Degradates and Impurities List

Background – Why consider degradates and impurities?

Degradates and impurities can also be water pollutants. In some cases, degradates have similar or greater toxicity than the parent compound. A few degradates and impurities are regulated water pollutants.

EPA Office of Pesticide Programs (OPP) identifies degradates and impurities of known toxicological or ecotoxicological concern when pesticides are registered and during periodic reviews.[1] In the last few years, OPP has started developing aquatic life and human health benchmarks for pesticide degradates. Nonetheless, many data gaps currently exist. These can be addressed through other types of monitoring (e.g., aquatic toxicity monitoring to determine aquatic life effects levels) and, in the long-term, through EPA's pesticide reviews (risk assessments which cover both human health and aquatic life).

Degradates and Impurities List Development

EPA OPP includes some—but not all—degradates in its lists of Human Health Benchmarks for Pesticides (HHBP) and Aquatic Life Benchmarks. These two lists are the primary resources for identifying degradates and obtaining reference values for use in prioritization.

Because the two EPA lists are currently incomplete with regard to degradates—and in some cases unclear about which degradate links to which pesticide—the attached reference table has been created. The table clarifies where enforceable drinking water standards and EPA Health Advisories exist for pesticides, since these values are expressly omitted from the HHBP table.

The table also includes a small number of pesticide impurities, since no EPA listing of pesticide impurities currently exists. The most common impurities of toxicological importance identified in EPA documents are chlorinated aromatics, specifically dioxins, furans, polychlorinated biphenyls, and hexachlorobenzene. These are the only impurities that are included in the table. Only dioxins were thoroughly reviewed; this was due to both the availability of reliable reference information and the presence of water quality standards and downstream 303(d) listings. Reliable impurity concentrations were only identified for one pesticide (2,4-D).

The table was assembled entirely from EPA documents, primarily OPP risk assessments.

Pesticides reviewed for inclusion on this table were:

(1) Pesticides identified by DPR in examples of the application of its pesticide monitoring prioritization tool to statewide agricultural pesticide use as ranked on the basis of aquatic toxicity (see materials for September 2014 workgroup meeting)
(2) Pesticides well known to degrade to other chemicals of interest
(3) Pesticides identified by EPA as containing dioxins (EPA 2006)
(4) Pesticides with human health or aquatic benchmarks for degradates where the benchmark tables do not clearly identify the linkage between degradate and parent chemical.

The table excludes pesticides for which the EPA benchmark tables clearly link parent and degradate (i.e., where degradates are listed immediately following the parent pesticides).

[1] For more information see http://www.epa.gov/oppefed1/ecorisk_ders/toera_analysis_exp.htm

Dioxins Details

Pesticides containing dioxins and furans were identified based on a list in the EPA Dioxins inventory (EPA 2006) and information in EPA pesticide Reregistration and Registration Review risk assessments. Most pesticides on this list were excluded from the table for the following reasons:

(1) Low-risk use patterns: Tetrachlorvinphos (all products are pet collars and bait blocks), pentachlorophenol (no agricultural use), triclosan (irgasan) (no agricultural use)
(2) Dioxins/furans concentrations below reporting limit in EPA-required measurements: Bromoxynil and Dichlobenil (Per EPA 1998 REDs), MCPA and MCPB (per EPA 2014 registration review workplans)
(3) No identified concentration data: 2,4-DB, 2,4-DP, Dicamba, Diflubenzuron, Oxadiazon, 2,6-Dichloro-4-nitroaniline (dichloran), Mecoprop-p (MCPP)
(4) No longer registered in California: 4-CPA, diclofop-methyl

For most purposes, dioxins/furans and (in some cases) dioxin-like PCBs concentrations are usually expressed as a single toxicity value based on the sum of "toxic equivalents" (TEQ) based on the toxicity of 2,3,7,8 tetrachlorodibenzodioxin (TCDD). The sum totally of the concentrations of all measured dioxins and furans is usually significantly higher than the TEQ concentration.

