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Short Communication

Re-evaluation of groundwater monitoring data for glyphosate and bentazone by taking detection limits into account

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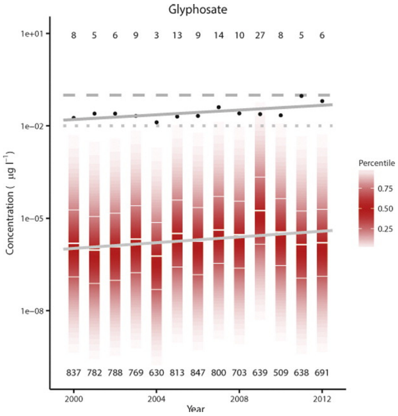
HIGHLIGHTS

- It is imperative to include all samples – including those falling below detection levels.
- Samples with pesticide concentrations below detection limits result in left-censored observations.
- Groundwater pesticide medians are 10^4–10^5 lower when including than when excluding “non-detect”
- Excluding “non-detect” samples significantly overestimates pesticide load in groundwater.

GRAPHICAL ABSTRACT

The size of glyphosate contamination in Danish groundwater without including samples with glyphosate below detection level is 10,000 to 100,000 higher than doing a parametric event-time model, where non-detect samples are left censored. The trend lines are rather similar. The broken lines are the EU drinking water directive maximum value 0.1 μg l^{-1} and the dotted line the detection limit of 0.01 μg L^{-1}. Numbers are number of samples above detection line and total number of samples.



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ABSTRACT

Current regulatory assessment of pesticide contamination of Danish groundwater is exclusively based on samples with pesticide concentrations above detection limit. Here we demonstrate that a realistic quantification of pesticide contamination requires the inclusion of “non-detect” samples i.e. samples with concentrations below the detection limit, as left-censored observations. The median calculated pesticide concentrations are shown to be reduced 10^4 to 10^5 fold for two representative herbicides (glyphosate and bentazone) relative to the median concentrations based upon observations above detection limits alone.

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1. Introduction

Since 1989, Danish groundwater has annually been analysed for pesticide residues in order to safeguard that the EU drinking water directive limit of 0.1 μg pesticide L^{-1} is met (Thorling et al., 2013). By contrast to other countries in the EU, the Danish drinking water is minimally treated groundwater. Therefore, the result of this long time monitoring of pesticide residues in groundwater is a crucial factor in the various Pesticide Action Plans agreed upon in the Danish Parliament in order to protect the groundwater (Kudsk and Jensen, 2014). However, in contrast to normally accepted practice the samples below the detection limits (non-detect samples) were excluded from the statistical analysis (Thorling et al., 2013). As examples of normal practice using non-detect samples, Köck-Schulmeyer et al. (2014) in a four-year monitoring of polar pesticides in groundwater included samples below the detection limit as a surrogate value of half the detection limits for the pesticides, although they did not explicitly describe the statistical method used. Fram and Belitz (2011) explicitly described how the data, including a surrogate concentration for samples below the detection limit, were analysed by the method outlined by Helsel and Hirsch (2002).

The herbicides bentazone and glyphosate are important in a number of crops and they can be found in the upper groundwater. Thus, they are appropriate representative pesticides for the evaluations carried out in this study. The weakly acidic herbicide, bentazone, is mobile and considered moderately persistent in soil. The Freundlich adsorption isotherm does not vary much among soils with clay contents, whether it is used under conventional or reduced tillage cultivation. The first order degradation constant in the soils does not significantly change in response to clay soils. However, tillage system has been demonstrated to affect macro-pore connectivity in some soils (Larsbo et al., 2009). Glyphosate is the most used herbicide in agriculture. It is a zwitterion with three pK_a values. In contrast to bentazone it is rarely freely dissolved in the soil water. In the pH range 4–8 the mono- and divalent anion is adsorbed to aluminium and ferric oxides (Borggaard and Gimsing, 2008). The leached glyphosate is likely to be colloidally adsorbed in wet soils with preferential flow (Vereecken, 2005). Degradation of glyphosate appears to be dependent on microbial activity (Borggaard and Gimsing, 2008).

The objective of this communication is twofold: First, we re-evaluate monitoring data for the two representative herbicides bentazone and glyphosate by estimating median concentrations in groundwater through the utilization of all available monitoring data (including non-detect samples) (Helsel, 2006, 2012). We demonstrate that a re-evaluation of monitoring data on this basis will provide a more balanced indication of both actual median herbicide concentration levels in groundwater as well as changes in concentration levels over time. Secondly, we discuss implications beyond Danish environmental policies.

