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Swedish Chemicals Agency

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Authorisation and Guidance

A proposed new method for calculating predicted environmental concentrations (PEC) for plant protection products in surface water

English version

This document contains an English translation of the report in Swedish *Förslag till ny beräkningsmetod för predikterade miljökoncentrationer (PEC) för växtskyddsmedel i ytvatten* by Centre for Chemical Pesticides Swedish University of Agricultural Sciences. Authors are Gustaf Boström, Nicholas Jarvis, Mikaela Gönczi and Jenny Kreuger.

The Swedish Chemical's Agency is responsible for the translation.

The purpose of this translation is make the results available to other competent authorities for Regulation (EC) No 1107/2009 in the EU. The results in the report serve as an example of possibilities to reduce the complexity of the environmental risk assessment of plant protection products. This translation is part of Swedish Chemicals Agency's work to streamline the authorisation process.

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A proposed new method for calculating predicted environmental concentrations (PEC) for plant protection products in surface water

Background report for the Swedish Pesticide Council 2019

Kompetenscentrum för kemiska bekämpningsmedel **Uppsala 2019**
Sveriges lantbruksuniversitet

Centre for Chemical Pesticides
Swedish University of Agricultural Sciences

CKB
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Centre for Chemical Pesticides, CKB

Swedish University of Agricultural Sciences (SLU). 2019

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Summary

The Swedish Chemicals Agency is conducting a long-term project to investigate whether the environmental risk assessment used for plant protection products can be simplified, which would enable a stronger focus to be placed on substances where there is greatest uncertainty as to whether or not authorisation can be granted. The Swedish Board of Agriculture has commissioned the Centre for Chemical Pesticides (CKB) at the Swedish University of Agricultural Sciences to investigate whether it is possible to develop a simple new method for calculating predicted concentrations in surface water (PEC) corresponding to FOCUS Step 1, but with a stronger link to actual conditions, without compromising the level of protection afforded by the assessment. The study is funded by the Swedish Pesticide Council, in which the Swedish Board of Agriculture and the Swedish Chemicals Agency collaborate. The project also included a comparison of the estimated concentrations of each substance with measured concentrations from the national environmental monitoring programme for plant protection products (NMÖ) 2009 - 2017 in order to assess the level of protection.

A simple formula for estimating surface water concentrations, PEC (Predicted Environmental Concentration, µg/l), in small catchments with a time resolution of one week is proposed. Using a number of assumptions and standard values based on results from the national environmental monitoring programme for plant protection products, the formula can be simplified to:

$$PEC = 0.5\ D$$

The field dose, D, which is used for calculating PEC CKB was produced based on data from the national environmental monitoring programme. PEC CKB was also calculated using the maximum authorised annual field dose from the Swedish Chemicals Agency's product authorisation, for 20 substances.

The formula has been refined with substance-specific K_{foc} values using the formula for F_w (the proportion of the amount applied that ends up in surface water rather than in sediment) used in the calculations for FOCUS Step 1. It is the PEC value calculated using the mean annual field dose from the national environmental monitoring programme and including F_W, which is referred to as 'PEC CKB' in this report.

$$\boldsymbol{PEC = 0.5\ D\ F_w}$$

The comparisons with the environmental monitoring data (Measured Environmental Concentrations, MEC) are based on three separate data sets:

1. **87 substances** which were included in the chemical analyses and which had a registered use in the national environmental monitoring programme for 2009 - 2017
2. **43 substances** which have at least a 90th percentile of measured environmental concentrations (MEC) and which were used on at least 20 occasions between 2009 and 2017
3. **20 substances** which have at least a 90th percentile of measured environmental concentrations (MEC), which were used on at least 20 occasions during the period 2009 - 2017, and for which data is available from the Swedish Chemicals Agency's product authorisation.

The results show that the proposed method for calculating estimated concentrations in surface water in small catchments with a time resolution of one week (PEC CKB) provides a good estimate of the highest concentrations that can be measured in the model catchments of the national environmental monitoring programme with a time resolution of one week, without being overly conservative.

All measured concentrations and the 99th percentile of MEC and all PEC values (PEC CKB, FOCUS PEC Step 1, PEC Step 3 (EFSA) and PEC Step 3/4 (Swedish Chemicals Agency)) are shown in the same figure for the 87 substances included in the study. In many cases, PEC CKB lies between PEC Step 3/4 and Step 1, but in 26-55% of cases, PEC CKB lies below PEC Step 3/4. Compared with measured concentrations, PEC CKB lies above the 99th percentile of MEC in the vast majority of cases, and in most cases also above the maximum measured concentration from the national monitoring programme during 2009 - 2017.

Statistical correlation calculations have been performed for comparison between all calculated percentages of MEC and PEC CKB (calculated using the mean annual hectare dose used in the national monitoring programme 2009 - 2017 and using the maximum authorised dose from the Swedish Chemicals Agency's product authorisation, and with and without the factor F_w). Comparisons have also been made between all MEC and PEC Step 3 or 4 from the Swedish Chemicals Agency's product authorisation (for 20 substances), as well as directly against the various doses and directly against F_w.

The report only presents correlations against the 99th percentile of MEC, as this generally produced the best results. All percentiles of MEC values and all calculated PEC values can be found in the Excel file entitled "Rådatarapport 2019-06-27.xlsx" submitted to the secretariat of the Swedish Pesticide Council. All correlation coefficients and other estimated measures of the relationships are presented in Appendix 3.

The method proposed for calculating estimated concentrations in surface water (PEC CKB) can be viewed as a variant of FOCUS Step 1, where the effective dilution is adjusted based on data from the national environmental monitoring programme in Sweden. The results show that the estimated concentrations in surface water will be lower and that more products could therefore be subject to an environmental risk assessment, without having to go through the more complicated Step 3 calculation methods.

However, a number of questions must be addressed before PEC CKB or another similar method could be used in the environmental risk assessment which is carried out as part of the product authorisation process. These questions concern issues such as protection level, how the risk of wind drift should be handled, and whether the environmental monitoring data that is used can be considered to be representative of all situations, e.g. for crops which are not grown in the model catchments.

The results of the study indicate that the correlation between PEC CKB and measured concentrations is relatively good, even though the proposed calculation method is very simple and requires minimal input data. However, there is obviously some spread in the underlying data, and further work could possibly achieve even closer conformity between predicted and measured concentrations by making more factors substance-specific.

1. Introduction

In order for a plant protection product to be used, the constituent active substances must be approved at EU level by the European Commission, and individual products that are to be placed on the market in Sweden must be authorised by the Swedish Chemicals Agency. Pesticide companies prepare comprehensive background information, including information concerning the substances' inherent properties, efficacy, health and environmental effects, and perform simulations using models as a basis for the environmental risk assessment. The authorisation authorities evaluate and assess the background information and reach a decision concerning authorisation. This is a major task both for pesticide companies and for the government agencies involved.

The Swedish Chemicals Agency is conducting a long-term project to investigate whether the environmental risk assessment used for plant protection products can be simplified, which would enable a stronger focus to be placed on substances where there is greatest uncertainty as to whether or not authorisation can be granted. The Swedish Pesticide Council, in which the Swedish Board of Agriculture and the Swedish Chemicals Agency collaborate, has commissioned the Centre for Chemical Pesticides (CKB) at the Swedish University of Agricultural Sciences to investigate whether it is possible to develop a simple new method for calculating predicted concentrations in surface water (PEC) corresponding to FOCUS Step 1, but with a stronger link to actual conditions, without compromising the level of protection afforded by the assessment. The project also included a comparison of the estimated concentrations of each substance against measured concentrations from the national environmental monitoring programme for plant protection products in order to assess the level of protection.

2. Method

2.1 Calculation of PEC CKB – basis

A simple formula for estimating surface water concentrations, PEC (Predicted Environmental Concentration, µg/l), in small catchments with a time resolution of one week is as follows:

$$PEC = \frac{\sum_{i=1}^{i=n} A_i D_i M_i}{A_c\, q}$$

where n is the number of fields sprayed during the week, A is the field area (m^2), D is the field dose (mg/m^2), M is the proportion of the applied dose lost to surface water, q is run-off during the week (m) and A_C is the catchment area (m^2). Assuming that both D and M are constant, we obtain:

$$PEC = \left[\frac{A_s}{A_c\, q}\right] D\, M$$

where A_s is the area sprayed during the week (m^2), which in turn can also be described as:

$$A_s = \frac{f\, A_c}{N_s}$$

where f is the proportion of the catchment's area which is sprayed every year, and N_s is the duration of the spraying season in weeks. This produces:

$$PEC = \left[\frac{f}{N_s\, q}\right] D\, M$$

The terms $\left[\frac{A_s}{A_c q}\right]$ and $\left[\frac{f}{N_s\, q}\right]$ in the above equations are effective dilution factors which enable extrapolation from the field scale to a complete catchment.

The values for the constituent parameters have been set on the basis of general knowledge based on results from the model catchments which are studied in the national environmental monitoring programme for plant protection products. In this case, we choose values that can be considered to define a worst-case situation.

- $f = 0.2$
  The proportion of the catchment which is sprayed each year can vary greatly between the different substances, depending on various factors including which crops they are used on. The proportion can also vary between areas and from year to year for the same substance. Based on data from the national environmental monitoring programme, the *f* value per substance, year and area have been calculated. Figure 1 shows a histogram of the maximum values (A) and the 90th percentile (B) of the proportion of the area which is sprayed (*f*) calculated per substance, area and year. The standard value of 20% was chosen as a mean value, but is conservative for most substances.

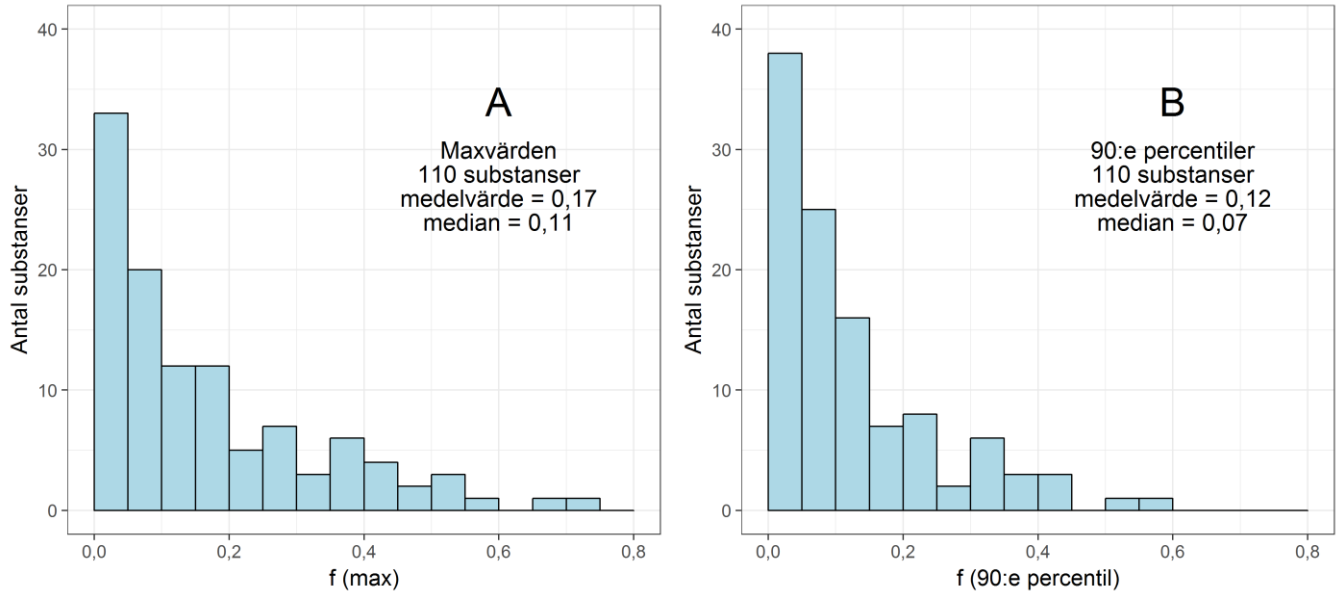

Figure 1. Histogram of substances' maximum (A) and 90th percentile (B) proportion of the catchment area of the four model catchments which has been sprayed (*f*), calculated per substance, area and year.

- $N_s = 4$
  The duration of the spraying season is set to four weeks. This can vary both between substances and between areas and years. The shorter the season, the more worst-case the scenario.

