

Occurrence and fate of sulfonamides (p-TSA, o-TSA, BSA) in an urban water cycle

vorgelegt von
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Fachbereich Geowissenschaften
der Freien Universität Berlin
zur Erlangung des akademischen Grades

Doktorin der Naturwissenschaften
- Dr. rer. nat. -

genehmigte Dissertation

Promotionsausschuss:

Gutachter: Prof. Dr. Asaf Pekdeger

Gutachter: Priv.-Doz. Dr. Michael Schneider

Tag der wissenschaftlichen Aussprache: 18.12. 2007

Berlin 2007

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A dissertation submitted to the
Fachbereich Geowissenschaften
der Freien Universität Berlin
for the degree of Doctor of Science
- Dr. rer. nat. -

presented by
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Berlin 2007

Preface

The research project “Bewertung der organischen Zusammensetzung des Grundwassers im Einzugsgebiet der Nordgalerien des Wasserwerks Friedrichshagen, Berlin” – English title "Evaluation of organic compounds in the groundwater of a catchment area of the waterworks Friedrichshagen (Berlin, Germany)" – was a cooperation between the Freie Universität of Berlin and the Berliner Wasserbetriebe (BWB). Financial support was provided by the BWB.

This thesis contains the following contributions by scientist, technicians and students:

- The standard water analysis presented in chapter 5 was undertaken by technicians of the BWB.
- Data of groundwater level, filter depths and coordinates of the observation and abstraction wells for the Friedrichshagen investigation area were kindly provided by the BWB and Hydrogeologie GmbH (HGN).
- Wastewater, groundwater, surface water and drinking water samples were collected by the technical staff of the PIGADI and the BWB.
- The installation and, in part, the supervision of the experimental filter was performed by the technical staff of the BWB.
- The incubation experiment in chapter 5 was undertaken in collaboration with Dr. Thomas Taute, Dr. Gudrun Massmann and co-workers at the Freie Universität Berlin.

Parts of this thesis have been published in:

1. RICHTER, D., DÜNNBIER, U., MASSMANN, G., PEKDEGER, A., 2007. *Quantitative determination of three sulfonamides in environmental water samples using liquid chromatography coupled to electrospray tandem mass spectrometry*. Journal of Chromatography A, 1157, 115-121.
2. RICHTER, D., MASSMANN, G., DÜNNBIER, U., 2008. *Identification and significance of sulfonamides (p-TSA, o-TSA, BSA) in an urban water cycle (Berlin, Germany)*. Water Research, 42, 1369-1378.

3. RICHTER, D., MASSMANN, G., DÜNNBIER, U., 2008. *Behaviour and biodegradation of sulfonamides (p-TSA, o-TSA, BSA) during drinking water treatment*. Chemosphere, 71, 1574-1581.
4. RICHTER, D., MASSMANN, G., TAUTE, T., DÜNNBIER, U., *The influence of sewage farming and redox conditions on the distribution and persistence of sulfonamides in groundwater*. submitted to Journal of Contaminant Hydrology.

Summary

Sulfonamides are used worldwide as pharmaceuticals and as industrial chemicals (benzene- and toluenesulfonamides, BTS). Therefore, para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA) and benzenesulfonamide (BSA) have various sources in wastewater. Thus, their environmental occurrence and fate is of particular interest in partly closed water cycles. However, poorly degradable compounds can be problematic as they may travel along the water path from wastewater to the raw water used for drinking water production. P-TSA is applied as a plasticizer, an intermediate for pesticides and drugs and is the primary degradation product of the common disinfectant chloramine-T in water. Chloramine-T is used as an antimicrobial agent in the food industry to disinfect surfaces, instruments and machinery. The substance is also used as a therapeutic drug for bacterial gill diseases of fish species, and for bacterial diseases of swine and poultry. The main field of application of o-TSA is in the production process of the artificial sweetener saccharin. BSA is used for synthesis dyes, photo chemicals and disinfectants.

