**Fate of Synthetic Pyrethroids Permethrin, Deltamethrin, Bifenthrin, Cyfluthrin, *Lambda*-cyhalothrin, Cypermethrin, Esfenvalerate, and Fenpropathrin in Simulated Bench-Scale Processes that Occur in Wastewater Treatment Plants**

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|---|---|
| **Report:** | Cleary, J.G. and J. McGrath. 2012. Laboratory Investigation of the Fate of Pyrethroid Insecticides in Wastewater Treatment Processes. Unpublished study performed by HDR\|HydroQual, Mahwah, N.J. and submitted by the Pyrethroid Working Group, Greensboro, N.C. HDR\|HydroQual Project Identification PYWG-153304.005. January 2012. |
| **Document No.:** | MRID **48762906** |
| **Guideline:** | Not applicable, this is a non-guideline study. |
| **Statements:** | The study WAS NOT conducted in compliance with Good Laboratory Practice Standards (GLPS) set forth in Title 40, Part 160 of the Code of Federal Regulations (p. 4). The authors indicate that GLP standards do not apply to this document (p. 4). Signed and dated Data Confidentiality was provided (p. 2). GLP Compliance, Quality Assurance, and Authenticity Certification statements WERE NOT provided. |
| **Classification:** | This study is considered **supplemental**. The study **WAS NOT** conducted in compliance with Good Laboratory Practice (GLP) Standards. |

| | | |
|---|---|---|
| **PC Codes** | Permethrin | 109701 |
| | Bifenthrin | 128825 |
| | Cyfluthrin | 128831 |
| | *Lambda*-cyhalothrin | 128897 |
| | Cypermethrin | 109702 |
| | Deltamethrin | 097805 |
| | Esfenvalerate | 109303 |
| | Fenpropathrin | 127901 |

**Signature:** José Luis Meléndez

**Reviewer:** **Jose Melendez, EPA** **August 19, 2014**

**Signature:**

**Reviewer:** **Stephen P. Wente, EPA** **August 19, 2014**

**Executive Summary**

The fate of the pyrethroids permethrin, deltamethrin, bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin, esfenvalerate, and fenpropathrin was studied in a bench scale study simulating four processes that occur in wastewater treatment plants (WWTPs): primary settling, aerobic biological treatment, anaerobic digestion, and ultra-filtration. These processes were evaluated separately

from each other (i.e., they were treated as modules, although in WWTPs they occur simultaneously). Primary settling, anaerobic digestion, and ultrafiltration were measured in batch mode (*i.e.*, a sample was submitted to the process and evaluated after a period of time, *e.g.*, two hours for primary settling, up to 34 days for anaerobic digestion). The aerobic biological treatment was evaluated in a continuous process (*i.e.*, sample was continuous and partially recirculated in the process and evaluated throughout the process for 50 days, with a target solids retention time (SRT) of 10 days). The following are highlights from the study.

- Primary settling did not remove substantial amounts of pyrethroids from the primary influent. The primary effluent had concentrations of pyrethroids that were very similar to the concentrations in the primary influent. Despite the fact that the solids had higher amounts of pyrethroids, these chemicals did not appear to be adsorbed by the solids substantially.
- Pyrethroids were removed from sludge obtained from the process of primary settling, submitted to the anaerobic process. Pyrethroids were removed moderately from primary sludge under these testing conditions in the anaerobic chamber. Among eight pyrethroids tested, removals ranged from 32 to 81 percent, for bifenthrin and cyfluthrin, respectively, attributed to anaerobic biological digestion.
- Pyrethroids were removed moderately from the secondary influent (or primary effluent), in the aerobic chamber. Removals ranged from 52 to 87 percent, for bifenthrin and permethrin, respectively.
- Ultrafiltration appeared to be the process that removed the highest percentage of pyrethroids from the secondary effluent, with over 90% of pyrethroid removed from the final effluent. Slightly higher levels of removal were observed when the effluent was filtered through a 1.0 µm pore size filter, compared to a filter with 0.1 µm pore size. No reasonable justification was provided for this unusual behavior.

**Table 1** provides a results synopsis of the study (note that he estimated removals are for specific modules and not overall removals).

