#### TEXTE

# 54/2016

Causes of findings of veterinary antibiotics in groundwater samples – investigation of vulnerable location in Northern Germany Summary



TEXTE 54/2016

Environmental Research of the Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety

Project No. (FKZ) 3714 23 210 0 Report No. (UBA-FB) 002344 /SUM

## Causes of findings of veterinary antibiotics in groundwater samples – investigation of vulnerable locations in Northern Germany

#### Summary

by

Dr. Stephan Hannappel, M. Sc. Claudia Köpp HYDOR CONSULT GmbH, Berlin, Germany

Dr. Sebastian Zühlke Technische Universität Dortmund, Institut für Umweltforschung (INFU), Dortmund, Germany

On behalf of the Federal Environment Agency (Germany)

#### Imprint

#### **Publisher:**

Umweltbundesamt Wörlitzer Platz 1 06844 Dessau-Roßlau Tel: +49 340-2103-0 Fax: +49 340-2103-2285 info@umweltbundesamt.de Internet: www.umweltbundesamt.de

f /umweltbundesamt.de
/umweltbundesamt

#### Study performed by:

HYDOR CONSULT GmbH Am Borsigturm 40 13507 Berlin Germany

## Study completed in:

May 2016

#### Edited by:

II 2.9 Section Rural Development, Agriculture and International Soil Protection Frederike Balzer

#### Publication as pdf:

http://www.umweltbundesamt.de/publikationen/aufklaerung-der-ursachenvon-tierarzneimittelfunden

ISSN 1862-4804

Dessau-Roßlau, June 2016

The Project underlying this report was supported with funding from the Federal Ministry for the Environment, Nature Conservation, Building and Nuclear safety under project number FKZ 3714 23 210 0. The responsibility for the content of this publication lies with the author(s).

Aufklärung der Ursachen von Tierarzneimittelfunden im Grundwasser - Untersuchung eintragsgefährdeter Standorte in Norddeutschland

#### **Report Cover Sheet**

Report No.	UBA-FB
Report Title	Causes of findings of veterinary antibiotics in groundwater samples – investigation of vul- nerable locations in Northern Germany
Author(s) (Family Name, First Name)	Dr. Hannappel, Stephan (HYDOR) M.Sc. Köpp, Claudia (HYDOR) Dr. Zühlke, Sebastian (INFU TU Dortmund)
Performing Organisation (Name, Address)	HYDOR CONSULT GmbH       Am Borsigturm 40       13507 Berlin       Institut für Umweltforschung (INFU),       der Fakultät Chemie und Chemische Biologie       Technische Universität Dortmund       Otto-Hahn-Str. 6       44221 Dortmund       in cooperation with:       NLWKN -Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz       Betriebsstelle Cloppenburg       Drüdingstraße 25       49661 Cloppenburg
Funding Agency	Umweltbundesamt Postfach 14 06 06813 Dessau-Roßlau
Report Date (Year)	2016
Project No. (FKZ)	3714 23 210 0
No. of Pages	18
Supplementary Notes	
Keywords	Antibiotics, groundwater, live stock, agriculture, manure, vadose water, sulfonamide, ni- trate, groundwater measurement points, tracer, indicator substances, Lower Saxony, North Rhine Westphalia, Schleswig-Holstein

#### **Table of contents**

Lis	t of F	igures	4	
1	Bac	ckground of the project	5	
	1.1	Initial situation	5	
	1.2	Stated aim	6	
2	Project realisation		7	
	2.1	Identification of the influx areas and the agricultural parcels	7	
	2.2	Sampling of groundwater, domestic waste water and seepage water	8	
	2.3	Cooperation with the farmers	9	
	2.4	Effects of the investigation	9	
3	Results		10	
	3.1	Evaluation of the questionnaires	10	
	3.2	Results of the analysed manure	11	
	3.3	Results of the analysed seepage water	12	
	3.4	Results of the analysed domestic waste water	12	
	3.5	Results of the analysed groundwater	13	
4	Inte	rpretation14		
5	Rec	ecommendations16		
6	Ref	References17		

#### **List of Figures**

Figure 1: Overview of the 11 investigated locations in regions with high livest density in SH, NI, NRW	
Figure 2: Identification of the influx area and the agricultural parcels at one in NRW	
Figure 3: Sampling of domestic waste water	8
Figure 4: Technical structure of the fixed suction probe and look into the see collection point	
Figure 5: Livestock breading of the farms and applied fertilisers (2009 to 201 parcels in the influx area	
Figure 6: Findings of sulfonamide in liquid manure and fermentation residues according to species	
Figure 7: Time variability of the analysed waste water from five waste water treatment works	
Figure 8: Percentages and amount of findings of active substances in groundy from 2012 until 2015	
Figure 9: Comparison of the content of boron, measured since 1990, and SMX measured since 2008 at the location in NRW	

#### **1** Background of the project

In Germany, the consumption of antibiotic veterinary medicine products (Tierarzneimittel, TAM) remains with 1238 metric ton in 2014 (BVL<sup>1</sup>) on a very high level at agriculture. However, between 2011 and 2014, the use of antibiotics shrunk by 27%. Up to 2013 the proportional administration of reserve antibiotics was increasing, e.g. the delivery of fluoroquinolones was doubled. The trend has to be considered critically with regards to the development of resistance and unknown eco-toxicological effects on terrestrial and aquatic non-target organisms (Ji et al. 2012, Balzer & Schulz 2015, MKULNV 2014<sup>2</sup>).

