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Autor: Müller, Stephan R. / Singer, Heinz / Stoob, Krispin
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Occurrence and fate of antibiotics in manure, soil and water*

Stephan R. Müller, Heinz Singer, Krispin Stoob, Michael Burkhardt, Niccolo Hartmann, Christian Götz, Christian Stamm and Christopher Waul
Swiss Federal Institute for Environmental Science and Technology (EAWAG),
Division Water and Agriculture, Duebendorf, Switzerland

Introduction

Due to the increase of resistant bacteria, the interest in the fate of antibiotics in the environment has strongly increased during the last years. About 50% of the antibiotics administered in Switzerland are used in animal production. The antibiotics are mainly excreted again in unaltered form. Accordingly, a pre-study on sulfonamides and trimethoprim revealed that up to 10 mg/l per compound and up to 30 mg/l for the sum of all measured antibiotics can be found in liquid manure of pigs that received medicated feed (1). Typical application rates of 30–50 m³/ha liquid manure may lead to an input of a few 100 g of antibiotics per ha. This is in the same order of magnitude as the application rate of herbicides, e.g., of atrazine in corn production. Note that atrazine can be found in surface waters up to a few µg/l during the application period in Switzerland (2). This clearly illustrates the importance of also investigating the fate and transport behaviour of sulfonamides in the environment. Therefore, beside the earlier developed analytical method for the quantification of sulfonamides in manure, an online SPE-LC-MS/MS method was developed for water samples, and two field studies were conducted.

Quantification of sulfonamides in natural waters using online SPE-LC-MS/MS

A new method was developed by coupling an automated solid phase extraction (SPE) online with a liquid chromatography tandem mass spectrometer (LC-MS/MS). The online coupling allows the easy, fast, and reliable determination of sulfonamide antibiotics and metabolites in environmental water samples at the low ng/l level. Reliable results were achieved by using isotope labeled sulfonamides as

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internal standards for almost each analyte. Due to the identical behaviour of analytes and internal standards during enrichment and measurement, problems with variable extraction recoveries and ion suppression effects in the MS were eliminated.

The online SPE coupling was developed with commercial available standard equipment. A PAL-Autosampler equipped with two additional switching valves and a diluter was used for the automated enrichment (sample volumes up to 20 ml) and for the elution from the OASIS HLB enrichment column. The elution was performed with a 1:1 mixture of methanol and water with 0.1 % formic acid (pH=2.4). By pumping a 10 mol/l ammonia acetate (pH=7) solution to the eluted fraction before the separation column, the methanol concentration was decreased to less than 50 ml/l and the analytes could be trapped and separated on the analytical column (C18 Nucleodur). The detection and quantification of sulfonamides in the MS/MS system were done in the Selected Reaction Monitoring (SRM) mode. The validation data for the method are summarized in Table 1.

Table 1
Method validation data

<i>compound</i>	<i>ion suppression</i> ¹	<i>SPE recovery</i> ¹	<i>reproducibility</i> ²	<i>limit of quantification</i> ³
Sulfadiazine	20 %	91 %	3 %	10 ng/l
Sulfathiazole	35 %	79 %	1 %	25 ng/l
Acetylsulfathiazole	4 %	86 %	2 %	25 ng/l
Sulfamethazine	25 %	83 %	1 %	10 ng/l
Sulfamethoxazole	23 %	74 %	3 %	25 ng/l
Acetylsulfamethoxazole	13 %	88 %	9 %	25 ng/l
Sulfadimethoxine	6 %	84 %	1 %	10 ng/l

¹in river water; ²% RSD (n=2); ³in nanopure water

With the developed online-SPE-LC-MS/MS system it was possible to enrich, measure and quantify simultaneously the following sulfonamides and metabolites with a minimum of sample preparation during a 30-minute-run: sulfadiazine*, sulfathiazole*, sulfamethazine*, sulfamethoxazole*, sulfadimethoxine*, acetylsulfadiazine, acetylsulfathiazole*, acetylsulfamethazine, acetylsulfamethoxazole*, acetylsulfadimethoxine (* isotope labelled compounds available). For illustrative purpose a chromatogram of a sulfonamide standard solution is shown in Figure 1. Measurements of already more than fifty field samples have demonstrated the robustness of the developed online-system during routine operation.