Previous to this study, a gas chromatography-mass spectrometry screening revealed elevated concentrations (high microgram per litre level) of these substances in groundwater below one of the former sewage farms in Berlin, Germany. The elevated concentrations occur in the catchment area of the Friedrichshagen drinking water treatment plant, located downstream of the former sewage farm at Münchehofe. Motivated by these alarming values, the occurrence, behaviour and fate of the three sulfonamides p-TSA, o-TSA and BSA in the urban water cycle of Berlin was intensively investigated in this study. Their entry into the aquatic environment was explored in field studies. In addition, laboratory experiments were performed. The toxicological relevance of p-TSA in drinking water was determined by the German Federal Environmental Protection Agency (UBA). The report recommends a tolerable maximum p-TSA concentration of 0.3 µg/L in drinking water. A maximum concentration of 0.1 µg/L is recommended for unknown substances (e.g. o-TSA, BSA) in drinking water, if toxicological and environmental information on the substances is insufficient.

First, an **analytical method** was developed for the sensitive and simultaneous determination of the three sulfonamides p-TSA, o-TSA and BSA in water samples. Solid phase extraction (SPE) and reversed phase liquid chromatography, coupled to tandem mass spectrometry (HPLC-MS/MS), were used for the quantitative analysis of the compounds in wastewater, surface water, groundwater and drinking water samples. The limit of quantification was 0.05 µg/L for all substances. The use of a deuterated sulfonamide as an internal standard (p-TSA-d₃) provided an optimal quantification of the analytes p-TSA, o-TSA and BSA in aqueous matrixes. The analyte recoveries were between 94 % and 120 % for aqueous samples.

Due to the nature of the Berlin **water cycle**, a number of persistent wastewater residues are present in the surface water and may potentially reach the groundwater via bank filtration and artificial recharge. The next step was to investigate the occurrence and behaviour of the wastewater residues p-TSA, o-TSA and BSA during wastewater treatment, in surface water, bank filtrate and ambient groundwater as well as during drinking water treatment. All three compounds are ubiquitous in the aquatic environment of Berlin. P-TSA concentrations (up to 50.8 µg/L) were much higher than those of o-TSA (up to 8 µg/L) and BSA (up to 0.64 µg/L) in wastewater. The highest concentrations of these substances were found in wastewater influents and in groundwater under the former sewage farm. P-TSA is considerably depleted during waste- and drinking water treatment (~90 % reduction each). No significant elimination during wastewater treatment and drinking water treatment was observed for o-TSA and BSA. The behaviour of o-TSA during wastewater treatment varied largely between different wastewater treatment plants where concentrations increased, remained constant, or decreased. BSA formed during treatment. The investigations showed that these compounds can help to identify the influence of treated wastewater in environmental water samples. The study makes clear that these sulfonamides should be monitored in abstracted groundwater and in drinking water, because of their omnipresence in the aquatic environment.

Their **behaviour during drinking water treatment** showed a significant reduction of p-TSA and a non-efficient removal of o-TSA and BSA. The degradation

pathways of p-TSA, o-TSA and BSA were investigated with incubation experiments and an experimental sand filter, which was constructed similar to the sand filters applied at the drinking water treatment plants in Berlin. Incubation experiments of p-TSA showed a high reduction during the treatment depending on specialised microorganisms. The degradation is performed by adapted microorganisms which were only present in polluted groundwater. O-TSA and BSA were stable in all incubation experiments and proved to be persistent. In the experimental filter, the microbial removal potential appeared to be higher when p-TSA concentrations were elevated. In total (after 1.6 m of flow through the column), the elimination of p-TSA yielded similarly good removals at all filtration velocities (from 2 to 6 m/h). The reaction rate was constant (around 0.0063 1/s) for all filtration velocities. Drinking water treatment did not reduce the concentration of o-TSA and BSA with the treatment applied in Berlin (aeration and rapid sand filtration). However, o-TSA and BSA were measured in very low ranges in the raw water used for drinking water production. P-TSA, o-TSA and BSA were only measured in low $\mu\text{g/L}$ concentrations in purified water (p-TSA: $< 0.3 \mu\text{g/L}$, o-TSA and BSA: $< 0.1 \mu\text{g/L}$).