- q = 0.001 m/week
  Run-off per week varies considerably depending on the weather. Run-off is often fairly low during the summer period. 0.001 m/week is a very low run-off. The lower the value specified, the more worst-case the scenario.

- M = 0.01
  The proportion of the applied dose that is lost to surface water varies greatly depending on the substance's characteristics and from time to time, depending on soil and weather conditions. Based on previous studies using environmental monitoring data, 1% represents a worst-case scenario. Losses to surface water for most substances are well below this value (Boström et al., 2017; Graaf et al., 2010).

With the above standard values, the above formula can be rewritten as:

$$\boldsymbol{PEC = 0.5\,D}$$

The field dose, D, which is used for calculations of PEC CKB was produced based on data from the national environmental monitoring programme 2009 - 2017 (see section 2.6 below). In the model catchments of the environmental monitoring programme, an inventory of cultivation and use of plant protection products is prepared annually through interviews with farmers in each area. Based on this data, a mean field dose was calculated for each substance (g active substance/treated area/year). If the same field is treated on several occasions in a single year, the area is not counted several times.

PEC CKB was also calculated using the maximum authorised annual field dose from the Swedish Chemicals Agency's product authorisation, for 20 substances.

2.2 Calculation of FOCUS PEC Step 1

FOCUS Step 1 is the method that is used in the authorisation of plant protection products as an initial worst-case step to calculate PEC (FOCUS, 2001) at the edge of the field. The formula used is:

$$PEC = \left[\frac{A_f}{A_w Z_w}\right] D\ M\ F_w$$

where A_f is the field area, A_w and Z_w are area (m^2) and depth (m) of the water recipient respectively, and F_w is the proportion of the applied quantity which ends up in the water rather than in sediment. This parameter is calculated using a simple equilibrium adsorption equation which depends on the substance's K_{oc} value (cm^3/g) and constant values for water depth (= 0.3 m), thickness of adsorbing sediments, Z_s (= 0.01 m), weight by volume, γ (= 0.8 g/cm^3), and organic carbon content, f_{oc} (= 0.05 kg/kg) :

$$F_w = \frac{Z_w}{Z_w + (Z_s \gamma K_{oc} f_{oc})}$$

The recipient is assumed to have an area that is ten times smaller than the field area. These assumptions mean that the factor $A_f/(A_w Z_w)$ is effectively set to 33.3 m^{-1}. Losses to surface water in FOCUS occur both via wind drift and surface run-off/drainage. It is assumed that 10% of the dose ends up in the recipient via surface run-off/drainage (i.e. M = 0.1 in this case). In addition to this are

losses to surface water via wind drift, but we ignore this transport path here. The outcome of all these assumptions is:

$$PEC = 3.33\ D\ F_w$$

which gives concentrations in surface water which are a factor of 6.66 times greater (= 3.33/0.5) than the method for PEC CKB, if F_W is set to 1 (i.e. everything ends up in the water and nothing in the sediment). It must also be remembered that FOCUS Step 1 calculations include wind drift, so that in practice the actual PEC will be even higher.

2.3 Calculation of final PEC CKB – with substance-specific K_{foc}

The formula for calculating PEC has been generalised, so that it can be used in connection with registration when the proportion of a catchment that the product will be sprayed on or the proportion that will be lost to surface water is not known. However, it is possible to adjust the formula with more substance-specific parameters. In this case, we have used the formula for F_w (the proportion of the quantity applied which ends up in surface water rather than in sediment) which is used in the calculations for FOCUS Step 1 in order to adjust the concentration which is calculated using PEC CKB as follows:

$$\boldsymbol{PEC = 0.5\ D\ F_w}$$

This makes the method for the proposed PEC CKB more comparable to the method for FOCUS Step 1. This requires substance-specific K_{foc} values.

The PEC value calculated using the mean annual field dose from the national environmental monitoring programme and including F_w is hereinafter referred to as 'PEC CKB'.

2.4 PEC and K_{foc} from EFSA Conclusions

EFSA Conclusions for 219 substances were reviewed by CKB as part of a project funded by the Swedish Environmental Protection Agency in 2018 and published in a background report entitled "Comparisons of PEC and PNEC from EFSA with guideline values and measured levels of plant protection products in surface water"[1] (Berggren et al., 2018). PEC Step 3 for the scenarios D1 and D4, which are the most relevant to Swedish conditions, was noted and has also been used in this project. The K_{foc} values used in this report were also taken from the previous compilation of EFSA conclusions.

2.5 PEC and doses from the Swedish Chemicals Agency's product authorisation

In 2017, CKB carried out a project funded by the Swedish Environmental Protection Agency where plant protection products that regularly exceed their water quality objectives for surface water were examined for root causes for the exceedances. The findings were published in CKB report 2017:2 (Boström et al., 2017). In connection with this work, the Swedish Chemicals Agency provided background data used in the product authorisation evaluation for the identified 12 substances, including PEC. In this project, they provided PEC and other related information, including doses, for a

[1] Translators note: Original title in Swedish is *Jämförelser av PEC och PNEC från EFSA med riktvärden och uppmätta halter av växtskyddsmedel i ytvatten - Underlagsrapport till Naturvårdsverket 2018*.

further ten substances in order to provide a broader basis including substances that are not considered to be as problematic for the aquatic environment.

2.6 Comparison of different PEC values with environmental monitoring data (MEC)

2.6.1 Environmental monitoring data

The various PEC values considered in this report have been compared with analysis data from the national environmental monitoring programme for plant protection products in agricultural areas (NMÖ) (Lindström et al, 2015; Nanos & Kreuger, 2015). Data was obtained from the ordinary sampling programme (May - November) in the four 'model catchments' of Skåne, Halland, Östergötland and Västergötland between 2009 and 2017. This period was chosen because chemical analysis methods remained relatively unchanged during this period with regard to detection and quantification limits and the handling of trace concentrations. The model catchments were selected to represent small catchments (8-16 km^2) with intensive agriculture (85-92% arable land) in the four agricultural regions in which they are located.

In the national environmental monitoring programme's model catchments (streams), time-integrated sampling is carried out using automatic ISCO samplers, which take a sub-sample every 90 minutes for a week. These composite samples show the mean concentration for the substances transported in the watercourse during the week.

The measured concentrations were then cleansed per year and area, so that only concentrations measured during the years in which the substance was used in the area were retained. This is done because significant measurable concentrations of a substance cannot be expected if the substance has not been used, and removing them ensures that the zero values do not impact on the subsequent percentile calculation.

In total, background data was available for 87 substances which were both included in the chemical analyses and had a registered use within the national environmental monitoring programme 2009 - 2017.

From the measured concentrations (Measured Environmental Concentration, MEC), different percentiles of MEC (max. concentration; 99th, 97.5th, 95th and 90th percentiles) were then calculated for each substance. The calculations are based on all values, i.e. including zero values (concentrations below the detection limit). Trace levels, concentrations between the detection limit and quantification limit are reported as numerical values and have also been included in the percentile calculations.

2.6.2 Statistics which are calculated

To assess the level of conformity between the predicted levels (PEC) and measured concentrations in the environment (MEC), four different statistical measures were calculated:

- Mean Absolute Error (MAE):

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|MEC_{Si} - \mathrm{PEC}_{Si}|$$

Where "n" is the total number of substances included in the analysis, "MEC_{Si}" is a percentile for measured concentrations in the environment for the "i'th" substance Si, and "PEC_{Si}" is the predicted concentration in the environment for the same substance.

MAE is the mean of the absolute values of the differences between the measured concentration and the predicted concentration for all substances. In the scatter chart shown in the results section, MAE can be interpreted as the mean distance between the points and the 1:1 line, in both the horizontal and the vertical direction.

The MEC_{Si} values tested in this report are the estimated percentiles of measured concentrations (max. concentration; 99%; 97.5%; 95% and 90%). The PEC_{Si} values tested in this report are PEC CKB values calculated using mean annual field doses from the national environmental monitoring programme, PEC CKB calculated using the maximum annual field dose from the Swedish Chemicals Agency's product authorisation, and PEC Step 3/4 from the Swedish Chemicals Agency's product authorisation.

- Bias:

$$Bias = \frac{1}{n}\sum_{i=1}^{n}(MEC_{Si} - \mathrm{PEC}_{Si})$$

Bias is the mean of the differences between the measured concentration and the predicted concentration for all substances. Bias can be positive or negative, whilst MAE can only be positive. Bias thus indicates whether the model (the predicted concentrations) has a tendency to systematically over- or underestimate the measured concentrations.

- Root Mean Square Error (RMSE):

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(MEC_{Si} - \mathrm{PEC}_{Si})^2}$$

RMSE has a less explicit interpretation than MAE and Bias because the difference between MEC and PEC for each substance is squared before a mean is calculated and the square root is taken from this mean. The squaring of the differences means that large errors have a substantial effect on the RMSE and it is therefore sensitive to outliers. However, RMSE is a commonly used measure of conformity between predicted and observed values.

- Correlation coefficient (Pearson's):

$$r = \frac{\sum_{i=1}^{n}(MEC_{Si} - \overline{MEC})(\mathrm{PEC}_{Si} - \overline{PEC})}{\sqrt{\sum_{i=1}^{n}(MEC_{Si} - \mathrm{MEC})^2}\sqrt{\sum_{i=1}^{n}(\mathrm{PEC}_{Si} - \overline{PEC})^2}}$$

The correlation coefficient is a measure of the strength and direction of the linear relationship between two variables and varies between -1 and 1, where ±1 indicates the strongest possible relationship (all points on a chart fall in a straight line) and 0 indicates that there is no linear relationship.

The various statistical measures should only be used to compare "models" calculated using the same substances and the same type of reference statistics (same percentile of MEC); otherwise, there is a risk for incorrect interpretations. Therefore, two different subsets of the substances were selected for the correlation analyses (Appendix 1)

1. 43 substances which have at least a 90th percentile of measured environmental concentrations (MEC) and which were used on at least 20 occasions between 2009 and 2017
2. 20 substances which have at least a 90th percentile of measured environmental concentrations (MEC), which were used on at least 20 occasions during the period 2009 - 2017, and for which data is available from the Swedish Chemicals Agency's product authorisation.

Both MEC and PEC values have been log-transformed (base 10) before the statistical measures were calculated to ensure that high values (high concentrations) do not have a disproportionate impact on the results.

2.7 Analysis of sensitivity to changes in K_{foc}

The two parameters in the formula for PEC CKB which are substance-specific are dose and K_{foc}. The K_{foc} value which is stated for the same substance can vary greatly depending on the conditions under which the measurements were taken. A simple variant of sensitivity analysis was performed in order to show how differences in K_{foc} used in the calculations of PEC CKB impact on the results. As mentioned previously, the K_{foc} values from EFSA Conclusions were used, and these were then multiplied by 1.1; 1.2; 1.5 and 2.0 in order to see how this impacts on PEC CKB.

2.8 Delimitations

Under the national environmental monitoring programme, a limited number of degradation products are analysed, primarily for substances which have a short half-life. However, degradation products are not included in this analysis, partly because of the difficulty of determining the proportion of parent substance which is converted into the specific degradation product.

3. Results

All background data and underlying results can be found in the Excel file entitled "Rådatarapport 2019-06-27.xlsx"[2] submitted to the secretariat of the Swedish Pesticides Council on 28 June 2019. This submission also included the document entitled "Förklaring av parametrar i rådatarapport 2019-06-27.docx"[3].

3.1 Comparison of different PEC values with environmental monitoring data (MEC)

The comparisons are based on three different data sets (see Appendix 1):

4. **87 substances** which were included in the chemical analyses and which had a registered use in the national environmental monitoring programme for 2009 - 2017
5. **43 substances** which have at least a 90th percentile of measured environmental concentrations (MEC) and which were used on at least 20 occasions between 2009 and 2017

[2] Translator's note (TN): The Excelfile is in Swedish. "Rådatarapport" means raw data report in English.
[3] TN: The Wordfile is in Swedish. "Förklaring av parametrar i rådatarapport" means explanation of parameters in English.

6. **20 substances** which have at least a 90th percentile of measured environmental concentrations (MEC), which were used on at least 20 occasions during the period 2009 - 2017, and for which data is available from the Swedish Chemicals Agency's product authorisation.

