INCLUDING DEGRADATION PRODUCTS OF ORGANIC CHEMICALS IN A GLOBAL MULTI-MEDIA MODEL TO ASSESS THEIR CONTRIBUTION TO PERSISTENCE AND LONG-RANGE TRANSPORT

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Introduction

Multi-media box models are widely used to assess the fate of chemicals in the environment. Most of those models ignore the formation of degradation products from parent compounds, that is, if a chemical is degraded, it disappears from the modeled system. In the real environment, however, chemicals are usually transformed into similar substances before they are completely mineralized. It has been shown that the degradation products that appear after such transformation processes can sometimes have very similar properties to the initial substances: persistence, bioaccumulation potential, and toxicity can be as high or even higher than those of the parent compound[1].

There are some models that include degradation products[2,3,4,5,]: studies with those models have shown that chemical hazard indicators such as persistence can increase if degradation products are included in the model. However, those models are only unit world; they can be applied only to a regional environment but not to the global environment. It is thus impossible to use them for the assessment of long-range transport, cold condensation, and other aspects of the global environmental fate of Persistent Organic Pollutants (POPs). The global fate of POPs has been shown to be strongly influenced by the varying properties of the global environment: in the cold arctic climate, degradation is much slower than in temperate regions, and the lower vapor pressure leads to an accumulation of such substances in the surface media (cold condensation[6,7]).

Therefore, there is a strong need to assess the importance of degradation products in a global environment. This is of particular importance for DDT, Aldrin, or similar substances which are known to have persistent and toxic degradation products, and which are know to be globally distributed. Therefore, we have extended an existing spatially resolved, global multi-media model to include degradation products.

Materials and Methods

We selected three pesticides to assess the importance of their degradation products. They had to be known to be globally distributed, for instance because they could be found in the Arctic, or because they were known to be persistent and have a high vapor pressure (properties that favor a global distribution). In addition, those substances had to have known degradation products. The substances selected are the insecticides DDT and Aldrin, and the herbicide 2,4-D. As DDT is a very well studied substance, it was selected for an in-depth case study.

Degradation pathways for those substances were compiled, where possible, from literature. If such information was unavailable or contradictory, stable degradation products from the pathway predicted by the CATABOL QSAR prediction software[8] was checked against predicted degradation products from the Minnesota University Biocatalysis / Biodegradation Database[9]. If no major contradictions could be observed, the suggested pathway was selected. It was not attempted to identify a complete inventory of all degradation products of a given parent compound, as only stable products will significantly contribute to the overall impact, as shown by Fenner et al[4].

For the parent compounds and the selected degradation products, partition properties were selected from literature (where available). If no literature values could be found for a substance (which was the case for many of the

degradation products), then values from the EPIWin Suite (a frequently used QSAR program[10]) were used. To check for biased property measurements, and to make the properties internally consistent, the least-squares adjustment procedure[11] was applied to all literature and QSAR data.

Degradation half-lives were assembled from literature where possible. Usually degradation half-lives could only be found for parent compounds. Where no literature values could be found, a method presented by Arnot et al.[12] was used, which extrapolates biodegradation half-lives from the QSAR software BioWin, and the results were compared to the biodegradation half-lives calculated by the CATABOL estimation software.

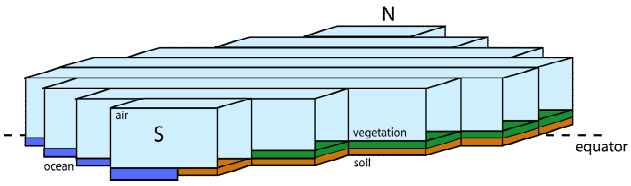

Figure 1: CliMoChem is a global, zonally averaged multi-media model with atmosphere, ocean, soil, and vegetation compartments in each of the 30 zones.