Groundwater pollution was monitored downstream of the former sewage farm at Münchehofe, which operated for almost 70 years until the 1980s. Sulfonamides were found to have a strong impact on the production wells of the Friedrichshagen drinking water treatment plant. The distribution of the sulfonamides in the anoxic groundwater was investigated. For this purpose a large number of observation and production wells were sampled. The locally monitored high concentrations of p-TSA, o-TSA and BSA in groundwater showed that the sulfonamides persist over decades in an anoxic aquifer environment. Wastewater irrigation will continue to influence the quality of the abstracted groundwater of the Friedrichshagen drinking water treatment plant for decades. Increasing concentrations of the sulfonamides in the abstracted groundwater can be expected in the future. For further information, another incubation experiment was conducted under in-situ pressures (~ 2 bar) in aluminium tanks to study the behaviour of these trace organic compounds under different redox conditions (oxic and anoxic). Sterile groundwater sampling was done to distinguish between microbiological processes occurring in the aquifer and those representing sampling and storage artefacts (non-sterile

incubation experiments). The results confirmed that the substances are persistent under anoxic conditions. P-TSA and o-TSA are more degradable in the presence of oxygen. BSA was not eliminated in any of the experiments. Hence, maintaining in-situ conditions with regard to the oxygen concentration and the microbiology and possibly pressures is essential to ensure that the groundwater concentrations of the sulfonamides remain unchanged after sampling.

The study presented here provides a representative investigation of three sulfonamides of industrial use in an urban water cycle and is a prerequisite for more profound environmental risk assessments. The results from the Berlin water cycle showed the significance of the various parameters (e.g. redox conditions and microbiology) with regard to the elimination of sulfonamides in wastewater treatment plants as well as during bank filtration and in drinking water treatment plants.

Zusammenfassung

Sulfonamide werden weltweit sehr vielseitig aufgrund ihrer bakteriostatischen Wirkung (Bakterienhemmer) verwendet, so z.B. in der Human- und Tiermedizin oder als Industriechemikalien (Benzen- und Toluensulfonamide, BTS). Durch die Verwendung von para-Toluensulfonsäureamid (p-TSA), ortho-Toluensulfonsäureamid (o-TSA) und Benzensulfonsäureamid (BSA) gelangen diese in die Abwasseraufbereitung. Das Vorkommen und Verhalten dieser Sulfonamide in der aquatischen Umwelt ist deshalb von besonderem Interesse. Die Verbindung p-TSA wird als Weichmacher, als Zwischenprodukt in der Pestizid- und Medikamentenherstellung, wie auch in Anstrichen und Farben als Fungizid verwendet. P-TSA ist ein charakteristisches Abbauprodukt des Desinfektionsmittels Chloramin-T. Die Verbindung Chloramin-T, das Na-Salz des p-Toluensulfonsäure-N-chloramids, wird wegen seiner bakteriziden Wirkung als Medikament in der Tiermedizin, Humanmedizin und als Desinfektionsmittel für Flächen, Geräte und Maschinen in der Lebensmittelindustrie (Landwirtschaft, Schlachthäuser und Küchen etc.) verwendet. Wegen seiner raschen Wirkung und seinem breiten Wirkungsspektrum gegenüber saprophytischen und pathogenen Keimen wird Chloramin-T in der Tiermedizin z.B. bei verschiedenen Fischkrankheiten, sowie bei bakteriellen Krankheiten von Schweinen und Geflügel eingesetzt. O-TSA wird bei der Herstellung vom künstlichen Süßstoff Saccharin benötigt. BSA ist ein Zwischenprodukt bei der Produktion von Farbstoffen, Chemikalien für die Photoentwicklung und von Desinfektionsmitteln.