**Table 1. Results Synopsis: Removal Percent of Eight Pyrethroids in Certain Treatment Processes Simulated in a Bench Scale Wastewater Treatability Study[1]**

| Process | Bifent. | Fenprop. | *l*-Cyhal. | Permet. | Cyflut. | Cypermet | Esfenval. | Deltamet. |
|---|---|---|---|---|---|---|---|---|
| Primary Settling | LR[2] | LR[2] | LR[2] | LR[2] | LR[2] | LR[2] | LR[2] | LR[2] |
| Aerobic Chamber[3] | 51.9 | 80.1 | 48.6 | 86.6 | 73.2 | 76.3 | 56.1 | 59.1 |
| Anaerobic Digestion[4] | 32.1 | 45.5 | 57.0 | 43.5 | 81.2 | 78.1 | 79.2 | 77.1 |
| Ultrafiltration[5] | 91.7 | 95.7 | 93.1 | 96.9 | 95.7 | 95.4 | 93.6 | 92.6 |

[1] The percent shown is for each of the individual modules (refer to text).
[2] LR means limited removal was achieved in this process. The concentrations of the influent and primary effluent were nearly the same (see p. 23 of study report).
[3] These results represent a likely best case scenario and removals should be lower whenever the solids retention time is lower than 10 days. Data obtained from Table 2-3, p. 92 of study report.
[4] Removal represents the amount remaining in the secondary effluent minus the amount applied of each pyrethroid. Data obtained from Table 9, p. 35 of study report.
[5] Results presented are the means of two values, using a 0.1 µm filter. The 1.0 µm filter yielded unexpectedly higher removal and are not reported in **Table 1**. Data were obtained from Table 2-5, p. 94 of study report

## I. Material and Methods

## A. Materials:

1. **Test Material:** For structures of the test substances, see **Attachment 1**. The test materials were not radiolabeled. Batch numbers were not provided.

**Table 2. Table of test materials[1]**

| Applicant's Code Name | PC Code | Chemical Name | Purity (%)[2] |
|---|---|---|---|
| Bifenthrin | 128825 | (2-Methyl[1 , 1 '-biphenyl]-3-yl)methy I 3-(-2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropane carboxylate | >95 |
| Cyfluthrin | 128831 | Cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate | >95 |
| *Lambda*-cyhalothrin | 128897 | [1a(S*),3a(Z)]-(±)-cyano(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl]-2,2-dimethyl cyclopropanecarboxylate | >95 |
| Cypermethrin | 109702 | (+/-)-a-cyano(3-phenoxyphenyl)methyl(+/-) cis. trans- 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylate | >95 |
| Deltamethrin | 097805 | (S)-Cyano(3-phenoxyphenyl)methyl(1R,3R)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate | >95 |
| Esfenvalerate | 109303 | ((S)-Cyano(3-phenoxyphenyl)methyl(S)-4-chloro-a/p/7a-(1-methylethyl)benzeneacetate) | >95 |
| Fenpropathrin | 129701 | Alpha-cyano-3-phenoxybenzyI-2,2,3,3-tetramethylcyclopropane carboxylate | >95 |
| Permethrin | 109701[3] | (3-Phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethyl cyclopropanecarboxylate | >95 |

1 Refer also to **Attachment I** for structures of these compounds.
2 Source of chemical purity, p. 11 of study report. Lot/batch numbers and certificates of analysis were not provided.
3 This DER will be filed under PC Code **109701** in the file room.

2. **Reference Compounds:** Analytical grade (not further described) reference compounds for each of the above mentioned chemicals were used.

3. **Source of Wastewater:** The wastewater used in this study was obtained from the Ridgewood Wastewater Treatment Plant, in Ridgewood, NJ. "Healthy" aerobic and anaerobic biomass was used to startup the aerobic and anaerobic processes, respectively, obtained from the same treatment plant.

4. **Stock Solution:** Stock solution was prepared by measuring 50 mg of each pyrethroid (except 500 mg permethrin), added to a 1 L volumetric flask containing 100 mL reagent grade acetone, and brought to volume with acetone, to generate a stock solution containing each pyrethroid at a target concentration of 50 µg/mL (except 500 µg/mL for permethrin). This sample was tested for each pyrethroid content (reference substances used to calibrate the system presumably analytical grade - see item #2 above), and the percent difference between the target and measured concentration was within a range of ≤10.6%, except for permethrin and cyfluthrin (-23.8 and -34.2% recovered, respectively). It was not clear whether corrections were performed in the calculations.

