Species Sensitivity Distribution of Dichlorvos in Surface Water Species

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Abstract

During the last years, dichlorvos has had an extremely high occurrence in monitoring campaigns, showing concentrations that would result in severe environmental impact. Environmental quality concentrations (EQC) for dichlorvos in surface waters vary by more than two orders of magnitude among different regulations. Regulatory EQC-values are based on toxicity data where species sensitivity distributions (SSDs) are mostly used as a basis. Hence, what makes the difference between the different national and regional EQC-values? And will they all protect the aquatic fauna? To investigate these questions, we constructed an SSD based on our laboratory data and compared this with SSDs based on literature data for technical and formulated products and species of different taxa. Finally, we compared the SSD-derived EQCs with a meta-study on monitored environmental concentrations to determine the EQC-exceedance. The following hypotheses were tested: (i) formulated dichlorvos will result in lower EQCs, as formulated products may include synergists; (ii) different taxon will have different sensitivities with arthropods being the most sensitive group; (iii) environmental concentration of dichlorvos represents a risk for aquatic organisms. As a result, experimental SSD defined a protective concentration of 6.5 ng L^{-1} for 5% of the species, which is in line with the European limit values, but one to two-fold lower than the limit values of the USA, China, and Argentina. The EQCs of three of the four regions included in this study are therefore not enough to protect the aquatic fauna.

Introduction

The aquatic environments are under pressure due to human activities where xenobiotics such as pesticides, pharmaceuticals, and industrial chemicals are daily released to surface waters [1, 2, 3]. Pesticides are easily spread in the environment as they may reach water matrices during their application (drift), by run-off and/or by leaching, therefore representing a risk on the preservation of aquatic environments [4, 5]. In fact, adverse effects of pesticides on non-target organisms have been widely reported [6, 7]. Despite the relatively low occurrence and concentration of neuroactive insecticides in natural waters, they have been identified as being of high concern [8, 9] being the organophosphates the group of insecticide that has received more attention in terms of aquatic toxicity. Dichlorvos (2,2-dichloroethyl dimethyl phosphate) is an organophosphate insecticide that acting as an acetylcholinesterase enzyme inhibitor by irreversible binding [10, 11]. Dichlorvos is mainly used in agriculture, for grain storage, and for pest control for livestock and households [10, 12, 13 - 15]. In consequence, it has been detected in surface waters from agricultural and non-agricultural areas [5, 16, 17, 18, 19, 20]. Moreover, monitored mean concentration for resulted higher than the sum of the rest of the organophosphates compounds [5]. The mean reported value (130 ng L^{-1}) exceeds restrictive regulatory acceptable concentrations (EQC-exceedance) for water wildlife protection in Argentina, the USA, and Europe [21 - 23].

Toxicological data is the principal input used to define environmental benchmarks, such as the predicted no-effect concentration [24] or more recently, environmental quality criteria [25]. Benchmarks, defined as protective environmental concentration, can be achieved following two methodologies. The first approach uses toxicity data, such as the 50% effect concentration (EC_{50}) or No Observable Effect Concentration ($NOEC$), from the most sensitive tested species, which is divided by an assessment factor (AF) [24, 26]. The AF can be up to 1000, depending on the type of data available, and is used to estimate a predicted no-effect concentration (PNEC), or a threshold above which an unacceptable risk may occur. As a low-risk tier approximation, the ratio between the PNEC and the predicted environmental concentration (PEC) can be used to describe the risk of undesirable environmental effects. Hence, the risk is described as the fraction between the acceptable concentration and the environmental concentration of the worst-case predicted. This methodology is called the deterministic approach. The second approach requires species sensitivity distribution curves (SSDs) to obtain environmental benchmark concentrations. This method has become popular after the '90 within European and North American countries [27]. The SSD analysis evaluates several species belonging to an ecosystem, hence, it can be also used to estimate the affected fraction of species at each dichlorvos concentration. Using the SSD approach, the concentration affecting to a specific fraction of the community (usually 5%) is determined with the associated 95% confidence interval. The value is called hazardous concentration (HC_p), where p represents the affected fraction of interest [28]. An assessment factor is also applied to the HC_p value or its lower confidence limit. Here, the AF used for SSD's is usually smaller than that used for the lower tier fraction-approach [24, 25, 29, 30] because collected data are provided from a group of organisms that includes several species. To construct an SSD, toxicity data from a representative number of species must be considered and finally, the value and certainty of the HC_p estimation will depend on the amount and quality of the collected data [28, 31]. If data collected are not enough, the deterministic approach (AF method) is considered more appropriate, as it often results in more conservative EQCs than those based on SSDs [32, 33].