Are sulfonamides transported into surface water?

In a field study in spring/summer 2003, liquid manure from a pig farm containing sulfamethazine was applied on two grasslands (each area 0.4 ha). Additionally, we spiked the manure for one field with sulfamethoxazole and for the other with sulfadimethoxine.

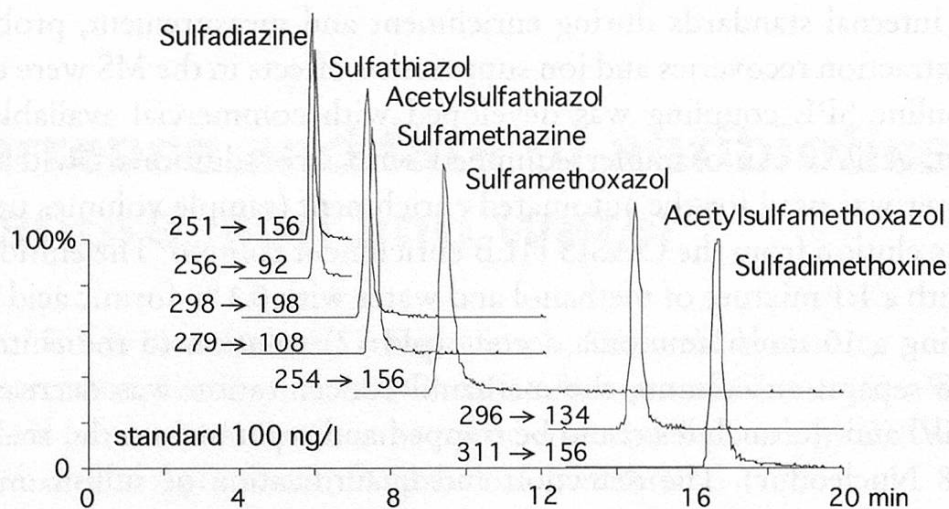


Figure 1 LC-MS/MS chromatogramm of a sulfonamides standard solution

After application, soil samples of the topsoil (5 cm depth) were collected at ten different days to determine the field dissipation rate. The ground water table was monitored with five piezometers along a transect of the two fields. Furthermore, soil water dynamic was monitored with TDR-probes and tensiometers every hour. The weather conditions were recorded by a meteorological station every ten minutes. In the nearby brook, we measured the water temperature, electrical conductivity and the discharge in five-minute-intervals. Flow proportional water samples were taken using an automatic sampling station.

Surface water samples were quantified with the above described analytical method. Soil extraction will be done by accelerated solvent extraction using buffered water (pH 9) as extraction solvent. This method is currently being developed.

First results show a dynamic input of sulfonamide antibiotics into the brook following the water discharge. Concentrations of up to 4000 ng/l were measured during the first rain event directly after application. The preliminary results show that sulfonamide antibiotics can reach surface waters and that system properties influence the behaviour of the compounds.

Factors influencing the transport into surface water

The second study aimed at investigating factors affecting the surface and subsurface transport of sulfonamides under different experimental conditions: varying irrigation amounts (30 and 60 mm), sulfonamide application with and without manure and varying manure contact time between one or three days. The experiment was conducted on a grassland site on twelve sloped field plots with an area of 2 m² and a slope between 6 and 9%. We used liquid pig manure containing sulfamethazine, which we additionally spiked with two other sulfonamides (sulfadi-

azine and sulfathiazole). Further, the herbicide atrazine, the conservative water tracer bromide and the dye tracer Brilliant Blue were added. After the application of liquid manure on selected plots (corresponding to 30 m³/ha) we irrigated deionized water with an automatic sprinkler. We compared the runoff and infiltration dynamic of sulfonamides with the different tracers by sampling the surface runoff and soil.