In einem semi-quantitativen gaschromatographischen und massenspektrometrischen Screening von Grundwasser unterhalb des ehemaligen Rieselfeldes Münchehofe (Berlin, Deutschland) wurden p-TSA, o-TSA und BSA in hohen Konzentrationen nachgewiesen. Die erhöhten Konzentrationen befinden sich im weiteren Einzugsgebiet des Wasserwerkes Friedrichshagen und sind deswegen von besonderem Interesse. Ziel dieser Arbeit war es, die Herkunft, das Vorkommen und das Verhalten dieser Sulfonamide im Wasserkreislauf von Berlin detailliert zu untersuchen. Die Konzentrationen der Einzelstoffe in der aquatischen Umwelt wurden in umfangreichen Feldstudien erhoben. Zusätzlich wurde eine Reihe von Laborexperimenten durchgeführt. Der gesundheitliche

Orientierungswert (GOW) für Substanzen, für die nur unzureichende toxikologische und ökologische Informationen existieren (z.B. o-TSA und BSA), liegt im Trinkwasser bei 0,1 µg/L. Das Umweltbundesamt (UBA) hat eine humantoxikologische Bewertung für p-TSA vorgenommen und empfiehlt eine maximal Konzentration von 0,3 µg/L im Trinkwasser.

Es bestand zunächst die Notwendigkeit, ein geeignetes quantitatives, sensitives, simultanes und routinefähiges **Analyseverfahren** zu entwickeln, um matrixreiche Wasserproben mittels Flüssigchromatographie und Massenspektrometrie (HPLC-MS/MS) auf p-TSA, o-TSA und BSA zu analysieren. Die zu untersuchenden wässrigen Proben werden mittels Festphasenextraktion (SPE) aufkonzentriert und mit der HPLC-MS/MS vermessen. Ein wichtiger Kernpunkt der Methodenentwicklung war die Trennung der isomeren Zielanalyten p-TSA und o-TSA. Um eine sichere Isomeren-Quantifizierung der polaren Verbindungen vorzunehmen, wurde eine isokratische LC-Trennung mittels einer Sunfire C18 Säule angewendet. Zur sicheren Quantifizierung wird zu Beginn der Probenvorbereitung ein geeigneter Referenzstandard (p-TSA-d₃) zugegeben. Die Bestimmungsgrenzen der drei Sulfonamide im entwickelten Analyseverfahren liegen jeweils bei 0,05 µg/L im Abwasser, Oberflächenwasser, Grundwasser und Trinkwasser. Die Wiederfindungsraten der einzelnen Analyten betragen 94 % bis 120 % für Wasserproben.

Das gereinigte Abwasser in Berlin wird zum größten Teil in das Berliner Oberflächenwasser eingeleitet. Zahlreiche persistente Reststoffe aus dem Abwasser sind somit im Oberflächenwasser enthalten und können durch die Uferfiltration und die künstliche Grundwasseranreicherung potentiell in das Grundwasser und letztlich in das Trinkwasser gelangen. Somit wurde die Herkunft, das Vorkommen und das Verhalten der Substanzen p-TSA, o-TSA und BSA im **Wasserkreislauf** bei der Abwasserreinigung, im Oberflächenwasser, im Uferfiltrat und im landseitigem Grundwasser, sowie bei der Trinkwasseraufbereitung untersucht. Alle drei Substanzen sind in der aquatischen Umwelt von Berlin ubiquitär vorhanden. Es wurden deutlich höhere Konzentrationen von p-TSA (bis zu 50,8 µg/L) als von o-TSA (bis zu 8 µg/L) und BSA (bis zu 0,64 µg/L) in Abwasserproben ermittelt. Die maximalen Konzentrationen wurden in den

Klärwerkszuläufen und im Grundwasser unterhalb eines ehemaligen Rieselfeldes gefunden. Während der Abwasserreinigung und Trinkwasseraufbereitung findet eine deutliche Elimination von p-TSA (jeweils $\approx 90\%$ Abbau) statt. Bei den Verbindungen o-TSA und BSA wurde kein signifikanter Konzentrationsrückgang beobachtet. Das Verhalten von o-TSA während der Abwasserreinigung variiert deutlich zwischen den unterschiedlichen Kläranlagen. Die Konzentrationen von o-TSA nehmen im Verlauf des Klärprozesses je nach Klärwerk entweder zu, bleiben konstant oder nehmen ab. Die BSA Konzentrationen erhöhen sich während der Abwasserklärung signifikant. Als Ursache für die Entstehung von BSA im Klärprozess ist ein Umbau und/oder Abbau höher molekularer Sulfonamide denkbar. Die an den Uferfiltrationsstandorten in Berlin gefundenen Werte belegen den Einfluss von gereinigtem Abwasser im Uferfiltrat. Somit können diese Substanzen auch dazu genutzt werden, Uferfiltrat zu identifizieren. Aufgrund der Allgegenwärtigkeit dieser drei Substanzen im Wasserkreislauf von Berlin ist eine Aufnahme der Substanzen in Routineanalysen des Trinkwassers zur Qualitätskontrolle unerlässlich.

