

Pesticides: Risks to Lakes and Streams?

Pesticide residues are most undesirable in surface waters. By applying a global quality criterion of 0.1 µg/l, the Swiss Water Protection Ordinance to date does not discriminate between the different effects of the over 400 registered active substances. To improve this situation, Eawag proposes an effect-based risk assessment approach for individual pesticides and pesticide mixtures.

For many years, Swiss surface waters have been contaminated by a wide variety of pesticides [1]. Due to their toxic function in curbing damaging pests and weeds, pesticides are also hazardous to flora, fauna and microorganisms in lakes and streams.

Water pollution, resulting from agricultural use of pesticides, usually follows a seasonal pattern. Pesticide concentrations are particularly high if applied to fields during or shortly after rain events: values of up to a few µg/l have then been measured in streams and medium-sized rivers [2]. The quantity of pesticides reaching water bodies

from farmland is dependent on the physico-chemical properties of the substances, topography of the landscape and soil characteristics [2]. Some 20 – mostly herbicides – of the more than 400 active pesticides registered in Switzerland are found regularly in surface waters (Tab. 1).

Some of these substances are extremely toxic, others less toxic. For effective water protection, a realistic assessment of the risks presented by individual pesticides or pesticide mixtures is therefore essential. Such a risk assessment requires the integration of as much ecotoxicity data as pos-

sible, currently lacking in most evaluation methods. Eawag is therefore developing an effect-based risk assessment system in collaboration with the Federal Office of Environment, Forest and Landscape (FOEFL). Based on the available ecotoxicity data, this system allocates an individual water quality criterion to each pesticide expressing the specific pesticide concentration, which should not be exceeded in surface waters in order not to endanger aquatic organisms. A second step involves the integration of the effect-based quality criteria in the risk assessment.

Traditional Risk Assessment

The risk presented by a pesticide is usually calculated by means of Formula 1 (see Box “Formulas”) [3]. If the risk factor is below 1, the probability for aquatic organisms to be damaged by the pesticide is relatively low. If the factor is above 1, the damage probability is high. The quality criterion of 0.1 µg/l, established by the Swiss Water Protection Ordinance, allows identification of polluted water bodies, but not performance of a risk evaluation, since this quality criterion has been arbitrarily defined without any consideration of the varying effects of the different pesticides.

In other countries, effect-based quality criteria are used for risk assessment [4–7].

Application as	Product
Herbicide	2,4-D, atrazine, dicamba, dimefuron, dimethenamid, diuron, ethofumesat, isoproturon, linuron, MCPA, mecoprop, metolachlor, metolachlor, napromide, propachlor, simazine, tebutam, terbuthryn, terbuthylazine, and triclopyr
Insecticide	Diazinon and primicarb
Fungicide	Metalaxyl, oxadixyl and penconazole

Tab. 1: Some 20 pesticides are regularly detected in Swiss water bodies.

Formulas

Formula 1

$$\text{Risk quotient of a pesticide} = \text{RQ} = \frac{\text{pesticide concentration in water body}}{\text{quality criterion}} = \frac{\text{MEC}}{\text{quality criterion}}$$

Formula 2

$$\text{Risk quotient of an individual pesticide} = \text{RQ}_i = \frac{\text{MEC}}{\text{HC5-95\%}}$$

Formula 3

$$\text{Risk quotient of a pesticide mixture} = \text{RQ}_m = \sum_{i=1}^n \text{RQ}_i = \sum_{i=1}^n \frac{\text{MEC}_i}{\text{HC5-95\%}_i} = \frac{\text{MEC}_1}{\text{HC5-95\%}_1} + \dots + \dots + \frac{\text{MEC}_n}{\text{HC5-95\%}_n}$$

RQ = risk quotient, MEC = see Glossary, i = individual substance, m = mixture, n = number of pesticides in mixture

However, these assessment criteria also have weak points. The currently most widespread, effect-based quality criterion is the PNEC value (see Glossary). When calculating the PNEC value, all ecotoxicity test data (EC50 and NOEC values, see Glossary) are taken into consideration. However, as the PNEC value is ultimately based on the lowest EC50 or NOEC value, criticism to that effect that the PNEC is reliant on a single data point is justified. In addition, the PNEC value is provided with arbitrarily selected security factors (see Glossary).