The effects of the veterinary antibiotics entering the environment have so far not been fully investigated. Recent detections of antibiotics in fermentation residues and slurry (Sattelberger et al. 2005, Harms 2006, LfL 2006, Ratsak et al. 2013) in soil (Kim et al. 2011, Hembrock-Heger et al. 2011, Tauchnitz et al. 2013) respectively in the unsaturated zone ((Jechalke et al. 2014). Also in Austria, antibiotics have been found in near-surface groundwater (Clara et al. 2010). The German Scientific Advisory Board classifies the control of groundwater on antibacterial substances as crucial (BMEL 2015).

Since there are no existing standards or thresholds on antibiotic residues in groundwater, the input of these substances into near-surface groundwater was not studied systematically within the monitoring programme of the EC Groundwater Directive (2006/118/EC) and the German Groundwater Directive (GrwV 2010).

#### 1.1 Initial situation

In 2008 for the first time a reliable evidence of an antibiotic residue in the near-surface groundwater has been detected in line of a soil and groundwater screening in North Rhine-Westphalia (Nordrhein-Westfalen, NRW). A second analysis confirmed this result (Hembrock-Heger et al. 2011). The first systematic approach followed in 2012 and 2013 within a screening program (Hannappel et al. 2014a). At 48 locations in 4 federal states in Germany, the potential input of substances was determined. Observation wells based on a so-called "worst case" scenario were selected: high local livestock density associated with high amount of organic fertilizer, a sandy composition of the infiltration zone, low groundwater levels with short residence time of seepage water in the unsaturated zone as well as high nitrogen contents in the groundwater. Based on a world-wide literature study, the antibiotic substances have been selected with regards to usage, physicochemical characteristics and detection to the groundwater. Within this project at 9 of 48 locations (19 %) sulfonamide residues could be detected. They were highly variable in terms of time and mostly in very low concentrations of a few ng/l (Hannappel et al. 2014). Research in Schleswig-Holstein (SH) came to a similar conclusion with 2 positive detections at 10 observation wells (20%). All results refer to only three single substances all of the group of sulfonamides. Other antibiotic substances (among others tetracycline) could not be detected in the groundwater investigated. The evaluation of the results does not represent a general problematic contamination of the groundwater. In individual cases under very adverse conditions higher

<sup>&</sup>lt;sup>1</sup> http://www.bvl.bund.de/DE/08\_PresseInfothek/01\_FuerJournalisten/01\_Presse\_und\_Hintergrundinformationen/05\_Tierarzneimit-tel/2015/2015\_07\_28\_pi\_Antibiotikaabgabemenge2014.html?nn=1401276 (02/2016)

<sup>&</sup>lt;sup>2</sup> https://www.foodnetcenter.uni-bonn.de/events/der-fachveranstaltung-keime-und-antibiotika-resistenzen-aus-der-tierhaltung-undihre-folgen-fur-die-menschliche-gesundheit (03/2016)

concentration of a substance was measured. In May 2014 the 53<sup>rd</sup> conference headed by the environmental federal state departments (Amtschefkonferenz der Umweltressorts der Länder) asked the federal government to continue the investigation due to the lack of knowledge and the novelty of the issue.

In 2015 a state wide screening of antibiotics in groundwater in selected observation wells in Lower Saxony (NI) was performed. Sulfonamides were found in 14 of 148 locations (9,5 %) in spring 2015 (Germershausen 2015). The findings were significantly increased in areas with high livestock density (about 20 %). Indeed there were also positive detections in areas outside high local livestock density, with no identification of the source of contamination yet. The main water supplier verified the content of medical substances in groundwater in 2014 and 2015 (OOWV 2014 and 2015). The percentage of the observation wells with positive results (17 %) was comparable to the UBA study in 2012 und 2013. The observation wells are located in water protection areas with a groundwater protection scheme. However, this relates to decrease the nitrate and pesticide values in groundwater, not antibiotics.

#### 1.2 Stated aim

The origins of the findings were not identified at the previous projects because of their screening purposes. The intention was to get an overview about the occurrence of sulfonamides in groundwater and their potential relevance for ground- and drinking water protection scheme.

The main aim of the present study was, to examine the findings of antibiotic residues in groundwater, known as single spots, at eleven locations. A sampling with a high temporal and spatial resolution was initiated to identify the source and fate of the substances. However, not all of the three verified sulfonamides are used in veterinary medicine. Sulfamethoxazole (SMX) is used mostly in human medicine. Thus, other input sources, like wastewater treatment facilities, were analysed as well.