5. **Decontamination of the Equipment:** An eight step process was used to clean the equipment, tubing and glassware. Equipment was wrapped in aluminum foil once cleaned. Drums and sampling containers were new and dedicated.

6. **Analytical Methods:** Methanol is used to partition eight pyrethroids from the wastewaters, and partitioned with hexane. (For sludge samples, a similar process is followed, except that a centrifuge is used to partition the liquid layer from the solids.) The upper hexane layer is passed through sodium sulfate, evaporated to dryness, re-disolved in hexane, and submitted to a silica solid phase extraction (SPE) procedure. The extracted sample is analyzed via GC/MS. The analytical methods for influent/effluent and sludge have been previously submitted to the Agency and evaluated under DP Barcode D395988 (dated 11/09/2011, USEPA 2011, MRIDs 48638501 & 48638601, studies were found to be supplemental). Additional data was requested in the past to upgrade the methods as they were reported. The LOQs claimed in the current report (MRID 48762908), are provided in **Table 3**. Spiked samples were tested for eight pyrethroids and recoveries ranged from 64-119% of the applied.

**Table 3. Limits of quantitation for the bench scale treatability study**

| Chemical | Permethrin | Deltamethrin | All other six pyrethroids[1] |
|---|---|---|---|
| Influent (ng/L) | 50 | 10 | 5 |
| Effluent (ng/L) | 5 | 1 | 0.5 |
| Sludge (ng/mL) | 25 | 5 | 2.5 |

[1] Bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin, esfenvalerate, and fenpropathrin

**B. Study Design:** Four processes were simulated in this study as separate modules. An overview of the processes follows:

In **primary settling,** the wastewater is kept in a quiescent state for a specified period of time (in this study, 2 hours), to allow heavy particles to settle. The resulting supernatant is named primary effluent, and the solids are the primary sludge. In this experiment, the primary sedimentation process was conducted in batch mode.

The primary (but also the secondary) sludge is added in the **anaerobic digestion** system. The chamber is kept at *ca.* $35^0$C under anaerobic conditions (in the absence of oxygen). As a result of this process, the remaining solids are the biosolids. The anaerobic digestion was run in a batch mode.

The primary effluent is added to the **aerobic biological treatment** system to reduce its organic content. The aerobic system is kept at room temperature (*ca.* $20^0$C) and it consists of two submodules: the aeration system in which dissolved oxygen promotes aerobic biological degradation, and secondary settling. This part of the experiment was run in a continuous flow system, where the secondary sludge is fed with the primary effluent to the aerobic chamber. The target solids retention time (SRT) was 10 days. The solids resulting from the secondary settling are the secondary sludge and the supernatant is the secondary effluent.

This process a named **ultrafiltration**, run in batch mode, the supernatants from the secondary settling are filtered and remaining solids are removed, reducing further the suspended particles, and consequently the organic matter associated with those particles (*e.g.*, pyrethroids).

**Figure 1** shows a schematic or diagram of the modules involved in this study. Following this section, there is a brief description of each module setup/procedures, and later (**Section II**), results relative to each process.