Eine deutliche Elimination von p-TSA und keine Konzentrationsabnahme von o-TSA und BSA konnte während der **Trinkwasseraufbereitung** festgestellt werden. Weiterführende Untersuchungen zum Abbauverhalten der Substanzen während der Trinkwasseraufbereitung wurden mit Hilfe von Inkubationsexperimenten und eines Versuchsfilters durchgeführt, der in Anlehnung an den Aufbau und Betrieb der in Berlin durchgeführten Sandfiltration errichtet wurde. Die Inkubationsexperimente zeigten, dass der Abbau von p-TSA während der Trinkwasseraufbereitung über spezialisierte Mikroorganismen erfolgt. Dieser Abbauprozess wird von adaptierten Mikroorganismen durchgeführt. Diese spezialisierten Mikroorganismen sind nur im Wasserwerk Friedrichshagen vorhanden, welches mit Sulfonamiden verunreinigtes Grundwasser aufbereitet. In den Inkubationsexperimenten wurde unter den vorherrschenden Bedingungen o-TSA und BSA nicht abgebaut. Im Fall von p-TSA lag das mikrobiologische Abbaupotential im Versuchsfiler anscheinend höher, bei erhöhten p-TSA Konzentrationen im Zulauf. Die Eliminationsraten von p-TSA zeigen bei Filtergeschwindigkeiten von 2 m/h bis 6 m/h keine signifikanten Unterschiede. Die Reaktionsraten liegen bei ca. 0,0063 1/s. Im Rohwasser (belüftetes Grundwasser)

wurden sehr niedrige Konzentrationen von o-TSA und BSA nachgewiesen. Letztendlich sind alle drei Substanzen im Trinkwasser in einem niedrigen Konzentrationsniveau vorhanden (p-TSA: < 0,3 µg/L; o-TSA und BSA: < 0,1 µg/L).

Die Sulfonamide sind dort in hohen Konzentrationen im Rohwasser vorhanden, wo das geförderte Grundwasser durch den Anstrom von ehemaligen Rieselfeldern beeinflusst wird. Die fast 70jährige Abwasserbeaufschlagung des Rieselfeldes Münchehofes (bis in die achtziger Jahre des 20. Jahrhunderts) hatte eine starke **Schadstoffbelastung des Grundwassers** zur Folge. In den Förderbrunnen des Wasserwerkes Friedrichshagen wurde eine starke anthropogene Belastung durch die Substanzen p-TSA, o-TSA und BSA festgestellt. Für eine Untersuchung der Verbreitung dieser Sulfonamide im anoxischen Milieu des Grundwasserleiters wurden zahlreiche Grundwassermessstellen und Trinkwasserbrunnen im Einzugsgebiet des Wasserwerks Friedrichshagen beprobt. Die auch nach Einstellung des Rieselfeldbetriebes unvermindert hohen Konzentrationen im anoxischen Grundwasser zeigen, dass diese Substanzen offensichtlich über Jahrzehnte unter diesen Redoxbedingungen persistent sind. Die vor Jahrzehnten praktizierte Rieselfeldbewirtschaftung beeinflusst seitdem die Qualität des geförderten Grundwassers vom Wasserwerk Friedrichshagen. Die Ausbreitung der Kontaminationsfahne zeigt, dass in Zukunft unter dem herrschenden hydrogeologischen Bedingungen zunehmende Konzentrationen der Sulfonamide im geförderten Grundwasser zu erwarten sind. Die Elimination von p-TSA scheint durch die Verfügbarkeit von Sauerstoff limitiert zu sein. Aus diesem Grund wurde das Verhalten der Substanzen unter verschiedenen Redox-Bedingungen mit Hilfe von Inkubationsexperimenten untersucht. Für den Versuchsaufbau wurde das Grundwasser in Aluminium-Vorratsgefäßen unter in-situ Druckverhältnissen (≈ 2 bar) mit jeweils oxischen und anoxischen Ausgangsbedingungen gelagert. Um die mikrobiologischen Prozesse im Grundwasser von denen durch die Probenahme verursachten zu unterscheiden, musste die Grundwasserprobenahme unter sterilen Bedingungen durchgeführt werden. Die Ergebnisse der Experimente bestätigen, dass die Substanzen unter anoxischen Bedingungen nicht abgebaut werden. Dagegen zeigen p-TSA und o-TSA unter oxischen Bedingungen eine gute Abbaubarkeit. Das Aufrechterhalten der in-situ Bedingungen im Laborversuch, in Bezug auf das Redoxmilieu und eventuell auch den