#### 2 Project realisation

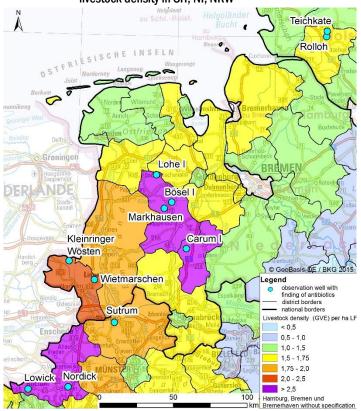
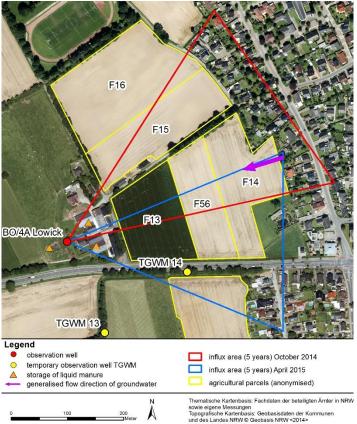


Figure 1: Overview of the 11 investigated locations in regions with high livestock density in SH, NI, NRW

Figure 2: Identification of the influx area and the agricultural parcels at one location in NRW



Altogether sampling sites at eleven locations, two in SH, three in NRW and six in Niedersachsen (NI) were investigated (figure 1). At the beginning a comprehensive data analyses was performed. Aim was to identify the local and potential none-agricultural sources of antibiotics surrounding the observation wells, i.e. domestic waste water treatment facilities or sewage sludge. To identify former appearance of antibiotic substances, water quality data of communal water suppliers in the recent past were analysed.

# 2.1 Identification of the influx areas and the agricultural parcels

At ten of the eleven locations, one site is located in a region of fissured rocks, a minimum of two temporary observation wells per existing groundwater measuring point have been built in October 2014. The percussion core drillings were performed on public alleys. Aim was to identify the influx area of the near-surface groundwater of the stationary observation wells. With the information gained (e.g. groundwater level) the groundwater influx area and the flow regime was investigated to identify the five-year-travel-time at each observation well. Additionally, at the temporary wells, two samples have been taken to analyse the sulfonamide residues and to gain more information about the surrounding of the stationary observation points. Finally, the temporary wells were removed or, as agreed with the local authorities, left in place for further usage.

Information about the quantities and content of organic fertiliser used in the past was inquired in order to correlate the data with the content and concentration on antibiotics measured in groundwater. The groundwater influx direction of each observation well has been identified (figure 2). With the help of the local agriculture associations, contact has been made to the farmers, cultivating on the sampling sites of interest. At almost all locations, farmers' voluntary provided these information and were co-operating at this project. Farmers Associations have been actively involved at this project and farmers were extensively informed about the aim of the study in advance.

#### 2.2 Sampling of groundwater, domestic waste water and seepage water

At the state-owned observation wells, groundwater samples have been taken on a monthly or quarterly basis between October 2014 and September 2015. These samples were analysed on sulfonamide residues, as well as main and accessory solutes. Suitable samples of domestic wells or wells of water suppliers (groundwater monitoring sites) close to the observation points are also included. For comparison of samples analysed it was ensured, that all sampling was performed at the near-surface groundwater. All actions were made in agreement with the owner, with the option of early and confidential communication of the water quality results.

Figure 3: Sampling of domestic waste water



with high troughput.

Supplementary, at two locations with high concentrations in sulfamethoxazole (SMX) in 2012 and 2013, waste water samples (figure 3) were taken at the domestic water treatment facitilies in the neighbouring area of the observation wells. The samples were analysed on sulfonamides at the laboratory, and examined to understand the possible fate of sulfamethoxazole, used mainly in human medicine and entering the aquatic environment via municipal waste water (Heberer et al. 2008, Hein 2011). For analysis in the laboratory samples from pre-treatment of the KKA were taken. It has to be assumed that the sulfonamides accumulate there than in the treated water

The State Authority for Mining, Energy and Geology (Landesamt für Bergbau, Energie und Geologie Niedersachsen, LBEG) is running permanent soil observation programs (Höper 2011, Höper 2016). One of the soil observation areas (Bodendauerbeobachtungsfläche, BDF, figure 4) is located near an observation well. Here seepage samples have been taken at a fixed suction probe in autumn 2015. Due to the investigation of the BDF it was possible to study the fate of the sulfonamide residues, found in near-surface groundwater, and to understand the pathways from slurry to soil and seepage water to groundwater. In spring 2015 the weather conditions were unusual dry and the period of seepage was subsiding at late winter (March) 2015. Thus, the samples were taken in November and December 2015 and integrated in project results.

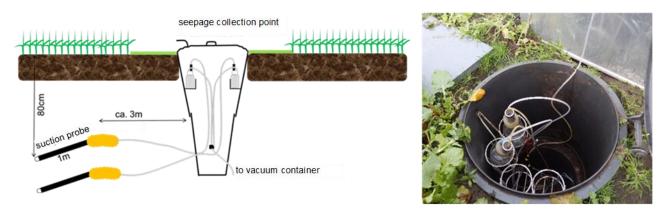


Figure 4: Technical structure of the fixed suction probe (scheme: LBEG, left) and look into the seepage collection point (right)

#### 2.3 Cooperation with the farmers

Negotiations with the stakeholders of the farmers have been held at the beginning of the project. The aim was an agreement with associations and affected farmers, who are cultivating the surrounding areas of the observation wells. This could be reached for all sampling sites concerned. With some stakeholders (e.g. Landvolk NI) an agreement with precise conditions of the co-operation was arranged. A questionnaire was handed out to farmers, working on the influx areas of the groundwater observation wells. This required information of the used veterinary medicine products as well as kind and quantity of applied farmyard manure at the influx areas in the recent past. The gained data were anonymised and handled strictly confidential. It was also agreed, that further samples of manure and/or fermentation residues would be taken in spring 2015. The sampling of the organic fertilisers was professionally performed by the responsible Chambers of Agriculture (Landwirtschaftskammern in NI and NRW) and an extern engineering office (SH).