2. Materials and methods

We re-evaluated data from the monitoring report (Thorling et al., 2013) for the two representative herbicides, bentazone and glyphosate, by including all samples. Specifically, we included data covering the period 1995 to 2012 for bentazone and 2000 to 2012 for glyphosate. Since 2003, sampling was predominantly from monitoring points where the groundwater was formed after 1950. From 2007, sampling focus was on wells where previous samples had shown pesticide concentrations above detection limits. For the latter, monitoring points with no pesticides above detection limit were only sampled every third year (2007–2010), and only twice for 2011–2015. Thus the monitoring plan changed to an increased focus on “groundwater at risk” (Thorling et al., 2013). Consequently, the distribution of wells was not representative of the whole country, but targeted regions with a track record of high herbicide concentrations.

Pesticide concentrations were assumed to follow a log-normal distribution, i.e., concentrations were assumed to be normally distributed when transformed to the logarithmic scale (e.g. Gilbert, 1987; Helsel, 1990, 2012). Specifically, for each herbicide we fitted a parametric event-time model assuming a linear trend in time and log-normally distributed concentrations. Concentrations below the detection limit of 0.01 μg L^{-1} were treated as left-censored observations, i.e. the concentrations were not measured precisely and it was only known that their value is smaller than the detection limit (Helsel, 2006, 2012). Thus, for each herbicide a joint model that included monitoring data from all years was fitted; thus data from all years were used to estimate the standard deviation of a common log-normal distribution. In fact, the model may be viewed as a simple linear regression model of logarithm-transformed concentrations and with year as a quantitative explanatory variable except for the large proportion of left-censored observations. By means of back-transformation using the exponential function, estimated medians and percentile concentrations were obtained on the original scales. Approximate z-tests were used to evaluate the linear trends. Sensitivity analyses were carried out assuming log-logistic and Weibull distributions, which are both suitable for right-skewed data, but in practice less used than log-normal distribution (Cox and Oakes, 1984). Additionally, logistic regression models for the reduced binary endpoint detected/non-detected were also fitted; these analyses did not assume any distribution for the concentrations. A significance level of 5% was used. Statistical analysis was carried using R (R Core Team, 2014).

3. Results and discussion

It is illustrative to compare estimated herbicide concentrations in the groundwater to the actual use of the herbicides. Sales of bentazone and glyphosate in Denmark are illustrated in Fig. 1. Field rates of pure bentazone products (Fig. 1A) were reduced by 33% of the original recommended rate in 1995 in order to protect the groundwater against potential contamination; and from 1995 bentazone use has been declining and is focused on crops such as maize, field peas, grass and clover for seed production as well as spring cereals with various under-sown crops. Due to increasing problems with *Geranium sp.* weeds in maize, use of bentazone is increasing in maize where it is the only active ingredient with high efficacy. A large proportion of glyphosate (Fig. 1B) is used pre-harvest in cereals, cruciferous crops and peas and pre-emergence in maize, potatoes and other slow germinating crops in order to effectively manage the first flush of weeds. It is also used extensively in reduced tillage cropping systems (conservation tillage).

During the whole period the median trend for bentazone concentrations estimated on the basis of all samples increased 5% per year ($p = 0.005$; 95% CI: 2–9%). The estimated median trends are shown in Fig. 2A. By contrast results based on samples with concentrations above the detection limit showed a negative trend ($p = 0.025$) in medians (Thorling et al., 2013). Moreover, estimated medians from analyses with and without non-detect samples differed 10^4–10^5 fold.

For glyphosate the discrepancy between estimated medians from the analyses with and without non-detect samples was also about 10^4–10^5 fold. The estimated trend line for glyphosate based on all samples (Fig. 2B) showed an increase by 11% (95% CI: 4–20%) per year ($p = 0.004$). This positive trend followed the total sold amount of glyphosate (Fig. 1B). However, if the year 2009 is omitted due extremely high concentrations among the actual observed concentration, the positive trend was weakened substantially ($p = 0.16$). In comparison the analysis without non-detects showed a positive trend in the medians ($p = 0.017$) (Thorling et al., 2013).

Using alternative distributions of the concentrations (log-logistic and Weibull distributions) resulted in estimated medians in the range from 10^{-5} to 10^{-8} for glyphosate compared to approximated 10^{-6} for the assumed log-normal distribution (Fig. 2B) and from 10^{-5} to 10^{-7} for bentazone compared to approx. 10^{-6} for the assumed