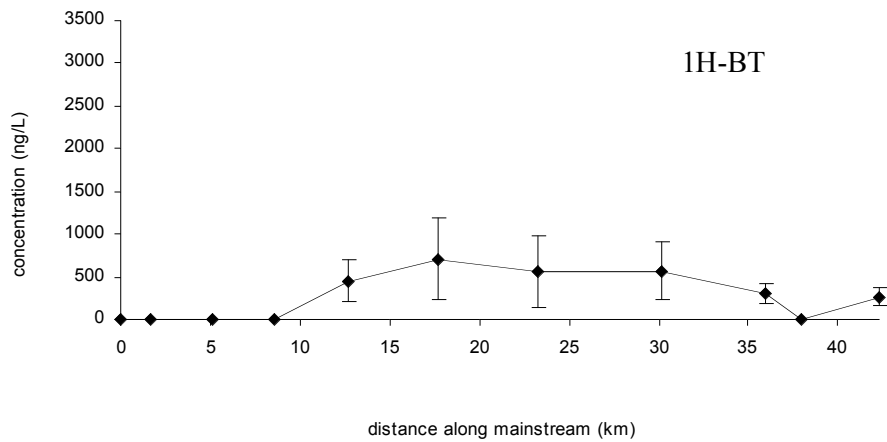


Figure 21b. Average concentrations of 1H-BT in the mainstream measured during summer (n=2) (error bars reflect min./max. values for different sampling times, n≤6).

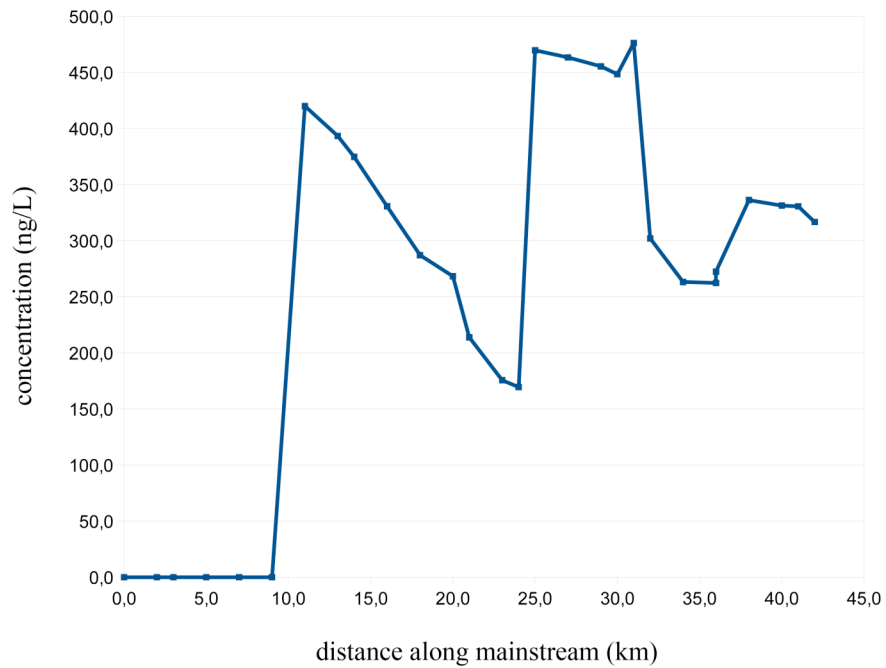


Figure 22a. Concentration profile of 4Me-BT in the mainstream, simulation (Pollmeier, 2008).

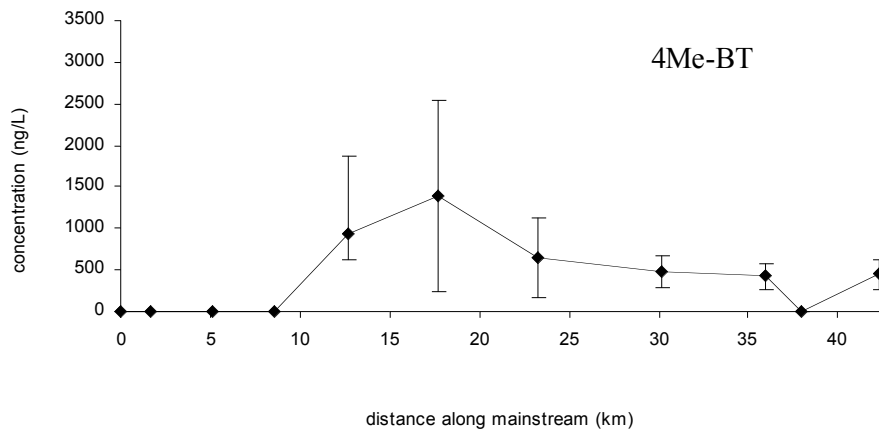


Figure 22b. Average concentrations of 4Me-BT in the mainstream measured during summer (n=2) (error bars reflect min./max. values for different sampling times, n≤6).

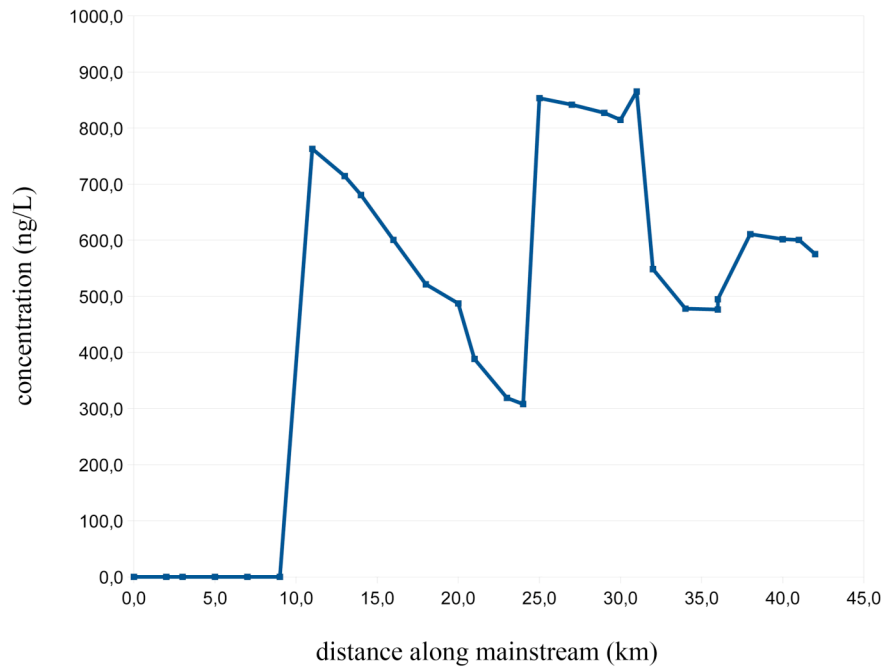


Figure 23a. Concentration profile of 5Me-BT in the mainstream, simulation (Pollmeier, 2008).