Figure 2 shows a plot of all measured concentrations and the 99th percentile of MEC and all PEC values in the same figure for the 87 substances included in the study. The figure shows that the so-called "tiered approach" is followed for most substances, i.e. lower steps in the risk assessment (Step 1) result in higher PEC values than the subsequent Step 3 or Step 4 calculations. However, this does not apply to all substances (e.g. alpha-cypermethrin and hexythiazox), for which PEC Step 3 is higher. However, it is important to remember here that the PEC Step 1 shown in the figure was calculated as PEC CKB * 6.66 and does not include wind drift, which is a very plausible explanation.

As regards PEC CKB, the results lie between PEC Step 3 and Step 1 in many cases, but there are several exceptions where PEC CKB is also below PEC Step 3. For 21 out of 38 substances (55%), PEC CKB is below PEC Step 3 D1 from EFSA, for 16 out of 62 (26%) PEC CKB is below PEC Step 3 D4 from EFSA, and for 6 out of 22 (27%) PEC CKB is below PEC Step 3 or 4 from the Swedish Chemicals Agency's authorisation. In comparison with measured concentrations, PEC CKB lies above the 99th percentile of MEC in the vast majority of cases, and in most cases above the maximum measured concentration within the national environmental monitoring programme 2009 - 2017. See Appendix 2 for the ratios between all calculated percentiles of MEC and PEC CKB, where ratios above 1 (percentile of measured concentration is higher than PEC CKB) are indicated.

Comparisons have been made between all calculated percentiles of MEC and PEC CKB calculated using the mean annual hectare dose used in the national environmental monitoring programme 2009 - 2017 and the maximum authorised dose from the Swedish Chemicals Agency's product authorisation, and with and without the factor F_w, which adjusts for the distribution between water and sediment. Comparisons have also been made between all percentiles of MEC and PEC Step 3 or 4 from the Swedish Chemicals Agency's product authorisation, as well as directly against both the various doses and F_w.

This results section only presents correlations with the 99th percentile of MEC, as this generally produced the best results. Similarly, Root Mean Square Error and Mean Absolute Error are not shown. Only Bias is shown, as this measure has a relatively simple interpretation as the mean difference between the measured concentration and the predicted concentration of all substances. All percentiles of MEC values and all calculated PEC values can be found in the Excel file entitled "Rådatarapport 2019-06-27.xlsx". All correlation coefficients and other estimated measures of the relationships are presented in Appendix 3.

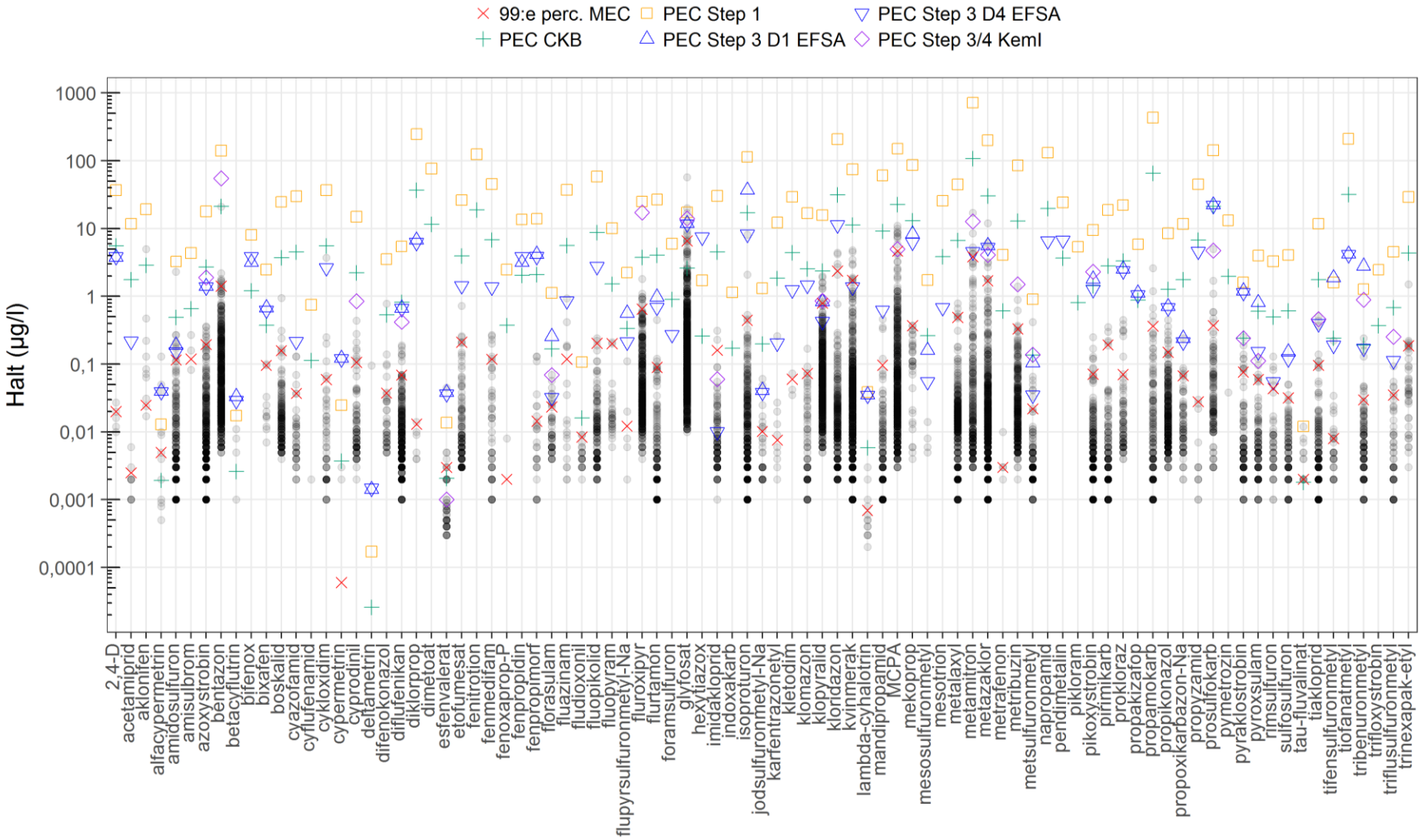

Figure 2. Plot showing all measured concentrations (MEC, grey to black dots), 99th percentile of MEC (red crosses), PEC CKB (calculated using the mean annual field dose, green plus signs), FOCUS PEC Step 1 (without wind drift, calculated as PEC CKB * 6.66, orange squares) PEC Step 3 D1 and D4 from EFSA Conclusions (Berggren et al., 2018, blue triangles), and PEC Step 3 or 4 from the Swedish Chemicals Agency's product authorisation (for 20 substances; purple rhombuses), for all 87 substances included in the study. Note that the y-axis is logarithmic. [TN: Substance names in Swedish.]

3.1.1 Correlations with 43 substances

Figure 3 shows all MEC and PEC data for the 43 substances included in the following correlation calculations in this section (substances with both a 90th percentile of MEC and at least 20 registered uses).

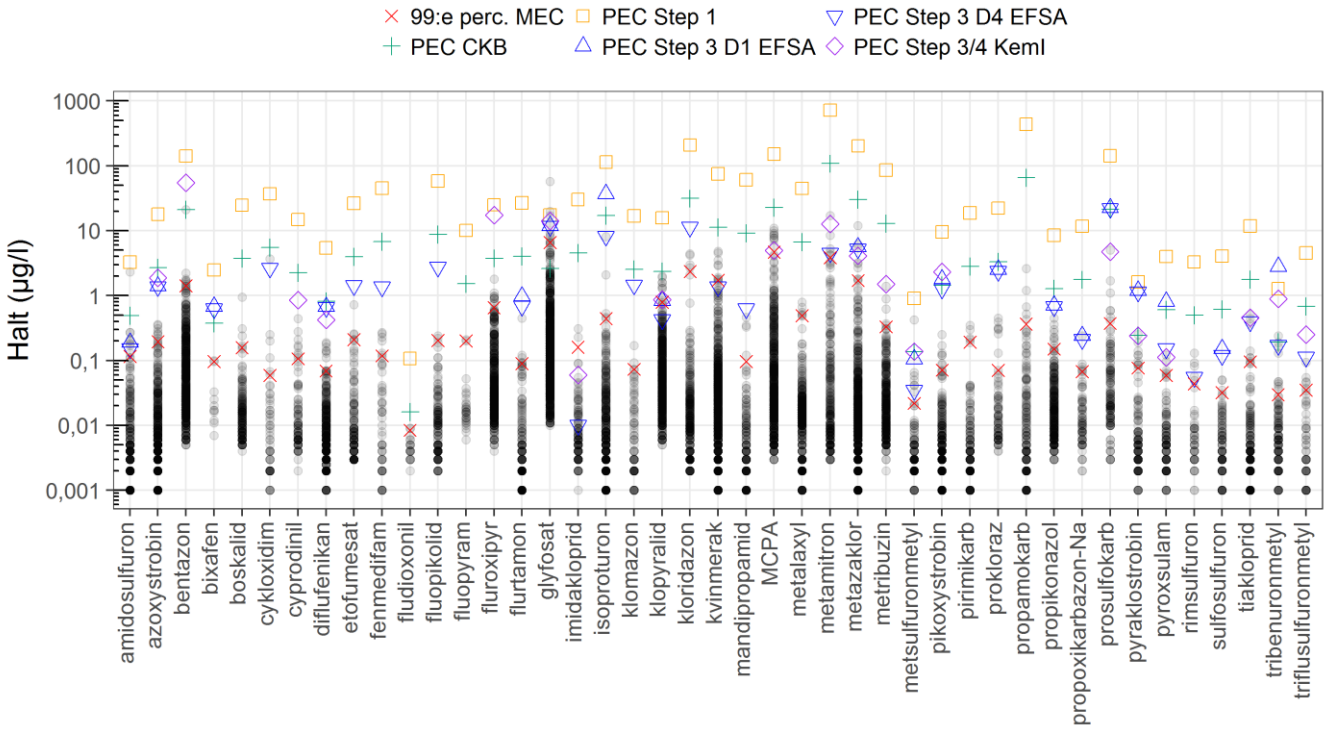

Figure 3. Plot showing all measured concentrations (MEC, grey to black dots), the 99th percentile of MEC (red crosses), PEC CKB (calculated using the mean annual field dose, green plus signs), FOCUS PEC Step 1 (without wind drift, calculated as PEC CKB * 6.66, orange squares), PEC Step 3 D1 and D4 from EFSA Conclusions (Berggren et al., 2018, blue triangles), and PEC Step 3 or 4 from the Swedish Chemicals Agency's product authorisation (for 20 substances; purple rhombuses), for all 43 substances included in the correlation calculations. Note that the y-axis is logarithmic. [TN: Substance names in Swedish.]

Figure 4 shows the correlation between PEC CKB, calculated using the mean annual hectare dose from the national environmental monitoring programme for 43 substances and the 99th percentile of MEC. The three substances propyzamide, dichlorprop and mecoprop have 90th percentiles of MEC, but were only used on four or five occasions during the period 2009 - 2017. They are shown in the diagram as grey dots, but are not included in the correlation calculations.

Glyphosate stands out as the only one of these substances to have an under-estimated PEC CKB compared with the 99th percentile of MEC. Other substances are relatively concentrated around the regression line.