For dichlorvos, an array of different benchmark concentrations exists. For instance, the environmental protection agency of the US (USEPA) set an acute benchmark concentration for dichlorvos of $0.035 \text{ } \mu\text{g L}^{-1}$ and chronic $0.0058 \text{ } \mu\text{g L}^{-1}$ for aquatic invertebrates [22]. However, the European Commission adopted a benchmark concentration for dichlorvos three orders of magnitude lower, with maximum concentrations of $0.0007 \text{ } \mu\text{g L}^{-1}$ [23]. In Argentina, the National Agency of Hydrological Resources established an acute benchmark concentration for dichlorvos of $0.078 \text{ } \mu\text{g L}^{-1}$ and chronic of $0.0078 \text{ } \mu\text{g L}^{-1}$ [21]. A value of $0.10 \text{ } \mu\text{g L}^{-1}$ has been proposed in China based on the SSD approach considering native species [34]. As is observed, there is a remarkably broad range of guide concentrations varying >100 fold between the highest and lowest concentration values. The reason could be attributable to several factors such as differences in the used method (deterministic versus SSD approach), the elected assessment factor, the use of formulated versus technical substances in the assays and the exclusion criteria for data quality and species selection for SSDs studies [33, 35].

The aim of this work was therefore to provide a more reliable benchmark concentration for dichlorvos based on the SSD approach. SSDs analysis based on both experimental data conducted under comparable laboratory conditions and reported data in the literature for technical and formulated products were compared and combined with environmental monitoring data to estimate exposure conditions. The following hypotheses were tested: (i) tests using formulated dichlorvos will have lower EC_{50} values, as formulated products may well include other compounds with synergist effects or facilitating the uptake of dichlorvos; (ii) different taxon will have different sensitivities with arthropods being the most sensitive group; (iii) environmental concentration of dichlorvos represents a risk for aquatic organisms in terms of EQC based on SSD analysis.

Materials And Methods

2.1. Chemicals

Standard dichlorvos (2,2-dichlorovinyl dimethyl phosphate) was purchased from Sigma-Aldrich (Germany), together with the reagents used to prepare the media M7 [36] and K medium [37] for maintenance of organism cultures (see additional file 1). Acetone (Baker, USA, HPLC grade) was used to prepare a dichlorvos stock solution.

2.2 Cultures

The organisms used to derive the SSD were *Daphnia magna*, *Chaoborus crystallinus*, *Chironomus riparius*, *Hyalella azteca*, *Gammarus pulex*, *Tubifex tubifex*, *Potamopyrgus antipodarum* and *Lemna minor*. The organisms were cultured under standard conditions according to standard protocols. Different protocols were followed for *Daphnia magna* [38], *Chironomus riparius* [36], *Hyalella azteca* [39], *Tubifex tubifex* [40], *Potamopyrgus antipodarum* [41] and *Lemna minor* [42]. All organisms were kept in culture at University of Copenhagen except *Chaoborus crystallinus*, which was obtained from a specialized store while *G. pulex* was collected in a local stream from Mølleåen, Allerød, Denmark (coordinates 55°48'58"N 12°18'45"E). The catching method consisted of gently waving a metal 1 mm sieve submerged under native macrophytes at the river-edges. Then, animals and the rest of the aquatic vegetation were kept in plastic containers with stream water. Water temperature was measured and set in the climate chamber once the *Gammarus* arrived in the lab and native plants were used to feed and emulated the natural condition [43]. Both species were acclimated to standard lab conditions [36, 44]. Previous to the test, *G. pulex* and *C. crystallinus* were acclimated for 4 days to M7 media. During the first three days, the medium was changed gradually to increase the ratio of M7 and river water (1st day 100:0, 2nd day 50:50, and day 3th 0:100).

2.3 Acute toxicity tests

In this work, evaluated endpoints were immobilisation (for animals) and growth (for plants). Immobilization was defined as individuals not being able to change their position after stimulation (manually stirring the media for 10 seconds). The effect is estimated as the ratio between the number of immobilised organisms regarding the total exposed and all animals were monitored for 48 h according to the OECD guidelines. In the case of *L. minor*, frond growth was monitored using a digital camera. Images were taken at the beginning and the end of the incubation period (7 days). Further details of acute tests are summarized in Table 1 and media compositions are given in supplementary data (Table A1).

