Short Communication

More Realistic Concentrations of Agrochemicals for Environmental Risk Assessments

Francisco SÁNCHEZ-BAYO*

Faculty of Horticulture, Chiba University, Matsudo, Chiba 271-8510, Japan

(Received October 20, 2003; Accepted January 5, 2004)

Given the strict protocols for the registration of agrochemicals in developed countries there is a need to re-consider whether the use of PECs for the assessment of risks and/or hazards in aquatic environments is a valid approach. As the exposure of aquatic organisms in natural systems is reduced by several processes, more realistic values of effective concentrations should be estimated. A correcting factor for such effective exposure is proposed here based on the partitioning and dissipation features of organic pesticides. The validation of this model is limited by the data available at the moment, but the evidence so far is quite promising.

Keywords: regulatory, risk assessment, models, acute toxicity, effective concentration.

1. Introduction

Environmental risk assessments for the registration of agricultural chemicals usually compare estimated or predicted environmental concentrations (EEC or PEC, both referred to as EC in this paper) of such substances in water, air, soil and sediment matrices with toxicological endpoints for particular non-target species. In regulatory assessments in the USA, Canada, Australia, OECD and Japan, acute toxicity data for the aquatic environment are required in the early tiers of this assessment process, in which acute lethal or effective concentrations (LC₅₀, EC₅₀) for representative taxa are compared against the ECs using simple hazard quotients. In this way, high-risk chemicals are screened, while reserving more demanding data in later tiers for those compounds that have passed earlier tests need confirmation about their safety.

It has been recognized, however, that the acute effective concentrations (AEC) estimated in laboratory bioassays are not necessarily comparable with the calculated ECs, because in natural systems several environmental factors would reduce the exposure of organisms to such concentrations. Indeed, the presence of algae, macrophytes, soil or sediment in natural aquatic ecosystems implies the partitioning, to a greater or lesser extent, of some of the dissolved chemical into its components, thus resulting in lower concentrations in the water itself during the time of exposure (typically 48 or 96 hr, depending on taxa). It is important to realise that the initial concentration level will not remain constant during this time of exposure. The existence of inevitable decay and degrading processes, on the other hand, would reduce those concentrations even further, and so minimise the presumed acute impacts.

Because ECs indicate the maximum initial levels expected under normal agricultural usage and practices, current risk assessments for the registration of agrochemicals tend to be conservative, though this is often justified on the grounds of more safety towards the environment. It would be reasonable, however, to use AECs that represent realistic exposure levels, at least in the first tier of the assessment process, since risk assessments aim at prioritising risks using sound objective data. The problem is, how can we estimate the real effective concentrations in the environment given the multiplicity of factors and situations found in natural ecosystems? Basically there are two ways of tackling the problem: i) to develop new protocols for aquatic toxicity bioassays that take into account those factors present in natural environments (e.g. inclusion of aquatic vegetation, sediment, etc.), so more realistic AECs can be derived; and ii) to correct either the calculated EC or AEC in aquatic ecosystems by a certain factor, so as to obtain true estimates of the effective concentrations (Ce) expected in real situations.

Proposals for conducting more realistic toxicity bioassays have been introduced in the past, i.e. using mesocosms or multispecies tests in standardised microcosms. However, the cost and variability of the former tests have been recognized, and for this reason are no longer required for registration purposes in the USA since 1997. As for the multispecies tests, though the impacts are measured within a trophic structure akin to natural aquatic ecosystems, current standardised bioassays are suitable only for microphytes (i.e. algae) and plankton (e.g. Cladocera, etc.): aquatic macrophytes, fish and sediment with organic matter are excluded for analytical reasons, although they occur undoubtedly in natural ecosystems. In fact, it would not be feasible to standardize a microcosm bioassay including the latter components, because the inherent variability of the plant material and sediment types make it very difficult to reproduce the same testing conditions. It seems that no alternatives are left to overcome this hurdle, and while microcosms provide essential insights into the ecological effects of chemicals at the lower echelons of the ecosystem, acute toxicity endpoints for higher organisms such as fish would still be needed.