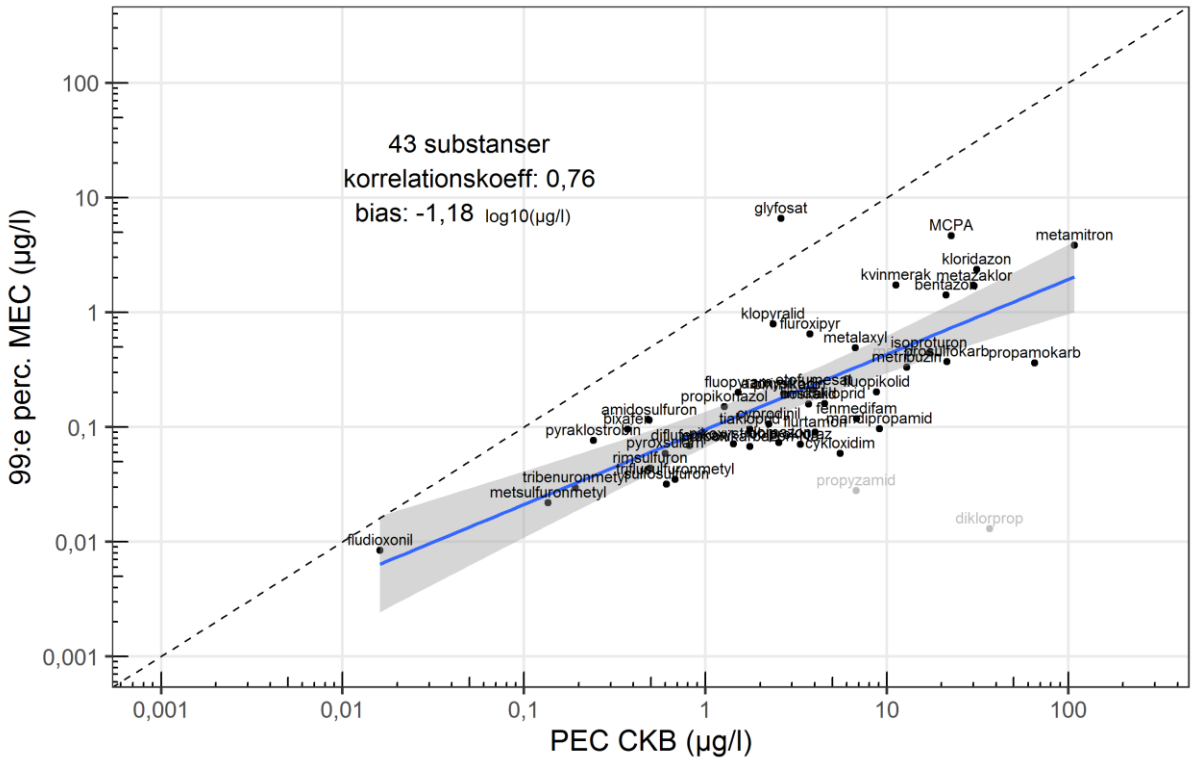

Figure 4. Scatter plot for PEC CKB (calculated using the mean annual hectare dose) against the 99th percentile of measured concentrations (MEC) in the national environmental monitoring programme, for 43 substances which have at least a 90 percentile of MEC and which were used on at least 20 occasions in the national environmental monitoring programme's model catchments during the period 2009 - 2017. The blue line shows the linear regression with a 95% confidence interval and the dotted line is x = y. The figure also shows the correlation coefficient and bias. Three substances with a 90th percentile but with <20 uses are shown as grey dots and were not included in the correlation calculations. Note that both axes are logarithmic. [TN: Substance names in Swedish.]

Figure 5 shows the correlation between PEC CKB, calculated using the mean annual hectare dose from the national environmental monitoring programme, but without the factor F_w for distribution between water and sediment based on K_{foc}, for the same 43 substances and the 99th percentile of MEC. The correlation coefficient here is slightly inferior and the value for bias is lower, indicating a greater over-estimation of the concentrations when F_w is excluded. However, with this calculation of PEC CKB, glyphosate is not under-estimated.

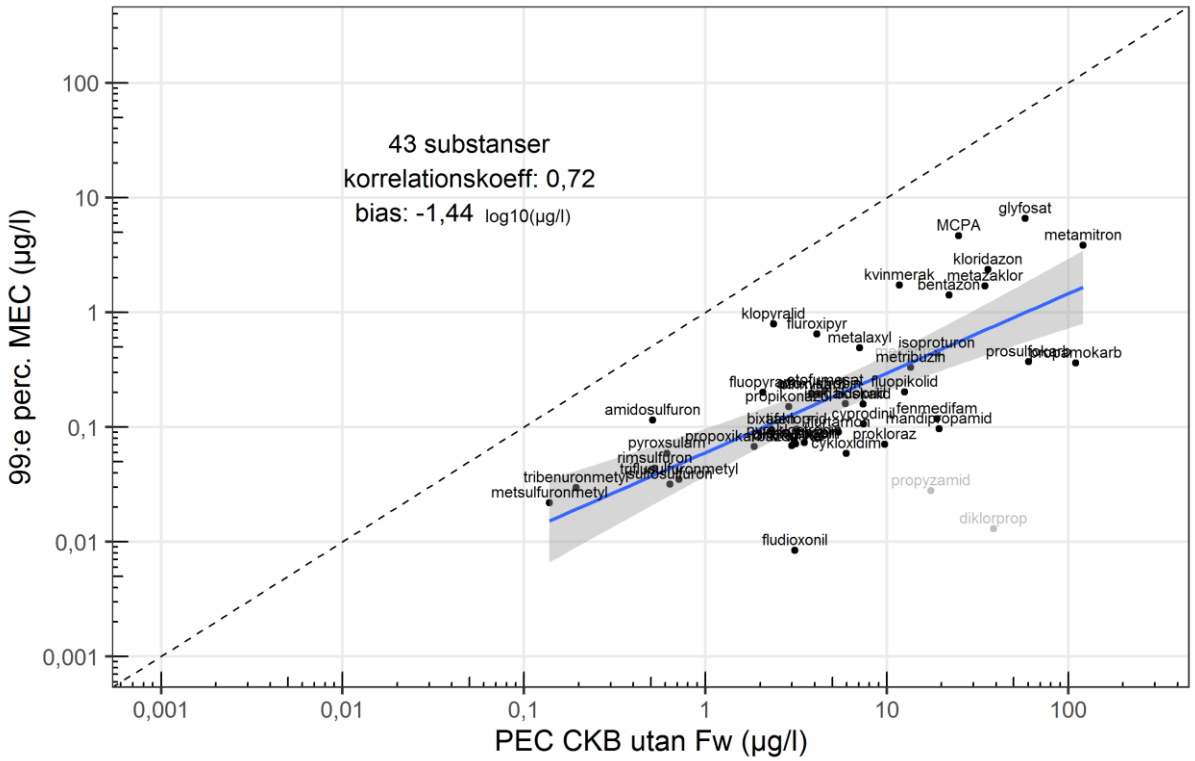

Figure 5. Scatter plot for PEC CKB (calculated using the mean annual hectare dose, but without FW - the distribution between water and sediment) against the 99th percentile of measured concentrations (MEC) in the national environmental monitoring programme, for 43 substances which have at least a 90th percentile of MEC and which were used on at least 20 occasions in the national environmental monitoring programme's model catchments during the period 2009 - 2017. The blue line shows the linear regression with a 95% confidence interval (grey area around the line) and the dotted line is x = y. The figure also shows the correlation coefficient and bias. Three substances with a 90th percentile but with <20 uses are shown as grey dots and were not included in the correlation calculations. Note that both axes are logarithmic. [TN: Substance names in Swedish.]

3.1.2 Correlations with 20 substances

Figure 6 shows all MEC and PEC data for the 20 substances included in the following correlation calculations in this section (the substances with both a 90th percentile of MEC and at least 20 registered uses, and for which data is available from the Swedish Chemicals Agency's product authorisation). Data from the Swedish Chemicals Agency's product authorisation (pgk) enables a comparison of PEC CKB and PEC Step 3 or 4 which was used for the authorisation, and a comparison of PEC CKB calculated using the mean dose used by the national environmental monitoring programme compared with PEC CKB calculated using the maximum authorised dose.

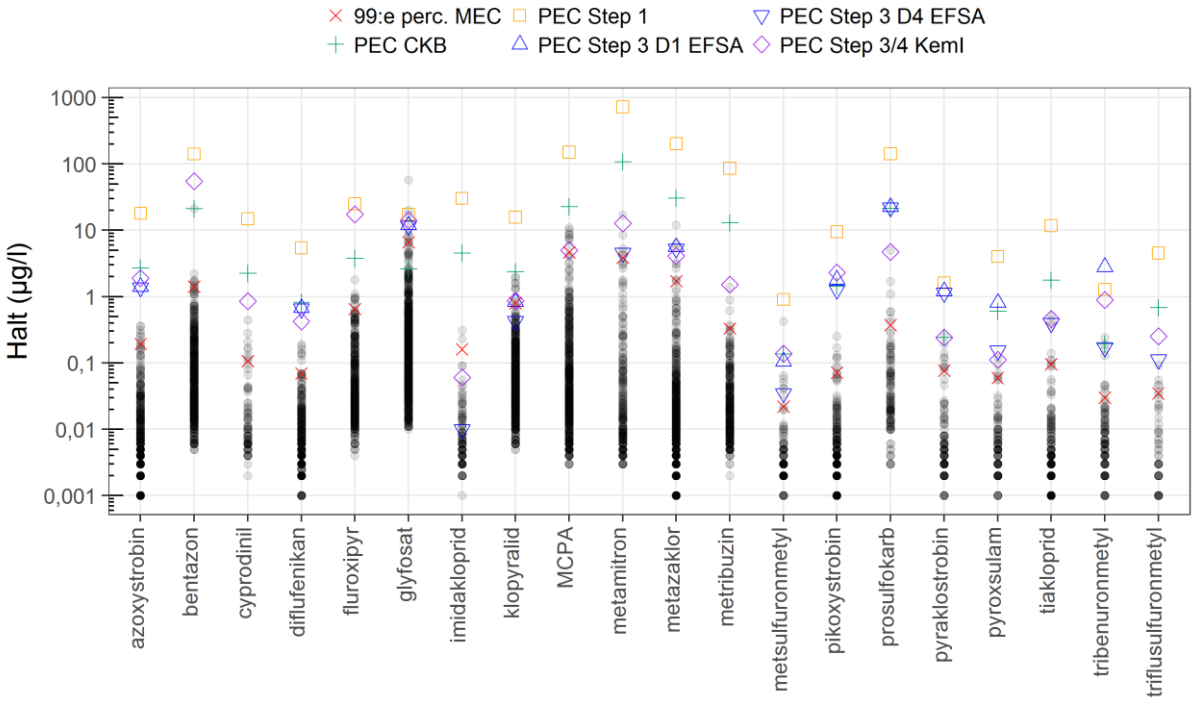

Figure 6. Plot showing all measured concentrations (MEC, grey to black dots), the 99th percentile of MEC (red crosses), PEC CKB (calculated using the mean annual field dose, green plus signs), FOCUS PEC Step 1 (without wind drift, calculated as PEC CKB * 6.66, orange squares), PEC Step 3 D1 and D4 from EFSA Conclusions (Berggren et al., 2018, blue triangles), and PEC Step 3 or 4 from the Swedish Chemicals Agency's product authorisation (purple rhombuses), for the 20 substances included in the correlation calculations. Note that the y-axis is logarithmic. [TN: Substance names in Swedish.]

Figure 7 shows the same correlation between PEC CKB and the 99th percentile of MEC as shown in Figure 4, but in this case only with the 20 substances for which we have data from the Swedish Chemicals Agency's product authorisation, so that the results are comparable to subsequent plots. Figure 8 corresponds to Figure 5, i.e. PEC CKB calculated without F_w compared with the 99th percentile of MEC, but with the smaller subset of 20 substances.