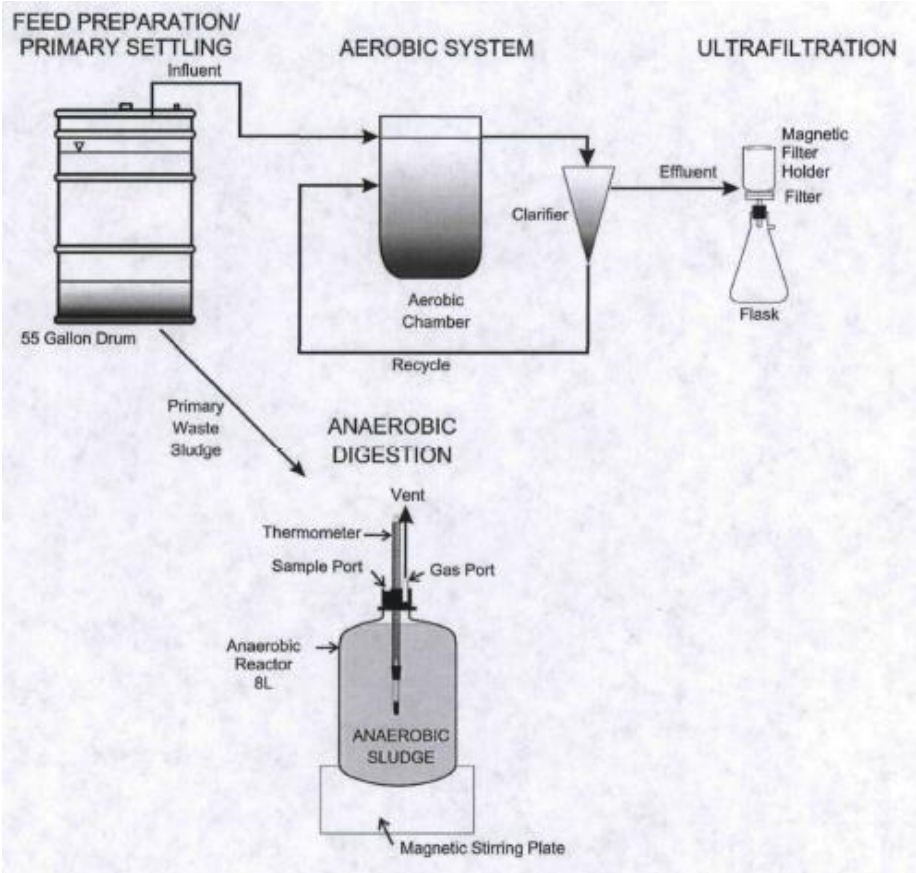



**Figure 1. Diagram of the bench-scale laboratory treatability study** (refer to p. 11 of report)

1. **Primary Settling:** This module of the study was run in batch mode. It was used to measure the removal via adsorption to sludge, and to produce primary sludge for the anaerobic digester. The settling drum had a capacity of 55 gal, to which 40 gal of primary influent were added and a 500 mL sample was pulled to prepare a composite sample for analysis of pyrethroids. The primary influent was stirred after the addition of the appropriate amount of stock pyrethroids solution to obtain a spiking level of 5 µg/L of each pyrethroid (50 µg/L permethrin). The spiked mixture was stirred for 30 minutes and another 500 mL grab sample taken for analysis. After mixing was stopped, the mixture was allowed to settle for 2 hours and a third 500 mL grab sample was taken. This process was repeated five times and the combined resulting sludge (totaling 1 gal), was used in the anaerobic digestion study. Composite samples of primary influent, primary effluent and primary sludge were analyzed for each of eight pyrethroids.

2. **Anaerobic Digestion:** The capacity of the anaerobic reactor was 8 L, which was wrapped with heat tape to keep a target temperature of 35-37$^0$C, and equipped with a magnetic stirrer. The process was maintained for 35 days and it was started with 3.2 L of healthy anaerobic seed from the Ridgewood plant. To this 2.8 L of primary sludge from the previous step were added, for a total of 6 L sludge. The vessel was purged with nitrogen to exclude any oxygen from the system, and maintained under anaerobic conditions. This module was run as a batch process, and sludge was measured for pyrethroids prior to start of the analysis, and at 6, 13, 20, and 35 days of anaerobic digestion. No additional pyrethroids were added to the system.

3. **Aerobic Biological System:** A glass rectangular chamber (10 L active biomass) was constructed for this analysis. After its construction, changes were made to the original design to improve mixing (*e.g.*, equipped with a paddle mixer to improve mixing of the samples), and to increase dissolved oxygen in the corners of the vessel. Further, an external secondary clarifier was used (1 L capacity). The aerobic chamber was fed with fresh feed prepared twice per week in 25 gal batches as described in the section on primary settling. A pump was used to deliver the feed and recycle the secondary sludge into the aerobic chamber in a continuous flow design. The solids retention time (SRT) was set to a target level of 10 days, and maintained by adjusting the feed flow rate.[1] It is noted that the target of 10 days SRT is a best case scenario for removal process for pyrethroids and it may not be representative of all treatment plants. This module was run as a continuous flow process, and sludge was measured for pyrethroids prior to start of the analysis (initial), and at 12, 23, and 32 days of aerobic biological process (corresponding to approximately 1, 2 and 3 SRTs, respectively). During the process, pyrethroids were added to the system continuously via the delivered feed which was prepared twice per week, as indicated above.