Using Degradate and Impurity Toxicity Reference Values in Monitoring Prioritization

STRAWMAN PROPOSAL FOR DISCUSSION

Including degradates in the pesticide prioritization process will clarify priorities, even if monitoring is not currently practical, (e.g., if no practical chemical analysis methods are available). When evaluating the pesticides ranked on the basis of degradates and impurities for potential monitoring, considerations in the Step 3 evaluation process, such as availability of chemical analysis methods, will be important in making final monitoring recommendations. If a degradate or impurity ranks highly, the monitoring could entail a novel approach, such as measurements of an indicator[2] or use of a monitoring method other than chemical analysis for the degradate or impurity. For example, since monitoring of the impurities on the attached list at environmentally relevant concentrations is expensive, measurements of the parent chemical may be an appropriate surrogate approach.

Degradates: Identify relevant degradates and obtain reference values.

1. Identify the degradates of pesticides used in a monitoring watershed for inclusion in the preliminary ranking process from the following three sources:
    a. EPA's table of pesticide Aquatic Life Benchmarks. This table lists most (but not all) degradates immediately following the parent pesticides.
    b. EPA's table of Human Health Benchmarks for Pesticides. This table includes degradates, but because it currently does not clearly identify pesticide parent/degradate relationships it cannot currently be used to identify relevant degradates. This table should be consulted because the parent/degradate linkage will likely to be clarified in future updates.

[2] For example, water column and/or sediment toxicity testing, which may already be an element of required monitoring, could be an appropriate indicator. Toxicity testing is appropriate to consider for the potential aquatic life effects of the pesticide parent chemical, its degradates (and the formulated ingredients and their degradates) in the environment, but it does not capture potential human health risks.

c. The attached table. This table lists degradates of interest that are not clearly listed in the EPA benchmark tables and provides the source(s) of reference values, which include water quality criteria, enforceable drinking water standards, and drinking water Health Advisories in addition to EPA pesticide benchmarks. This table identifies the parent/degradate linkages for pesticide degradates with human health benchmarks.

2. Once the degradates are identified, find the reference value for each degradate by looking in EPA's human health and aquatic life benchmark tables, California and EPA water quality criteria lists, and enforceable drinking water standards and health advisories tables (see "Information On Drinking Water Standards And Guidance Values"). [Item for discussion: should specific values or detailed instructions on how to obtain non-benchmark reference values for degradates (e.g., enforceable drinking water standards and water quality criteria)? If specific values are provided in the table, they will need to be updated regularly.]
3. Select the lowest reference value among parent and degradate(s) and use that reference value in the Step 2 preliminary ranking process. Alternatively, if desired (this is not required), the degradate fraction applicable to the application setting, which may be available in EPA OPP documents, can be used as a multiplier for the use quantity, to create a more realistic use estimate for the degradate prioritization. If this optional approach is used, the remaining use quantity of the pesticide should be included in the Step 2 preliminary ranking as parent chemical or other degradates (as appropriate).
4. When two or more pesticides have a common degradate, complete a separate Step 2 preliminary ranking for the degradate, based on the sum total of all use of the parent pesticides. Sum up the use of all pesticides in the group (i.e., triazole derivatives and pesticides with common degradates named in the "notes" column) before completing the special degradate ranking for the group. (This approach is the equivalent of EPA's "total toxic residue" approach.) In this situation, continue to include the parent pesticides separately in the ranking.

Impurities: Multiply the impurity concentration by the pesticide use to estimate total impurity use in the monitoring watershed. Obtain the reference values for the impurity. Calculate the ratio of impurity use to reference value during the Step 2 preliminary ranking process.

A reliable concentration estimate is available for only one impurity in one pesticide (dioxins/furans in 2,4-D). Available maximum values for other impurities are provided in the attached table for information.

Limitations of Document and Considerations for Future Updates

This document may not be complete. Resources were not available to review EPA risk assessments for every registered pesticide. Older EPA documents were less complete in their identification of degradates of toxicological or ecotoxicological concern.

Available information on degradates and impurities is rapidly improving in both accuracy and completeness. Changes to EPA's benchmarks lists may eventually eliminate the need for a degradates reference table. Annual review and updating of the table would be appropriate.

Reference

EPA (2006). An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000. EPA/600/P-03/002F. Table 8-31