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Comparing ecotoxicological standards of plant protection products potentially toxic to groundwater life with their measured and modelled concentrations

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ABSTRACT

Trigger values (TVs) for groundwater ecosystems in the European Union (EU), as elsewhere, are not based on toxicity data for the biota of that ecosystem. At present, very few toxicity tests have been conducted with groundwater organisms so the true sensitivity of groundwater ecosystems is largely unknown. In a previous published study, we set groundwater TVs for all plant protection products (PPPs) allowed for use at the time of the study based on toxicity data for surface water organisms as surrogates for groundwater organisms and calculated TVs lower than the current EU standard of 0.1 μg/L for 16 PPPs. This thus reveals that the effect assessment of these PPPs may not be fully adequate, but would still only indicate risk if the (expected) concentrations of these PPPs are greater than their calculated TVs. The present study was therefore initiated to evaluate whether predicted and measured concentrations of these PPPs are higher than the previously calculated TVs lower than 0.1 μg/L. To this end, predicted environmental concentrations (PECs) were calculated using the PELMO and SCI-GROW models that are currently used for this purpose in the EU and USA, respectively, and measured concentrations (MECs) were obtained from the open literature. In addition, the empirical PERPEST model was used to assess the severity and probability of effects that may be expected at these concentrations on taxonomic groups known to be well represented in groundwater ecosystems. In addition, only for dimethoate a PEC greater than 0.1 μg/L was calculated. However, when considering concentrations actually measured in the field, 99.7% showed risk quotients (RQ, as MEC/TV) values higher than 1 and 36.7% even higher than 100. Future field monitoring studies are needed to validate and eventually calibrate the way PEC values are currently calculated with the different models and scenarios currently in use. Such studies would also aid in the question to what extent the high MEC values may be attributed to diffuse or point-source pollution.

1. Introduction

Groundwater has long been considered as an extreme environment inhabited by only a few specialized species. Up to the 1980s, the subsurface was even generally considered to be sterile (Gibert, 2001). In the past decades, however, research into groundwater biodiversity has revealed that groundwater environments harbour diverse communities of animals (e.g., Gibert et al. (1994), Galassi et al. (2009)). Many authors subsequently started to dispute groundwater legislation for only considering groundwater as a source of drinking water and not as an ecosystem (e.g., Notenboom (2001), Daam et al. (2010)). In the EU, this was acknowledged with the implementation of a new Groundwater Directive (GWD) in 2006, which states in recital 20: "Research should be conducted in order to provide better criteria for ensuring groundwater ecosystem quality and protection" (EC (European Commission), 2006). The GWD maintained the EU-wide groundwater quality standards of 0.1 μg/L for any individual compound and 0.5 μg/L for the sum of all individual pesticides as was laid down in the "old" Groundwater Directive (80/68/EEC) (EC (European Commission), 1980). These trigger values relate to the contemporary detection limits for pesticides, and hence lack any ecotoxicological base. What is new is that if these groundwater quality standards are considered not to be adequate for achieving the environmental objectives as set out in the Water Framework Directive (2000/60/EC) (EC (European Commission), 2000), more stringent threshold values (TV) have to be established by Member States (MS), in which local or regional conditions should also be taken into account (EC (European Commission), 2006).

Daam et al. (2010) set groundwater TVs based on ecotoxicological data for all PPPs allowed for use at that time in the EU. In the almost complete lack of data for groundwater organisms, they used data for surface water taxa known to be well represented in groundwater as surrogates. Three different approaches were used: (i) a "first-tier" approach, using toxicity data for the crustacean

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Daphnia magna and the bacterium *Vibrio fischeri* since crustaceans and bacteria have been reported to be the most diversified, dominant and fundamental components of groundwater ecosystems, respectively (e.g., Notenboom (2001); (ii) species sensitivity distributions (SSDs), constructed with toxicity data of surrogate surface water organisms for the truncated groundwater diversity in accordance with Hose (2005); (iii) the case-base model PERPEST (Van den Brink et al., 2002). Although the trigger value of 0.1 μg/L appeared to be sufficiently protective for the majority of pesticides, TVs lower than 0.1 μg/L were calculated for 16 PPPs, most of which have an insecticidal mode of action. This thus reveals that the effect assessment of these PPPs may not be fully adequate, but would still only indicate risk if the (expected) concentrations of these PPPs are greater than their calculated TVs.

In the present study, the TVs for the PPPs for which Daam et al. (2010) calculated a TV lower than 0.1 μg/L were compared with their expected and measured concentrations in groundwater. To this end, predicted environmental concentrations (PECs) were calculated using the models PELMO, one of the FOCUS (FOrum for Co-ordination of pesticide fate models and their Use) models as currently used in the PPP registration procedure in the EU, and SCI-GROW (Screening Concentration In GROundWater), a screening model frequently used in the USA for this purpose. In addition, measured environmental concentrations (MECs) of these PPPs were obtained from the open literature. Subsequently, the PECs and MECs were compared with the TVs as calculated in Daam et al. (2010) to evaluate whether actual risks are likely to occur for these PPPs. Where possible, species sensitivity distributions (SSDs) and the empirical PERPEST model were used to assess the severity and probability of effects that may be expected at the calculated and measured concentrations. Ultimately, this was aimed at evaluating whether the previously calculated TVs lower than 0.1 μg/L may potentially lead to risks for groundwater life under the current EU legislation.