4. **Ultrafiltration:** The secondary effluent resulting from the aerobic biological system was filtered to determine the levels of additional removal of pyrethroids in ultrafiltration. This was done through an apparatus and method similar to the one used to measure total suspended solids (TSS). Two glass fiber filter pads were used, with pore retention times of 0.1 and 1.0 µm, and analyses were conducted in duplicate. Secondary effluent from the aerobic biological system was collected for this analysis on days 24 and 32 (when steady state should have been achieved). Both the secondary effluent (which served as the influent to the filtering system), and the filtrate, were analyzed for pyrethroids, to estimate the levels of removal.

## II. Results and Discussion

### A. Background Samples

[1] The SRT is the average time the activated biomass is in the system. According to the submission, 1-3 days is used in plants that do not nitrify, while 8-12 days are used for nitrification. The longer the SRT, the level of removal is higher for difficult to degrade substances.

1. Samples of primary influent, primary sludge, aerobic biomass and anaerobic biomass from the Ridgewood treatment plant, were analyzed for pyrethroids, in order to determine whether the concentrations of pyrethroids were high enough to interfere with the spiking levels of pyrethroids. All pyrethroids, except deltamethrin, were detected in the primary influent, with permethrin showing the highest concentration. Meanwhile, no pyrethroids were observed above the detection limits in sludge or biomass samples.

**B. Findings**

2. **Primary Settling:** Based on analysis of the total suspended solids (TSS) in the primary influent, primary effluent and primary sludge, it was determined that the solids material balance was 86.3% TSS recovered, from what was initially applied. Analysis of concentrations of pyrethroids in primary influent and effluent resulted in very similar concentrations, suggesting that the settling process did not remove substantial levels of pyrethroids. The authors suggested two possible explanations for this unexpected behavior: (1) the amount of time was not sufficient to allow for adsorption to occur (2 hours of settling), and (2) the dissolved organic carbon (DOC) may have prevented the adsorption of pyrethroids to the solids. Nonetheless, the primary sludge had measurable amounts of pyrethroids ranging from 59.1 ng/mL for bifenthrin to 704 ng/mL for permethrin. In order to obtain sufficient sludge for the anaerobic digestion process, the settling was repeated until an appropriate amount of sludge could be extracted for the anaerobic process (see below).

3. **Anaerobic Digestion:** The reactor temperature was 34-36$^0$C, the pH was between 7 and 7.5, gas production was steady and volatile solids decreased throughout the test, all of which appear to be indicative of a reasonable anaerobic system. The initial concentration of pyrethroids ranged from 2620-5670 ng/g, except for permethrin (32400 ng/g); concentrations decreased after 35 days to 537-3090 ng/g, except for permethrin (18300 ng/g). The removal rates ranged from 32-81% in anaerobic condition. There was an apparent anomaly with the day 20 samples, which exhibited abnormally high pyrethroid concentrations, compared to the established trend from all other measurements. Using first order kinetics, the authors estimated the biodegradation rates for the pyrethroids. Permethrin showed the highest rate, while for bifenthrin, the concentration remained fairly constant and no rate could be calculated.

3. **Aerobic Biological System:** The aerobic system was maintained for a period of 50 days, of which the first 14 days were used to start up the system, which was monitored and any needed adjustments were performed. The test conditions included the solids retention time (SRT) target value of 10 days (range 4-27 days), a target F/M (the ratio of food (F) delivered to system to mass (M) of biological solids in the system) of 0.3 g/g-day (range 0.36-1.3 g/g-day), and a constant flow of 20 L/day. A higher F/M was required to maintain the mixed liquor suspended solids (MLSS) in the aeration chamber. The variability in the SRT was due to fluctuation in effluent total suspended solids (TSS). The pH remained between 7.0 and 8.0 in the aeration chamber and the temperature was within the range 15-20$^0$C. Due to the aeration of the aerobic chamber, the dissolved oxygen (DO) was maintained at 8-10 mg/L. Measures of ammonia-nitrogen, and nitrate-nitrogen in the

influent and effluent suggested that nitrification did occur. The pyrethroid concentration in the influent was variable and it was attributed to the preparation of different batches of influent, while the concentrations in the effluent was less variable, and appeared to decrease slowly (suggesting that the system was acclimating). Permethrin appeared to be the chemical with highest levels of removal. Three measurements are available for each pyrethroid, based on measurements separated by approximately one SRT each. Kinetic calculations performed with the aerobic system results yielded that permethrin had the highest biodegradation rate was for permethrin, with $1.1 \times 10^{-5}$ $day^{-1}$.