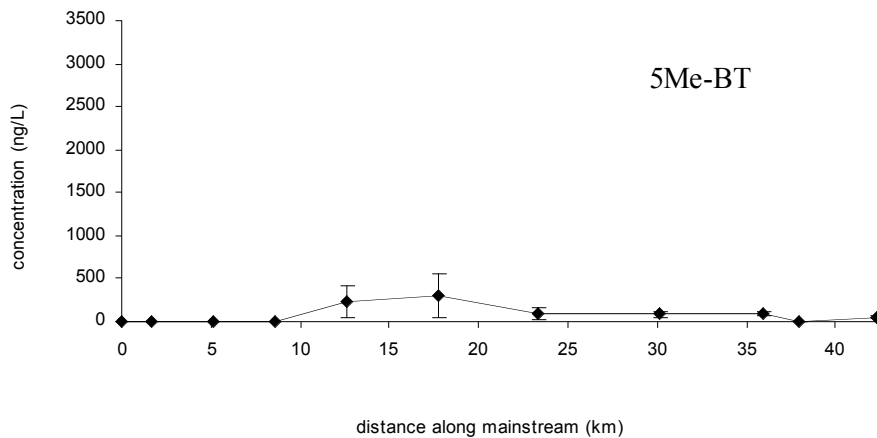


Figure 23b. Average concentrations of 5Me-BT in the mainstream measured during summer .

At 4Me-BT the measured average concentrations in mainstream also indicate underestimated simulated concentrations. The measured concentrations were 2 times higher than the simulated values. The best correspondence between the simulated model and measurement in Schwarzbach/Hengstbach River was found at 5Me-BT. In the longitudinal

profiles of the distribution of the compounds 4Me-BT showed the highest concentrations, followed by 1H-BT and 5Me-BT. In our study TTs were never detected above LOD in dishwasher detergent tablets used in Germany. In contrast by Weiss et al. (2006) and by Janna et al. (2011) the presence of either 1H-BT or TTs in all dishwasher detergent products was confirmed in tablets as well as powders. It could be possible that the concentrations of 4Me-BT might originate from the household wastewater containing dishwasher detergents or industrial wastewater.

In the simulated model, a strong increase was demonstrated in mainstream after the 25th km (P7). P6 and P7 were located downstream of the discharge point of the industrial WWTP operated by Frankfurt Airport. At measured concentrations for all BTs a slight decrease of constant values was observed after the 15th km (P5). P5 was located downstream from one municipal WWTP and the detection of BTs in river water may indicate an input of BTs from the household wastewater containing dishwasher detergents or other temperature independent application fields.

The simulation of BTs exposition and outcome with GREAT-ER WATER was not perfect and realistic, but it was a good base to determine the exposition sources of BTs in the research area.

3.4 Occurrence of BTs in Wastewater

3.4.1 24-h Flow Proportional Composite Samples

According to matrix effects it was impossible to determine the exact concentrations of 4Me-BT and 5Me-BT in untreated wastewater. However, a relative comparison of concentrations and resulting mass flows was conducted. BTs were detected in all 24-hours composite samples with relatively high concentration variations dependent on the month of sampling. Figure 24 a, b, c shows the daily mass flows in influents of WWTP-S, WWTP-N and WWTP-G. Mass flows were calculated relatively to the highest mass flow, which was set to 100%.

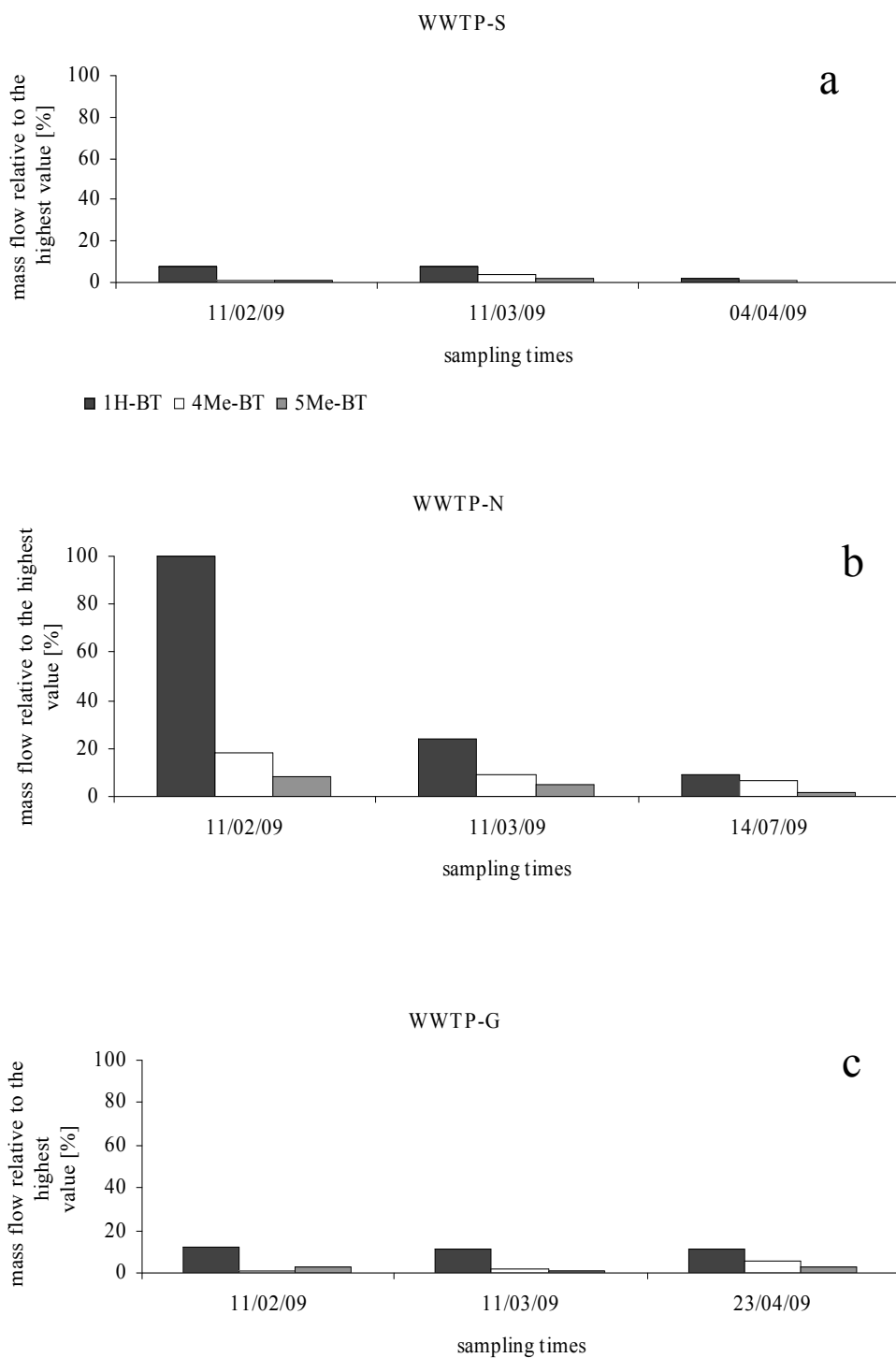


Figure 24. Comparison of daily mass flows in 24-hours composite samples of untreated wastewater collected at WWTP-S (a), WWTP-N (b) and WWTP-G (c).

The maximum concentrations and mass flows of BTs were determined at WWTP-N in February. In July, when the mean daily air temperature was the highest, the concentrations and mass flows of all three substances at WWTP-N were much lower. This might be an indication for an influence of temperature dependent applications of products containing BTs. The Airport Frankfurt directed a part of its wastewater into WWTP-N (Institute Fresenius 2004). This wastewater consisted of domestic sewage, fire extinguisher wastewater; aircraft wash water in winter periods and wastewater from runway cleaning (Institute Fresenius 2004). BTs were identified in AAF (Type IV) used also at Frankfurt Airport (Kiss and Fries 2012).