Interestingly, the manure increased the surface runoff by a factor of four to six compared to plots without manure. Furthermore, on manured plots the concentrations in the runoff of all compounds were also higher. Accordingly, the load was between five and ten times higher on manured plots compared to plots without and different for each substance. Moreover, after three days contact time the load was higher compared to one day.

Based on the varying loads of the different substances chemical properties seem to influence the total mass of substances mobilised. Further, after analyzing the soil samples we will get information about the fate in soils and the leaching potential to groundwater. Note, that the results of both field studies are preliminary and the sample measurements and their interpretation is still ongoing.

Summary

Sulfonamides are important veterinary antibiotics used in livestock production, e.g. for pig farming. Between 0.1 and 30 mg/l of sulfonamides were measured in liquid manure of pigs that received medicated feed. The typical manure application rates of 30–50 m³/ha may lead to an input of a few 100 g/ha. This illustrates the importance of understanding the environmental fate and transport behaviour of sulfonamides. Therefore, an online LC-MS/MS method was developed for water samples, and two field studies were conducted. First results show a dynamic input of sulfonamide antibiotics into the brook following the water discharge. Highest concentrations were measured during the first rain event directly after application. These results showed that a small part of the sulfonamides might reach surface waters. The transport seems to be enhanced due to the temporary sealing of the soil surface by the manure.

Zusammenfassung

Sulfonamide sind wichtige Antibiotika, welche in der Tierproduktion, z.B. in der Schweinemast, eingesetzt werden. Zwischen 0,1 und 30 mg/l Sulfonamide konnten in der Gülle von Schweinen, welche aus tiergesundheitlichen Gründen mit Medizinalfutter behandelt worden waren, mit einer LC-MS/MS-Methode nachgewiesen werden. Beim Ausbringen der Gülle gelangen die Sulfonamide auf Kulturland. Bei einer typischen Güllemenige von 30–50 m³/ha kann dies zu einem Austrag von einigen 100 g/ha führen. Dies zeigt, dass es wichtig ist, den Stofffluss und das Abbauverhalten der Sulfonamide in der Umwelt zu verstehen. Um den Transport der Antibiotika in die Gewässer zu verfolgen, sowie das Vorkommen und Verhalten der Antibiotika in den Flüssen und Seen zu bestimmen, wurden an der

EAWAG eine neue analytische Methode (LC-MS/MS) entwickelt und zwei Feldstudien durchgeführt. Dabei konnte festgestellt werden, dass Sulfonamide kurz nach der Gülle-Applikation auf Grasland während Niederschlagsereignissen in Bäche gelangen können. Dieser Prozess wird offenbar durch die kurzfristige Bodenverschlammung durch die Gülle verstärkt.

Résumé

Les sulfonamides sont des antibiotiques importants utilisés dans la production de bétail, notamment dans les porcheries. Entre 0.1 et 30 mg/l de sulfonamides peuvent être mesurés dans le purin de porcs ayant reçu ces médicaments. L'application normale du purin sur les champs est de 30–50 m³/ha ce qui peut conduire à une entrée de quelques 100 g/ha dans l'environnement. Ceci illustre l'importance d'une meilleure compréhension du devenir environnemental des sulfonamides, notamment du transport de ces substances dans l'environnement. Une méthode online avec un LC-MS/MS a donc été développée pour analyser les échantillons d'eau et deux études sur le terrain ont été menées. Les premiers résultats montrent que les concentrations en sulfonamides dans les ruisseaux suivent la dynamique du débit. Les plus hautes concentrations ont été mesurées lors du premier évènement pluvieux après l'application. Ces résultats ont également montré qu'une petite partie des sulfonamides est susceptible de rejoindre les eaux de surface.

Key words

Transport behaviour, antibiotics, manure, environment, quantification, sulfonamides

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Address of correspondent: Dr. Stephan R. Müller, Swiss Federal Institute for Environmental Technology and Science (EAWAG), P.O. Box 611, Ueberlandstrasse 133, CH-8600 Dübendorf, stephan.mueller@eawag.ch