4. **Ultra-Filtration:** Pyrethroids were removed upon filtering the aerobic effluent for both the 0.1 and 1.0 µm filters. Removal of pyrethroids ranged from 91.4-98.2%, whereas removals in the 1.0 µm pore size filters were slightly better than in the 0.1 µm filters (which were opposite to the expected trend). The authors did not offer an explanation for this behavior.

## III. Study Deficiencies and Reviewer's Comments

**A.** The study WAS NOT conducted in compliance with Good Laboratory Practice Standards set forth in Title 40, Part 160 of the Code of Federal Regulations (p. 4 of the study report). The study does not provide any indications as to which were the main procedures that departed substantially from GLPs.

**B.** Stock solution was prepared at a target pyrethroid concentration of 50 µg/mL (except 500 µg/mL for permethrin). Testing of the stock solution for pyrethroid content showed that the percent difference between the target and measured concentration was within a range of ≤10.6%, except for permethrin and cyfluthrin (-23.8 and -34.2% recovered, respectively). No further information was provided to evaluate the calibration process. No certificates of analysis were provided for the test substances or the standards. It is unknown whether any type of corrections were performed in the calculations.

**C.** The pH remained between 7.0 and 8.0 in the aeration chamber, and between 7 and 7.5 in the anaerobic chamber. Pyrethroids are known to be more susceptible to hydrolysis under alkaline conditions. According to the submission, these pHs appear to be typical of treatment plants.

**D.** The target solids retention time (SRT) was set to 10 days. According to the submission, for plants that do not nitrify, the SRTs are 1-3 days and for plants that nitrify, the SRTs are 8-12 days. Since the retention of 10 days is longer, besides achieving nitrification, the levels of removal will be higher under aerobic biological system, resulting in a "best case" scenario which may not be typical of a number of treatment plants that do not nitrify.

**E.** Multiple monitoring measurements were performed throughout each module, in order to make sure that the appropriate testing conditions were maintained. Only key measurements are reported in this brief DER.

**F.** Even though the ultrafiltration achieved a high level of removal, it is uncertain how many treatment plants will have such level of treatment. Ultrafiltration is usually associated with tertiary treatment plants.

## IV. Comparison of Studies Reviewed Concurrently

A major complicating factor for interpreting the studies of pyrethroid fate in publically-owned treatment works (POTWs) is understanding the uncertainty inherent in the mass balances presented in these studies. Two of these studies, MRID 48072901 and MRID 48857505, model the fate of pyrethroids in POTWs in New York (denoted POTW NY) and California (POTW CA), and the third study (MRID 48762906) is a bench scale laboratory model of the POTW treatment processes and influent from POTW NY (denoted Lab NY). The basic mass balance follows a parcel of water through real POTWs (POTW CA and NY) or a simulated POTW (Lab NY) from plant influent concentration to plant effluent concentration both of which are measured and therefore, relatively certain values. As the parcel of water moves through the POTW, pyrethroids are lost from the water parcel due to partitioning to solids or sludge, metabolism, and volatilization.

The concentration of pyrethroids in sludge is another measured value; however the uncertainty associated with these measured values should increase with increasing solids in the medium measured. Pyrethroids tend to bind to the organic material in the solids. Because all of these POTW studies used non-radiolabeled pyrethroids, it is likely that a significant fraction of the pyrethroid residues were not extracted in those samples with a lot of solids. For example, radiolabeled alpha-cypermethrin aerobic aquatic metabolism studies (MRID 48425011 and 48425012) found un-extracted residues in excess of 40% of applied radioactivity. Therefore, the effluent concentration (very little solids) is more certain than the influent concentration (more solids), which is more certain than the sludge concentration.

The amount of pyrethroids volatilized is based on the Henry's Law Constant of each pyrethroid and the amount time spent undergoing aerobic biological treatment in each facility. However, it would also be decreased by how much partitioning to solids and biodegradation had already occurred within the POTW. Therefore, if the actual sludge concentration was higher (due to un-extracted residues) than measured, the amount volatilized should be lower.

Biodegradation was estimated from the difference between the measured influent and the measured effluent, measured sludge, and estimated volatilization (biodegradation = influent – sum [effluent, sludge, and volatilization]). Therefore again, if the actual sludge concentration was higher (due to un-extracted residues) than measured, the amount of pyrethroids biodegraded should be lower. Based upon the dependence on the sludge measurement and the way this value is calculated, the biodegradation value should probably be treated as the least certain value reported.