Previous studies have already reported that airports are point sources of BTs emissions (Cancilla et al. 1997; Cancilla et al. 2003; Weiss et al. 2006). The fact that no significant increase of BTs mass flows in February was observed at WWTP-S, even though it receives airport wastewater (Institute Fresenius 2004), therefore it can not be claimed with certainty, that anti-icing operations at the airport enhanced BTs mass flows in wastewater influents at WWTP-N. Since BTs mass flows showed also slightly temporal variation at WWTP-G, where no wastewater from any airport was discharged, contributions from other seasonal dependent sources e.g. windshield wiper systems of vehicles must be also considered. Due to moderate daily mean temperatures in April and July the discharge of BTs from temperature dependent sources can be excluded at these times. The BTs detected those times in untreated wastewater must be originated from dishwasher detergents or other additional but unknown temperature independent sources.

BTs were also detected in all effluent wastewater samples. This result demonstrates that BTs is only partially removed during conventional wastewater treatment. The concentration in all three WWTPs ranged between 0.3 and 9.5 $\mu\text{g/L}$ for 1H-BT, 3.2 and 10.1 $\mu\text{g/L}$ for 4Me-BT and 0.1 and 3.6 $\mu\text{g/L}$ for 5Me-BT. The effluent mass flows were calculated for 24-hours composites by the individual effluent concentration times the mean daily effluent discharge. The mass flows ranged between 0.01 and 1.2 kg/day for 5Me-BT. According to matrix effects it was impossible to determine the exact concentrations of BTs in untreated wastewater and therefore the removal efficiencies, which could be calculated by the difference between the mean influent and effluent mass flows.

3.4.2 2-h composite samples

On 23/04/09, every 2 hours influent composite samples were taken at WWTP-G. The concentrations of BTs in wastewater influents showed great daily fluctuations.

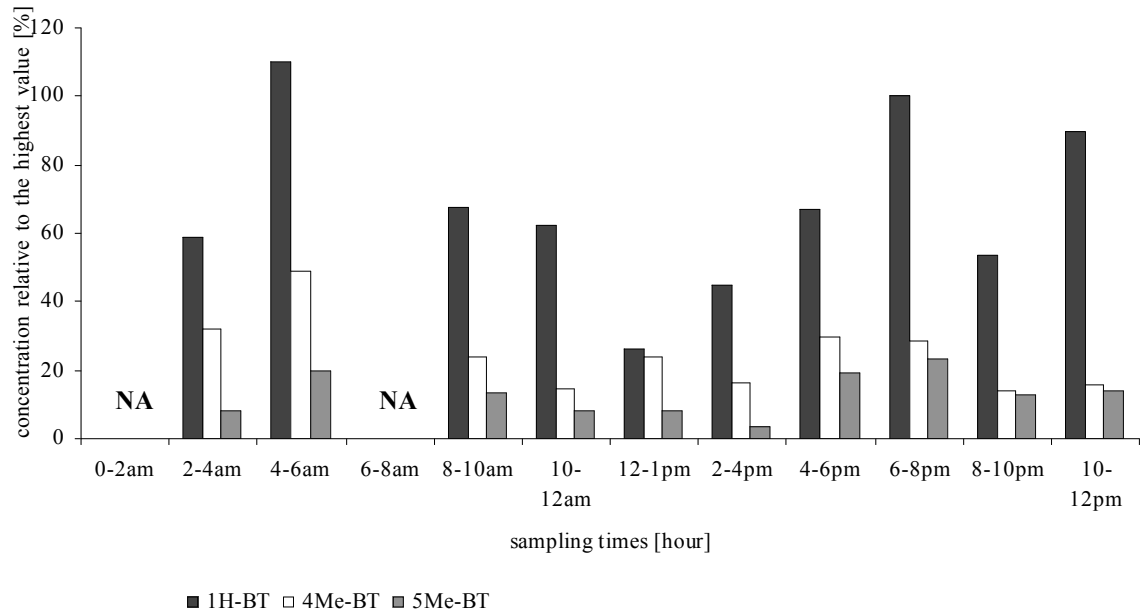


Figure 25. Daily variations of 1H-BT, 4Me-BT and 5Me-BT concentrations in 2-hour composite samples of untreated wastewater collected at WWTP-G on 23/04/09.

In Figure 25 the concentration of BTs are shown. The daily variations in influents could be directly associated with the household activities occurring and dishwasher detergent products used during the sampling day. Variable concentrations in wastewater influents may result in variable exposure concentrations in river water when treated wastewater is discharged into receiving waters. Considering toxic effect on aquatic organism organisms (Pillard 1995; Cancilla et al. 1997; Novak et al. 2000; Cancilla et al. 2003b; Corsi et al. 2006, Seeland et al. 2011), one can conclude that daily fluctuations of BTs should be considered in risk assessments.

On account of daily fluctuations of flow velocity and discharge flow of wastewater in sewer systems the calculation of individual mass flows is required to represent the diurnal mass flows of BTs in the influent. At this WWTP-G the flow course of wastewater varies from 1 km to over 10 km. Due to the large catchments area wastewater can take its way from the households to the WWTP during dry weather conditions from a few min to 4 h (with flow

velocity 0.8 – 1 m/s). The daily variations of BTs mass flows in this wastewater influent are not only related to flow variations, but also to the composition of the incoming wastewater. Moreover it also depends strongly on the hydraulic situation including influence on precipitation. In general the mass flows did not follow the concentration fluctuations. Mass flows of 1H-BT and 5Me-BT were clearly higher after 4 pm. Daily fluctuation of mass flows is showed in Figure 26.

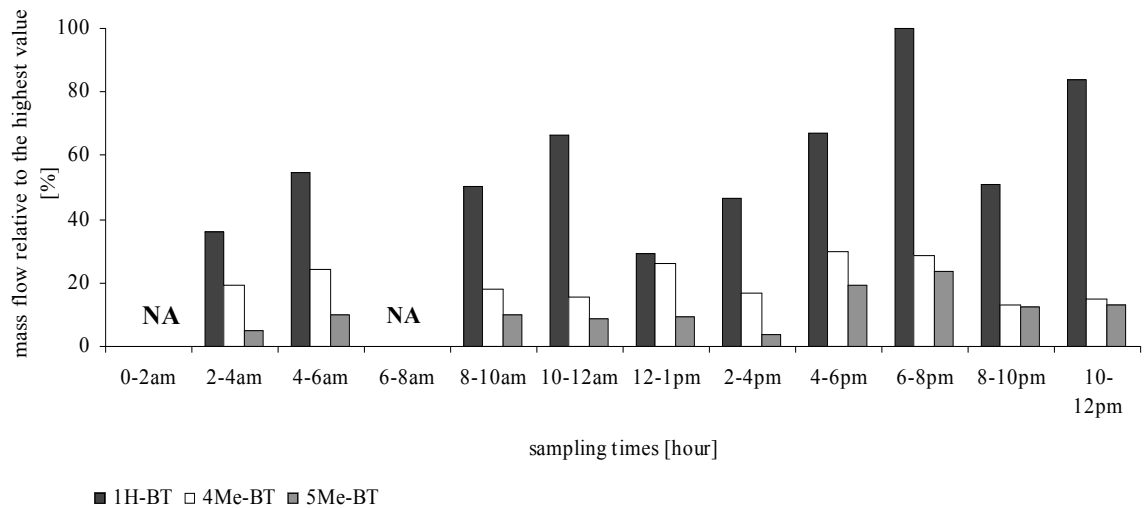


Figure 26. Daily variations of 1H-BT, 4Me-BT and 5Me-BT mass flows in 2-hour composite samples of untreated wastewater collected at WWTP-G on 23/04/09.