This paper outlines a possible way to overcome this problem, using the second path indicated above to estimate the real effective concentrations in natural environments by means other than testing. The task is urgent given the conservative bias implicit in current regulatory risk assessments.

* To whom correspondence should be addressed. E-mail: sanchezbayo@faculty.chiba-u.jp
2. Exposure Factor

It is proposed that the effective concentrations (Ce) acting upon aquatic organisms decline after a short time due mainly to the combined effect of fugacity\(^{11}\) and degradation processes, as in fact happens in experimental trials.\(^{19}\) Therefore, during the 48 or 96 hr of exposure required in standard bioassays, the estimated acute effective concentration needs to be corrected by a certain factor, which we will call here forth the exposure factor (X)

\[
Ce = AEC \times X \quad \text{where} \quad 0 < X < 1
\]

(1)

The following parameters modify the actual exposure of organisms:

- adsorption by all organic materials present in the system, \(i.e.\) plankton, macrophytes and the organic component (OC) of sediments. It is well established that such adsorption is directly proportional to the logarithm of the octanol-water partitioning coefficient \((K_{ow})\),\(^{12}\) a physicochemical property of each substance;
- uptake by plants, a biological process directly related to the solubility of chemicals in water.\(^{15}\) As solubility and \(K_{ow}\) are inversely correlated,\(^{16}\) we can take the \(\log K_{ow}\) as the only parameter that explains both processes;
- overall decay/degradation rate in water and sediments, of which half-lives \((DT_{90})\) are common measurements in environmental studies - in this sense, half-lives are the reciprocal of such degradation rates. Obviously, such a half-life considers all physical, chemical and biological processes involved, and although it matters to know the contribution of each component in the degradation process, only a figure reflecting the overall disappearance of a chemical from the system is useful, because half-lives \(per\) \(se\) are not additive.

Thus, the reduction of a chemical's concentration in water within the time of exposure of organisms can be expressed as a function of the above parameters

\[
dC/dt = -(\log K_{ow}/DT_{90}) \times C
\]

(2)

and after integration

\[
Ce = C_0 \times \exp (-\log K_{ow}/DT_{90})
\]

(3)

where \(C_0\) is the sought effective concentration and \(C_0\) the initial concentration of chemical. In risk assessments, this initial concentration is given by the estimated or predicted ECs, which for calculation purposes are the same as AEC. Taking it into equation (1), the exposure factor becomes

\[
X = \exp (-\log K_{ow}/DT_{90})
\]

(4)

As half-lives usually differ markedly between water and sediment, it would be more appropriate to express the dissipation in both media as

\[
X = \exp [-\{(\log K_{ow}/wDT_{90}) + (\log K_{ow}/sDT_{90})\}]
\]

(5)

where \(wDT_{90}\) and \(sDT_{90}\) are the respective half-lives in water and sediment, and \(K_{ow}\) is the organic carbon partitioning coefficient, derived from either water solubilities or \(K_{ow}\).\(^{19}\)

The proposed exposure factor is an approximation of the reducing effect that partitioning and dissipation processes have in natural environments, where a variety of aquatic plants, microorganisms and soil or sediment substrates influence decisively the effective concentrations of any chemical. Consequently it can be used as a reasonable correcting factor of the calculated ECs or AECs.

An example will help understand the use of this exposure factor in risk assessments. Let's suppose the 96 hr LC\(_{90}\) of a new pesticide to a standard surrogate species of fish is 250 \(\mu g/l\), and its highest concentration at the outlet of paddy fields draining into a local stream has been estimated as 300 \(\mu g/l\). Based on simple hazard quotients, the assessor may think that the risk of using this pesticide is far too great, as it will certainly kill more than 50% of the fish population (EC/LC\(_{90}\)=1.2) in four days. However, this pesticide shows great adsorption onto organic matter (say \(\log K_{ow}=4\)) and has an average half-life in water of one week. Considering only the presence of waterplants and algae in the paddy drains, the real effective concentration will be lowered by a factor of 0.56 within the same time of exposure of fish, giving a more realistic 168 \(\mu g/l\) at the outlets, which translates into a hazard quotient of 0.67. Moreover, suppose the half-life of this pesticide in non-sterile soil was estimated as 14 days, so the partitioning and degradation in the layer of sediment deposited along the bottom of the stream will further reduce the effective concentration in water by a combined factor of 0.44, giving a final figure of 132 \(\mu g/l\) at the receiving stream and a hazard quotient of 0.53. Fairly, the assessor should conclude the effective risk is not as dramatic as originally thought, since less than 50% of the fish population would likely be dead.