#### 2.4 Effects of the investigation

The Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency (NLWKN), took the opportunity of the project, to initiate further own studies for its', known until then, single spot findings of substances of the sulfonamide group in groundwater at six locations in Lower Saxony (NI). The project runs until November 2016. The studies have a conceptual linkage, the same observation wells have been sampled with the same temporal and spatial range. At the NLWKN also soil, seepage and soil drainage water samples were taken at these six locations. As tracer for human impact, the sweetener acesulfame K was considered. The investigations in NI (HYDOR 2016) are very important to clearify the reasons of the observed contamination.

During the course of the project, interim results were continuously reported to the working group of the project and relevant technical details were coordinated. At the beginning of the project in October 2014, after intense discussions, it was mutually agreed to exclude the sampling and analysis of soil, the focus was concentrated on groundwater. However, soil is also a very important environmental compartiment. In further investigation, contamination of soils by pharmaceuticals should also be observed. At the final presentation of the project in April 2016, the results of the study were presented to an extended circle of participants.

During the course of the project, relevant parts of the results have been published in scientific journals, on colloquiums (Groundwater workshop NLWKN) and congresses, i.e. Berlin September 2015 (Balzer et al. 2015b), partly published. However, consistent and complete interpretation of the data was ensured at the end of the project. At the end of the former project of UBA and its publication in spring 2014, the impression in media occurred, that the sources of antibiotic substances in groundwater were not fully understood. To successfully deliberate this impression this time, it was focused on early communication to the professional public and agricultural associations.

#### 3 Results

With assistance of the local agricultural associations and the Chamber of Agriculture, there was a high voluntary co-operation of farmers, who provided samples of slurry and digestates for analyses, at most of the locations.

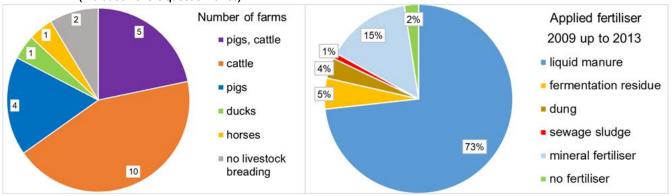
Within the groundwater-influx areas of the observation wells, only at one of eleven locations, the cultivating farmer was not co-operating. Thus, at this location no information from questionnaires or manure samples were available. At two further locations in NRW, most of the farmers cultivating the influx area of the observation well were not co-operating. At these observation wells, the repeated findings of antibiotics detected in groundwater could not be clarified. However, the central target of the project was achieved with an active and complete co-operation of all relevant persons and institutions at the other eight locations with positive findings on antibiotic substances in groundwater.

#### 3.1 Evaluation of the questionnaires

The influx areas of the eleven observation wells are located on 56 agricultural parcels and cultivated by 30 farm businesses, with up to 18 parcels lying at the influx to one groundwater observation well. 21 farms (70 %) were completely answering the questionnaires. This built the data information base for the years 2009 to 2013. In SH, the parcels were used mainly as pastures. In NI and NRW the main use was growing arable crops. In NRW half of the parcels were used for corn, in NI additionally cereals and grass are grown. In total, one third of the parcels is used for growing corn, one third as pasture and one third for cultivation of other arable crops (for example potatoes).

Figure 5 shows livestock farming at 23 cooperating farms, working on parcels in the influx area. zeigt die Viehhaltung in den 23 Betrieben, die auf den Schlägen im Zustromgebiet zu den Messstellen wirtschaften und sich an dieser Untersuchung beteiligt haben. For the farms in SH cattle is the main type of livestock breading, in NRW pig farming and cattle. At the six locations investigated in NI the husbandry is heterogenic, with all main types of breading animals, at one location ducks are produced. The figure also shows the compound of manure, which have been applied on the fields in the influx area. Liquid manure is the preferential fertiliser as shown on the right side of figure 5. Furthermore dung, fermentation residues, mineral fertilisers and sewage sludge are added.

Figure 5: Livestock breading of the farms (left) and applied fertilisers (2009 to 2013, right) on the parcels in the influx area (Evaluation of the questionnaires)



At three quarters of the farms, no sulfonamides were used at factory farming between 2009 and 2013. At 25 % sulfamethazine and sulfadiazine were used with the same quantity or in combination. The questionnaires contained detailed information about the used medicines. Most commonly (41 % of farms) medicine with sulfonamides was used at porkers, followed by calves (25 %) and dairy cattle and sows (17 % each).

The precise locations of the influx areas were determined with the construction of temporary observation wells, repeated measurements of water tables and calculation of the hydrological triangle. They often showed slightly seasonal varying directions of groundwater flow. However, they had no effects on the selection of parcels for the sampling of manure. Thus, strong correlation between samples of farmyard and groundwater samples can be guaranteed.

#### 3.2 Results of the analysed manure

At nine of the eleven locations samples of farmyard manure were provided and analysed. At seven of these, the samples showed the active substances sulfamethazine (SDM), sulfadiazine (SDZ) and additionally sulfathiazole. The results showed a high variation of concentrations between the samples and the locations. The analysed concentrations of sulfonamides at this project corresponds with the known content of antibiotic substances of farmyard manure from literature (Ratsak et al. 2013). The maximal content of 1350  $\mu$ g/kg dry matter of SDM was meas-

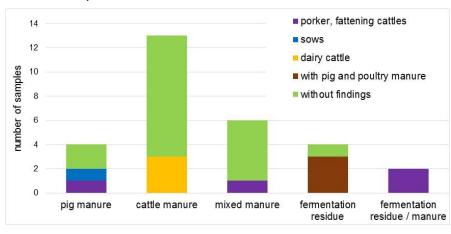


Figure 6: Findings of sulfonamide in liquid manure and fermentation residues according to species

ured at a mixture of slurry and digestate. At two locations, the analyses of manure showed no results although the groundwater confirms a content on SDM for many years.