Immobilisation tests were conducted in glass beakers containing 80 mL of media solution and a minimum of four individuals, which were gently transferred to the beaker. Four replicate beakers were used for each dichlorvos concentration and dissolved oxygen concentration (DO) was ensured to be higher than 3.00 mg L⁻¹ by 5 min of daily aeration. Assays of *G. pulex* and *L. minor* were carried out in six-well plates with 10 mL of media for each individual. Eighteen individuals of *G. pulex* per treatment were incubated individually in a well with a leaf (around 2 cm²) to allow hiding behaviour. For *Lemna*, three replicates of single fronds were used.

Main cultures and tests were conducted in the same media for animals (M7 medium) and *L. minor* (K medium). Temperature and light cycles were 20 ± 1 °C and 16:8 h for *D. magna*, *C. crystallinus*, *C. riparius*, and *P. antipodarum*. Conditions were adjusted for *G. pulex* (15 ± 1 °C, 12:12 h), *T. tubifex* (20 ± 1 °C, 0:24 h) and *H. azteca* (25 ± 1 °C, 16:8 h), to avoid temperature or light stress of the organisms. The climate chamber was set at 24 ± 1 °C with a light cycle of 16:8 h for growing and testing of *L. minor*.

For all organisms, pilot tests were conducted to adjust the range of dichlorvos concentration tested. The final test was performed with at least five treatment concentrations, controls, and solvent controls (maximal acetone concentration <0.01%).

2.4 Chemical analyses

Dichlorvos concentrations were evaluated by liquid chromatography coupled to a mass spectrometry detector adapted from [45]. The equipment consisted of UPLC-MS/MS, Waters® Acquity Iclass LMS Xevo TQD and the mobile phase selected was a 70:30 volumetric mixture of formic acid 0.1% in water and formic acid 0.1% in methanol. The employed column was a Waters® ACQUITY UPLC BEH_{C18} (2.1 mm x 50 mm, particle size 1.7 µm) with a constant flow of 1.2 ml min⁻¹. The retention time was 4.6 minutes. A six-level calibration curve was performed and the relative standard deviations on samples were under 10% (LOQ = 10 µg L⁻¹).

2.5 Data collection

In addition to the toxicity tests done in the laboratory, literature values on acute toxicity were collected from the following online databases: ECOTOX database [46], governmental agency reports [21, 47, 48] and from scientific journals using <https://www.sciencedirect.com>. For this, the following criteria were used for selecting data: i) manuscripts must be cited on a specialized database, ii) the entire manuscript must be available and be written in english, and iii) results must be obtained from experiments carried out under standard procedures including controls.

A total of 101 references have been checked and following the inclusion criteria, 74 articles match the selection criteria containing toxicity values of dichlorvos (Table A2.1 and A2.2 in additional file 1). These data were divided into two groups: The first group included 33 papers where standard protocols were used

(OECD, American Public Health Association or similar). These also include the use of controls (solvent and zero concentration), test solution prepared from technical grade compound (purity > 95%), and nominal or measured concentration declared. The second group included 41 papers, that matches the same quality standards as the first group, but using commercial formulations of dichlorvos. Toxicity values from the literature database were sorted into taxonomic groups (arthropods, annelids, molluscs, fishes, and anurans). Groups with low representation of species (< 8) were not considered for the taxon comparison.

Data on environmental concentrations of dichlorvos in surface waters were also reviewed. The ScienceDirect database was used following the keywords: “monitoring and dichlorvos”, “occurrence and dichlorvos”, “surface water and dichlorvos”, “water residue and dichlorvos”, “pesticide and water and dichlorvos”. From 21 reports, only those in the last 10 years of publication were included in this work to reflect reasonably recent exposure scenarios (Table 3). Other criteria for the selection were: inclusion of recovery values from spiked water samples and the use of control on the analytic methodology. Due to differences in reporting parameter format (sample concentration, not detected samples, mean concentration, minimum, maximum, etc), only the number of samples, maximum and mean concentration, from each sampling site and campaign were selected. In total, 16 papers were selected for the environmental occurrence analysis.

2.6 Data analysis

Assuming normal (growth data) or binary distribution (immobility data), a three-parameter model (equation 1) was used to calculate EC_{50} values [38].

$$y = \frac{d}{1 + \left(\frac{c}{e}\right)^b} \quad (\text{Eq. 1})$$

where y corresponds to the measured variable (immobilization or relative growth) as a function of c (concentration), d is the asymptotic maximum of the function (response of the non-treated individuals). The parameter e is the inflexion point in the sigmoidal function and represents the value causing 50% of individuals been affected (EC_{50}). The parameter b is proportional to the slope around the EC_{50} value.

