DEVELOPMENT OF A SCHEME TO ASSESS THE CONTRIBUTION OF TRANSFORMATION PRODUCTS TO THE ENVIRONMENTAL PERSISTENCE OF EMITTED CHEMICALS

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Introduction

The identification of potential persistent organic pollutants (POPs) is an extremely challenging field, given the many thousands of chemicals already in commercial production. For the majority of these chemicals, property data are largely missing. Thus, their environmental behavior and fate can be difficult to predict. As an added dimension of complexity, it has become widely recognized that a number of chemicals have transformation products or metabolites that are as or more hazardous (toxic, persistent or bioaccumulative) to the environment and organisms. As a result of this growing concern, the assessment of transformation products is now incorporated into several key pieces of environmental legislation, including the European REACH regulation. However, the knowledge base for transformation products is even scarcer than for intentionally produced chemicals. Thus, the routine assessment of multiple such products for thousands of chemicals could be considered an intractable problem. In order to better assess this tractability and provide a framework for the screening of potentially hazardous transformation products, we have developed a scheme that combines existing and easily accessible tools for the prediction of transformation products and their properties with a multispecies multimedia fate model. Focusing on the hazard metric of persistence, we assess the ability of our scheme to identify transformation products that substantially contribute to the overall persistence of a parent compound. We use previously published assessments of the tools employed together with 22 'test cases' of compounds with known degradation pathways[1,2,3] to evaluate the effectiveness of our scheme and identify important data gaps.

Materials and methods

We have chosen persistence as the hazard property with which to evaluate our screening scheme. Persistence is particularly useful because an integrated metric exists that incorporates the persistence of both parent compounds and their transformation products, the joint persistence (JP). It is defined as the sum of the steady state mass of the parent compound and all its transformation products relative to the parent compound emission rate.[4,1]

Thus, to calculate JP the following data are needed: parent compound emission rates; physico-chemical properties governing its environmental fate (namely, the octanol-water partition coefficient K_{OW}, the Henry's Law coefficient H, and the organic-carbon water partition coefficient K_{OC}); the identity and proportion of transformation products formed and their physico-chemical properties; media-specific transformation half-lives for both parent compound and transformation products. Here we focus on biodegradation as the dominant transformation process in water and soil and on reaction with hydroxyl radicals as the dominant transformation process in air. We chose two readily available and free to use resources to acquire these data: for the prediction of possible biodegradation products we use the University of Minnesota's Pathway Prediction System (UM-PPS)[5], and for the estimation of physico-chemical properties we use Syracuse Corporation's Estimation Programs Interface Suite (EPISuite).[6] One challenge of using UM-PPS is that it predicts all possible biodegradation products, rather than the set of most likely products. For a complex parent compound structure, this could lead to prediction of hundreds of possible structures. Thus, we also devised a pathway simplification scheme with which to reduce this combinatorial explosion.

Our assessment scheme thus consists of six steps (Figure 1): 1) estimation of parent compound properties using EPISuite; 2) prediction of possible degradation products with UMPPS; 3) reduction of products to representative set; 4) estimation of transformation product properties with EPISuite; 5) prediction of JP using a multi-species

multimedia model; 6) comparison of parent compound persistence and JP to regulatory thresholds (here, the 60-day REACH threshold for persistence, P).