Again, mass flows were calculated relatively to the highest mass flow, which was set to 100%. The highest mass flows were calculated for all BTs between 6 and 8 pm. 1H-BT had a second outstanding/maximum value between 10 and 12 pm. The maximum of mass flow may reflect dinnertime or the influence of other sources such as the gastronomy trade. Our results give an overview of the daily periodic emissions of BTs from dishwasher detergents through the human daily routine. In the study of Ort et al. (2005) 1H-BT also showed a daily fluctuation. Here the maximum values were after lunch (12 pm) and before people go to bed mainly after 8 pm. As a conclusion our results demonstrated that in exposure modeling of BTs in river catchments daily fluctuations of BTs in wastewater have to be necessarily considered in different scenarios.

3.5 Occurrence of BTs in products

BTs were identified in Type IV (anti-icing fluid), but were not found above LOD in either Type I (de-icing fluid) or in the SDF. Concentrations of BTs in Type IV were 0.715 $\mu\text{g/g}$ (0.764 mg/L) for 1H-BT, 1.425 $\mu\text{g/g}$ (1.522 mg/L) for 4Me-BT and 0.536 $\mu\text{g/g}$ (0.573 mg/L) for 5Me-BT. In the report of the Airport Cooperative Research Program (ACRP), the maximum concentrations of BTs in Type IV were between 281.3 mg/L (1H-BT), 427.9 mg/L (4Me-BT), and 731.7 mg/L (5Me-BT). In Type I, no BTs were detected, whereas pavement deicers contained only TTs (Seeland et al., 2011). At Zurich Airport, the measured 1H-BT concentration in ADAF was up to 240 $\mu\text{g/g}$ (Giger et al., 2006). Corsi et al. (2006) measured 4Me-BT and 5Me-BT in several ADAF used at the General Mitchell International Airport in Milwaukee, USA. In Type I, concentrations were between 196 and 230 $\mu\text{g/g}$ (4Me-BT) and 280 and 290 $\mu\text{g/g}$ (5Me-BT). In Type IV, the maximum concentrations of BTs were 782 $\mu\text{g/g}$ (4Me-BT) and 1130 $\mu\text{g/g}$ (5Me-BT) (Corsi et al., 2006). Our results demonstrate that no BTs were detected in the de-icing fluid used at German airports, whereas the anti-icing fluid contained 1H-BT and both TTs. The distribution patterns and amounts of BTs in ADAF used in different countries vary greatly. The concentrations of BTs were much lower in the anti-icing fluid analysed in this study than those used in the USA (Corsi et al., 2006). The ratio of 4Me-BT/5Me-BT observed in the anti-icing fluid analysed in this study contradicts the results observed in anti-icing formulations by Corsi et al. (2006), which contained more 5Me-BT than 4Me-BT.

Since the matrix of dissolved dishwasher detergent tablets was very different to that of ultrapure water, a qualitative analysis was performed. 1H-BT was detected in two tablet solutions; TTs were never detected above the LODs. In contrast, in Janna et al. (2011) the presence of either 1H-BT or TTs in all dishwasher detergent products was confirmed in tablets and powder commonly used in the UK. One can assume that the distribution patterns and quantities of BTs contained in dishwasher detergents vary greatly, too.

3.6 The persistence and eco-toxicological risk potential of BTs in the aquatic environment

The effects of BTs on aquatic organisms have been evaluated in previous studies (Pillard 1995; Cancilla et al. 1997; Novak et al. 2000; Cancilla et al. 2003b; Corsi et al. 2006, Seeland et al. 2011). In acute tests, the effective concentrations (EC_{50}) for *Vibrio fischeri* were 4.25 mg/L for 5Me-BT and 6.08 mg/L for 4,5-Me-BT (Corsi et al., 2006). 4,5Me-BT showed chronic toxic effects with a lowest inhibitory concentration (IC_{25}) of 5.7 mg/L for *Ceriodaphnia dubia* (Corsi et al., 2006).

The highest measured concentrations in effluent samples, which discharge into stream Hengstbach/Schwarzbach, were 1000 times lower than the effect concentrations. BTs are only partially removed during conventional wastewater treatment. According to their applications pharmaceuticals, household chemicals and detergents like BTs can exhibit seasonal, weekly and daily short-term fluctuations, which can provide some important information on their ecotoxicity and environmental risks (Ort et al., 2005; Ort and Gujer, 2008; Ort et al., 2009). Variable concentrations in wastewater influents may result in variable exposure concentrations in river water when treated wastewater is discharged into receiving waters. The concentrations of BTs in wastewater influents showed great daily fluctuations. These results give an overview of the daily periodic emissions of BTs from dishwasher detergents through the human daily routine. As a conclusion our results demonstrated that in exposure modeling of BTs in river catchments daily fluctuations of BTs in wastewater have to be necessarily considered in different scenarios.

Compared with the highest measured concentrations in the investigated streams, the concentrations were about 1000 times lower than the reported effect concentrations. However, the results indicate that a seasonal influence on concentrations of BTs must be considered in risk assessments. It must also be taken into account that mixtures of numerous organic contaminants usually occur in river water. Since the effects of such mixtures are still unknown, the release of frequently used organic additives, such as BTs, into natural waters may pose potential risks to ecosystems. More experiments are necessary to characterize the potential risk from these highly persistent chemicals for the aquatic environment. Above all, it is still unknown whether BTs pass or accumulate in food chains.

5. Conclusions and Outlook

The *first aim* was the development of an analytical method for the detection of BTs in environmental samples like river water and wastewater, as well as in products.

An analytical method based on SPE and GC-MS has been developed and optimized for the determination of the presence of the corrosion inhibitors 1H-BT, 4Me-BT and 5Me-BT in environmental samples. According to their different behaviors in environment, both TTs isomers have to be quantified separately. The separation of the two TTs isomers was possible with this analytical method. The LOD values for all three compounds were in the lower ng/L range demonstrating high sensitivity similar to LC-MS/MS. The application of GC-MS instead of LC-MS/MS enables the routine analysis of BTs.

The *second aim* was the evaluation of contribution of BT-input originating from ADAF and dishwasher detergents due to WWTP discharges and other sources; and the determination of content of BTs in ADAFs and dishwasher detergents.

The studied WWTPs receive wastewater from the City of Frankfurt am Main, from several smaller cities in the surrounding area and from Frankfurt Airport. One of these treatments, WWTP-Griesheim (WWTP-G) does not receive wastewater from the airport. At WWTP-Niederrad (WWTP-N) the mass flows of 4Me-BT, 5Me-BT and especially of 1H-BT in 12 x 2h time proportional composite samples was strongly influenced by the month of sampling. Highest mass flows were apparent in February, when the lowest mean daily air temperature was observed. Lower mass flows determined in wastewater influents collected in July at WWTP-N reflected emissions of corrosion inhibitors from temperature independent applications. Mass flows in 2-hours influent composite samples collected at WWTP-G in April were significantly higher between 6 and 8 pm, especially in the case of 1H-BT. They reflected the daily periodic emissions from dishwasher detergent products through the human daily routine, which have to be considered in risk assessments.

This study demonstrated the occurrence of 1H-BT, 4Me-BT and 5Me-BT in an anti-icing fluid used at German Airports for the first time. However, BTs were not detected in the de-icing fluid. Our studies revealed that the distribution patterns of BTs ADAF for the German/European market were different from those that were used at airports in the United States. The identification of 1H-BT in commonly used detergent tabs in Germany was also shown in this study for the first time.