EC_{50} values rather than No Observable Effect Concentration (NOEC) values were used for the SSD analysis, as they are more accurate and do not depend on the employed concentration range [27]. This criterion was used also for the bibliographic toxicological compilation data. A maximum likelihood method was applied to fit the toxicological data sets to SSD curves [49]. This method avoids losing censored data by reducing toxicological data to a single value instead of using their 95% confidence interval range. Using web tool MOSAIC_SSD (<https://mosaic.univ-lyon1.fr/ssd>), probability distributions were fitted based on the R-package fitdistrplus. Hazardous concentrations were calculated using a bootstrap method.

Different datasets were compared (experimental data SSD, technical dichlorvos SSD, formulated dichlorvos SSD and by taxonomic SSD) according to affected fraction results and actual regulatory concentrations.

To evaluate the associated risk to the environmental concentration of dichlorvos, a probabilistic risk assessment was attempted. As the exposure data, however, were rarely sampled and reported in a way facilitating the construction of exposure distributions, a hazard quotient approach was implemented. Mean and maximum concentrations were divided by HC_5 and HC_{10} obtained in the SSD analysis, and exceedance was discussed relative to regulatory EQCs. Then, temporal and basin linked observation was discussed in terms of occurrence frequency and EQC-exceedance.

Log-logistic fitting parameters were obtained by using the open-source statistical software R version 1.1.46 and plots were done in Sigmaplot v11.

Results And Discussion

3.1 Experimental acute test

The toxicity on aquatic organisms based on concentration-response curves is presented in Figure 1. Arthropoda, Annelida, Mollusca, and the vascular plant had shown different distribution curves along the concentration axis. A summary of the experimental setup and fit parameters are given in Table 1. The exposure verification showed all concentrations to stay above 80% of nominal concentrations (Table A3) and nominal concentrations were corrected by measured concentration. The relative stability of dichlorvos was expected based on previous experiments [45] and a half-lifetime of 3 days at pH $\approx$ 7 [46]. As expected for an insecticide, *L. minor* was the least sensitive species having an EC_{50} value five orders of magnitude bigger than *D. magna*; the standard test species, which was the most sensitive of the tested organisms (Figure 1). Although dichlorvos has not been designed for targeting chlorophytes, the toxic effect has been described as well [50, 51]. The acute EC_{50} values resulted similar to the values presented from previous reports. For instance, Sturm and Hansen [52] reported acute EC_{50} values for *D. magna* and *c. riparius* of 0.23 $\mu\text{g L}^{-1}$ and 10 - 20 $\mu\text{g L}^{-1}$, compared to the 0.22 ± 0.03 and $12.0 \pm 1.6 \mu\text{g L}^{-1}$ found in this study [52]. For *Hyalella Azteca*, a lower EC_{50} value was reported, 53.3 $\mu\text{g L}^{-1}$, but for an exposure time of 96 h rather than the 48 h used in our experiment giving an EC_{50} of $50 \pm 14 \mu\text{g L}^{-1}$ [53], while Johnson and Finley [54]. found an EC_{50} of 0.5 $\mu\text{g L}^{-1}$ (96h) for *Gammarus lacustris* which is considerably lower than the $54 \pm 14 \mu\text{g L}^{-1}$ found in this study on the related species *Gammarus pulex*. No previous reports were found for *T. tubifex*, *P. antiopdarum* and *L. minor*.

Reviewed reports on literature showed a wide range of EC_{50} values between the minimum and maximum (0.07 – 57700 $\mu\text{g L}^{-1}$, Table A2.1 and A2.2 in additional file 1). Arthropod species (crustaceans and insects) were more represented in technical dichlorvos based articles than for formulated ones with 52%

and 29% of the 33 and 41 EC_{50} values being on arthropods. The second most well-represented group was fish, with 33% and 54% of the EC_{50} values, respectively, for technical and formulated dichlorvos, followed by molluscs (11%), plants or algae (3%), frogs or toads (1.4%) and annelid worms (1.4%) out of the total 74 EC_{50} values.

3.2 SSD analysis

To analyse the available information about aquatic toxicity of dichlorvos, three SSDs graphs were constructed for comparison: A) our experimental data, B) literature data from assays performed with technical and formulated dichlorvos, and C) SSD's for different taxonomic groups (technical and formulated data separately for fish and arthropods), where a minimum of eight species was tested (Figure 2). For each curve, a log-logistic model was applied and their parameters were estimated together with the 5% and 10% Hazard Concentration (HC_5 and HC_{10}), protecting 95% and 90% of the species, respectively (Table 2). In the present review of the literature, not enough chronic studies were found on dichlorvos to be able to construct chronic SSD's.