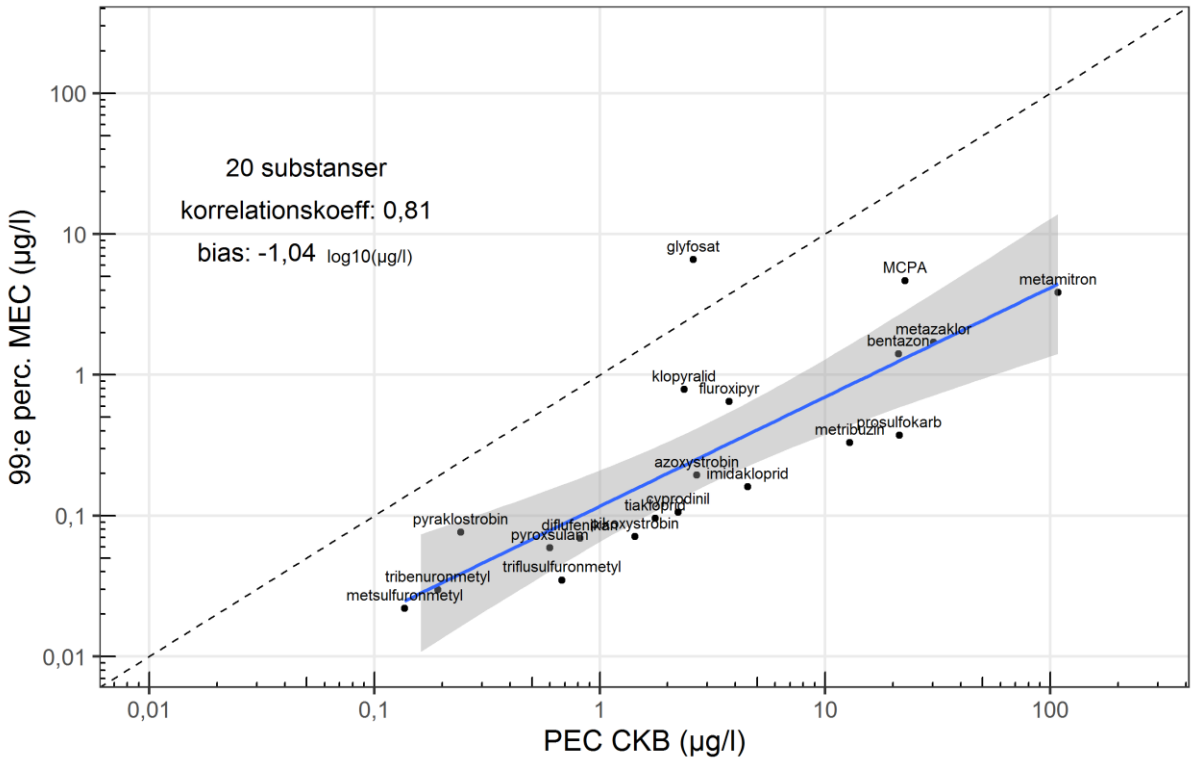

Figure 7. Scatter plot for PEC CKB (calculated using the mean annual hectare dose) against the 99th percentile of measured concentrations (MEC) in the national environmental monitoring programme, for 20 substances which have at least a 90 percentile of MEC, which were used on at least 20 occasions in the national environmental monitoring programme's model catchments during the period 2009 - 2017, and for which data is available from the Swedish Chemicals Agency's product authorisation. The blue line shows the linear regression with a 95% confidence interval (grey area around the line) and the dotted line is x = y. The figure also shows the correlation coefficient and bias. Note that both axes are logarithmic. [TN: Text in the graph is in Swedish.]

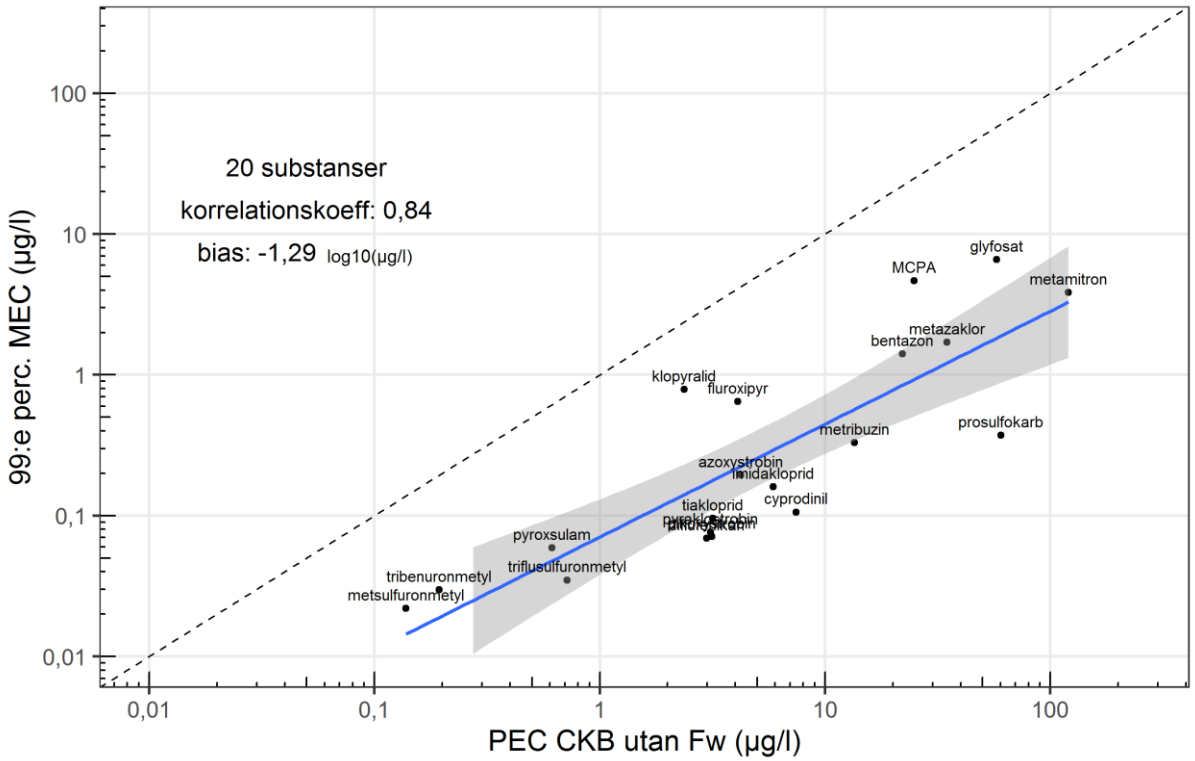

Figure 8. Scatter plot for PEC CKB (calculated using the mean annual hectare dose but without Fw – distribution between water and sediment) against the 99th percentile of measured concentrations (MEC) in the national environmental monitoring programme, for 20 substances which have at least a 90th percentile of MEC, which were used on at least 20 occasions in NMÖ's model catchments during the period 2009 - 2017, and for which data is available from the Swedish Chemicals Agency's product authorisation. The blue line shows the linear regression with a 95% confidence interval (grey area around the line) and the dotted line is x = y. The figure also shows the correlation coefficient and bias. Note that both axes are logarithmic. [TN: Text in the graph is in Swedish.]

Figure 9 shows the correlation between PEC CKB calculated using the maximum authorised dose from the Swedish Chemicals Agency's product authorisation and the 99th percentile of MEC. The correlation coefficient is marginally better than for PEC CKB calculated using the mean annual hectare dose from the national environmental monitoring programme, but the bias is bigger as most substances have a higher PEC CKB. Glyphosate still stands out compared with other substances, but is not under-estimated compared with the 99th percentile.

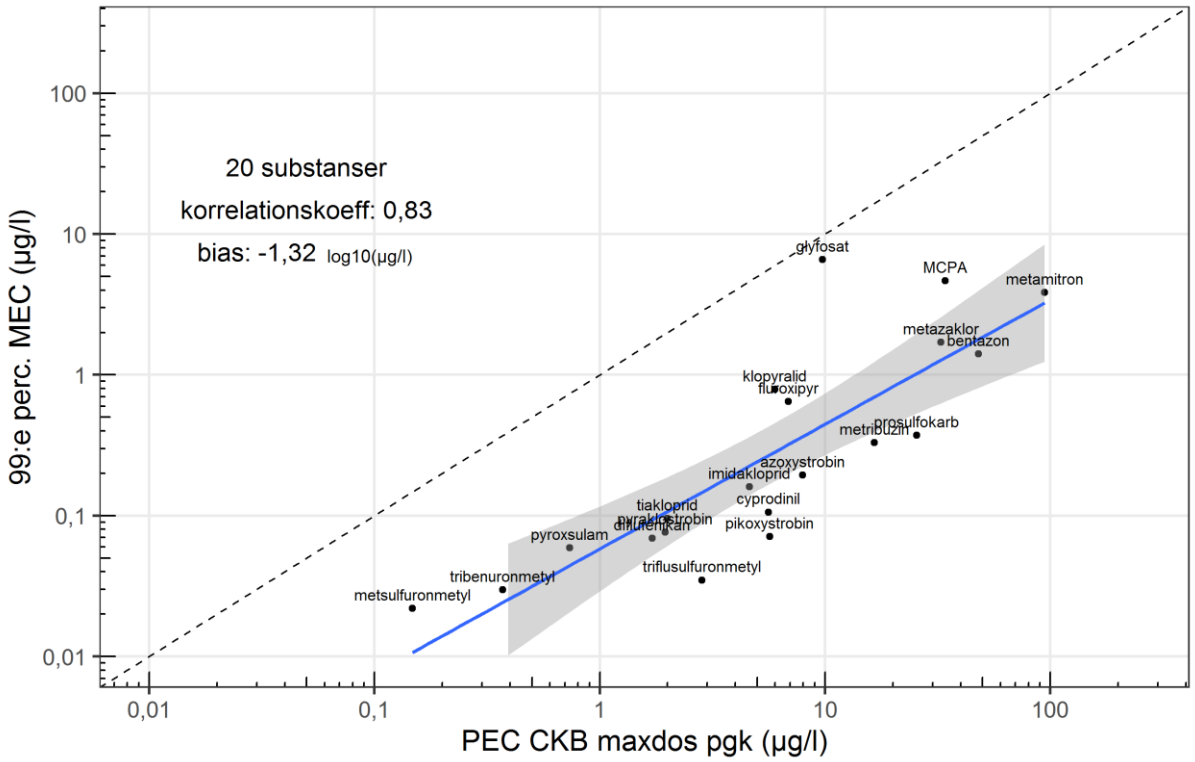

Figure 9. Scatter plot for PEC CKB (calculated using the maximum annual hectare dose in accordance with the Swedish Chemicals Agency's product authorisation (pgk)) against the 99th percentile of measured concentrations (MEC) in the national environmental monitoring programme, for 20 substances which have at least a 90 percentile of MEC, which were used on at least 20 occasions in the national environmental monitoring programme's model catchments during the period 2009 - 2017, and for which data is available from the Swedish Chemicals Agency's product authorisation. The blue line shows the linear regression with a 95% confidence interval (grey area around the line) and the dotted line is x = y. The figure also shows the correlation coefficient and bias. Note that both axes are logarithmic. [TN: Text in the graph is in Swedish.]

In Figure 10, PEC CKB was calculated using the maximum authorised dose from the Swedish Chemicals Agency's product authorisation, but without F_w.

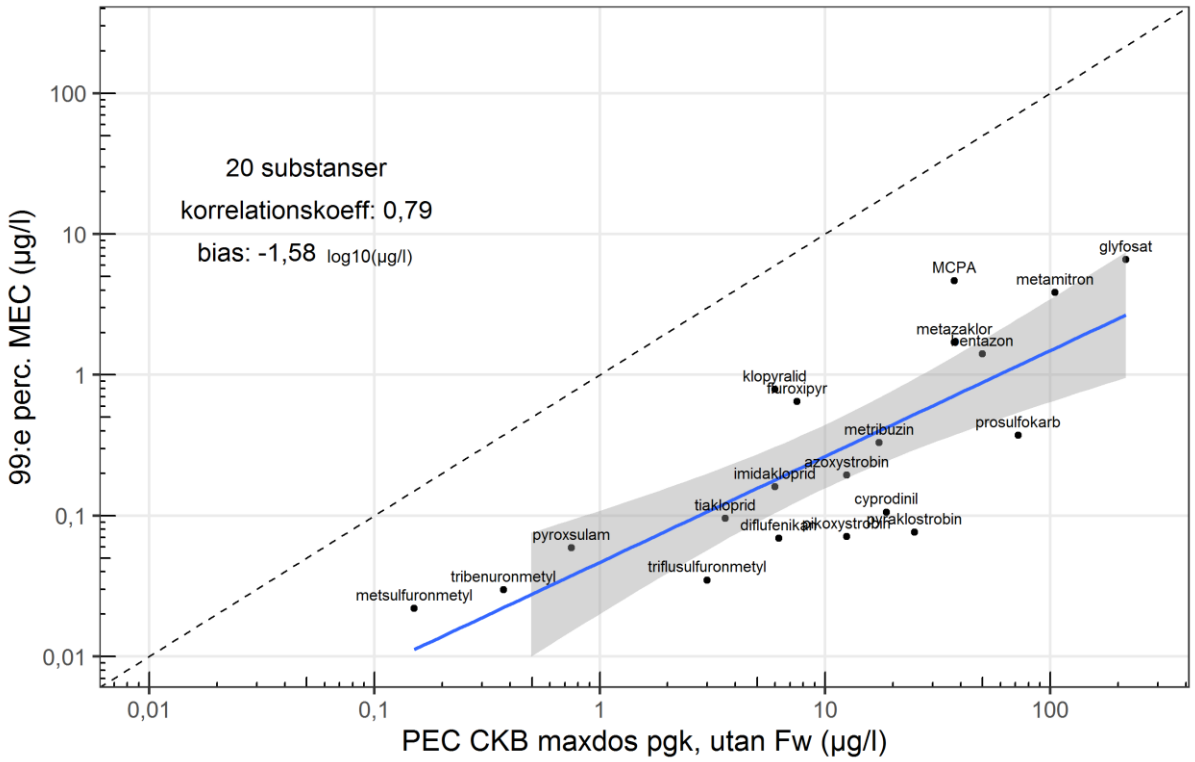

Figure 10. Scatter plot for PEC CKB (calculated using the maximum annual hectare dose in accordance with the Swedish Chemicals Agency's product authorisation (pgk), but without Fw – the distribution between water and sediment) against the 99th percentile of measured concentrations (MEC) in the national environmental monitoring programme, for 20 substances which have at least a 90 percentile of MEC, which were used on at least 20 occasions in the national environmental monitoring programme's model catchments during the period 2009-2017, and for which data is available from the Swedish Chemicals Agency's product authorisation. The blue line shows the linear regression with a 95% confidence interval (grey area around the line) and the dotted line is x = y. The figure also shows the correlation coefficient and bias. Note that both axes are logarithmic. [TN: Text in the graph is in Swedish.]