In order to compare the three studies investigating the fate of pyrethroids in POTWs, an attempt was made to summarize the generalized mass balance produced by each study (**Table 4**). The POTW NY values are based on Table 7 of Appendix 2 (page 36 of the study report) after converting to percent of influent. The Lab NY values are from Table 9 of page 35 of the study report. Because the primary settling portion of the lab study did not function, only values from the aeration system were used for this comparison. The POTW CA values are from Table 12 on page 12 and Table 13 on page 13 of Attachment 1 of the study report (values are medians of three calibrations and may not add to 100%).

**Table 4. Comparison of Pyrethroid Mass Balances within POTW across Studies.**

| Chemical | Study | Sludge (%) | Biodegraded (%) | Emitted (%) | Effluent (%) |
|---|---|---|---|---|---|
| Bifenthrin | POTW NY | 64.29 | 10.71 | 25.00 | 1.79 |
| | Lab NY | 10.5 | 41.4 | NE | 48.1 |
| | POTW CA | 41.75 | 44.01 | 1.79 | 9.99 |
| Cyfluthrin (α,ß)[1] | POTW NY | 61.29 | 32.26 | 0.32 | 6.45 |
| | Lab NY | 5.8 | 67.4 | NE | 26.8 |
| | POTW CA | 37.4 | 58.84 | 0.01 | 7.25 |
| Cypermethrin (α,ß)[1] | POTW NY | 67.54 | 29.32 | 0.02 | 3.14 |
| | Lab NY | 5.4 | 70.8 | NE | 23.7 |
| | POTW CA | 29.85 | 65.21 | <0.01 | 4.84 |
| Deltamethrin | POTW NY | Not Measured in NY POTW | | | |
| | Lab NY | 9.6 | 49.5 | NE | 40.9 |
| | POTW CA | Not Measured in CA POTW | | | |
| Esfenvalerate | POTW NY | 60.00 | 40.00 | 0.02 | 4.00 |
| | Lab NY | 12.5 | 43.6 | NE | 43.9 |
| | POTW CA | Not Measured in CA POTW | | | |
| Fenpropathrin | POTW NY | 75.00 | 50.00 | 0.06 | 2.50 |
| | Lab NY | 4.4 | 75.7 | NE | 19.9 |
| | POTW CA | Not Measured in CA POTW | | | |
| *Lambda*-cyhalothrin | POTW NY | 75.00 | 15.00 | 0.02 | 10.00 |
| | Lab NY | 14.4 | 34.2 | NE | 51.4 |
| | POTW CA | 42.04 | 50.68 | <0.01 | 8.23 |
| Permethrin | POTW NY | 62.60 | 36.13 | 0.05 | 1.27 |
| | Lab NY | 5.1 | 81.6 | NE | 13.4 |
| | POTW CA | 33.38 | 63.75 | <0.01 | 5.16 |

NE = Not Estimated

Comparing the percentage of the influent pyrethroids in the effluent (effluent values expected to be relatively certain due to low solids concentrations), it is clear that the Lab NY values do not align with the POTW NY and CA values. As explained in Lab NY report, the pyrethroids did not settle out with solids in the primary settling portion of the experiment, which appears to have allowed the pyrethroids attached to dissolved organic to carbon to resist biodegradation. Potentially, the Lab NY values are more representative of an overloaded or poorly functioning POTW.

Comparing the POTW NY and CA effluent values yields relatively good agreement for those pyrethroids that can be compared (bifenthrin: 1.79 *vs* 9.99%; cyfluthrin: 6.45 *vs* 7.25%; cypermethrin: 3.14 vs 4.84%; *lambda*-cyhalothrin: 10 vs 8.23%; and permethrin: 1.27 vs 5.16%) considering that the values come from different POTWs with differing waste streams. Notice that if the somewhat uncertain influent values were higher due to un-extracted pyrethroid residues, the effluent percentages would be lower.