The zonally averaged multi-media model CliMoChem[6] has been extended to include degradation products. A substance that is degraded may appear as one or several degradation products. It is possible that varying fractions of the parent compound are transformed into different degradation products in different media: for the DDT substance family, for instance, the parent compound DDT is degraded only to DDE in the atmosphere, whereas it is degraded to DDE and DDD in soil.

The model also calculates various indicators of environmental hazard, such as spatial range, persistence, cold condensation potential[6], and arctic contamination potential[7]. Those indicators were extended to take into account degradation products: Fenner et al[2,4] defined the joint persistence as the persistence of the parent compound and all the degradation products. The joint persistence represents the overall half-live of the substance and its degradation products in the system and can be separated into the primary persistence (the persistence of the parent compound), and the contributions of the different degradation products to the joint persistence. Similarly, Quartier and Muller-Herold[3] have introduced the secondary spatial range (the part of the circumference of the earth in which 95% of the pollutant's concentration appears), which is the spatial range of the degradation products. Here, we have calculated this indicator for the first time in a zonally averaged model, and also defined the joint spatial range, which is the spatial range of a parent compound and its degradation products.

Two more indicators were calculated for degradation products: the joint cold condensation potential is the cold condensation potential (Scheringer et al.[6]) of the parent compound and all its degradation products, and the joint arctic contamination potential is the arctic contamination potential (Wania[7,13]) of the parent compound and all its degradation products.

To confirm the model, the model results were compared to measured concentrations in the environment in an in depth case study on DDT and its degradation products, DDE and DDD. To this end, an emission scenario for DDT was compiled from various sources on the production and use of DDT between 1940 and today[14,15,16,17].

Measured concentrations of DDT and its degradation products are widely available: Halsall[18] and Hung[19] have recently measured DDT in the arctic atmosphere, Shen[20] in the atmosphere in North America, Tanabe[21] and Iwata[22] have determined DDT and its degradation products in the Pacific Ocean and overlaying atmosphere several times since 1980. Other studies report the temporal evolution of DDT at given places[23,24].

Results and Discussion

Figure 2 displays the joint persistence, the joint spatial range, and the joint arctic contamination potential of the three selected substances, including the contributions of the different substances in the respective substance families. For DDT, the first and second degradation products (DDE and DDD) are almost as important as DDT in terms of

persistence. Also the spatial range is increased by DDE (the first degradation product), so that the joint spatial range is almost twice as high as the primary spatial range of DDT. The degradation products of 2,4-D significantly increase the persistence and the spatial range of the substance family. Interesting results were found for Aldrin and its degradation products: the pathway prediction software CATABOL identifies a series of stable degradation products, which all contribute significantly to the joint persistence. Also the spatial range is increased by all the degradation products. Surprisingly, only Dieldrin (the first of the degradation products presented here) is frequently detected in the environment and known to be an important degradation product of Aldrin.

For the arctic contamination potential, 2,4-D has the highest value (close to 100%). This means that after 10 years, almost all the remaining 2,4-D is located in arctic zone. The ACP of DDT is about 18%, and that of Aldrin is below 2%. The ACP results exhibit a surprising feature: for all substance families, the degradation products have lower arctic contamination potentials than the parent compounds, and also the joint arctic contamination potential is lower than the one of the parent compound. This is somewhat counterintuitive, because including degradation products in the ACP indicator should result in a higher value of the indicator (indicating a higher risk). For the ACP, this is not the case: the more degradation products are included in the indicator, the lower it will be. The reason for this is that the ACP indicator is defined as the fraction of the overall substance mass that is present in arctic surface media (excluding atmosphere). As degradation is slow in the cold arctic climate, only small amounts of degradation products will be formed there, whereas in temperate regions, degradation products are built-up faster.