Figure 6 shows the findings in liquid manure and fermentation residues according to species. The content of the sulfonamides in the manure of porkers (50 %) was higher than in cattle (23 %). The mixed slurry consist of different percentages of pig- and cattle manure. The sample with the finding of sulfonamide contains 80 % cattle- and 20 % pig-manure (fattening animals). Three out of four fermentation residues contain renewable raw materials as well as cattle- and pig-manure and poultry manure respectively duck manure. These sample have findings of sulfonamides. One fermentation residue is only from cattle manure and shows no finding. The percentages in the mix of liquid manure and fermentation residue are 50 %. The manure consists of porker or porker and fattening cattle. However, the data are not representative, as the database is only 30 samples.

#### 3.3 Results of the analysed seepage water

Two samplings of seepage water at a depth of 1 m below surface using a suction probe at the soil observation area were performed in autumn 2015. A concentration of 24 ng/l (October 2015) and 4 ng/l (December 2015) SDM could be verified, other substances of the sulfonamide group could not be determined.

#### 3.4 Results of the analysed domestic waste water

The sampling and chemical analysesis of sewage from surrounding domestic small waste water treatment works (Kleinkläranlage, KKA) showed at one location in NI recurrent findings of SMX and his transformation product (N-Ac-SMX). Another KKA presented the active substance trime-thoprim, which is widely used in human medicine in combination with SMX.

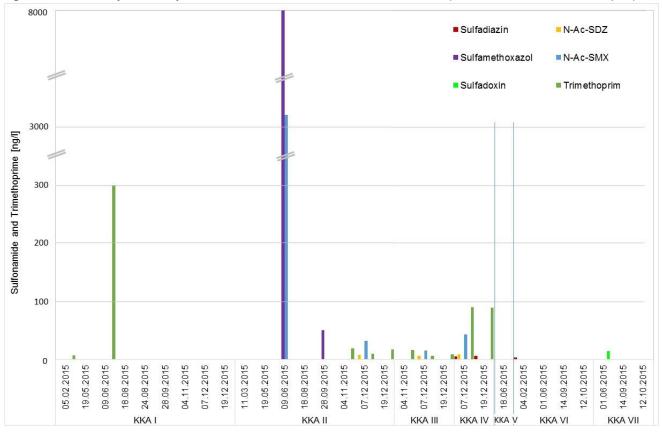


Figure 7: Time variability of the analysed waste water from five waste water treatment works (KKA, concentration axis is interrupted)

As characteristic for a domestic sewage system, the SMX concentrations are variable on an hourly basis. It shows concentrations from below detection limit up to 8000 ng/l in short time

scale (a few weeks). At a second location with proven long term high concentrations of SMX (as well as boron) in groundwater (NRW), no SMX was detected in several samples of sewage. Additionally, a samples of farmyard manure provided by co-operating farmers at this area showed no SMX content.

Figure 7 shows the time variability of findings in domestic waste water. SDM is exclusively administered as veterinary medicine and was not found in KKA. SDZ and its metabolite were detecteded occasionally in concentrations below 10 ng/l. Sulfadoxin was detected once in waste water but not in groundwater.

As tracer for human input of waste water into groundwater, caffeine was chosen. It was found in almost all KKA in high concentrations up to 400.000 ng/l. The anti-epileptic medicine carbamazepine was proven at very few samples and in low concentrations (up to 15 ng/l). It is understood that there is no clear relationship between the concentrations at the observation wells, influenced by human medicine, as caffeine was found in low concentrations of up to 60 ng/l in only one well. This corresponds with the known and comprehensive degradation behaviour of the substance caffeine at near-surface groundwater. Carbamazepine could be verified only sporadically at KKA, but at one location, it was repetitively found in groundwater in low concentrations up to 4.6 ng/l. Carbamazepine is a good tracer at municipal waste water treatment plants, which have a high number of connected inhabitants, but not at domestic waste water plants with few private persons and a high variability of medicine taken.

#### 3.5 Results of the analysed groundwater

The samples taken at all eleven groundwater observation wells over twelve month verified the assumed agricultural load situation in groundwater of the previous project. The nitrogen content of the groundwater was mostly significantly above the threshold of the groundwater directive. This limits nitrate to 50 mg/l and ammonium to 0.5 mg/l. The concentrations of further indicator-parameter as potassium or phosphate are clearly higher than the natural background. This result could be proven with the repetitively samples taken at the temporary groundwater wells. The nutrients clearly indicate an influence of agricultural production of the near-surface groundwater. The results of antibiotic substances show a wide spatial range of heterogeneities.

The both tracer for the influence of wastewater - caffeine and carbamazepine - were found in very difficult proportions at the eleven observation wells. The maximum concentration of caffeine was uniquely at 60 ng/l. At one location carbamazepine was found regularly in groundwater on average 3 ng/l.