All SSD curves showed good fitting ($R^2 > 0.95$) and the quality of the fits (lowest MLE values) increasing with the number of species included in the SSD. Previous works had calculated HC_5 for dichlorvos based on SSD curves, hence, Chèvre et al. [55] found a HC_5 of $0.0009 \mu\text{g L}^{-1}$ using 27 toxicological endpoints and a total species number of 13 (mainly invertebrates species). This value is one order of magnitude lower than our result, and most likely stems from the inclusion of chronic values. Differences in the criteria to include or exclude toxicological data could give contrasting results. Normally SSD's based on either acute or chronic data giving rise to acute and chronic EQC-values [22, 23]. Our SSD curve only considers acute parameters of EC/LC values, and can therefore not be compared to SSD's that includes chronic data. The experimental dataset ($n = 8$) showed a remarkably close fit to the SSD based on literature acute EC_{50} values for technical dichlorvos ($n = 33$) (Figure 2B, Table 2). Both HC_5 and HC_{10} were similar besides a slight difference in the 95% confidence interval (Table 2). The close correspondence between the experimentally derived SSD and that based on comparative and quality checked literature data gives confidence in the robustness of SSDs.

As expected, there was a large and significant difference between the SSD's based on technical dichlorvos and those based on the formulated (Figure 2B, C, Table 2). This difference, however, had contradicted the expectation due to the formulated products resulted in lesser toxicity than the technical dichlorvos. This was particularly evident for the arthropods (Figure 2C), whereas for fish, there was no difference between technical and formulated products. Deriving EQC's based on HC-values on formulated rather than technical compounds would shift the values two orders of magnitude upwards, disregarding whether lower confidence intervals or mean HC_5 -values are used. This is a very significant shift and may explain some of the different HC_5 values reported in the literature and used for deriving EQS-values in different countries and regions. We have no hypotheses regarding why the formulated compounds seems to be less toxic to arthropods compared to technical compounds. Particularly as there was no difference for the fish species tested. Spite of that, these results show the importance of discriminate experiments done on formulated versus technical products, as differences may be significant. Moreover, the inclusion of less sensitive taxonomic groups in the SSD did not affect the HC_5 value, as long as, the most sensitive species (in this case the arthropods) were also present (Figure 2B). Even when only considering eight species in total, as was the case from our experimental study, a representative SSD could be performed. However, the exclusion of the most sensitive species, as was done in the SSD with only fish (Figure 2C), markedly increased the HC_5 value (Table 2).

The main difference of including or excluding non-sensitive species was the steepness of the slope (Table 2). Steeper slopes are obtained when variance in sensitivity between species is small (hence, for specific phylogenetic groups), resulting in smaller 95% confidence limits of the EC-values. Hence, using the lower confidence limits of the HC_5 , to derive ecological benchmark concentrations, or Environmental Quality Concentrations (EQC's), as suggested by EC guideline [25], it could be argued that excluding non-sensitive species could result in higher EQC values than including them. In our case, however, EQCs derived from lower confidence limits would be 6.5 , 8.1 or 9.0 ng L^{-1} for the experimental data and the literature data on all species and arthropods, respectively. Using the mean HC_5 with an assessment factor of 10 [24, 33], the EQC would be then 12 , 8.4 and 6.5 ng L^{-1} for the same three groups, resulting in very similar values. In conclusion, as long as the data is obtained on technical compounds, making SSD's on a broad range of species including unsusceptible species such as plants, which do not have the molecular target of an insecticide, or selecting only the susceptible group of the arthropods, makes little difference for the derived HC-values and associated EQCs.

EQC values of this study were one order of magnitude lower than the acute EQC of the US-EPA [22] and Argentine [21], but according to their chronic EQC of 5.8 and 7.8 ng L^{-1} , respectively. However, it is one and two orders of magnitude higher than the European acute and chronic EQC's [23], and one to two orders of magnitude lower than the Chinese EQC [35] (Figure 3). Considering the relative robustness of the HC-values of our study, as long as arthropods are included and technical compounds are used, the large differences in regional EQCs must be due to other causes than species selections. He et al. [35], publishing two derived EQC values according to Chinese regulations based on native and non-native species from China or USA, respectively, being 0.355 and $0.0718 \mu\text{g L}^{-1}$. These difference could be attributable to the species selection of each studies. In fact, this is an important issue that need to be reconsidering to have reliable benchmarks. USEPA and European commission have historically been the first agencies to set guidance values, and have typically selected model species from their region [24, 25, 29, 56, 57]. Thus, geographical differences in species sensitivities cannot be ruled out. However, other comparisons between species sensitivities towards organophosphorus insecticides in mesocosm studies performed on different continents and using local species did not show any region-specific difference on sensitivity, even when they were performed under different environmental conditions [58]. The difference in the SSD's of He et al. [35] therefore likely is rather due to the selection of species composition rather than on the geographical origin of the species.