3. Validation of the Exposure Factor

The above model is based mainly on observations of several laboratory and glasshouse experiments with pesticides of different properties, and the consideration of fugacity in ecosystems. Those experiments were originally designed to measure the phyto-degradation of residual pesticides by aquatic plants using hydroponic systems without sediment layers.\(^{20}\) Thus, the concentrations in water after a few days reflected just the amounts remaining after hydrolysis and adsorption by those plants took place.

A close look at the concentrations obtained in water several times under various conditions revealed a pattern for most pesticides, independently of the degrading ability of the plant species tested. Such patterns seem to be correlated with the physico-chemical properties and half-life of each compound in water (Table 1), which was calculated from controls (e.g. no plants) tested at the same time or obtained from the literature. The exposure factor described in this paper fits well those experimental results, with the following regression coefficients obtained: \(r^2 = 0.80\) (\(n=8\) for day 1 or \(r^2=0.97\) (\(n=7\), excluding phthalide); \(r^2=0.92\) (\(n=8\), excluding phthalide) for days 7 and 14.

Despite the limited data available, and the fact that no sediments were used, the trend shown by such a range of different chemicals is encouraging. The only discrepancy was phthalide,
Table 1. Comparison between residues of nine different pesticides remaining in hydroponic greenhouse experiments (mean ± standard deviation) and those estimated by using the proposed exposure factor (X). The log $K_{oc}$ and the dissipation in water (wDT$_{50}$) of each chemical are indicated.

<table>
<thead>
<tr>
<th>Chemical a.i.</th>
<th>$C_{0}$ (µg/l)</th>
<th>Remaining concentrations (µg/l)</th>
<th>Exposure factor (X)</th>
<th>Estimated Ce (µg/l)</th>
<th>Log $K_{oc}$</th>
<th>wDT$_{50}$ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day 1</td>
<td>Day 3</td>
<td>Day 7</td>
<td>Day 14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldicarb*</td>
<td>40</td>
<td>42±12</td>
<td>37±12</td>
<td>33±8</td>
<td>1.00</td>
<td>40</td>
</tr>
<tr>
<td>Fluometuron*</td>
<td>100</td>
<td>107±15</td>
<td>87±15</td>
<td>79±11</td>
<td>0.97</td>
<td>97</td>
</tr>
<tr>
<td>Prometryn*</td>
<td>80</td>
<td>N/A</td>
<td>54±13</td>
<td>54±6</td>
<td>0.95</td>
<td>76</td>
</tr>
<tr>
<td>Diazinon**</td>
<td>1000</td>
<td>858±148</td>
<td>965±138</td>
<td>802±83</td>
<td>0.91</td>
<td>911</td>
</tr>
<tr>
<td>Fenobucarb**</td>
<td>1000</td>
<td>1040±195</td>
<td>1113±99</td>
<td>1000±127</td>
<td>0.92</td>
<td>918</td>
</tr>
<tr>
<td>Phthalidic*</td>
<td>1000</td>
<td>333±77'</td>
<td>378±74'</td>
<td>200±67</td>
<td>0.80</td>
<td>797</td>
</tr>
<tr>
<td>Chloryrifos*</td>
<td>10</td>
<td>8±5</td>
<td>7±5</td>
<td>4±4</td>
<td>0.91</td>
<td>9.1</td>
</tr>
<tr>
<td>Endosulfan*</td>
<td>20</td>
<td>15±10</td>
<td>7±1</td>
<td>5±1</td>
<td>0.39</td>
<td>7.7</td>
</tr>
<tr>
<td>Silafluoren**</td>
<td>1000</td>
<td>548±84</td>
<td>220±119</td>
<td>113±109</td>
<td>0.40</td>
<td>402</td>
</tr>
</tbody>
</table>

$\rho^2$ 0.80 0.69 0.73 0.74

$\rho^{***}$ 0.97 0.98 0.92 0.92

* Combined results of 6 aquatic plant species, 25–30°C ambient temperature (data from Ref. 16).