At two locations, one in NRW and one in NI, almost continuously high concentrations (> 100 ng/l) of the active substance SMX, also used in human medicine, were measured in groundwater. In August 2013, a maximum of 950 ng/l was measured at the sampling site in NI. The maximum concentration 2014/15 occurred in February 2015 with 234 ng/l. However, also concentrations below 100 ng/l have been measured. This documents a high variance of substance concentration in groundwater at this location within almost three years. SDM was constantly found in low concentrations.

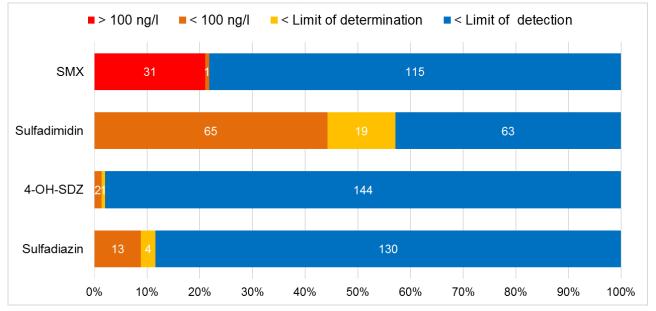
At the second location with a high SMX load (NRW), the concentrations are more constant between 150 ng/l to 300 ng/l. In addition, carbamazepine has been determined in low concentrations and boron, also a tracer for the influence of wastewater, was significantly increased. SDM was found in low concentrations in the groundwater as well.

At further eight locations without detection of SMX, repetitively low concentrations on SDZ and SDM, clearly below 100 ng/l were proven. The values were almost between 10 and 20 ng/l. SDM

was verified more often than SDZ. The maximum concentration of SDM was 69 ng/l and ranks amongst the highest documented concentrations in groundwater in literature (cf. 84 ng/l in Spain, Qian Sui et al. 2015). A transformation product of SDZ was repetitively found in groundwater on several locations. The concentrations of 4-hydroxy sulfadiazine (4-OH-SDZ) reached a peak of 64 ng/l in NI. In NRW a maximum of 90 ng/l was identified.

Figure 8 shows the distribution of four concentration classes for the active substances including the transformation product 4-Hydroxy-Sulfadiazin (4-OH-SDZ). A total of 147 samples were taken at the eleven groundwater observation wells from 2012 until 2015. SDM was the most common substance (57 %). SMX was found at two locations only, but there almost in concentrations > 100 ng/l. SDZ and 4-OH-SDZ were not consistently found at six locations.

Figure 8: Percentages and amount (white numbers) of findings of active substances in groundwater from 2012 until 2015; Limit of detection/Limit of determination [ng/l]: 4-OH-SDZ: 6/15; SMX: 4/10; SDM: 2/4; SDZ: 2/4



At a further location in NI, in 2012 and 2013 very low concentrations of SDM (5 ng/l) and SDZ (10 ng/l) were measured. This was also proved in 2014 and 2015 at the state-wide screening of NLWKN (Germershausen 2015). The influx direction of the groundwater is very variable, causing from a low hydraulic gradient, so the marginal finding could not be associate to a single source.

#### 4 Interpretation

For eight of the eleven locations, a reliable database with information on cultivation of the last years, could be built. This could be reached with the active assistance of the farmers at the parcels of the influx areas, who were providing information through a questionnaire. Generally, the groundwater samples taken at the projects represent substance input of organic fertilisers in the past and do not correspond to the samples of farmyard manure taken at the same time within the project. Due to this time lag, a direct assignment between the concentrations in manure and in groundwater is not possible. To close this time gap, the questionnaires have been evaluated to gain more information about the operational practise of the last years. The farmers declared a mostly stable stock of animal husbandry with some small variations in veterinary medicines administered.

The substance based comparison and interpretation of the input pathways and the findings of the study are drawing mainly a coherent picture with usage at farmers, proof in fertiliser and verification in groundwater. For SDZ at all evaluable locations and for SDM at four of seven locations an uninterrupted input pathway could be detected. In some cases, the substance was found in groundwater, but not at manure and, based on the available data of the farmers, was not used within the last years. It is assumed, that this could be an effect of low concentrations in groundwater caused by existing environmental burdens or an influx from greater distance. Thus, the low concentrations could be classified as diffuse load.

The findings of SDZ and 4-OH-SDZ confirm the assumption, that both substances are bound onto soil particles after application of manure containing the antibiotic residues. They remain there for a longer period but also leak out into groundwater in small quantities (Förster et al. 2009).

At one of the two locations with a long term background of SMX in groundwater, the source could be identified from repetitively tested KKA. The KKA are located at the immediate influx of the observation well and is emitting its water into the groundwater. The small distance between the input source and the observation well is causing a short redemption time of a few weeks to months. A numeric simulation of human medicine intake over pathways of waste water, soil and the unsaturated zone to the near-surface groundwater showed concentrations of the substances, used in human medicine, in comparable dimensions to the concentrations found in groundwater at the nearby observation wells. At the second location the input of SMX was probably caused due to a former leakage at a domestic waste water system. As indicator of waste water, the concentration of the element boron was measured. This was higher than in previous investigations of LANUV NRW. The boron concentrations, which are on a high level in the past years. To clarify the input, further studies should show the decrease of SMX and boron at the observation well, as indicated within the last ten years.

