Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Measurement and modeling of bentazone in the river Main (Germany) originating from point and non-point sources

M. Bach[a,*], M. Letzel[b], U. Kaul[b], S. Forstner[b], G. Metzner[b], J. Klasmeier[c], S. Reichenberger[a], H.G. Frede[a]

[a] Institute of Resources Management, University Giessen, Heinrich-Buff-Ring 26, 35392 Giessen, Germany
[b] Bavarian Environmental Agency, Lazarettstr. 67, 80636 München, Germany
[c] Institute of Environmental Systems Research, University Osnabrück, Barbarastr. 12, 49076 Osnabrück, Germany

ARTICLE INFO

Article history:
Received 12 June 2009
Received in revised form
9 February 2010
Accepted 10 April 2010
Available online 24 April 2010

Keywords:
Bentazone
Model DRIPS
Non-point source
Pesticide
Point source
River load

ABSTRACT

A Water Framework Directive pilot project combines measured data and model approaches to calculate fluxes and mass balance of the pesticide bentazone in an 81 km section of the river Main (Germany). During the study period (six weeks in spring 2004) the observed bentazone inflow and outflow in the river section amounted to 52.8 and 53.1 kg, respectively; the maximum concentrations reached 220 and 290 ng l^{-1}. Based on sampling of seven sewage treatment plants a specific loss of 0.87 g bentazone per farm was calculated. Extrapolation to the entire sub-basin results in 2.6 kg bentazone in total as point source contribution from farms. Diffuse input into the surface water network occurred after an intensive rainfall event on May 7th. Total bentazone load was simulated with the pesticide emission model DRIPS to be 23.2 kg. One third of this load was estimated to be degraded by photolysis before reaching the main waterway, the river Main. The ATV water quality model was applied to predict the concentration profile of bentazone in river Main between Schweinfurt and Würzburg with reasonable results. The difference between total measured and modeled fluxes amounted to 1.5 kg corresponding to 2% of the overall input. The combined approach of monitoring and modeling appears to be a valuable strategy to quantify the relevance of point and non-point sources and to focus effective mitigation measures to the most relevant origins within a river basin.

1. Introduction

Pesticides are perceived to pose a severe risk to human health and environmental contamination of soil, water, and air affecting acute and chronic toxicity to humans and aquatic biocoenosis, respectively. With respect to human health the EU Drinking Water Directive (EU 98/83/EC) sets the standard for the concentration of a pesticide compound in drinking water to 0.1 μg l^{-1}. A survey among waterworks in Germany in 2006 ranks bentazone as number three of the most relevant pesticides (after diuron and isoproturon) causing problems in drinking water supply from bank filtration (Sturm et al., 2007). To protect the drinking water supply from bank filtration along the river Rhine the International Commission for the Protection of the Rhine (ICPR) proposes a concentration limit of 0.1 μg l^{-1} as target value for bentazone. The EC Water Framework Directive (WFD) currently specifies no environmental quality standard for

* *Corresponding author*. Tel.: +49 641 9937375; fax: +49 641 9937389.
E-mail address: martin.bach@umwelt.uni-giessen.de (M. Bach).
0043-1354/$ – see front matter
doi:10.1016/j.watres.2010.04.010

bentazone, but the substance is subject to review for possible identification as priority substance according to WFD (European Parliament, 2007).

Bentazone is frequently detected in considerable concentrations in surface waters in several European countries. With detection frequencies of more than 30% of all samples (period 1985–2005), the long-term Swedish national water quality monitoring program ranks bentazone as the most commonly found substance in watercourses. However, there is a substantial decrease in the frequency of detection of concentrations above 0.1 $\mu g\ l^{-1}$ for the interval 1998–2005 compared to 1985–1991 (Törnquist et al., 2007). In the Belgian river Dyle watershed (ca 4580 km^2) the substance was detected at eight sampling sites mainly during and shortly after the application periods in spring 1998 and 1999 (Beernaerts et al., 2003). Among other pesticides bentazone was reported as one of the major pollutants in the Ebro river (Spain) estuary waters in 1993–1994 (Barcelo et al., 1996). Comoretto et al. (2007) linked the occurrence of bentazone in lagoons of the Rhone River (France) with post-emergence application of herbicides in nearby paddy fields.