Formationsdruck, sowie eine sterile Probenahme sind von großer Wichtigkeit, um die Korrektheit der gemessenen Werte sicherzustellen.

In dieser Arbeit wird eine repräsentative Untersuchung von drei Sulfonamiden in einem städtischen Wasserkreislauf gezeigt, deren Ergebnisse zu einer umfassenden Risikobetrachtung beitragen. In den einzelnen Komponenten des Berliner Wasserkreislaufes, in den Klärwerken, während der Uferfiltration, im anthropogen belasteten Grundwasser und in den Wasserwerken, lassen sich verschiedene Eliminationsfaktoren (z.B. Redoxmilieu und Mikroorganismen) differenzieren.

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Abbreviations

AOX	adsorbable organic halogens
B	boron
BIOXWAND	acronym for the research project entitled „ <i>Entwicklung und Erprobung einer Bio-Oxidationswand im Abstrom eines hoch mit Ammonium kontaminierten Grundwasserleiters.</i> “
BMBF	Federal Ministry of Education and Research
BSA	benzenesulfonamide
BTS	benzene- and toluenesulfonamide
BWB	Berliner Wasserbetriebe
DOC	dissolved organic carbon
DWTP BEE	drinking water treatment plant Beelitzhof
DWTP FRI	drinking water treatment plant Friedrichshagen
DWTP KAU	drinking water treatment plant Kaulsdorf
DWTP KLA	drinking water treatment plant Kladow
DWTP SPA	drinking water treatment plant Spandau
DWTP STO	drinking water treatment plant Stolpe
DWTP TEG	drinking water treatment plant Tegel
DWTP TIE	drinking water treatment plant Tiefwerder
DWTP WUH	drinking water treatment plant Wuhlheide
DWTP	drinking water treatment plant
EC	electric conductivity
eff	effluent
ESI	electrospray ionisation
EU	European Union

GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
GW	groundwater
HGN	Hydrogeologie GmbH
HPLC-MS/MS	high performance liquid chromatography coupled to tandem mass spectrometry
inf	influent
IS	internal standard
k_f	hydraulic conductivity
LC	liquid chromatography
LOQ	limit of quantification
MRM	multiple reaction monitoring
n	number of samples
NH_4^+	ammonium
NIDESI	acronym for the research project entitled „ <i>Entwicklung eines gekoppelten Nitrifikations-/Denitrifikations-Verfahrens zur in situ Reinigung stark stickstoffbelasteter Grundwasserleiter</i> “.
O_2	oxygen
o-TSA	ortho-toluensulfonamide
ow	observation well
PPCPs	pharmaceuticals and personal care products
p-TSA	para-toluensulfonamide
p-TSA-d ₃	deuterated para-toluensulfonamide
pw	production well
RSD	relative standard deviations
SPC	sulfophenyl carboxylates

SPE	solid phase extraction
SRM	single reaction monitoring
SW	surface water
SWTP	surface water treatment plant
UBA	German Federal Environmental Protection Agency
WWTP MÜN	wastewater treatment plant Münchehofe
WWTP RUH	wastewater treatment plant Ruhleben
WWTP SCH	wastewater treatment plant Schönerlinde
WWTP STA	wastewater treatment plant Stahnsdorf
WWTP WAS	wastewater treatment plant Wassmannsdorf
WWTP	wastewater treatment plant