2. Materials and methods

2.1. PELMO and SCI-GROW simulated PPP concentrations

In the lower risk assessment of PPPs before registration in the EU (Regulation (EC) No 1107/2009; EC (European Commission), 2009) a number of mathematical models are used to assess the fate of pesticides in the different environmental compartments ((FOCUS) Forum for the Co-ordination of Pesticide Fate Models and Their Use, 2000, 2009). For groundwater, four different models are currently used for this end: (i) the pesticide leaching model (PELMO), (ii) the pesticide emission assessment at regional and local scales model (PEARL), (iii) the pesticide root zone model (PRZM), and (iv) the macropore flow model (MACRO). In the present study, PELMO was chosen since this model was used for three out of five compounds for which previous PEC calculations were available for groundwater from published draft assessment reports (DARs; http://dar.efsa.europa.eu/dar-web/provision), enabling a comparison of our simulations with those made in the DARs. Furthermore, these three PPPs included dimethoate, the only PPP for which a PEC greater than 0.1 μg/L was reported in these five DARs.

The simulation model FOCUS PELMO 4.4.3 (Carsel et al., 1984) was used to estimate the PECs for the nine realistic worst-case scenarios as set by (FOCUS) Forum for the Co-ordination of Pesticide Fate Models and Their Use, (2000) as a realistic worst-case Tier-1 exposure assessment to represent agriculture across Europe. Using these scenarios, PECs were calculated for all representative uses of the PPPs in South and North Europe, as indicated in the DAR reports, EU review reports, and/or reasoned opinions on MRL modifications as published by EFSA (European Food Safety Authority; Table 1). For the simulations, worst-case values were used, i.e. highest application rate and shortest interval between applications. In order to calculate the amount of the PPP that actually reaches the soil surface after application, the dose rates were corrected for the amount of crop interception. Interception values for the different crops and growth stages were used according to (FOCUS) Forum for the Co-ordination of Pesticide Fate Models and Their Use, (2000, 2009).

The simulation model PELMO 4.4.3 contains a number of defined crop scenarios. However, no respective crop scenarios exist for olives and orchards within the FOCUS models. In these cases, a crop scenario that was considered most suitable for the missing crop was chosen based on similarity in cultivable area (location), root depth, leaf area index (LAI), and time between planting and harvest. In this way, citrus was considered to be the most suitable crop scenario for olives and the apple scenario for orchards. To calculate the application dates for each crop scenario, the harvest date as provided in (FOCUS) Forum for the Co-ordination of Pesticide Fate Models and Their Use, (2000, 2009) and the shortest interval between the applications and security interval as described in the representative uses were used. Values for the other input parameters were also selected from DAR and EU review reports (Table 1). For a number of input parameters (e.g., diffusion coefficients), substance specific data were not available. In these cases, default values as recommended by the FOCUS group ((FOCUS) Forum for the Co-ordination of Pesticide Fate Models and Their Use, 2000, 2009) were used. The simulation set-up and the output processing followed EU procedures ((FOCUS) Forum for the Co-ordination of Pesticide Fate Models and Their Use, 2000), i.e. a simulation period of 26 years, in which the first 6 years are used as a warming-up period in order to minimize the influence of the initial conditions, and the last 20 years are used as output. The yearly average pesticide flux concentration in leachate at 1 m depth was calculated and the 80th-percentile concentration (i.e. the year with the fourth largest average leachate concentration) was identified as the target output to be predicted by the meta-model.

SCI-GROW (Screening Concentration In GROundWater; available via http://www.epa.gov/oppefed1/models/water/#scigrow) is the model used by the US-EPA (United States Environmental Protection Agency) in the initial tier screening of pesticides in groundwater. This model provides an estimate of likely groundwater concentrations at the maximum allowable use rate for areas with groundwater systems that are exceptionally vulnerable to contamination. In most cases, a large majority of the use areas will have groundwater that is less vulnerable to contamination than the areas used to derive the SCI-GROW estimate. The model estimation procedure can't currently be adjusted (e.g., divided by a factor) to estimate a more realistic exposure level for groundwater that is not especially vulnerable to contamination ((US-EPA) United States Environmental Protection Agency, 2007). Version 2.3 of the SCI-GROW of the model was used to estimate the concentrations of the PPPs under study. This enabled a comparison between PECs calculated through the initial tiers of the registration procedures of the EU and USA, the more as the input data of the SCI-GROW simulations (application rate, number of applications, Koc, and soil DT50) were also selected from the DAR and EU review reports (Table 1).

2.2. Trigger value calculations using the first-tier and SSD approach

The trigger values (TVs) below which no effects on groundwater life is expected that were used in the present study were those as calculated by Daam et al. (2010). These authors calculated four different TV values: a short-term and a long-term value using