Figure 11 shows the correlation between PEC Step 3/4 from the Swedish Chemicals Agency's product authorisation and the 99th percentile of MEC. The correlation coefficient is slightly lower than for PEC CKB, but the bias is also smaller, as more substances are closer to the 1:1 line. Imidacloprid is underestimated compared with the 99th percentile of MEC.

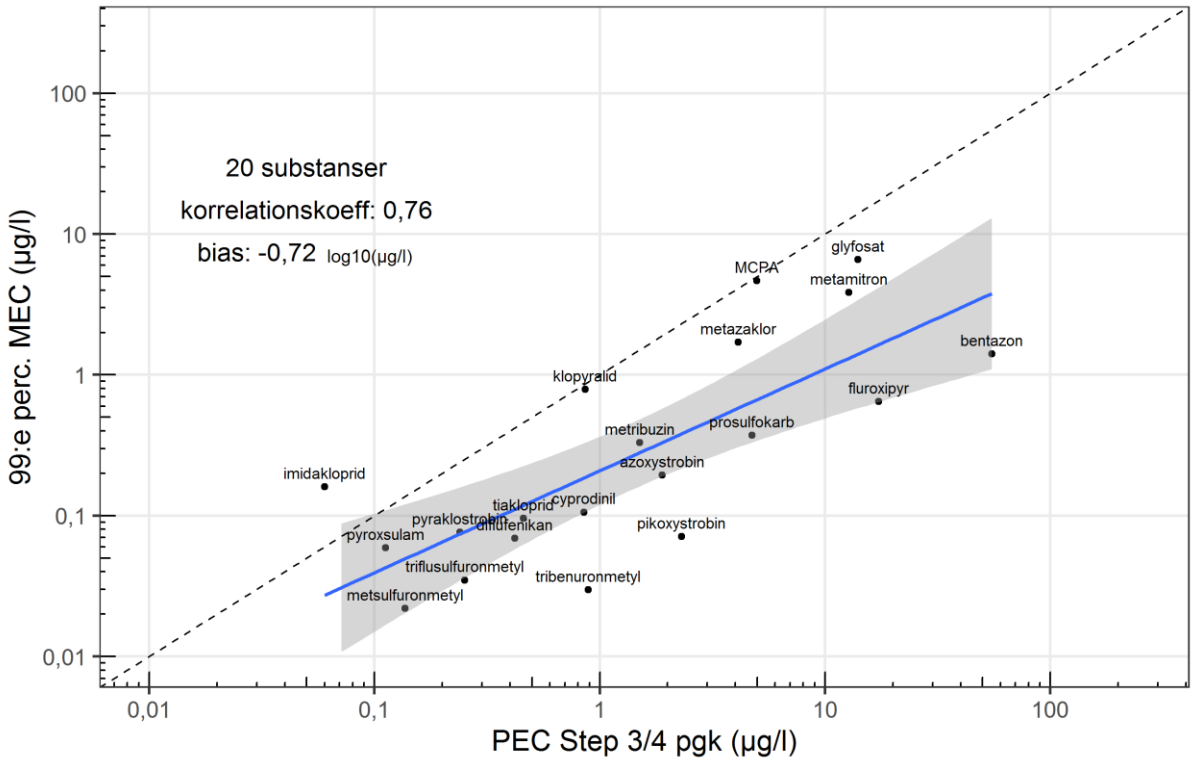

Figure 11. Scatter plot for PEC Step 3 or 4 from the Swedish Chemicals Agency's product authorisation (pgk) against the 99th percentile of measured concentrations (MEC) in the national environmental monitoring programme, for 20 substances which have at least a 90th percentile of MEC, which were used on at least 20 occasions in the national environmental monitoring programme's model catchments during the period 2009 - 2017, and for which data is available from the Swedish Chemicals Agency's product authorisation. The blue line shows the linear regression with a 95% confidence interval (grey area around the line) and the dotted line is x = y. The figure also shows the correlation coefficient and bias. Note that both axes are logarithmic. [TN: Text in the graph is in Swedish.]

3.2 PEC CKB for substances that are rarely detected

The drawback of the above correlation calculations is that they only cover substances that were measured in at least 10 % of the samples, and thus provide no information on how PEC CKB correlates for substances that are either never or only rarely measured above the detection limit. To illustrate how the proposed method works for these substances, PEC CKB for substances with <10% detection frequency (41 substances) was plotted on a box plot for comparison with PEC CKB for the substances which have a detection frequency ≥10% (46 substances). The figure shows that the PEC CKB values for the substances with a detection frequency ≥10% end up in a higher range, and a t-test shows that there is a statistically significant difference between the groups' mean values ($p = 0.0004$ for values logarithmised to base 10 and $p = 0.02$ without log transformation).

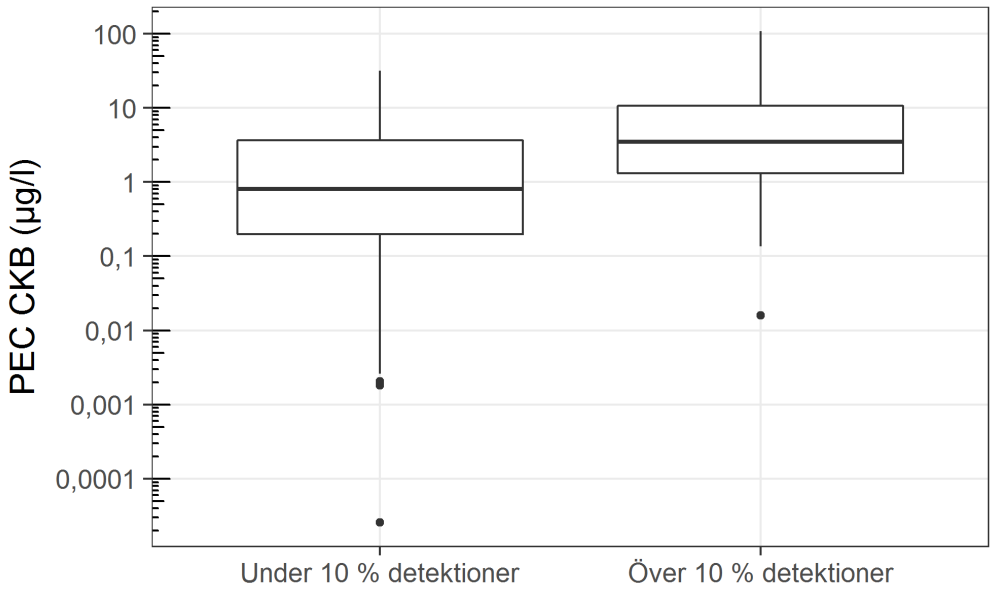

Figure 12. Box plot of PEC CKB for substances with over and under 10% detections in the national environmental monitoring programme. The thicker horizontal line shows the median, the box shows the 25th to 75th percentile range and the "whiskers" show the highest and lowest values which lie within the 1.5 * interquartile range from the 25th and 75th percentiles. Values outside this range are shown as separate points. Note that the y-axis is logarithmic. [TN: Text in the graph is in Swedish.]

3.3 Analysis of sensitivity to changes in K_{foc}

As the reported K_{foc} values for the same substance can vary relatively widely between studies, an attempt has been made here to illustrate how different K_{foc} values impact on the results when calculating PEC CKB using the proposed method. Figure 13 shows the percentage change in PEC CKB when K_{foc} is multiplied by different factors using different original values of K_{foc}. It can be seen here that the percentage changes are small for substances with low K_{foc} values if K_{foc} is multiplied by 1.1 - 2.0. For substances with a K_{foc} of about 100 or above, the impact on PEC CKB will be greater and asymptotically approaches a reduction by a specific factor with a K_{foc} value of about 100,000 or above (e.g. for K_{foc} * 2.0, PEC CKB will be about 50% lower). A literature study would be necessary to determine by how much K_{oc} and K_{foc} can vary between studies for the same substance.

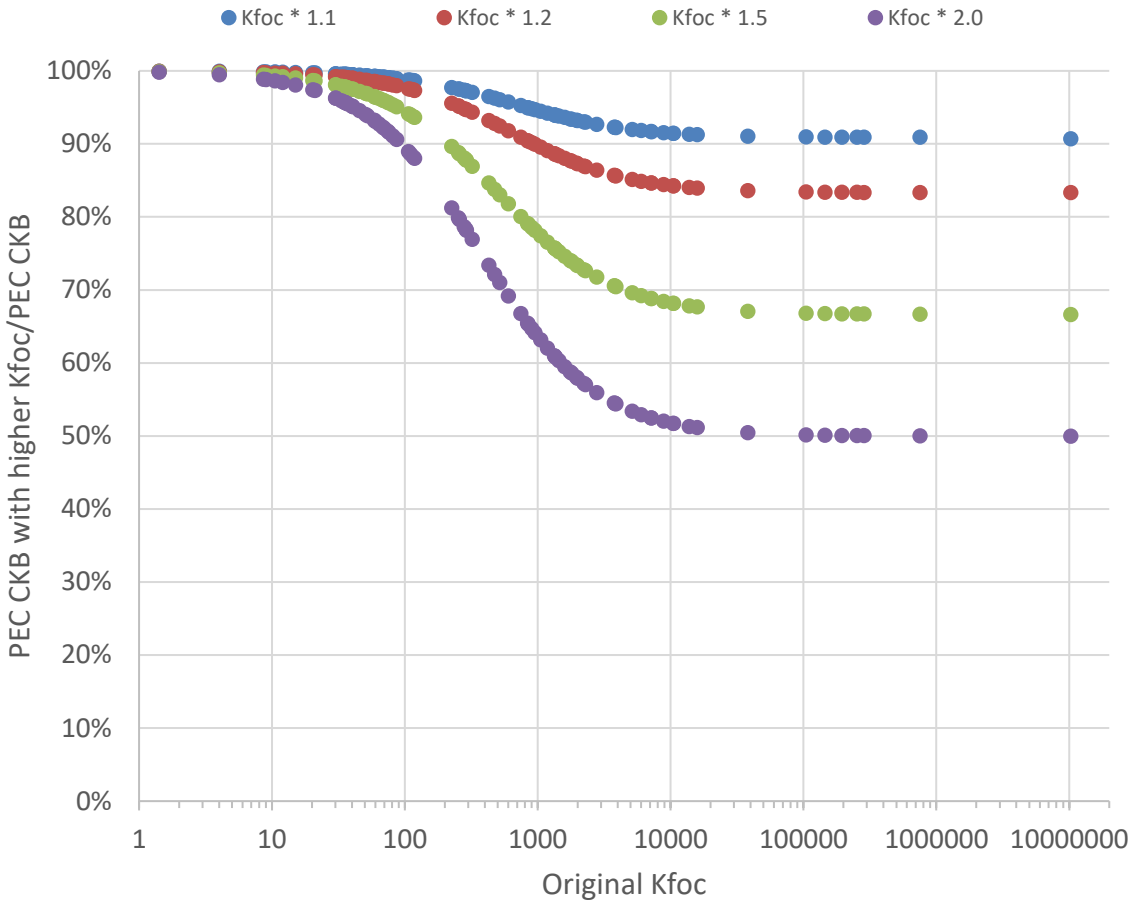

Figure 13. Diagram showing the difference in PEC CKB (y-axis) when Kfoc is multiplied by 1.1; 1.2; 1.5 and 2.0 (different colours) for substances with different original K_{foc} values (x-axis). Note that the x-axis is logarithmic.