The LAWA (working group of Federal states) network of ca 130 monitoring sites depicts the overall situation of surface water quality in Germany. According to this national monitoring program bentazone exceeded the 0.1 $\mu g\ l^{-1}$ drinking water standard up to 10% of the monitoring sites at least one time during the period 2002–2004 (BMU, 2006). In the German river Selz, bentazone was continuously detected nearly all over the year in 1997 and 1998 with a 14-day peak concentration above 2 $\mu g\ l^{-1}$ (Augustin et al., 2002). In Bavarian rivers, bentazone concentrations exceeded the detection limit of 0.05 $\mu g\ l^{-1}$ in 17 of 72 samples in 2002, with concentrations being partly above the drinking water standard (LfW, 2003).

Due to restricted monitoring capacities the German water authorities permanently lack information on the relevance of different sources of pesticide input as well as the temporal variability of pesticide occurrence in river basins. However, this knowledge is essential to design appropriate mitigation measures and to implement effective management plans. Holvoet et al. (2007) gave a state-of-the-art of the current knowledge related to the occurrence and modeling of pesticides in surface waters with an emphasis on sources and transport routes that contribute most to the pesticide loads found in river systems.

This was the background of a research project of the Bavarian Environmental Agency in 2004 which uses information from monitoring and modeling data to set up the mass balance for a selected pesticide in a larger stream. The methodological aspect of the study focuses on the capability of a combined approach to quantify the loads and the entry pathways of contaminants into a surface water body based on a combination of measured data with modeling results, exemplarily for a selected part of the river Main (Germany) which is known to receive large impacts from agricultural activities (Letzel, 2008). The approach considers both, point as well as non-point sources as main contributors of pesticides into the surface water network, which is not often reported as a hypothesis in water quality studies (Müller et al., 2002). Both sources deliver input data for the consecutive modeling of the transport and the turnover process of the substance in the stream water body. While bentazone is known to be sensitive to photolytic decay this process has to be regarded explicitly.

Point source input caused by sprayer leakage or spills from compound storage and handling on paved farmyards connected to a sewage treatment plant (STP) may contribute a serious fraction to the total pesticide river load (Carter, 2000; Gerecke et al., 2002). To a large extent, this load is emitted into the sewer system and transported to the respective STPs. In earlier studies up to 90% of the pesticide input into river basins in Germany was attributed to point sources (Bach et al., 2000), which was essentially ascribed to inappropriate handling of pesticide agents (Jaecken and Debaer, 2005). Due to the expected high relevance of this source of input it was decided for the study to measure bentazone directly in the effluents of nine STPs in the investigated area. Non-point emissions resulting from surface runoff were estimated using the model tool DRIPS (Drainage, Runoff, and spray drift Input of Pesticides into Surface waters), a semi-empirical approach adopted to the situation in Germany (Bach et al., 2001a). This information finally is used as input data to simulate the concentration profile along the river Main with the ATV water quality model. As a control and model quality check the concentration of bentazone was determined during the application period in spring 2004 at two sampling sites in the river Main representing start and end points of the study area.

2. Substance properties

Bentazone is a herbicide commonly used in German agriculture for post-emergence application in spring cereal and corn cropping. Bentazone is a weak acid with a pK_a value of 3.28. In aqueous solutions it is thus almost exclusively present as an anion explaining the relatively high water solubility and the low octanol/water partitioning coefficient (K_{ow}) at neutral pH. Sorption to soil is also low. The neutral molecule has a low vapor pressure indicating a negligible tendency for volatilization from water. Microbiological degradation in soil is moderate with observed DT_{50} values from 4 to 21 days (EU Commission, 2000). In an aqueous solution, the substance is stable against hydrolysis, but prone to photolytic decomposition (Huber and Otto, 1994; see also Section 5.2). Since no information about biodegradation of bentazone in surface water and in sewage treatment plants was available, this process was investigated in a laboratory experiment (see Section 4). Table 1 summarizes available substance data.

According to the Agricultural Census in 2004 within the selected part of the Main catchment 16,900 ha is cropped with spring cereals and an additional 1850 ha with maize. These areas form the potential land area to be treated with bentazone. According to an expert judgment of the regional plant protection advisory personnel approximately 20% of the potential fields were treated with bentazone-containing products. The recommended application rate is 1 kg bentazone per hectare. Thus, the absolute amount of bentazone sprayed onto the arable land of the sub-basin in spring 2004 can be estimated to be roughly 3750 kg.