The *third aim* was the determination of spatial and temporal variability of concentrations and mass flows for BTs in river water in the Hengstbach/Schwarzbach River and its tributaries. BTs were measured in all river water samples with concentrations up to 6013 ng/L for 1H-BT, to 5054 ng/L for 4Me-BT and to 1766 ng/L for 5Me-BT. BTs concentrations in river water showed great temporal and spatial variations that were higher in winter than in summer. The results from 15 monitoring stations in five rivers indicated a significant seasonal source influence on BTs mass flows in river water.

The *fourth aim* was the assessment of persistence and eco-toxicological risk potential of BTs in the aquatic environment.

Compared with the highest measured concentrations in the investigated streams, the concentrations were about 1000 times lower than the reported effect concentrations. However, the results of the present study indicate that a seasonal influence on concentrations of BTs must be considered in risk assessments. It must also be taken into account that mixtures of numerous organic contaminants usually occur in river water.

More wastewater samples are still needed for the evaluation of the contribution of BT-input originating from ADAF and dishwasher detergents due to WWTP discharges. According to matrix effects using SPE and GC-MS it was not possible to determine exact BTs concentrations in untreated wastewater. Therefore, the development of a more specific analytical method is necessary for the detection of BTs in untreated wastewater, and to eliminate the ME problem.

On account of the high polarity and the low biodegradability of BTs, they could not be reserved or degraded in soil and sediment, because they are too mobile in leading groundwater. Hence, BTs have a high entry potential into drinking water. It will be necessary to evaluate a batch test to investigate the elution behavior of BTs according to DIN 19527 Norm.

The potential for input of BTs into the groundwater is uncertain; as such it will be necessary to take groundwater samples in the catchments area of Hengstbach/Schwarzbach River.

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Appendix

Table A1. The values of the Pearson's correlation coefficient (r) for the correlation of the distance between the bottom of a bridge and the water surface of the river/stream and the measured values of Q ; R^2 -values of logarithmic regression line of the distance between the bottom of a bridge and the water surface of the river/stream and the measured values of Q at different sampling times.

	r	R^2	Date	Q_{lin}	Q_{log}	Q_{lin}/Q_{log}
P5	-0,99685	0,9921	01/2009	0,174508	0,174168	1,001955
			02/2009	0,192368	0,192138	1,001198
			04/2009	0,103068	0,104865	0,982864
			07/2009	0,14236	0,142485	0,999125
			02/2010	0,3031	0,310003	0,977731
			01/2009	0,603808	0,620505	0,973091
P6	-0,96926	0,9447	02/2009	0,104448	0,105504	0,989993
			04/2009	0,20432	0,201657	1,013208
			07/2009	0,241772	0,238526	1,01361
			02/2010	0,64126	0,662952	0,967279
			01/2009	0,073495	0,073462	1,000453
			02/2009	0,83672	0,870564	0,961124
P7	-0,90822	0,8222	04/2009	1,599945	1,763922	0,907038
			07/2009	-0,78132	-0,72796	1,073301
			02/2010	0,53143	0,541358	0,98166
			01/2009	0,31043	0,305871	1,014906
			02/2009	0,571075	0,569368	1,002999
			04/2009	0,381515	0,376546	1,013195
P8	-0,99931	0,9976	07/2009	0,12087	0,121535	0,994529
			02/2010	0,4526	0,4481	1,010042
			01/2009	0,452684	0,441993	1,024187
			02/2009	0,522732	0,503823	1,03753
			04/2009	0,6087	0,585658	1,039344
			07/2009	0,5291	0,509649	1,038165
P9	-0,86038	0,6853	02/2010	0,548204	0,527344	1,039556
			01/2009	0,11843	0,118415	1,00013
			02/2009	0,096365	0,097312	0,990273
			04/2009	0,180212	0,179498	1,003979
			07/2009	0,228755	0,229706	0,995859
			02/2010	0,47147	0,516878	0,912149
P11	-0,57545	0,3135	01/2009	1,070667	1,073266	0,997578

			02/2009	1,241315	1,235069	1,005057
			04/2009	1,13466	1,133309	1,001192
			07/2009	2,158548	2,211851	0,975901
			02/2010	2,073224	2,11219	0,981552
P12	-0,67746	0,4512				
			01/2009	1,117035	1,128427	0,989905
			02/2009	1,19847	1,203698	0,995657
			04/2009	1,784802	1,775954	1,004982
			07/2009	1,621932	1,611356	1,006563
			02/2010	0,87273	0,908201	0,960943
P13	-0,97198	0,9455				
			01/2009	1,05623	1,062004	0,994563
			02/2009	1,34581	1,370019	0,982329
			04/2009	0,62186	0,621119	1,001193
			07/2009	0,737692	0,736335	1,001843
			02/2010	1,432684	1,464783	0,978086

Table A2. Response factors with IS.

	R_{IS/SuS}	R_{IS/IH-BT}	R_{IS/4Mc-BT}	R_{IS/5Mc-BT}
10	13.53093826	7.229232165	7.888943821	3.180397155
10	12.62743265	7.451149769	7.364614398	3.644378533
10	12.99126707	7.619277671	8.294835791	3.298011286
20	9.922940651	4.041083056	2.537721785	2.006570798
20	9.157617137	4.033425165	2.557660069	1.4764031
20	7.202938637	3.998100808	2.554885714	1.511301342
30	1.676748213	1.98084166	1.358718484	0.707484794
30	1.486894049	2.303718919	1.221287682	0.770722614
30	1.630256247	1.913411042	1.295900597	0.732049818
40	0.785297273	1.065444595	0.789777085	0.455470968
40	0.819136922	1.072338129	0.774681741	0.451780975
40	0.830271394	1.069645636	0.762248735	0.453660958
50	0.683117477	0.936216975	0.680866727	0.395593471
50	0.874480446	1.019953244	0.76919997	0.475415359
50	0.757792844	1.098153228	0.647172843	0.401843912
100	0.291499206	0.401673086	0.300037129	0.164180891
100	0.294480302	0.4004257	0.303697643	0.162535083
100	0.315303716	0.362855452	0.309609811	0.171757428

Table A3. Mass of compounds in stock solution of response factor.

	g/25 mL MeOH
IS	0.0105
SuS	0.0105
1H-BT	0.0097
TTs	0.0169
4Me-BT	0.0113
5Me-BT	0.0075

Table A4. Concentrations of river water samples 2008.

Concentration (ng/L)	1H-BT	4Me-BT	5Me-BT
29/11/08 P1	0	0	0
29/11/08 P2	0	0	0
29/11/08 P3	0	0	0
29/11/08 P4	0	0	0
29/11/08 P5	481	1201	268
29/11/08 P6	1027	1317	173
29/11/08 P7	297	679	97
29/11/08 P8	1316	2359	354
29/11/08 P9	692	1408	156
29/11/08 P10	0	0	0
29/11/08 P11	667	1679	167
29/11/08 P12	89	2791	255
29/11/08 P13	1034	2130	328
29/11/08 P14	877	2300	265

Table A5. Concentrations of river water samples 2009.

