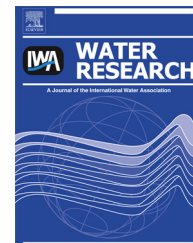




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Emerging pesticide metabolites in groundwater and surface water as determined by the application of a multimethod for 150 pesticide metabolites

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ABSTRACT

A recently developed multimethod for the determination of 150 pesticide metabolites was exemplarily applied to 58 samples of groundwater and surface water. 37 of these metabolites were detected in at least two samples with a concentration ≥ 0.025 $\mu\text{g/L}$. The detected metabolites were ranked according to their concentration and frequency of detection. Findings are clearly dominated by metabolites of chloroacetanilide herbicides, but metabolites of sulfonylurea and thiocarbamate herbicides and other herbicides (dichlobenil) together with metabolites of some fungicides (tolylfluanid, chlorothalonil, trifloxystrobin) were also prominent. A number of 17 of the ranked metabolites are denoted as emerging metabolites because no reports on their previous detection in groundwater or surface water were found. Most of them, however, were correctly predicted to occur in the summary reports of the European pesticide approval process. Median total concentrations of the analysed pesticide metabolites summed up to 0.62 $\mu\text{g/L}$ in groundwater and 0.33 $\mu\text{g/L}$ in surface waters. While the concentration of the individual metabolites is usually low (< 0.1 $\mu\text{g/L}$) the diversity of metabolites found in one sample can be large; between two and six metabolites were detected most frequently (maximum of 12 metabolites). Runoff from urban surfaces was investigated in this study and also here previously undetected pesticide (biocide) metabolites were detected. The emerging pesticide metabolites detected in environmental water samples in this study require more extended monitoring.

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1. Introduction

While groundwater is regularly monitored for the concentration of a large number of pesticides, the number of pesticide metabolites covered by such monitorings is comparatively limited. Traditionally a number of dealkylated and hydroxylated metabolites of the chloro-s-

triazines is considered or ethanesulfonic and oxanilic acid degradates of chloroacetanilide herbicides (Scribner et al., 2000). Furthermore, 2,6-dichlorobenzamide (BAM) from dichlobenil (Bjorklund et al., 2011; Schipper et al., 2008) or aminomethyl phosphonic acid (AMPA) from glyphosate (Schipper et al., 2008) may be monitored in groundwaters.

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In several cases in the past the occurrence of elevated concentrations of a pesticide metabolite gave rise to restrictions in use or to the complete withdrawal of the respective products from the market in European countries. In Germany this was the case for atrazine in 1990 and for dichlobenil in 2001. As a consequence groundwater concentrations of the respective metabolites decreased again, as found for desethylatrazine in Germany since the mid 1990s.

For several reasons the number of pesticide metabolites included in monitoring programmes is limited: (a) the need to limit the analytical effort, (b) the fact that the drinking water limit of 0.1 µg/L applies to relevant metabolites only, (c) the lack of appropriate analytical methods/data for further metabolites, and (d) the lack of indications that other metabolites could be of interest. Obviously the latter two points are closely connected in the way that information on the occurrence of other metabolites was hardly obtained as long as methods for their determination were unavailable.

Consequently the latest findings of pesticide metabolites in groundwater have been unexpected and made unintentionally, and they were related to parent pesticides that had been in use for several decades already. Among these metabolites are desphenyl chloridazon and methylphenyl chloridazon of the herbicide chloridazon (Weber et al., 2007; Buttiglieri et al., 2009) and N,N-dimethylsulfamide (DMS) formed from the fungicide tolylfluanid (Schmidt and Brauch, 2008). This metabolite has been shown to be a source for N-nitrosodimethylamine formation upon ozonation during drinking water treatment (Schmidt and Brauch, 2008). Since their determination a few years ago these three metabolites have been included in some groundwater monitorings and these metabolites are often found more frequently and at higher concentration than traditional metabolites such as desethyl atrazine (e.g. LUBW, 2011; Loos et al., 2010). The elevated groundwater concentrations of DMS led to restrictions in the use of the parent pesticides tolylfluanid by the German authorities in 2007.

These cases of unintentional discovery of previously unrecognized pesticide metabolites in groundwaters gave rise to the question, whether further pesticide metabolites of similar importance have remained undiscovered. To allow an answer to this question, we have recently developed a multimethod for the determination of 150 pesticide metabolites from groundwater and surface water (Reemtsma et al., 2013). This method avoids extraction of water samples but relies on the direct injection into the LC–MS/MS system. The selection of analytes to be included into that method was based on a variety of data sources, from data on previous findings in the environment to information provided in the respective pesticide approval processes (Tab. S1). The broader application of this method may give answer to several questions:

Are further so-far undetected pesticides metabolites occurring in higher frequency in groundwater or surface water? Even though most of the 150 pesticide metabolites included in the new multimethod are so-called ‘non-relevant’ metabolites for which the European drinking water limit of 0.1 µg/L does not apply (European Commission, 1998), the occurrence of pesticide metabolites in groundwater or surface water should not remain unrecognized. To ensure drinking water hygiene authorities and drinking water suppliers

should be aware of organic contaminants in the raw waters used for drinking water production.

Are the concentrations of metabolites found in groundwater and surface water in accordance (i.e. below) to the expected concentrations derived in the pesticide approval process? An answer to this question would allow to judge on whether or not assumptions and model calculations made in pesticide approval procedures do indeed reflect ‘realistic worst case’ scenarios and are suitable to ensure that pesticides do ‘not have any unacceptable effect on the environment’ as it is required in the EU regulation on pesticide approval of 2009 (European Union, 2009).

Here we report first data of the application of the multimethod for pesticide metabolites (Reemtsma et al., 2013) to groundwaters and surface waters. Since the number of samples in this study is limited to 58, the data are not representative and, thus, not suited to allow a reliable answer to the two questions above. However these data provide first indication, which of the 150 metabolites may emerge in groundwater or surface water and which previously unrecognized metabolites may be of top priority for inclusion into future monitoring programmes.

2. Materials and methods

2.1. Standards

All metabolite standards were of certified quality and were either commercially available or were provided by the approval holders of the respective pesticides. Details on the analytes included, the analytical method, detection conditions for the 150 individual metabolites and on method performance have been published elsewhere (Reemtsma et al., 2013; and Supplementary information therein).

2.2. Samples

A total number of 58 samples was analysed: samples of ground and surface water were received from the State Institute for Environment, Measurements and Nature Conservation Baden-Wuerttemberg (Karlsruhe, Germany) and the State Institute for Nature, Environment and Consumer Protection North Rhine Westfalia (Duesseldorf, Germany) in October 2009. A part of the groundwater wells were selected based on the previous determination of pesticide metabolites. Additionally samples of surface runoff from impervious urban areas were received from Berliner Wasser-Betriebe (Berlin, Germany). All samples were transported and kept cooled (approx 7 °C). Prior to analysis samples were filtered over 0.45 µm membrane syringe filters (regenerated cellulose, 4 mm diameter).

2.3. Liquid chromatography–mass spectrometry analysis

The multimethod is described in detail elsewhere (Reemtsma et al., 2013). It is based on liquid chromatography–electrospray ionization–tandem mass spectrometry (LC–MS/MS) with detection by multiple reaction monitoring (MRM) in positive

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