For some years, the hazardous concentration HC (see Glossary) has been used as an effect-based quality criterion in risk assessment [8]. Calculation of the HC is dependent on the statistical assessment of NOEC data available in the literature (see Box “Hazardous Concentration”). However, one of the difficulties in calculating reliable HC values is the required input of at least 10 NOEC values from chronic toxicity tests—a requirement not currently met by most pesticides.

A New Method to Calculate Sound, Effect-based Quality Criteria

Despite these drawbacks, the HC is currently the most reliable parameter we have.

Our project therefore focused on establishing a method allowing calculation of the HC value, even with few or no NOEC data available. Specifically, we have chosen the HC5-95% value (see Box “Hazardous Concentration”) as the effect-based quality criterion.

Our method comprises three stages (Fig. 1):
 1. SSD curves based on EC50 (see Glossary and Box “Hazardous Concentration”) were established for all pesticides in the mixture as well as for a reference pesticide. The more abundant EC50 data were chosen instead of the NOEC values. As a reference, a pesticide is chosen on which 8–10 long-term and short-term tests had been carried out ensuring sufficient NOEC and EC50 data. Subsequently, the so-called “toxicity ratio” is calculated between the individual SSD-EC50 pesticide curves and the SSD-EC50 curve of the reference pesticide.

2. A second SSD curve provided with confidence range is established for the reference substance – based this time on the NOEC values available in the literature.

3. The SSD-NOEC curves of the other substances, including the confidence range, are plotted on the basis of the SSD-NOEC curve of the reference substance. This is possible by using the toxicity ratio calculated at the

start. Finally, the HC5-95% for each substance was derived from the new SSD-NOEC curves.

However, our new method can be used in practice only if the following two hypotheses are verified:

- Pesticides with similar action modes show parallel SSD-EC50 and SSD-NOEC curves.

The “Hazardous Concentration” HC

HC values are calculated from so-called “Species Sensitivity Distribution” curves (SSD curves) [8] in which the distribution of the NOEC data is logarithmically plotted against the percentage of the species affected. In the ideal case, the NOEC data are distributed log-normal, resulting in an S-shaped curve in cumulative plotting of SSD. In practice, HC5 values have become established. They designate the pesticide concentration at which 5% of the total number of species are endangered or 95% of all the species are protected. The SSD curves may also be provided with a confidence interval. The smaller the confidence interval, the better is the quantity and quality of the available ecotoxicity data. This confidence interval allows calculation of the HC5-95% value. It expresses with a 95% probability the pesticide concentration at which 5% of the species are endangered and 95% are protected. The HC5-95% value is always lower than the HC5 value – the smaller the confidence interval, the more the two values converge [9].

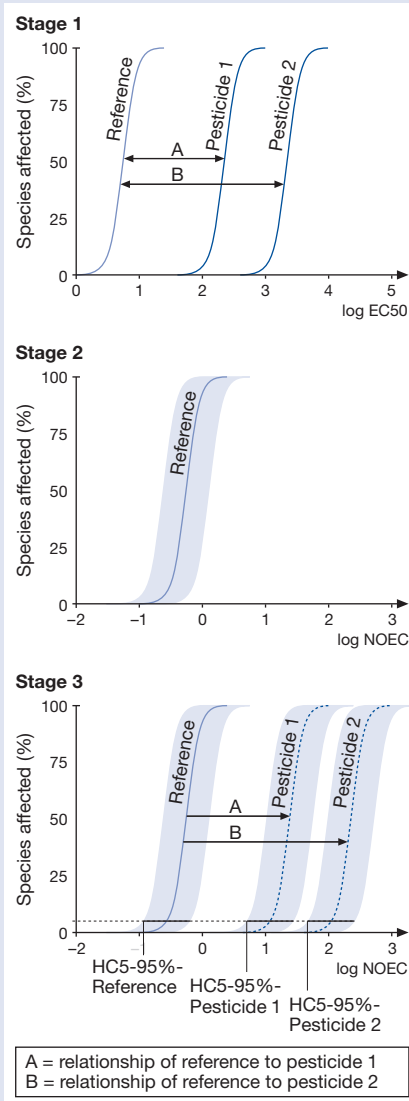
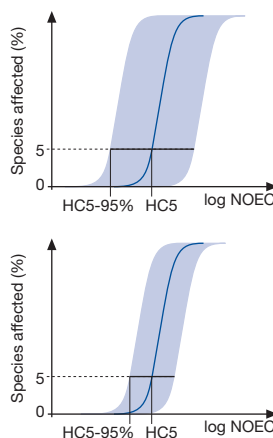


Fig. 1: The three stages of the recently developed calculation method for more consistent HC5-95% values. See text for further explanations.