4. Discussion

The method proposed for calculating estimated concentrations in surface water (PEC CKB) can be viewed as a variant of FOCUS Step 1, where the effective dilution is adjusted based on data from national environmental monitoring programme in Sweden. The results show that the estimated concentrations in surface water will be lower and that more products could therefore be subject to an environmental risk assessment, without having to go through to the more complicated Step 3 calculation methods.

However, a number of questions must be addressed before PEC CKB or another similar method could be used in the environmental risk assessment which is carried out as part of the product authorisation process. The level of protection provided by PEC CKB must first be discussed. In this report, PEC CKB has primarily been compared with the 99th percentile of MEC, but by adjusting the standard values in the formula, PEC CKB can be displaced linearly to better correspond with any other percentile of MEC. The level of MEC that PEC CKB should correspond to is a topic of further discussion.

Another aspect that is more conceptually built into PEC CKB is that the predicted concentrations correspond to concentrations at the outlet of a catchment, while the calculations for FOCUS Step 1

correspond to the (higher) concentrations that can occur at the edge of the field (" edge-of-field"). That PEC CKB corresponds to the concentrations at the outlet of a catchment means that the results are directly comparable to the national environmental monitoring programme. However, the way in which this should be related to the level of protection required under the authorisation process must be considered in more detail.

Another question that arose during the study is what proportion of concentrations in the surface water we could be at risk of overlooking, as PEC CKB does not explicitly include wind drift. As regards the areas monitored under the national environmental monitoring programme, the effects of wind drift on measured concentrations are likely to be low, especially in the two areas where most of the watercourses are located in culverts. However, the possibility that the impact of wind drift may be greater in other areas cannot be ruled out, especially in connection with the spraying of fruit trees, for example, where wind drift can be a very relevant dispersal path. FOCUS Step 1 assumes that 2.8% of the dose is dispersed to the recipient during the spraying of field crops (FOCUS, 2001). In connection with the spraying of certain other crops, a higher proportion is assumed to be lost via wind drift, e.g. 15.7 – 29.2% in the case of fruit trees (pome/stone fruit). A similar approach as in FOCUS Step 1 to include wind drift could be applied to PEC CKB by varying the M value depending on the crop. However, this is contradicted by the fact that the purpose of the MEC described here is to correspond to the in-field management of plant protection products. Since 1997 there are regulations that make it mandatory for farmers to handle wind drift, initially through SNFS 1997: 2 (Naturvårdsverket, 1997a) and thereto associated General advice 97: 3 (Naturvårdsverket, 1997b), and now through the NFS 2015: 2 (Naturvårdsverket, 2015a) and associated guidance (Naturvårdsverket, 2015b). The management of wind drift by the farmer should be done, among other things, by using fixed protection distances and protective distances adapted based on conditions on the site, proximity to water sources, lakes and watercourses, as well as surrounding land, e.g. by using the Helper[4] (https://www.sakertvaxtskydd.se/hjalpredan/), which has been in use since 1997. With this in mind, the fact that we do not explicitly include wind drift in the model should not be a general problem that causes the proposed method to underestimate levels in watercourses. PEC values for sediment are also included in FOCUS Step 1, but are not included in this proposal for PEC CKB. However, it could be investigated whether PEC values could be calculated in the same way as in FOCUS Step 1.

When calculating PEC CKB, no distinction is made between the spring and autumn treatment of crops. However, the application season is known to be an important factor as regards the risk of dispersal to surface water, where autumn generally results in a higher risk due to lower temperatures, which cause slower degradation, low evapotranspiration rates and higher water flows to drainage. An in-depth analysis of the substances that are mainly applied during the autumn could be carried out to determine whether PEC CKB also provides sufficient protection for these substances. In this context it is worth noting that the calculations of FOCUS Step 1 also make no distinction between spring and autumn application.

According to the "tiered approach", the lower steps in the risk assessment should always be more conservative than the higher ones. This means that if PEC CKB is to be used to replace FOCUS Step 1, PEC CKB should never produce lower predicted concentrations than PEC Step 3/4, as it does with the proposed method in 26-55% of cases. However, whether and, if so, how PEC CKB should replace Step 1 or act as a supplement in a later step of the assessment is a question for future consideration.

[4] TN: In Swedish: *Hjälpredan*.

Here, the question of protection levels arises once again, and it will also be necessary to investigate what is possible under the legislation.

The measured concentrations used in this study were obtained from the four model catchments included in the national environmental monitoring programme for plant protection products. It is therefore logical to ask how representative these types of areas are of Swedish agriculture in general. The model catchments were chosen to represent areas of intensive agriculture in the four largest agricultural regions of Sweden. They are small catchments of 8-16 km^2 high up in the water systems, with 85-92% arable land, so dilution from other areas is limited. This means that the model catchments represent relatively worst-case scenarios for Swedish conditions. However, as mentioned earlier, the measurements were taken in the model catchments at the outlets of the catchments, rather than at the edge of the field, which means that dilution from untreated areas will occur. This dilution is described by the factors *f*, N_s and *q* in PEC CKB and thus produces lower concentrations. The difference in the level of protection between the edge of the field and the outlet of the small, very agriculture-intensive model catchments is a topic for further discussion.

Although the national environmental monitoring programme is only being carried out in four model catchments, wider screenings have been carried out in many more areas scattered across the southern half of the country. In 2015, a screening programme was carried out where surface water samples were taken from 46 localities, while in 2016, a follow-up study was carried out covering 21 localities. These major screening studies produced results which are in line with the national environmental monitoring programme and support the view that model catchments represent worst-case conditions in Sweden. It should be noted that the areas studied in both screening studies were larger catchments (20 - 1202 km^2) and that most areas had a lower proportion of agricultural land (7% - 84%), but the vast majority were clearly agriculture-dominated areas.

When assessing measured concentrations from the model catchments, consideration should be given to the fact that certain measured concentrations may be the result of random circumstances such as accidents, spillages or leakage from spraying equipment. It is also not possible to rule out the possibility that the private use (class 3) of certain active substances such as glyphosate could occur in the areas, or that the use of substances which are also found in biocidal products, such as alpha-cypermethrin, deltamethrin and imidacloprid, also occurs. These considerations cannot be captured by any of the models discussed in this study.

There are crops that are not grown at all or only to a very limited extent in the model catchments, e.g. fruit trees, berries and horticultural crops. Thus, this method cannot be used to show that PEC CKB affords sufficient protection for this type of use.

As mentioned previously, the samples were taken in the model catchments using an automatic sampler which takes a sub-sample approximately every 90 minutes, which is then combined to produce one sample per week. These samples thus represent mean concentrations in the stream over the week and are therefore well-suited to comparison with PEC CKB, which conceptually estimates concentrations with a time resolution of one week. However, this method does not provide any data on the highest concentrations which can occur in the stream, e.g. in the event of peak flows following heavy rain. A review of data from the flow-proportional sampling carried out in the model catchment in Skåne shows that the concentrations in samples taken at elevated flows can be both higher and lower than the weekly samples, and in the vast majority of cases lie within an order of magnitude of the mean concentration during the same week (Boye et al., 2019). A high water flow can cause both a high mass flow of plant protection products and / or a high dilution of substances in the water.

In the comparisons between PEC CKB and measured concentrations where F_w (the effect of K_{foc}) is included, glyphosate stands out as the substance that deviates the most from the correlation. However, when F_w is not included, glyphosate falls much more into line with the other substances. This may be because glyphosate has a high K_{foc} value, which means that in the model that includes $F_{w,}$ it is assumed that a high proportion will be bound to the sediment. However, glyphosate is a special substance, as it is a 'zwitterion' and, along with a high K_{foc} value, also has a high water solubility. It is also a well-known mobile substance. These properties can adversely impact on the usefulness of the model as regards glyphosate in particular.

One consideration linked to this is the fact that the chemical analyses under the national environmental monitoring programme include particles, and thus the particle-bound fraction of the substances, rather than just what is dissolved in the water phase. This may mean that the model which includes F_w will not necessarily produce a better result. One hypothesis is that including the effect of K_{foc} on the binding of the substance in the soil before it enters the watercourse in the model would produce a better result. In the proposal presented here, this effect is primarily represented by the factor *M*, which concerns the percentage loss and is set to 1% for all substances.

One disadvantage of the statistical indicators that are used in the study is that they do not take into account substances that are rarely, if ever, detected. An attempt to illustrate the difference between PEC CKB for these substances compared with the substances which are detected more often is made in section 3.2. This shows that PEC CKB is generally lower for those substances that are either rarely or never encountered.

The results of the study indicate that the correlation between PEC CKB and measured concentrations is relatively good, even though the proposed calculation method is very simple and requires minimal input data. However, there is obviously some spread in the underlying data, and further work could possibly achieve even closer conformity between predicted and measured concentrations. Further work to improve the proposed method could be: more realistic scenarios for different product applications (corresponding to FOCUS Step 2) could be calculated by changing the values for *f* and N_s based on, for example, crop distribution and patterns of use. Data as a basis for this could be obtained from the national environmental monitoring programme. Making the percentage loss, *M*, substance-specific would be another "Step 2" variant. We have previously attempted to statistically explain the variation in measured *M* values from the model catchments based on substance properties, but this approach has not been very successful. However, this could be studied further in a future project.

5. Conclusions

- The proposed method for calculating estimated concentrations in surface water in small catchments with a time resolution of one week (PEC CKB) provides a good estimate of the highest concentrations that can be measured in the model catchments of the national environmental monitoring programme, without being overly conservative.
- The estimated concentrations can be adjusted linearly either upwards or downwards for all substances by changing the standard values in the formula, thus making it possible to adjust the level of protection for PEC CKB. This could for example be done based on the ratios between the measured concentrations and PEC CKB given in Appendix 2.
- PEC CKB has a relatively strong correlation with the 99th percentile of measured concentrations in the national environmental monitoring programme.

- In many cases, PEC CKB lies between PEC Step 3/4 and Step 1, but in 26-55% of cases, PEC CKB lies below PEC Step 3/4.
- On average PEC CKB provides lower estimated concentrations for substances that are rarely if ever detected in the national environmental monitoring programme.
- A number of proposals for further development of the model, by making more factors substance-specific, have been discussed.

6. Acknowledgements

The project was funded by the Swedish Board of Agriculture through the Swedish Pesticide Council (agreement ref. no. 4.1.11-14984/2018). We would like to thank everyone who contributed to the project in the form of valuable discussions and background data (Mats Allmyr, Johan Axelman, Sara Furuhagen, Abdul Ghafoor, Milena Ivansson, Maja Larsson, Julien Moeys and Markus Ollikainen). Special thanks must go to Claudia von Brömssen (Department of Energy and Technology, SLU) for her assistance with the statistical analyses.

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8. Appendices

Appendix 1 – Substance lists

Lists of all substances included in the study and substances included in the correlation analyses.

87 substances	43 substances	20 substances
2,4-D	amidosulfuron	azoxystrobin
acetamiprid	azoxystrobin	bentazone
aclonifen	bentazone	cyprodinil
alpha-cypermethrin	bixafen	diflufenican
amidosulfuron	boscalid	fluroxypyr
amisulbrom	cycloxydim	glyphosate
azoxystrobin	cyprodinil	imidacloprid
bentazone	diflufenican	clopyralid
betacyflutrin	ethofumesate	MCPA
bifenox	phenmedipham	metamitron
bixafen	fludioxonil	metazachlor
boscalid	fluopicholide	metribuzin
cyazofamid	fluopyram	metsulfuron-methyl
cyflufenamid	fluroxypyr	picoxystrobin
cycloxydim	flurtamone	prosulfocarb
cypermethrin	glyphosate	pyraclostrobin
cyprodinil	imidacloprid	pyroxsulam
deltamethrin	isoproturon	thiacloprid
difenoconazole	clomazone	tribenuron-methyl
diflufenican	clopyralid	triflusulfuron-methyl
dichlorprop	chloridazon	
dimethoate	quinmerac	
esfenvalerate	mandipropamid	
ethofumesate	MCPA	
phenitrotion	metalaxyl	
phenmedipham	metamitron	
fenoxaprop-P	metazachlor	
fenpropidin	metribuzin	
fenpropimorph	metsulfuron-methyl	
florasulam	picoxystrobin	
fluazinam	pirimicarb	
fludioxonil	prochloraz	
fluopicholide	propamocarb	
fluopyram	propiconazole	
flupyrsulfuron methyl-sodium	propoxycarbazone-sodium	
fluroxypyr	prosulfocarb	
flurtamone	pyraclostrobin	
foramsulfuron	pyroxsulam	
glyphosate	rimsulfuron	
hexythiazox	sulfosulfuron	

87 substances	43 substances	20 substances
imidacloprid	thiacloprid	
indoxacarb	tribenuron-methyl	
isoproturon	triflusulfuron-methyl	
iodsulfuron-methyl-sodium		
carfentrazone-ethyl		
clethodim		
clomazone		
clopyralid		
chloridazon		
quinmerac		
lambda-cyhalothrin		
mandipropamid		
MCPA		
mecoprop		
mesosulfuron-methyl		
mesotrione		
metalaxyl		
metamitron		
metazachlor		
metrafenone		
metribuzin		
metsulfuron-methyl		
napropamide		
pendimethalin		
picloram		
picoxystrobin		
pirimicarb		
prochloraz		
propaquizafop		
propamocarb		
propiconazole		
propoxycarbazone-sodium		
propyzamide		
prosulfocarb		
pymetrozine		
pyraclostrobin		
pyroxsulam		
rimsulfuron		
sulfosulfuron		
tau-fluvalinate		
thiacloprid		
thifensulfuron-methyl		
thiofanate-methyl		
tribenuron-methyl		
trifloxystrobin		
triflusulfuron-methyl		
trinexapac-ethyl		

Appendix 2 – Ratios between percentiles of measured concentrations and PEC CKB

Ratios of percentiles of measured concentrations (MEC) divided by PEC CKB (calculated using the mean annual hectare dose from the national environmental monitoring programme 2009 - 2017 and including F_w). Ratios over 1, i.e. where the percentile of measured concentrations is higher than PEC CKB, are indicated in red.