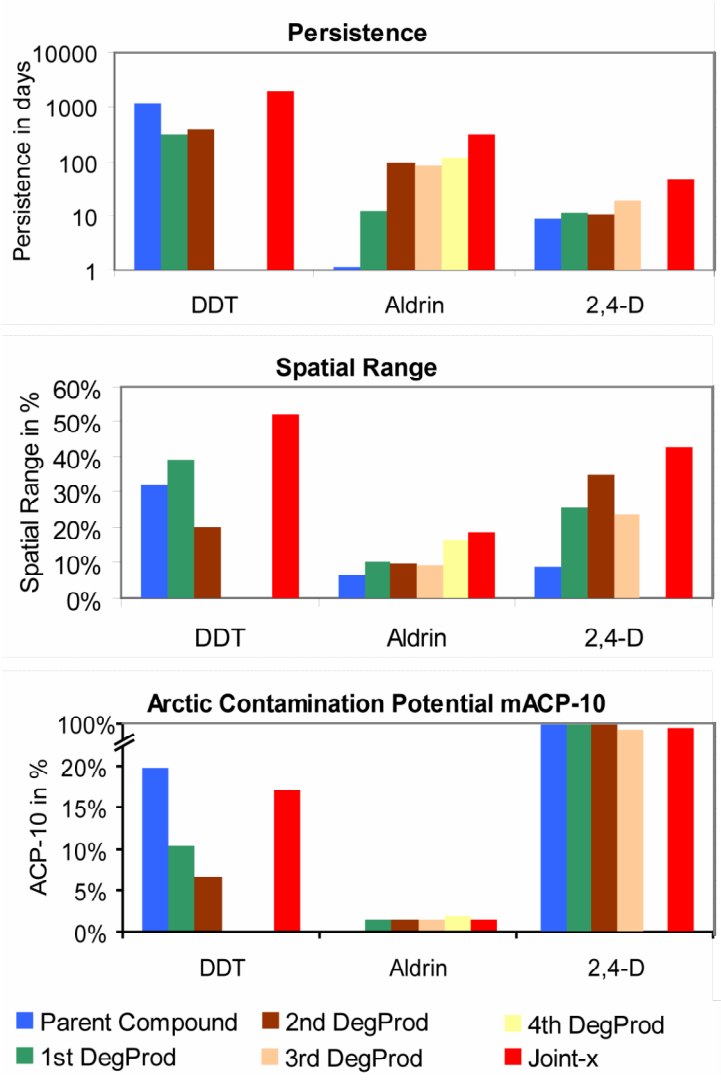

Figure 2: Persistence, spatial range and arctic contamination potential (ACP-10) of the three selected pesticides.

The results of the model runs with the realistic emissions inventory of DDT show that maximal DDT concentrations were reached in the temperate regions at the beginning of the 1960ies, whereas the maximal concentrations of the degradation products were reached about ten years later. Since then, pollutant concentrations have decreased by about one order of magnitude. Most studies on DDT in the environment have measured decreasing concentrations in the last 20 years[21,22,23,25]. In this area, the model is confirmed by the measurements in the environment.

Furthermore, the model predicts that the concentrations of DDT are higher than those of its degradation products until about 1990, and similar from there on. It is difficult to draw a general picture of the actual quantities of DDT

and its degradation products in the environment, but it rather seems that the concentration of DDE is highest most of the time, and that DDT and DDD are present in lower concentrations, especially in recent years[19,21,22,25]. This difference between model results and field data will lead to a further improvement of the input data used in the model.

The geographical distribution of the pollutants in the model runs shows that the pollutants should be mainly present in the Northern Hemisphere, at highest concentrations in the temperate and the tropical zones. These are the regions where DDT has been used most extensively. Global field studies confirm that the highest concentrations of DDT are to be found in the source regions[20,21]. In other studies, DDT and its degradation products have been identified (in lower concentrations) in remote regions such as the Arctic[19,25]. This is reflected by the model results as well: significant amounts of DDT are transported to the northernmost zone (84°–90° N) of the modeling domain.

In conclusion, evaluation of parent compounds and transformation products in one consistent environmental fate analysis makes the risk assessment of pesticides more informative. The case study on DDT shows that model findings can be confirmed with measurements in the environment, and that degradation products can play an important role in this confirmation process.

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