** Combined results of 4 aquatic plant species, 12–15°C ambient temperature.

*** Excluding phthalide.

1. Likely to be underestimates of true values due to poor analytical method.

but this could be explained by known analytical deficiencies.

The above data validates the model, although more experiments using plants as well as sediment layers would be necessary to confirm it, or else propose a more appropriate equation. The point here is to derive a model that may enable one to correct the acute effective concentrations of pesticides tested under standard toxicity bioassay conditions, so that more realistic figures of exposure could be obtained to compare them with the true concentrations present in natural systems. Indeed, the LC$_{50}$ would remain the same in any case, but the effective concentrations in a real environment would be lower than estimated by the initial ECs.

4. Sensitivity Analysis

The proposed exposure factor is more dependent on the half-life dissipation than the partitioning coefficients due to the range of values used: 0 to 9 for log $K_{oc}$ and log $K_{oc}$ compared to 0 to 200 for half-lives. However, considering that the volume of water in natural systems such as streams, rivers and lakes is surely larger than the volume of sediment there, it makes sense to think that the effect of hydrolysis in the ecosystem may outweigh that by other factors. According to our model, the effective concentrations (Ce) in water over a short period of time would be reduced substantially if the half-life is only one day (0 < X < 0.54) or up to a week (0.11 < X < 0.92), whereas it would be less marked for chemicals lasting one month (0.57 < X < 0.98) or for more persistent compounds (Fig. 1).

5. Data Requirements

The usefulness of the proposed model is that all the parameters involved are available, or can be obtained easily and at low cost by chemical companies and other laboratories. The partitioning coefficient $K_{oc}$ is known for most if not all pesticides, and the half-life in water can be easily derived from experiments carried out under normal laboratory or greenhouse conditions. In the latter case, it is advisable to test the dissipation in water under sunlight/dark cycles, since this is always the case with natural waters. The effect of sunlight in promoting the hydrolysis of many organic chemicals is well known and cannot be ignored when calculating realistic dissipation rates. For the same reason, a range of variable temperatures and pH, similar to those found in agricultural environments, should be used to obtain

Fig. 1. Sensitivity analysis of the exposure factor (X) for a variable range of partitioning coefficients (log $K_{oc}$) and half-lives (legend, days). Although in this graph equal dissipation rates for water (wDT$_{50}$) and soil (sDT$_{50}$) were used, different combinations would apply for individual chemicals.
more confidence about the variability of results. It can be argued that natural water systems carry a variety of microorganisms which would be responsible for part of the dissipation process, and therefore they should also be included; however, it might be difficult to standardise bioassay conditions that include microorganisms, though it is not impossible as exemplified in the case of microcosms.\(^{36}\)

Confirmation of the proposed model would rely to a large extent on trials carried out by other investigators. In this regard, it is important to test as many compounds as possible, using simple water-plant-sediment systems that meet the essentials described in this paper. The effect of plant biomass and the ratio of water volume to sediment volume (or adsorption area) need to be checked in the laboratory, because they might cause some variation in the exposure factor. On the other hand, minor influences are expected from the choice of plant species and soil or sediment composition, as evidence based on the sensitivity analysis and experimental data suggest.

ACKNOWLEDGMENTS

Mike Rose and Saori Ishikawa provided experimental data and Prof. Naoki Motoyama encouraged me to think about this issue and find practical solutions. I also thank Dr. Yukari Egashira for helping translate the synopsis into Japanese language.

REFERENCES