Concentration (ng/L)	1H-BT	4Me-BT	5Me-BT
16-17/01/09 P2	<LOD	<LOD	<LOD
16-17/01/09 P3	<LOD	<LOD	<LOD
16-17/01/09 P5	2226	3541	1496
16-17/01/09 P6	2316	3630	1766
16-17/01/09 P7	1098	1343	643
16-17/01/09 P8	3080	4222	694
16-17/01/09 P9	1608	2373	484
16-17/01/09 P10	<LOD	22	<LOD
16-17/01/09 P14	2087	2531	469
09-13/02/09 P1	<LOD	<LOD	<LOD
09-13/02/09 P2	<LOD	<LOD	<LOD
09-13/02/09 P3	<LOD	<LOD	<LOD
09-13/02/09 P4	<LOD	<LOD	<LOD
09-13/02/09 P5	571	530	310
09-13/02/09 P6	736	790	418
09-13/02/09 P7	297	301	96
09-13/02/09 P8	948	1193	262
09-13/02/09 P9	624	728	246
09-13/02/09 P10	63	32	10
09-13/02/09 P11	374	226	38
09-13/02/09 P12	1314	1069	183
09-13/02/09 P14	981	944	190
09-13/02/09 P15	67	24	17
24-25/07/09 P4	<LOD	<LOD	<LOD
24-25/07/09 P5	109	177	45
24-25/07/09 P6	120	208	46
24-25/07/09 P7	70	143	27
24-25/07/09 P8	105	201	107
24-25/07/09 P9	119	250	57
24-25/07/09 P10	<LOD	<LOD	<LOD
24-25/07/09 P11	97	229	66
24-25/07/09 P12	56	349	73
24-25/07/09 P14	79	227	36
24-25/07/09 P15	<LOD	<LOD	<LOD
17-20/11/09 P5	331	1186	245
17-20/11/09 P6	752	809	44
17-20/11/09 P7	390	880	24
17-20/11/09 P8	594	1273	343
17-20/11/09 P9	473	1046	55
17-20/11/09 P10	<LOD	79	6
17-20/11/09 P11	91	814	124
17-20/11/09 P12	453	1209	191
17-20/11/09 P13	384	990	148
17-20/11/09 P14	129	1175	206
17-20/11/09 P15	<LOD	<LOD	<LOD

Table A6. Concentrations of river water samples 2010.

Concentration (ng/L)	1H-BT	4Me-BT	5Me-BT
08/02/10 P5	423	738	206
08/02/10 P6	382	753	131
08/02/10 P7	396	711	205
08/02/10 P8	967	2039	684
08/02/10 P9	327	620	192
08/02/10 P10	<LOD	<LOD	<LOD
08/02/10 P11	211	479	125
08/02/10 P12	630	1704	222
08/02/10 P13	398	969	142
08/02/10 P14	259	662	141
08/02/10 P15	<LOD	<LOD	<LOD
07-09/07/10 P5	353	1392	422
07-09/07/10 P6	606	2120	566
07-09/07/10 P7	499	948	158
07-09/07/10 P8	461	542	127
07-09/07/10 P9	461	561	114
07-09/07/10 P10	<LOD	53	11
07-09/07/10 P11	361	482	86
07-09/07/10 P12	170	327	46
07-09/07/10 P13	<LOD	<LOD	<LOD
07-09/07/10 P14	191	530	70

Table A7. Mass flows for all three substances in January 2009, November 2009 and July 2009.

1H-BT			
(g/day)	Measure 1	Measure 2	Measure 3
Jan. 09	65,53	68,16	83,01
Nov. 09	9,95	22,60	51,93
July 09	2,62	7,94	13,64

4Me-BT			
(g/day)	Measure 1	Measure 2	Measure 3
Jan. 09	63,91	65,50	75,11
Nov. 09	21,86	14,91	70,44
July 09	2,6045518	19,213639	2,9530808

5Me-BT			
(g/day)	Measure 1	Measure 2	Measure 3
Jan. 09	22,56	26,62	12,79
Nov. 09	3,78	0,68	3,11
July 09	0,5479684	1,3137268	2,6241128

Table A8. Single factor analysis of variance (ANOVA) of 1H-BT.

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
<0° °C	3	216,6976	72,23253	88,86823
0-13 °C	3	84,48658	28,16219	463,8721
>13° C	3	24,21125	8,070417	30,36613

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	6462,65	2	3231,325	16,62471	0,003572	5,143253
Within Groups	1166,213	6	194,3688			
Total	7628,863	8				

F_{emp} 16,62471

F_{theo} 5,143253

1 - Confide.: 0,05

$F_{emp} > F_{theo}$:

true

=>

difference

Table A9. Single factor analysis of variance (ANOVA) of 4Me-BT.

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
<0° °C	3	204,5237	68,17458	36,72655
0-13 °C	3	107,2065	35,7355	915,3431
>13° C	3	24,77127	8,257091	90,06483

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	5397,463	2	2698,731	7,768857	0,02162	5,143253
Within Groups	2084,269	6	347,3782			
Total	7481,732	8				

F_{emp} 7,768857

F_{theo} 5,143253

1 - Confide.: 0,05

$F_{emp} > F_{theo}$:

true

=>

difference

Table A10. Single factor analysis of variance (ANOVA) of 5Me-BT.

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
<0° °C	3	61,97839	20,65946	50,54044
0-13 °C	3	7,566486	2,522162	2,663392
>13° C	3	4,485808	1,495269	1,102312

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	697,2825	2	348,6412	19,25977	0,002448	5,143253
Within Groups	108,6123	6	18,10205			
Total	805,8948	8				

F_{emp} 19,25977

F_{theo} 5,143253

1 - Confide.: 0,05

$F_{emp} > F_{theo}$:

true

=>

difference

Table A11. Concentrations of BTs in 2-hour composite samples of untreated wastewater of WWTP-G at 23/04/09.

(ng/L)	1H-BT	4Me-BT	5Me-BT
0-2am			
2-4am	2556	1388	350
4-6am	4801	2138	861
6-8am			
8-10am	2937	1050	573
10-12am	2711	633	363
12-2pm	1154	1030	357
2-4pm	1955	704	151
4-6pm	2922	1291	835
6-8pm	4362	1251	1016
8-10pm	2340	613	563
10-12pm	3914	694	607

Table A12. Mass flows of BTs in 2-hour composite samples of untreated wastewater of WWTP-G at 23/04/09.

(g/2h)	1H-BT	4Me-BT	5Me-BT
0-2am			
2-4am	19,49	10,58	2,67
4-6am	29,69	13,22	5,32
6-8am			
8-10am	27,13	9,70	5,29
10-12am	35,91	8,38	4,81
12-2pm	15,90	14,19	4,93
2-4pm	25,21	9,07	1,94
4-6pm	36,19	15,99	10,34
6-8pm	54,14	15,53	12,61
8-10pm	27,47	7,19	6,61
10-12pm	45,38	8,05	7,04