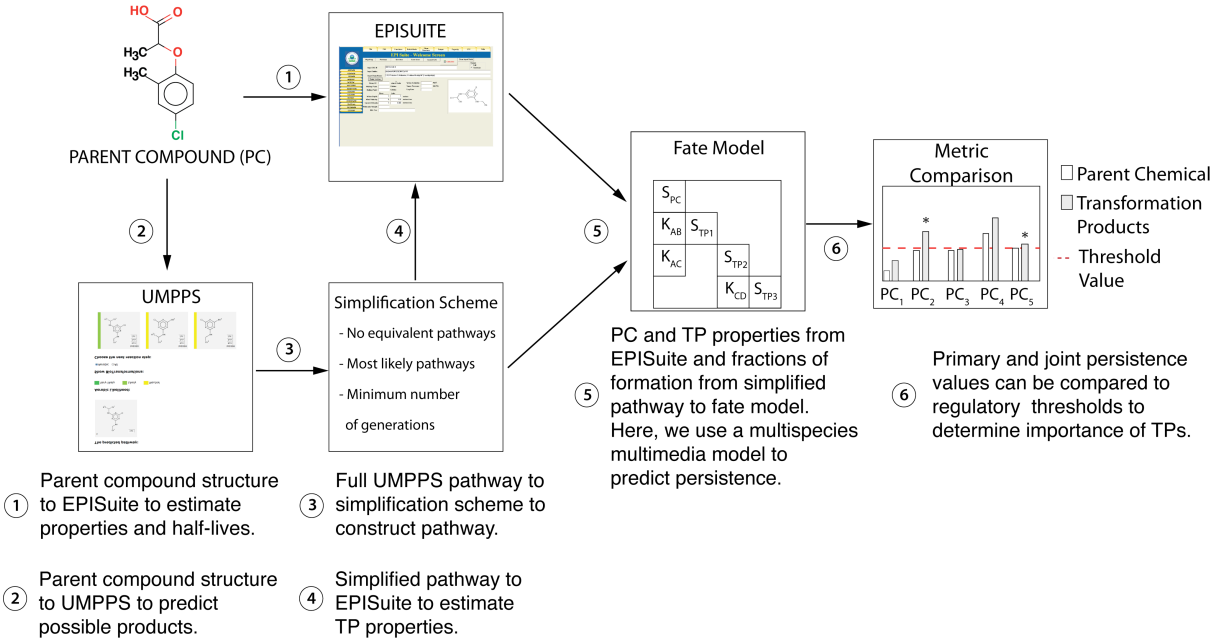

Figure 1: Scheme to identify transformation products that substantially contribute to parent chemical hazard. In this work, we focus on persistence as an important hazard metric.

In addition, we use previous assessments of EPISuite tools[7-13] to propagate the uncertainty in property estimates to the estimated persistence of the parent compound and the estimated joint persistence. We compare these values, as well as the 'representative transformation scheme' predicted by UM-PPS and our simplification method to known biodegradation pathways for 22 test compounds.

Results and discussion:

When considering the geometric means of the parent compound persistence (PP) and the joint persistence (JP) we find for our 22 test cases that 8 have PPs below the threshold and JPs above it (2,4-D, kresoxim-methyl, dicamba, orbencarb, alachlor, diuron, amidosulfuron and atrazine). This indicates that their classification would change if transformation products were included in the assessment. Four compounds have both values below the threshold (MTBE, glyphosate, perchloroethylene and mecoprop-P), while for ten compounds both PP and JP exceed the threshold (DDT, aldrin, heptachlor, mesotrione, sulcotrione, a-HCH, bromoxynil octanoate, chlorpyrifos, TCPN and fluoroglycofen-et). However, when the 95% confidence intervals resulting from propagation of physico-chemical property uncertainty are considered, the picture is far from clear (Figure 2). The confidence intervals for PP and JP cover up to two orders of magnitude and thus, for the majority of chemicals, cross the persistence threshold.

We find that the biodegradation half-life of either the parent compound or one of its transformation products is one of the most important parameters contributing to the uncertainty in JP estimates. In addition, the organic-carbon water partition coefficient (K_{OC}) and the Henry's Law coefficient (H) significantly contribute to the uncertainty in PP and JP. In most cases it is the uncertainty in the properties of the parent compound rather than its transformation products that dominates. Clearly, better estimates of these properties are needed and, more fundamentally, better empirical data on which to found more rigorous structure-property relationships will be key to the success of screening schemes of this type.

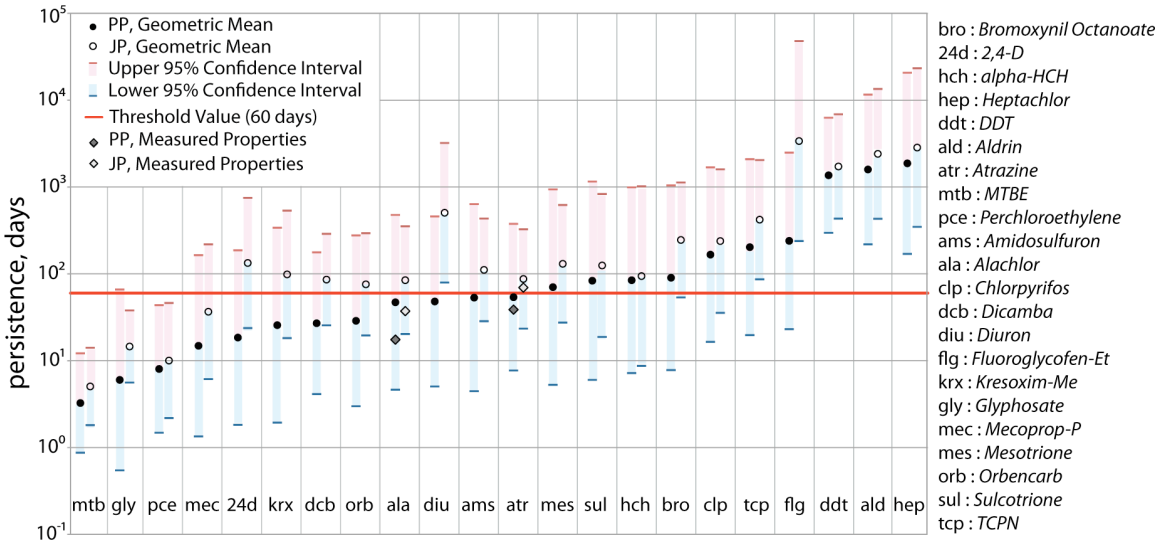

Figure 2: Geometric means and 95% confidence intervals for the parent compound and transformation product persistence (PP and JP) for 22 test cases.