The SSD approach could also be used to determine the affected fraction of a community at a specific environmental concentration. If a large monitoring dataset of the chemical in question is available, frequency and exposure concentrations can be plotted in a distribution describing the probability of exposure. The probability of exposure and probability of community effects can be combined in a probabilistic risk assessment [59]. A probabilistic risk assessment of a chemical gives the probability to affect the community under a specific exposure distribution. However, even though the concept has been available in the

literature for approximately two decades, it is rarely conducted. The most likely reason being the lack of good and representative exposure data. In the next section, affected fractions are calculated taking into consideration the environmental concentrations reported in literature and our experimental SSD.

3.4 Exposure concentrations and risk

Reports on environmental concentrations of dichlorvos were distributed over 10 different countries from America, Oceania, Europe and Asia (Australia, China, Greece, India, Iran, Portugal, South Korea, Thailand, US). The occurrence of dichlorvos in samples varies widely with an occurrence frequency ranging from 2 to 100% of the samples, which conforms a total of 2582 reported samples (Table 3). Reported concentration of dichlorvos present three order of magnitude between the lower and the highest value ($0.004 - 5.63 \mu\text{g L}^{-1}$) and the median value of the positive samples was $0.11 \mu\text{g L}^{-1}$. Approximately 14% of the values listed in Table 3 had a concentration $>1.00 \mu\text{g L}^{-1}$. Additionally, the findings of dichlorvos in freshwater organisms from Argentina and Belgium indicate not only its presence in water bodies but also the presence in biological matrices [60, 61].

Environmental data was ordered by sampling time, under the assumption that regulation would have lead to decreased environmental concentrations with time. No time-concentration relation was, however, observed. Instead, the main differences seemed to be geographic (Table 3). Maximum concentrations were observed in China and Portugal during 2015 and 2010, respectively. Only the sampling campaign from Tighara (India) and Dongjiang River (China) presented mean concentration values below the HC5 derived from our experimental data ($\text{HC}_5 = 6.5 \text{ ng L}^{-1}$), while all other mean values are higher, thereby potentially also affecting more than 5% of the species (Table 3). Not only mean and maximal values are of importance, but the frequency of detections above the LOQ likewise. The meta-data in Table 3 show that at least half of the sampling data-sets have a dichlorvos occurrence greater than 90%. Even though the time and sampling procedures vary and are likely focussed at seasons of the high probability of occurrence, the detection frequency is very high indicating close to chronic exposures for many sampling sites with little time for eco-system recovery. Besides, dichlorvos is most likely not the only pesticide present but may be accompanied by other pesticides and pollutants used in the agricultural sites, making the joint environmental impact larger than that predicted by dichlorvos alone.

To compare mean and maximum values, hazardous quotients were calculated considering the HC5 and HC10 obtained in the SSD analysis based on experimental data (Figure 4 and 5). Lower confidence interval (95%) was employed to calculate HQ in each case (see Table 2).

HQs offer a good first risk approach, as do the potentially affected fraction, but the result of both risk measures is very dependent on the sampling effort to elaborate a representative picture of the environmental exposure. In environmental risk assessment, the use of an SSD or HQ approach is still discussed [33, 75]. Despite a better community approximation of the SSD method, a more protective PNEC could be achieved with the deterministic method. The robustness of SSD will depend on distribution parameter of data set, with higher numbers of species (n) giving more robustness to the HC-values, and lower variance (σ) (steeper slopes) in sensitivity between species giving smaller 95% CI's for the HC-values. Sorgog and Kamo [33] suggest $\sigma < 0.9$ is desirable to choose the SSD method rather than the deterministic method [33]. However, the relative merits of the two methods are reverted when $\sigma > 0.9$; under those conditions, the AF method would be preferred. SSD curves obtained in the present work shows σ values > 0.9 , except fish SSD curves. This suggests that an AF (10) applied to EC_{50} of most sensitive species (i.e. *D. magna*) will give a protective concentration of $0.019 \mu\text{g L}^{-1}$. The HC5 (Table 2) in the case of arthropods and experimental SSD represent a lower concentration and choosing this parameter it could minimize the uncertainty of under-protect arthropods species.