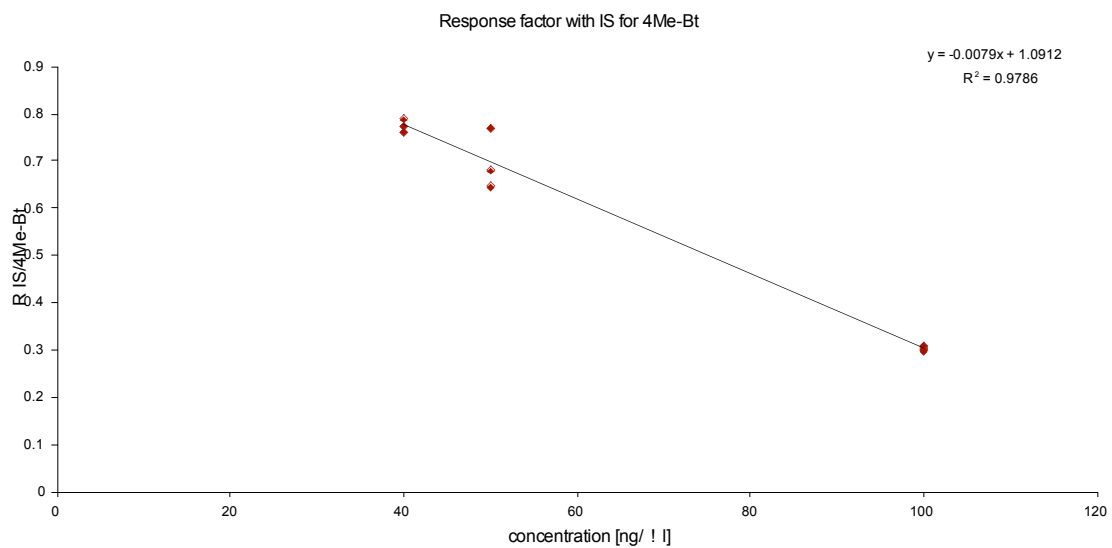
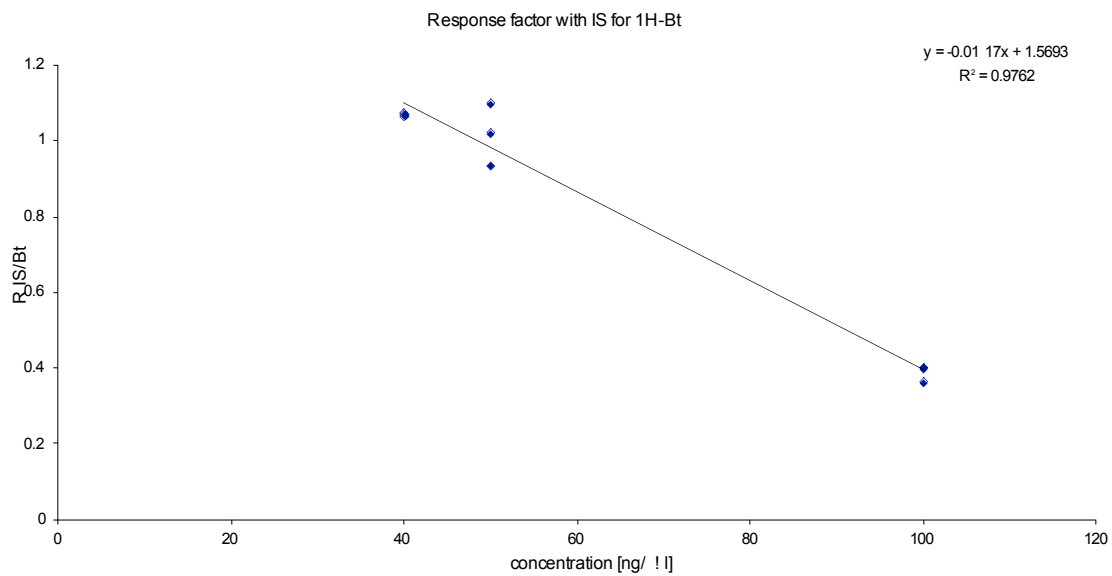
Table A13. Concentrations of wastewater samples at all WWTPs.

WWTP-S	Influent-S			Effluent-S		
(µg/l)	1H-BT	4Me-BT	5Me-BT	1H-BT	4Me-BT	5Me-BT
11.02.09	16,89	2,60	1,52	6,41	3,65	0,62
11.03.09	16,28	8,78	3,75	1,23	3,51	0,12
04.04.09	8,24	2,70	0,31			
26.06.09						
14.07.09						
WWTP-N/G	Influent-G			Effluent-G		
	1H-BT	4Me-BT	5Me-BT	1H-BT	4Me-BT	5Me-BT
11.02.09	12,30	1,13	2,48			
11.03.09	13,14	2,23	0,91			
23.04.09	18,45	9,34	4,84			
26.06.09						
14.07.09						
	Influent-N			Effluent-N		
	1H-BT	4Me-BT	5Me-BT	1H-BT	4Me-BT	5Me-BT
11.02.09	144,25	27,03	11,82	9,59	3,26	1,26
11.03.09	41,32	10,33	4,28	3,78	10,15	2,64
04.04.09						
26.06.09				5,93	5,33	0,58
14.07.09	10,17	7,31	1,97	0,30	3,95	3,65

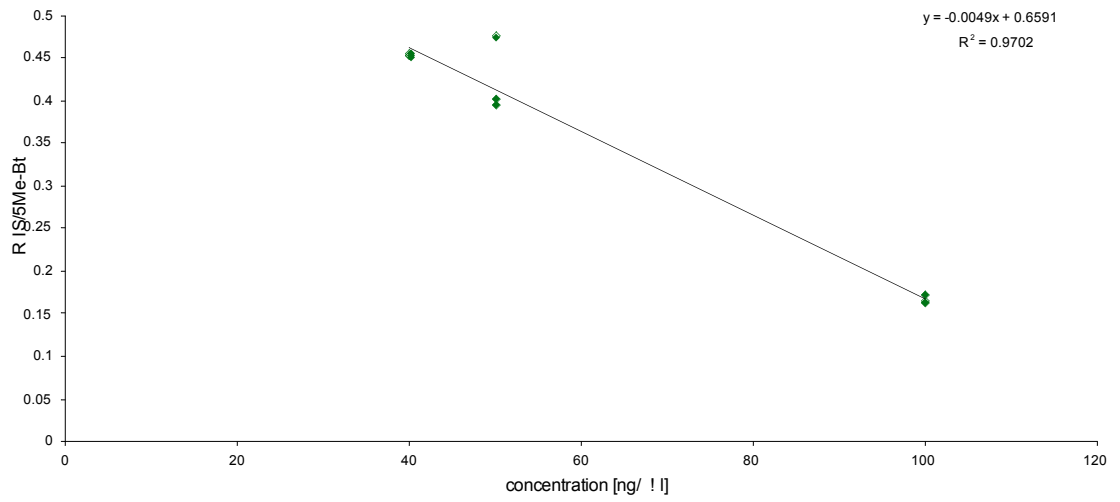
Table A14. Mass flows of wastewater samples at all WWTPs.

WWTP-S (g/day)	Influent-S			Effluent-S		
	1H-BT	4Me-BT	5Me-BT	1H-BT	4Me-BT	5Me-BT
11.02.09	1712	264	154	586	334	57
11.03.09	1542	832	355	112	318	10
04.04.09	465	152	18			
26.06.09						
14.07.09						
WWTP-N/G	Influent-G			Effluent-G		
	1H-BT	4Me-BT	5Me-BT	1H-BT	4Me-BT	5Me-BT
11.02.09	2501	231	504			
11.03.09	2368	401	164			
23.04.09	2387	1209	626			
26.06.09						
14.07.09						
	Influent-N			Effluent-N		
	1H-BT	4Me-BT	5Me-BT	1H-BT	4Me-BT	5Me-BT
11.02.09	21305	3992	1746	2842	967	374
11.03.09	5032	1861	1085	958	2572	668
04.04.09	0	0	0			
26.06.09						
14.07.09	2025	1456	393	102	1352	1248

Figure A1. Response factor of 1H-BT, TT and SuS for wastewater with linear regression.