To better illustrate the effect of parameter uncertainty on the identification of potentially important transformation products, we look at the effect of uncertainty on the classification of a chemical based on the geometric mean of JP relative to the threshold value. From a Monte Carlo sample (N=1000) for each chemical based on uncertain property estimate distributions, we calculate the fraction of the population that would be classified differently than what is indicated by the geometric mean of the JP (Figure 3).

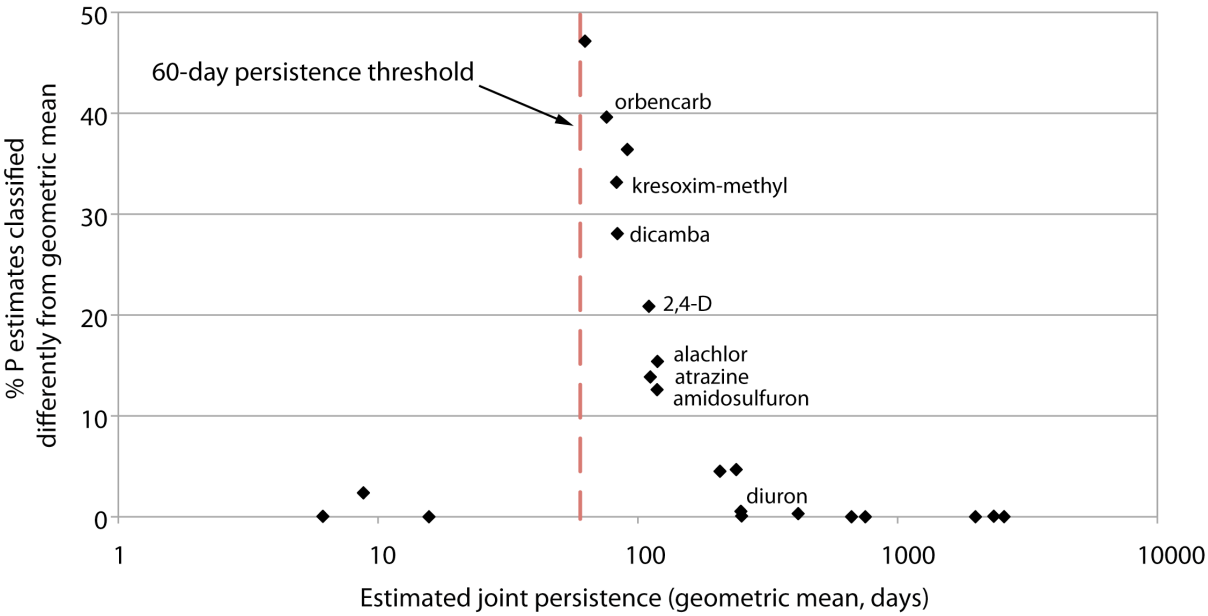

Figure 3: Effect of uncertainty on classification of chemicals based on the geometric mean of the joint persistence (JP) relative to a threshold value (here, 60 days).

As expected, we find that the uncertainty in JP has the greatest effect when the geometric mean is close to the threshold value. Close to the 60-day threshold, more than 45% of the sample is 'misclassified' relative to the geometric mean. However, this disagreement rate quickly decreases as the geometric mean moves away from the threshold value. By a mean JP value that is twice the threshold, less than 15% of the sample has a different

classification. Thus, in spite of substantial uncertainty surrounding both the identity of transformation products and the properties of both parent chemicals and their products, our scheme can identify chemicals with potentially problematic products, and thus help to guide the expensive and time-consuming process of experimental chemicals assessment.

By breaking down the seemingly intractable problem of transformation product inclusion in chemicals assessment into a series of systematic and largely independent steps (identification of products, estimation of properties, prediction of hazard metric of interest, comparison to threshold values), we have been able to show:

1) an initial screening of chemicals for identification of potentially persistent products is possible on the basis of structure alone;
2) the estimation of physico-chemical properties remains a major challenge in environmental chemistry, particularly with regards to degradation half-lives;
3) the UM-PPS is a particularly useful tool in preliminary identification and assessment of transformation products.

Although the landscape remains uncertain, we find these results promising in that they indicate that a systematic screening approach, when combined with sound predictive tools, can be of substantial assistance in the pressing problem of the necessary assessment of large numbers of chemicals with unknown properties.

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