Measures to manage the risk of pesticide could be listed by effectiveness [76]. In order to prevent surface water contamination, similar strategies from groundwater protection policies could be applied to reduce environmental risk. Particularly, sustainable agriculture practices are listed as the most effective action. Nevertheless, limitation or prohibition represent the most applied strategy followed by governmental agencies to manage the risk of pesticides use. Boucaud-Maitre et al. [77] proposed that withdrawal measures were effective to reduce the number of poisonings reported in humans. This withdrawal action was applied when dichlorvos was banned in France in 2007. Besides this, dichlorvos was the most frequent compound illegally imported from African countries.

Conclusion

An SSD analysis was performed for dichlorvos and new EC_{50} report were presented for three species (*L. minor*, *T. tubifex* and *P. antiopdarum*). Experimental SSD defines a protective concentration of 6.5 ng L^{-1} for 5% of the species, which is in line with the European limit values, but one to two fold lower than the limit values of the USA, China and Argentina. During the last years, dichlorvos has had an extremely high occurrence frequently in monitoring campaigns, showing concentrations which would result in severe environmental impact. The EQCs of three of the four regions included in this study is therefore not sufficient to protect the aquatic fauna.

Declarations

Acknowledgement

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Authors' contributions

NC conceived the idea and supervised the entire work. NJB designed and performed experiments (in-vitro experiment and data collection). NC provided materials. NJB, AI, NC and AFC interpreted and discussed the data. NJB, AI and NC wrote the first draft. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are available upon request.

Competing interests

The authors declare they have no competing interests.

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Tables

Table 1. Condition of acute test in different selected species. <i>EC</i> ₅₀ (µg L ⁻¹) concentrations (conc.) of acute species tests.	Slope	2.33 ± 0.60	1.65 ± 0.35	3.37 ± 1.14	1.62 ± 0.43	2.71 ± 1.04	1.39 ± 0.33	4.99 ± 1.83	1.25 ± 0.25	¹ Rank o
	<i>EC</i>₅₀ ± SE³	0.22 ± 0.03	2.52 ± 0.56	12.0 ± 1.6	54 ± 14	70 ± 14	181 ± 44	7320 ± 930	31220 ± 4762	² Rando (RS).
	Conc. ranges³	0.022–4.60	1.00 – 88	2.56 – 40	3.60 – 362	25 – 460	20 – 600	1.00 – 85	1020 – 70 000	³ Concent and star error (SE given in Dichlorv
	n	200	200	175	162	140	140	96	30	concent was with 80% of nominal
	n by conc.	4 x 5 ind.	4 x 5 ind.	5 x 5 ind.	4 x 5 ind.	6 x 3 ind.	4 x 5 ind.	4 x 4 ind.	3 x 1 frond	concent through experim
	Time	48h	48h	48h	48h	48h	48h	48h	7 days	
	Stage²	24h old	10 mm Larvae	4th instar Larvae	RS>5mm	RS >1mm	RS>10mm	RS >1mm	2 week old	
	Class	Arthropoda	Arthropoda	Arthropoda	Arthropoda	Arthropoda	Annelida	Mollusca	Tracheophyta	
	Specie	<i>D.magna</i>	<i>C. crystallinus</i>	<i>C. riparius</i>	<i>G. pulex</i>	<i>H. azteca</i>	<i>T. tubifex</i>	<i>P. atipodarum</i>	<i>L. minor</i>	
	R¹	1	2	3	4	5	6	7	8	

Table 2. Hazardous coefficient estimations (HC).

Data set	Hazardous concentration ¹		Model parameters			
	HC ₅ / µg L ⁻¹	HC ₁₀ / µg L ⁻¹	<i>b</i>	<i>e</i> / µg L ⁻¹	<i>n</i>	<i>MLV</i>
Experimental data (this work)	0.12 (0.0065 -7.1)	0.58 (0.046 – 20)	0.47 (0.34-1.1)	65 (5.4 - 1200)	8	-30.1
Technical dichlorvos	0.084 (0.0081 – 0.85)	0.47 (0.066-3.30)	0.44 (0.34-0.61)	72 (18 – 290)	33	-223.5
Formulated dichlorvos	13 (4 – 46)	38 (14 – 100)	0.72 (0.58-0.96)	780 (390-1600)	41	-362.4
Technical dichlorvos (Arthropods)	0.065 (0.009 – 0.49)	0.19 (0.035 – 1.00)	0.71 (0.5-1.1)	4.3 (1.3-14)	17	-60.4
Technical dichlorvos (Fish)	100 (15 – 680)	220 (45 – 1100)	0.93 (0.63- 1.8)	2400 (760-1000)	11	-104.2
Formulated dichlorvos (Arthropods)	4.8 (0.87 – 26)	10 (2.4 – 42)	1 (0.69 – 1.9)	87 (33-240)	12	-74.4
Formulated dichlorvos (Fish)	420 (180 – 1000)	690 (330 – 1500)	1.5 (1.1 – 2.3)	3100 (1800-5200)	22	-200.9

¹Estimation are based on SSD analysis and model parameters of Eq. 1 with *d* set to 1, *e* giving the mean *EC*₅₀ value of the analysed group, and *b* giving the slope of the SSD. All values are given with 95% CI and the Maximum Likelihood values (MLV) of the fits are given in the final column. Web tool MOSAIC_SSD [49].