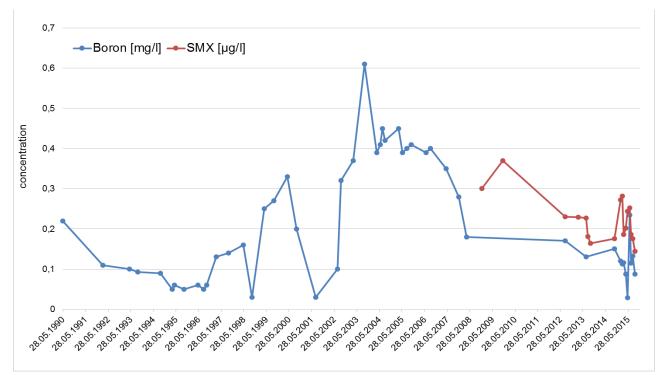


Figure 9: Comparison of the content of boron, measured since 1990, and SMX, measured since 2008 (Data: LANUV), at the location in NRW

It is assumed that the antibiotic substance SDM, founding continuous and long-standing in groundwater, was the result of agricultural application of manure. Since 14 years it will be used exclusively in veterinary medicine and qualify it as tracer for agricultural influence (Jekel & Dott 2013). The identification of SDM and SMX at the same groundwater sample shows a possible exposure of two different input sources, farmyard manure and water emitted from domestic waste water treatment plants.

#### 5 Recommendations

The methodical approach, to actively involve the local farmers at the investigation, was very successful. With their help, most of the input sources of antibiotic substances into groundwater could be verified on a local level. It is an advisable model for future investigations on primary agricultural substance input, to detect continuous intake and an accumulation within the underground. At rural areas, it is important to identify the origins of the substances, which may be also used in human medicine and could be transferred with the waste water. The aim should be, that all causer and the local authorities for agriculture and water management as well as the regulatory authorities would minimise the substance input into the groundwater.

Necessary is the evaluation of all environmental compartments and the complete process of the substance input, from the application in farm to the detection in groundwater. The biotic soil zone is important since here accumulation and degradation processes take place. A suitable model for such investigations could be the BDF in NI. It offers favourable conditions because of a thorough site survey and long-time-data of soil and seepage water. The increased sulfonamide concentrations found here, should furthermore be monitored.

Monitoring of antibiotics in groundwater in Germany is necessary as shown by the results and demanded by BMEL (2015). Regions with high livestock densities should coordinate and standardize their criterions to choose observation wells and parameter transnational (for example within LAWA in coordination with UBA).

It seems necessary to implement further groundwater monitoring programmes on antibiotic substances across the borders of the federal states. Additionally, other environmental compartments like soil and seepage water should be integrated to holistically understand the substance input and its fate.

A German threshold value for antibiotics in groundwater as precautionary principle is considered useful. It should be based on the threshold value for plant protection and biocides of  $0,1 \mu g/l$ . This would provide a clear legal basis for the protection of groundwater (approval / measures). The legal immission protection minimization (precautionary principle) would apply below the threshold. Thus, a monitoring of the environmental development of the pollution level ought to be installed and sustainable strategies in order to reduce the pollution ought to be developed.

#### 6 References

- Balzer, F. & D. Schulz (2015): Umweltbelastende Stoffeinträge aus der Landwirtschaft; Möglichkeiten und Maßnahmen zu ihrer Minderung in der konventionellen Landwirtschaft und im ökologischen Landbau.- Hrsg.: Umweltbundesamt, Fachgebiet I 3.6 Landwirtschaft.
- Balzer, F., Zühlke, S. & S. Hannappel (2015b): Antibiotics In Groundwater Under Locations With High Livestock Density In Germany.- DIPCON Berlin (accepted).
- BMEL (2015): Wege zu einer gesellschaftlich akzeptierten Nutztierhaltung.- Wissenschaftlicher Beirat Agrarpolitik beim Bundesministerium für Ernährung und Landwirtschaft, Berlin.
- Clara, M., O. Gans, F. Humer, S. Weiß & I. Zieritz (2010): Antibiotika im Grundwasser, Sondermessprogramm im Rahmen der Gewässerzustandsüberwachungsverordnung.- Hrsg.: Umweltbundesamt Österreich REP-0258, Wien
- EG (2006): Richtlinie des Europäischen Parlaments und des Rates zum Schutz des Grundwassers vor Verschmutzung und Verschlechterung.- 2006/118/EG, (ABl. L 372 vom 27.12.2006, S. 19, L 53 vom 22.2.2007, S. 30, L 139 vom 31.5.2007, S. 39
- Förster, M., Laabs V., Lamshöft M., Groeneweg J., Zühlke J.S., Spiteller M., Krauss M., Kaupenjohann M. & W. Amelung (2009): Sequestration of manure-applied SDZe in soils.- Environmental Science and Technology 43, 1824-1830.
- Germershausen, L. (2015): Ergebnisse der niedersächsischen Sonderuntersuchungen zu Tierarzneimitteln im Grundwasser.- Vortrag 20. Grundwasser-Workshop NLWKN Ckoppenburg, Oktober 2015, NLWKN, Hannover-Hildesheim (unveröff.)
- GrwV (2010): Verordnung zum Schutz des Grundwassers, Grundwasserverordnung GrwV, Ausfertigungsdatum: 09.11.2010, BGBL. I S. 1513.
- Hannappel, S., Groeneweg, J. & S. Zühlke (2014): Antibiotika und Antiparasitika im Grundwasser unter Standorten mit hoher Viehbesatzdichte.- Texte 27/2014, Umweltforschungsplan des Bundesministeriums für Umwelt, Naturschutz, Bau und Reaktorsicherheit, Forschungskennzahl 3711 23 225, UBA-FB 001897, ISSN 1862-4804, Dessau-Roßlau, März 2014
- Harms, K. S. (2006): Untersuchungen zum Nachweis und Vorkommen von Antibiotika und deren Metaboliten in Schweine-Gülle, Lehrstuhl für Tierhygiene, Department für Tierwissenschaften, Dissertation Technische Universität München.
- Hein, A. (2011): Verbleib und Verhalten von Makrolid- und Sulfonamid-Antibiotika bei der künstlichen Grundwasseranreicherung mit behandeltem Kommunalabwasser.- Schriftenreihe des Institut für Technischen Umweltschutz, Bd. 16, Berlin.
- Hembrock-Heger, A., M. Nießner & R. Reupert (2011): Tierarzneimittel in landwirtschaftlich genutzten Böden und oberflächennahem Grundwasser in NW. Bodenschutz 4, 2011, S. 100-104.
- Höper, H. (2011): Langzeituntersuchungen zum Vorkommen von Tierarzneimitteln in Boden und Sickerwasser in NI. Landesamt für Bergbau, Energie und Geologie, Statusseminar Arzneistoffe in der Umwelt, 07./08.08.2011, Dresden (unveröff.).
- Höper, H. (2016): Langzeituntersuchungen zum Vorkommen von Tierarzneimitteln in Boden und Sickerwasser, Ergebnisse der niedersächsischen Bodendauerbeobachtung.- Expertengespräch Tierarzneimittel in der Umwelt (FKZ 3715 63 4301), 09./10.03.2016, Berlin.
- HYDOR (2016): Ergänzende Untersuchungen zum UBA-Projekt: "Ursachen der Funde von Tierarzneimitteln im Grundwasser (FKZ 3714 23 210)" - Ingenieurleistungen und Probenahme 2015 -

