

VETERINARY DRUGS IN THE ENVIRONMENT: OCCURENCE OF SULFONAMIDES IN GROUNDWATER

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The occurrence of antibiotics in the environment has become a subject of major concern among scientists due to the potential spread and maintenance of bacterial resistance (Halling-Sorensen et al., 1998). Amongst them, the family of sulfonamides is one of the most widely used in human and especially in veterinary medicine. They have been detected in all kind of water matrices (Díaz-Cruz et al., 2008), not only because of their high consumption rates, but also to their amphoteric properties, rather poor chelating ability and low sorption to soils tendency. Other reasons for greater occurrence may be due to their relatively low elimination efficiency during sewage treatment procedures and to the increase in the number of confined animal feeding operations, which often lack proper waste management practices. Furthermore, the extensive use of manure as fertilizer on agriculture can be a significant source of diffuse contamination of ground waters by these compounds.

Sulfonamides are metabolized to a considerable and varying extent in the organism, (i.e. by acetylation and hydroxylation) and these metabolites, together with the not assimilated parent substances, are excreted mainly via urine and faeces. Therefore, very small amounts of these substances are being continuously introduced in the aquatic environment, and concentrations that had previously been considered as harmless are leading to the emergence of antibiotic resistant bacteria strains. The application of manure from treated animals in crop soils can also constitute a main entrance pathway for these antibiotics in the natural media.

In the present work the occurrence of 20 selected sulfonamides, both for veterinary and human medicine use and including some of their metabolites, were investigated in groundwater samples taken from surveillance and operational monitoring networks located in two groundwater bodies, Plana de Vic and La Selva, in the northwest of Catalonia (Spain). Both of them include areas designated as nitrate vulnerable zones under the provisions of Directive 91/676/CEE (“nitrate directive”) and are at risk of not reaching WFD environmental objectives in 2015.

The samples were analyzed by a highly selective and sensitive analytical method based on on-line solid phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS). This new analytical method developed is fully automated and, in addition, requires smaller sample volumes, only 40 mL, compared to

conventional off-line SPE methods that require between 100 and 500 mL of ground water for each analysis.

For quantitative analysis, and in order to get enough IPs to achieve analyte confirmation (Commission Decision 93/256/EEC), data acquisition was performed in selected reaction monitoring (SRM) mode, recording the transitions between the precursor ion and the two most abundant product ions for each target analyte. Quantification, based on peak areas, was done by the internal standard (IS) method, using a deuterated sulfonamide. The performance of the method was evaluated through estimation of the linearity, sensitivity, repeatability, recovery, and matrix effects of the method. Five to seven point-calibration curves were built (matrix matched) with a concentration ranging from 0.01 to 1000 ng/L. The developed method allowed detecting concentration values as low as 0.02 ng/L.

Results indicated that sulfadimethoxine, sulfamethazine and the N⁴-acetylated metabolite of sulfamethazine were the three sulfonamides more frequently detected and at the highest concentrations in both sampling areas, with concentrations in the range 0.1 - 228 ng/L. Nearly all the target sulfonamides could be detected in most of the samples as well, although at lower concentrations.

The relationship between the occurrence of the sulfonamides and nitrates coming from organic fertilizers is also being investigated, in order to assess their common origin.

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