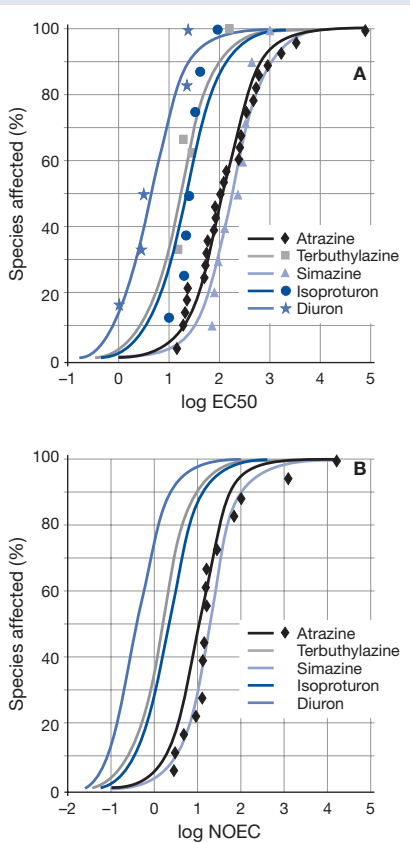


Fig. 2: Individual HC5-95% values for the five pesticides in a pesticide mixture were calculated with the new method. SSD curves were plotted from EC50 data (A), allowing the corresponding SSD-NOEC curves to be derived (B).

■ The “toxicity ratio” between the SSD-EC50 and the SSD-NOEC curves is constant.

Since studies on the SSD curves are fairly recent, it is unclear whether these hypotheses are correct. A comparison of the SSD-NOEC curves, derived by this method with the few NOEC data available from literature, indicates that our assumptions are acceptable.

The HC5-95% values will have to be regularly updated if additional effect data become available. Availability of more data increases HC significance.

Our Recommendations

In future, our method will allow calculation of consistent HC5-95% values. We therefore recommend the following measures:

■ The global quality criterion of 0.1 µg/l, established by the Swiss Water Protection Ordinance, should be replaced by individual HC5-95% values.

■ For risk assessment of individual substances, the individual HC5-95% pesticide values should be used in Formula 2 as effect-based quality criteria (see Box “Formulas”).

■ The HC5-95% values can also be used in risk assessment of pesticide mixtures, provided the mixtures contain pesticides with

similar action modes. This is where the concept of concentration additivity can be applied. According to this theory, concentrations of substances with similar effect mechanisms can be weighted and added according to their toxicity [10], and their risks then calculated by using Formula 3 (see Box “Formulas”).

Example: Risk Assessment of 5 Herbicides

The risk of a herbicide mix in the small river Aa near Mönchaltorf, Canton of Zurich was assessed with the method described above. The mixture comprised 5 herbicides, each an inhibitor of photosynthesis affecting the photosystem II. Although their sites of action are not identical [11], these herbicides follow the concept of concentration additivity [Chèvre et al., soon to be published]. Atrazine was chosen as the reference herbicide. To calculate the SSD curves, only toxicity data from tests on aquatic primary producers (algae and aquatic flora) were used, since they are the most sensitive to this type of pollutant. Figure 2A classifies the 5 herbicides according to their SSD-EC50 curves. Diuron is the most toxic herbicide, followed by isoproturon, terbutylazine, atrazine, and simazine. In Figure 2B, the SSD-EC50 curves are transposed to the SSD-NOEC