2016.- 2. Zwischenbericht HYDOR Consult GmbH an den Niedersächsischen Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz, BS Cloppenburg, März 2016, Berlin (unveröff.).

- Jechalke, S., Heuer, H., Siemens, J., Amelung, W. & K. Smalla (2014): Fate and effects of veterinary antibiotics in soil.- Trends in Microbiology, 1-10.
- Jekel, M. & W. Dott (2013): Leitfaden Polare organische Spurenstoffe als Indikatoren im anthropogen beeinflussten Wasserkreislauf, Ergebnisse des Querschnittsthemas "Indikatorsubstanzen".- BMBF-Fördermaßname "Risikomanagement von neuen Schadstoffen und Krankheitserregern im Wasserkreislauf" RiSKWa im Auftrag des BMBF.
- Ji, K, Kim, S, Han, S, Seo, J, Lee, S, Park, Y, Choi, K, Kho, YL, Kim, PG & J. Park (2012): Risk assessment of chlortetracycline, oxytetracycline, sulfamethazine, sulfathiazole, and erythromycin in aquatic environment: are the current environmental concentrations safe? Ecotoxicology. Oct 2012, 21(7):2031-50.
- Kim, K. R., Owens, G., Kwon, S. I., So, K. H., Lee, D. B., & Ok, Y. S. (2011): Occurrence and Environmental Fate of Veterinary Antibiotics in the Terrestrial Environment. Water, Air, & Soil Pollution, January 2011, Volume 214, Issue 1, pp 163-174
- LfL (2006): Schweinegülle Quelle für potentiell unerwünschte Stoffe.- Hrsg: Bayerische Landesanstalt für Landwirtschaft und Technische Universität München, Schriftenreihe 12/2006, 5. Kulturlandschaftstag, ISSN 1611-4159.
- OOWV (2014): Grundwasseruntersuchungen 2014 auf Rückstände aus Tierarzneimitteln.- Da-ten des Oldenburgisch-Ostfriesischen Wasserverbandes, Brake (unveröff.).
- OOWV (2015): (Tier-)Arzneimittel, Antibiotika-Rückstände im oberflächennahen Grundwas-ser, Ergebnisbericht 2015.- Autoren: M. Penning & J. Teppema, Brake (unveröff.).
- Ratsak, C., Guhl, B., Zühlke, S. & T. Delschen (2013): Veterinärantibiotikarückstände in Gülle und Gärresten aus NW.- doi:10.1186/2190-4715-25-7, Environmental Sciences Europe 25:7.
- Sattelberger, R., E. Martinez & O. Gans (2005): Veterinärantibiotika in Dünger und Boden.-Hrsg.: Umweltbundesamt Österreich, Berichte 272, Wien.
- Tauchnitz, N., Gildemeister, D. & S. Berkner (2013): Mixtures of veterinary medicinal compounds in manured soils.- Workshop "Pharmaceuticals in Soil, Sludge and Slurry" of the German Federal Environment Agency, 18th June to 19th June 2013, Dessau (unveröff.)
- UMWELTBUNDESAMT & AGES (2015): Humer, F. & Inreiter, N.: Monitoringprogramm von Pharmazeutika und Abwasserindikatoren in Grund- und Trinkwasser. Forschungsprojekt im Auftrag des Bundesministeriums für Gesundheit, Endbericht Juni 2015, ISBN 978-3-902611-97-0, Wien