Substance	max. MEC / PEC CKB	99th percentile MEC / PEC CKB	97.5th percentile MEC / PEC CKB	95th percentile MEC / PEC CKB	90th percentile MEC / PEC CKB
2,4-D	0.0049	0.0036	0.0025		
acetamiprid	0.0034	0.0014	0.0011	0.0006	
aclonifen	1.7321	0.0086			
alpha-cypermethrin	67.3830	2.5813			
amidosulfuron	4.7015	0.2355	0.0899	0.0435	0.0155
amisulbrom	0.4120	0.1811			
azoxystrobin	0.1335	0.0721	0.0356	0.0175	0.0091
bentazone	0.9908	0.0667	0.0379	0.0245	0.0142
betacyflutrin	4.2154				
bifenox					
bixafen	0.2684	0.2580	0.0794	0.0468	0.0220
boscalid	0.2560	0.0427	0.0153	0.0101	0.0059
cyazofamid	0.0290	0.0082	0.0029	0.0013	
cyflufenamid	0.0177				
cycloxydim	0.6697	0.0107	0.0033	0.0010	0.0002
cypermethrin	0.8058	0.0161			
cyprodinil	0.1970	0.0475	0.0109	0.0045	0.0022
deltamethrin	3687.9145				
difenoconazole	1.4700	0.0707	0.0325	0.0141	
diflufenican	0.2324	0.0844	0.0500	0.0278	0.0171
dichlorprop	0.0004	0.0004	0.0003	0.0003	0.0002
dimethoate					
esfenvalerate	21.8942	1.4596	0.4865	0.2433	
ethofumesate	0.1821	0.0531	0.0245	0.0088	0.0032
phenitrotion					
phenmedipham	0.0397	0.0174	0.0050	0.0010	0.0001
fenoxaprop-P	0.0215	0.0054			
fenpropidin					
fenpropimorph	0.0622	0.0069	0.0019		
florasulam	0.4111	0.1396	0.0536	0.0238	
fluazinam	0.1677	0.0211	0.0014		
fludioxonil	0.5610	0.5236	0.3740	0.3117	0.2493
fluopicholide	0.0274	0.0231	0.0128	0.0089	0.0041
fluopyram	0.1387	0.1323	0.0301	0.0200	0.0126
flupyrsulfuron methyl-sodium	0.3282	0.0364	0.0052		
fluroxypyr	0.4786	0.1725	0.1223	0.0665	0.0346
flurtamone	0.1118	0.0223	0.0144	0.0044	0.0012
foramsulfuron					

Substance	max. MEC / PEC CKB	99th percentile MEC / PEC CKB	97.5th percentile MEC / PEC CKB	95th percentile MEC / PEC CKB	90th percentile MEC / PEC CKB
glyphosate	21.8626	2.5315	1.3137	0.7288	0.3414
hexythiazox					
imidacloprid	0.0683	0.0354	0.0141	0.0078	0.0053
indoxacarb					
isoproturon	0.4739	0.0259	0.0140	0.0076	0.0037
iodsulfuron-methyl-sodium	0.3088	0.0514	0.0152		
carfentrazone-ethyl	0.1413	0.0041			
clethodim	0.0165	0.0136	0.0094	0.0071	
clomazone	0.0671	0.0288	0.0186	0.0092	0.0028
clopyralid	0.8447	0.3341	0.1818	0.1229	0.0760
chloridazon	0.1405	0.0753	0.0071	0.0038	0.0019
quinmerac	0.4278	0.1536	0.0736	0.0276	0.0098
lambda-cyhalothrin	0.5172	0.1203	0.0556		
mandipropamid	0.0505	0.0106	0.0041	0.0022	0.0011
MCPA	0.4854	0.2053	0.0529	0.0278	0.0130
mecoprop	0.0285	0.0285	0.0281	0.0246	0.0212
mesosulfuron-methyl	0.0535				
mesotrione					
metalaxyl	0.1178	0.0731	0.0176	0.0087	0.0051
metamitron	0.1573	0.0356	0.0134	0.0029	0.0008
metazachlor	0.3964	0.0563	0.0189	0.0059	0.0022
metrafenone	0.0163	0.0049	0.0011		
metribuzin	0.1088	0.0257	0.0162	0.0109	0.0065
metsulfuron-methyl	3.0879	0.1610	0.0616	0.0368	0.0221
napropamide					
pendimethalin					
picloram					
picoxystrobin	0.1747	0.0497	0.0179	0.0112	0.0054
pirimicarb	0.1243	0.0682	0.0124	0.0055	0.0021
prochloraz	0.1351	0.0211	0.0078	0.0036	0.0015
propaquizafop					
propamocarb	0.0399	0.0056	0.0025	0.0009	0.0003
propiconazole	0.3533	0.1178	0.0636	0.0416	0.0220
propoxycarbazone-sodium	0.1365	0.0384	0.0161	0.0097	0.0046
propyzamide	0.0044	0.0041	0.0037	0.0020	0.0004
prosulfocarb	0.2339	0.0174	0.0075	0.0033	0.0012
pymetrozine	0.0192				
pyraclostrobin	1.0333	0.3159	0.0620	0.0248	0.0124
pyroxsulam	0.1996	0.0984	0.0335	0.0166	0.0100
rimsulfuron	0.2627	0.0884	0.0182	0.0113	0.0004
sulfosulfuron	0.0820	0.0523	0.0335	0.0259	0.0144
tau-fluvalinate	6.6504	1.1084			
thiacloprid	0.2894	0.0544	0.0119	0.0068	0.0028
thifensulfuron-methyl	0.9153	0.0333	0.0127		
thiofanate-methyl					

Substance	max. MEC / PEC CKB	99th percentile MEC / PEC CKB	97.5th percentile MEC / PEC CKB	95th percentile MEC / PEC CKB	90th percentile MEC / PEC CKB
tribenuron-methyl	1.2532	0.1554	0.0788	0.0470	0.0157
trifloxystrobin					
triflusulfuron-methyl	0.1366	0.0513	0.0188	0.0059	0.0015
trinexapac-ethyl	0.3433	0.0428	0.0140	0.0065	

Appendix 3 – Calculated statistics

Various statistical measures of the relationships (correlation coefficient, Root Mean Square Error, Mean Absolute Error and Bias) between different percentiles (maximum; 99th; 97.5th; 95th and 90th percentile) of measured concentrations (MEC) in the national environmental monitoring programme 2009 - 2017 and various PEC values; PEC CKB (calculated using the mean annual field dose from the national environmental monitoring programme and the factor F_w (the proportion that ends up in water rather than in sediment)), and PEC CKB without F_w calculated for a subset of 43 substances and a sub-set of 20 substances. For the subset of 20 substances, statistics concerning the relationship with MEC percentiles were also calculated for PEC CKB using the maximum authorised dose from the Swedish Chemicals Agency's product authorisation (pgk) with and without F_w, against PEC Step 3 or 4 from the Swedish Chemicals Agency's product authorisation, as well as directly against different ways of calculating the field dose and directly against the factor F_w. All statistics were calculated on values logarithmised to base 10.

Correlation coefficients

	PEC CKB	PEC CKB without F_w	PEC CKB	PEC CKB without F_w	PEC CKB max. dose product authorisation	PEC CKB max-dose product authorisation without F_w	PEC Step 3/4 Swedish Chemicals Agency's product authorisation	Max. dose product authorisation	Area-weighted yearly hectare-dose	Median dose per application	F_w
	43 substances	**43 substances**	**20 substances**	**20 substances**	**20 substances**	**20 substances**	**20 substances**	**20 substances**	**20 substances**	**20 substances**	**20 substances**
MEC (max.)	0.74	0.66	0.75	0.80	0.75	0.73	0.82	0.73	0.80	0.81	-0.13
MEC (99%)	0.76	0.72	0.81	0.84	0.83	0.79	0.76	0.79	0.84	0.84	-0.11
MEC (97.5%)	0.73	0.70	0.79	0.80	0.81	0.75	0.80	0.75	0.80	0.80	-0.06
MEC (95%)	0.65	0.64	0.74	0.75	0.75	0.70	0.78	0.70	0.75	0.76	-0.05
MEC (90%)	0.54	0.57	0.69	0.71	0.70	0.66	0.73	0.66	0.71	0.73	-0.06

RMSE - Root Mean Square Error (log10[µg/l])

	PEC CKB	PEC CKB without Fw	PEC CKB	PEC CKB without Fw	PEC CKB max. dose product authorisation	PEC CKB max. dose product authorisation without F_w	PEC Step 3/4 Swedish Chemicals Agency's product authorisation				

	43 substances	43 substances	20 substances	20 substances	20 substances	20 substances	20 substances				
MEC (max.)	0.81	1.05	0.69	0.83	0.87	1.11	0.50				
MEC (99%)	1.28	1.53	1.14	1.36	1.39	1.66	0.89				
MEC (97.5%)	1.68	1.93	1.52	1.76	1.78	2.06	1.23				
MEC (95%)	1.99	2.24	1.83	2.08	2.10	2.37	1.52				
MEC (90%)	2.39	2.63	2.16	2.41	2.43	2.70	1.85				

MAE - Mean Absolute Error (log10[µg/l])

	PEC CKB	PEC CKB without Fw	PEC CKB	PEC CKB without Fw	PEC CKB max. dose product authorisation	PEC CKB max. dose product authorisation without F_w	PEC Step 3/4 Swedish Chemicals Agency's product authorisation				
	43 substances	43 substances	20 substances	20 substances	20 substances	20 substances	20 substances				
MEC (max.)	0.71	0.91	0.58	0.71	0.80	0.98	0.40				
MEC (99%)	1.20	1.44	1.08	1.29	1.32	1.58	0.76				
MEC (97.5%)	1.60	1.86	1.45	1.69	1.72	1.98	1.12				
MEC (95%)	1.90	2.17	1.74	2.00	2.03	2.29	1.43				
MEC (90%)	2.28	2.55	2.07	2.33	2.36	2.62	1.76				

Bias (log10[µg/l])

	PEC CKB	PEC CKB without Fw	PEC CKB	PEC CKB without Fw	PEC CKB max. dose product authorisation	PEC CKB max. dose product authorisation without F_w	PEC Step 3/4 Swedish Chemicals Agency's product authorisation				
	43 substances	43 substances	20 substances	20 substances	20 substances	20 substances	20 substances				

MEC (max.)	-0.59	-0.85	-0.39	-0.65	-0.68	-0.93	-0.08				
MEC (99%)	-1.18	-1.44	-1.04	-1.29	-1.32	-1.58	-0.72				
MEC (97.5%)	-1.59	-1.86	-1.43	-1.69	-1.72	-1.98	-1.12				
MEC (95%)	-1.90	-2.17	-1.74	-2.00	-2.03	-2.29	-1.43				
MEC (90%)	-2.28	-2.55	-2.07	-2.33	-2.36	-2.62	-1.76				