Table 3. Surface water sampling data since the last 10 years.

Site (#)	n	Frec. %	Mean $\mu\text{g L}^{-1}$	AF-mean ¹	Max $\mu\text{g L}^{-1}$	AF-max	Sampling Time	Ref.
Mae Sa, Thailand	370	23	0.018	0.06	1.1	0.32	2007 - 2008	[62]
Haihe River, China (1)	17	100	0.03	0.08	0.05	0.10	2008	[63]
Haraz River, Iran	8	100	1.12	0.32	1.9	0.38	May 2008	[64]
(1 & 2)	8	100	0.64	0.27	1.4	0.35	Dec-2008	
Douro River, Portugal	12	91	0.08	0.12	0.09	0.13	Mar -2009	[65]
(1, 2 & 3)	48		0.29	0.20	0.51	0.25	Apr - 2009	
	24		0.12	0.14	0.19	0.17	May - 2009	
Corner Inlet rivers, Australia	40	5	0.01	0.05	0.01	0.05	Summer 2009/10	[66]
Douro River, Portugal	24	100	0.06	0.11	0.87	0.3	Mar-Sep 2010	[17]
(4)								
Nakdon - Han Rivers, Korea	477	60	0.10	0.13	0.15	0.16	Jul-Nov 2010	[18]
Great Lakes, USA	709	8	0.041	0.09	0.29	0.20	Sep 2010 - Sept 2013	[67]
Volvi Lake, Greece	12	—	—	—	0.002	0.03	Oct-Nov 2010	[68]
(1)								
Amravati region,India	156	—	0.186	0.17	0.25	0.19	Sep 2011 - Jul 2012	[69]
(1)								
Volvi Lake, Greece	12	—	—	—	0.003	0.03	Mar-Jun 2011	[68]
(2)								
Kosynthos river , Greece	270	4	—	—	0.027	0.08	2011-2012	[70]
(3)								
Tighara , India	64	100	0.017	0.06	0.022	0.07	winter 2014	[71]
(2, 3, 4 & 5)	64	100	0.004	0.03	0.012	0.05	Summer 2014	
	64	100	0.005	0.04	0.010	0.05	Pre-monsoon 2014	
	64	94	0.004	0.03	0.006	0.04	Post-Monson 2014	
Shangyu, China	49	100	1.56	0.36	5.63	0.49	Aug 2014	[72]
(2)								
Dongjiang River, China (3)	26	100	0.004	0.03	0.014	0.06	July & Aut 2015	[73]
Shahid Rajaei dam, Iran	20	90	0.24	0.19	0.52	0.25	June 2015	[74]
(3, 4,5 & 6)	16	38	0.10	0.13	0.47	0.24	July 2015	
	13	0	—	—	—	—	September 2015	
	15	0	—	—	—	—	February 2016	

¹The affected fraction according experimental SSD curve are calculate for mean and max environmental concentrations (AF-mean and AF-max respectively).

Figures

Figure 1

Please see manuscript for full Figure Caption

Figure 2

SSD curves based on EC50 values are presented by groups of data. A) Experimental SSD curve obtained in this work. B) Comparison among technical and formulated SSD curves based on literature reports and our experimental SSD curve (this work, pink line). Taxonomic groups were arthropods (black), fish (grey), molluscs (yellow), plants or algae (green), frogs or toads (blue), and annelid worms (red). In both cases confidence intervals (95%) are presented in blue lines. C) SSD curves of invertebrates and fishes for technical and formulated dichlorvos.

Figure 3

Comparison between regulatory concentrations and compiled data sets.

Figure 4

Hazardous quotient using mean sampling values, calculated as HC5 (coars pattern) or HC10 (fine pattern) ratio from experimental SSD analysis. Basin origins are indicated by number and chronologically (see Table 3).

Figure 5

Hazardous quotient using maximum sampling values, calculated as HC5 (coars pattern) or HC10 (fine pattern) ratio from experimental SSD analysis. Basin origins are indicated by number and chronologically (see Table 3).

Supplementary Files

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