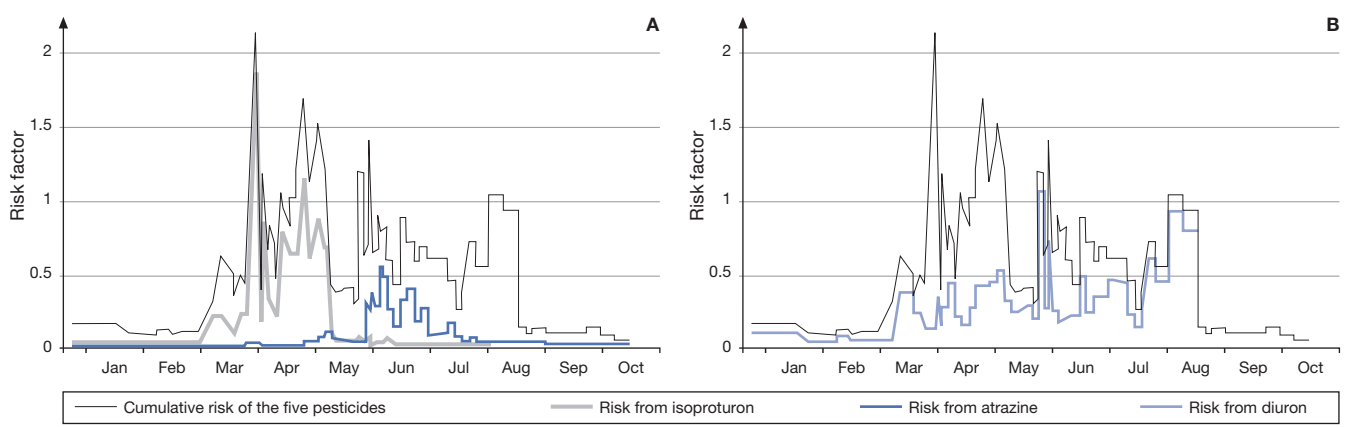


Fig. 3: Risk assessment of the five pesticides in a pesticide mixture.

curves as described in stage 3 of our method.

The risk of damage of this herbicide mixture to aquatic ecosystems in spring (March to May) sometimes clearly exceeds 1 (Fig. 3A). If we consider the risks posed by the individual herbicides in the mixture, two phenomena can be observed: Firstly, the impact risks for the herbicides in water can also be superimposed if they are applied at different times. This is the case for isoproturon and atrazine used in March to April and May to June respectively, showing a risk of super-

position in May (Fig. 3A). Secondly, some herbicides occur not only during their application period, but have also been regularly detected throughout the year. These substances reveal a constant baseline load as in the case of our study on diuron, which is not only used as a herbicide, but also as a preservative in paints. Diuron appears to be continuously washed off from house surfaces and subsequently transported into lakes and streams (Fig. 3B). In our research region, diuron is not used as a herbicide, but mainly applied in viticulture. Nevertheless, this should not be underestimated, since it largely contributes to the total risk, along with the baseline risks of the other herbicides.

Our results indicate the importance of integrated herbicide management.

detected regularly in the water. Further pesticide groups will soon follow.

In the context of standardization, it is of utmost importance to establish clear rules for pesticide sampling. Definition of these rules and selection of sampling sites are the subject of a parallel project. The results of both projects could be useful as reference material for revision of the Swiss Water Protection Ordinance.



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Risk Parameter Glossary

MEC = Measured Environment Concentration – indicates the pollutant concentration actually detected in the water body.

EC50 = Effect Concentration 50% – usually determined by laboratory testing for acute toxicity. It expresses the pollutant concentration at which 50% of the exposed organisms show the tested effect. Mortality is generally used as the indicator.

NOEC = No-Observed Effect Concentration – usually determined by laboratory testing for chronic toxicity. It expresses the pollutant concentration at which no effect is detectable. Usually reproduction or growth is used as the indicator.

PNEC = Predicted No-Effect Concentration – calculated from EC50 and NOEC data. It expresses the pollutant concentration at which no effect is expected in the field. The PNEC is based on the lowest EC50 and/or NOEC values and is also provided with a security factor. The lower this factor, the greater the availability of chronic toxicity data (NOEC data) and number of tested trophic levels (levels in the nutrition pyramid). The security factor includes the uncertainty obtained when the limited amount of laboratory toxicity data are extrapolated to natural conditions.

HC = Hazardous Concentration, derived from SSD curves, indicates the concentration corresponding to a given level of environmental protection (see Box “Hazardous Concentration”).

SSD Curves = Species Sensitivity Distribution Curves – represent the percentage of species affected as a function of the pollutant concentration (log NOEC) (see Box “Hazardous Concentration”).

Outlook

The recommended method is currently used to calculate new quality criteria for the most commonly detected herbicides in water (triazine, phenylurea, chloroacetanilide), as well as for a specific group of insecticides, the organophosphates, of which diazinon is

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