Response factor with IS for 5Me-Bt



Response factor with IS for SuS

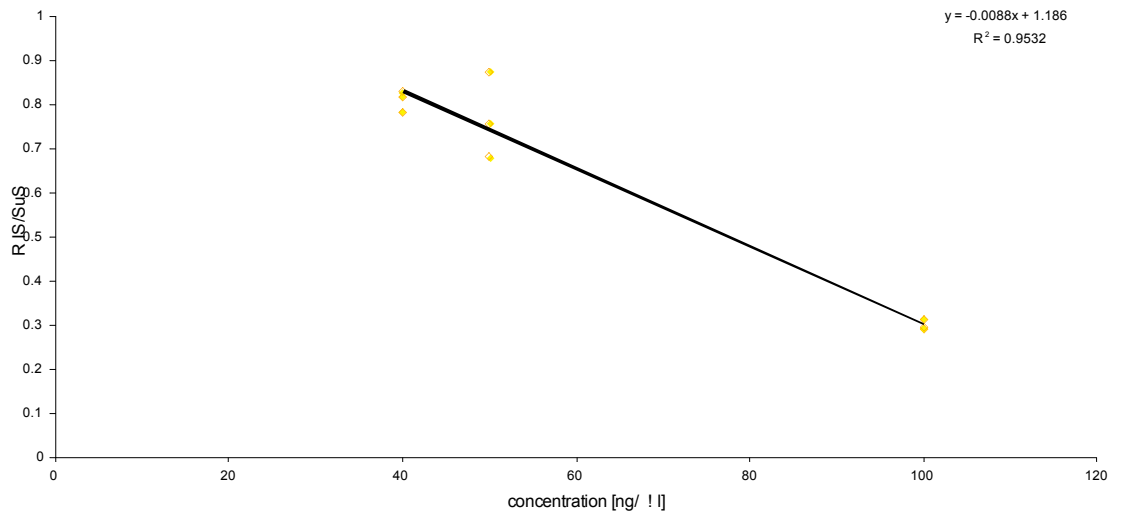
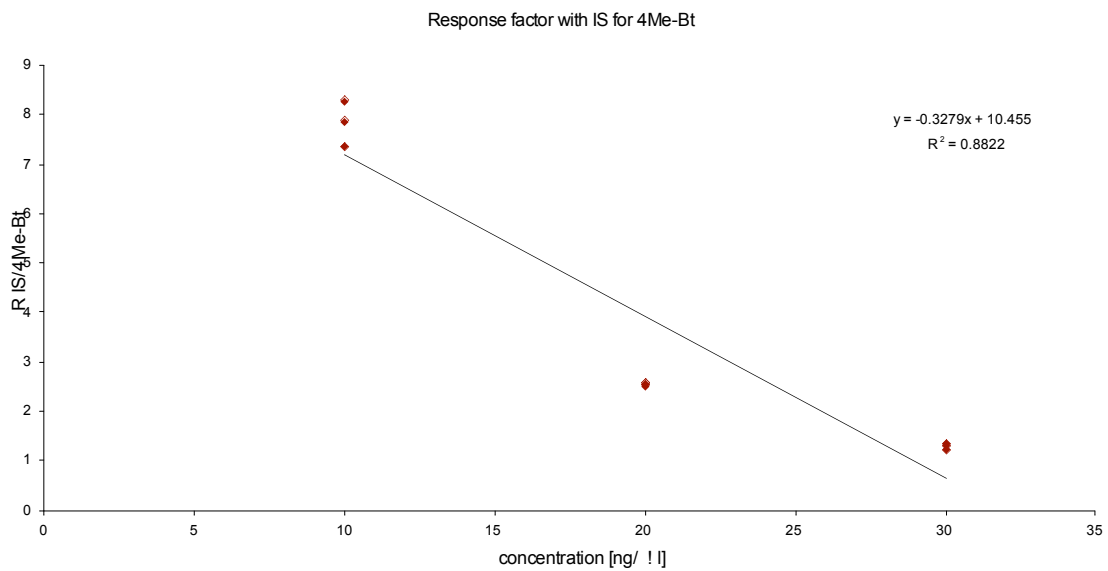
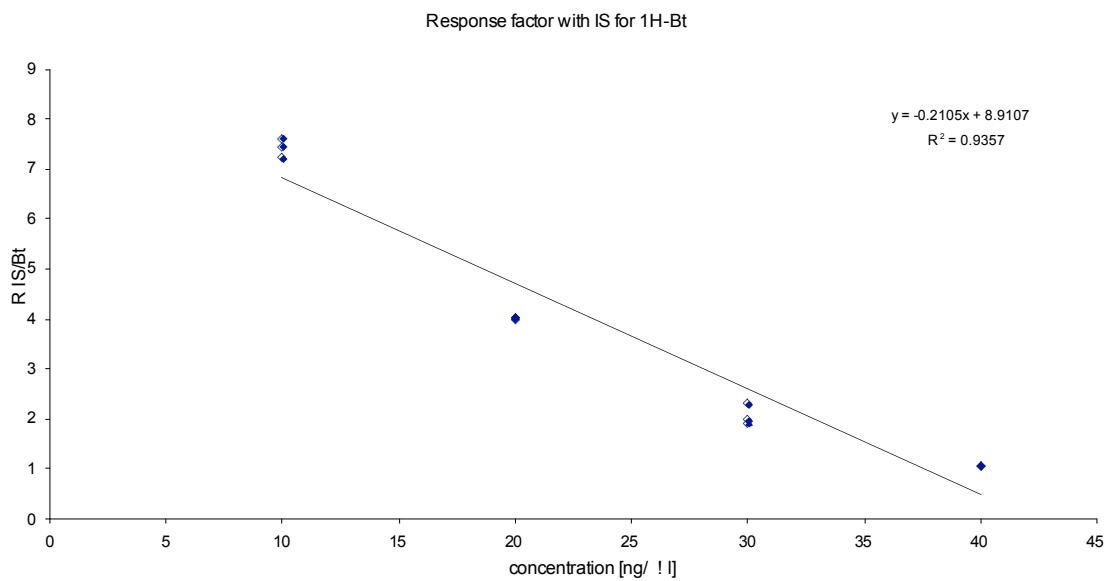
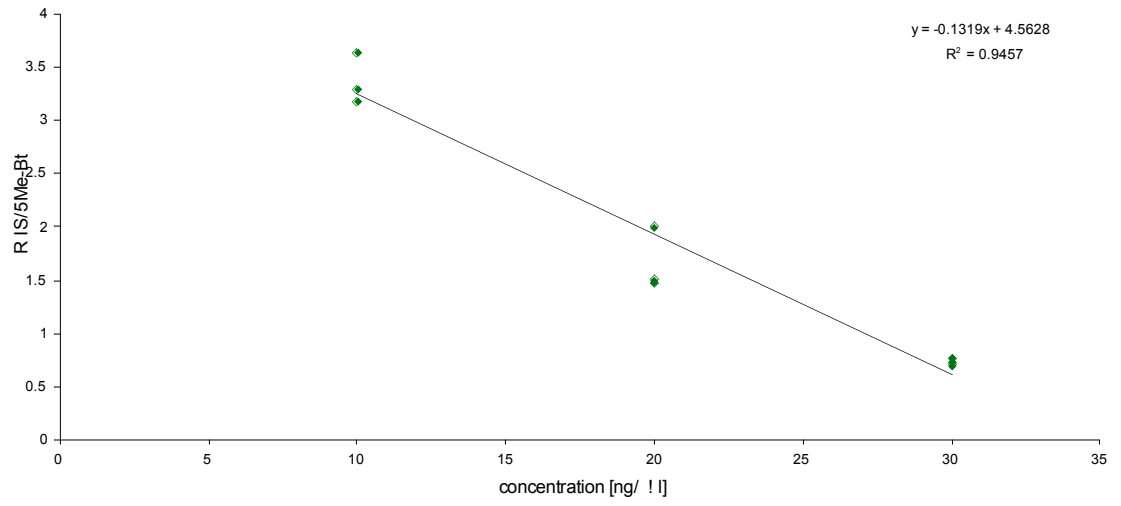


Figure A2. Response factor of 1H-BT, TT and SuS for river water and products



Response factor with IS for 5Me-Bt



Response factor with IS for SuS