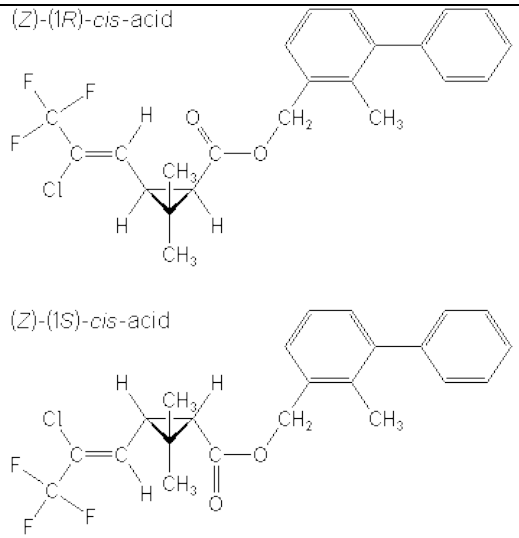
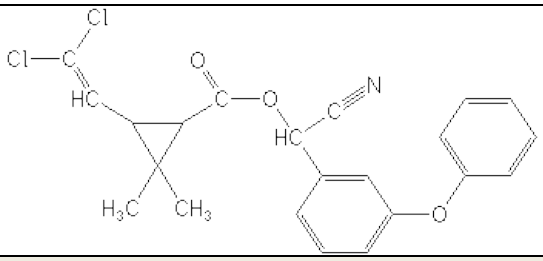
Other than the effluent values, the sludge values are the next most useful values from these studies for pyrethroid risk assessment. Considering the potential for un-extracted residues, the listed sludge percentages should probably be considered minimum values (i.e., the percentages of influent pyrethroids in biosolids are at least the values given in Table 1, but could be substantially higher).

## V. References

U.S. Environmental Protection Agency (USEPA). 2011. EFED Comments on the Pyrethroid Working Group's Environmental Chemistry Methods for Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin for the Analysis of Influent and Effluent (*i.e.*, Wastewaters), Primary Sludge and Dewatered Cake (*i.e.*, Biosolid) Samples from Publicly Owned Treatment Works. Memorandum from Jose Melendez to Monica Wait dated November 9, 2011. (Review of MRIDs 48638501 and 48638601 and associated DERs.)

## Attachment 1: Chemical Names and Structures

**TABLE 1.1. Test Compounds Nomenclature[2]**

| **Common name** | **Bifenthrin** |
|---|---|
| **IUPAC name** | 2-Methylbiphenyl-3-ylmethyl (Z)-(1RS,3RS)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS Name** | (2-Methyl[1,1'-biphenyl]-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS #** | 82657-04-3. |
| **Structure** |   |
| **Common name** | **Cypermethrin.** |
| **IUPAC name** | (RS)-α-Cyano-3-phenoxybenzyl (1RS,3RS;1RS,3SR)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS Name** | Cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS #** | 52315-07-8. |
| **Structure** |  |
| **Common name** | **Cyfluthrin.** |
| **IUPAC name** | (RS)-α-Cyano-4-fluoro-3-phenoxybenzyl (1RS,3RS;1RS,3SR)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate. |
| **CAS Name** | Cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropancecarboxylate. |
| **CAS #** | 68359-37-5. |

[2] Structures were obtained at http://www.alanwood.net/pesticides/index_cn_frame.html (accessed 02/26/14).

**TABLE 1.1. Test Compounds Nomenclature[2]**

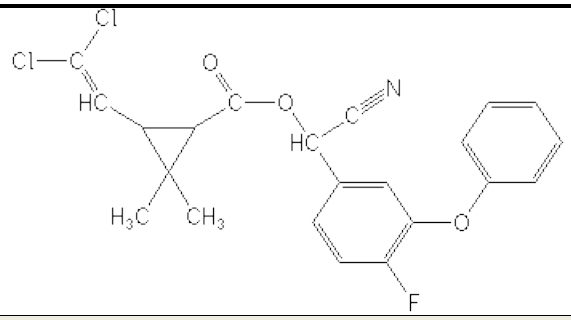
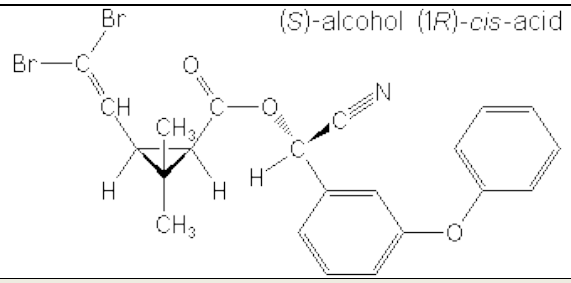
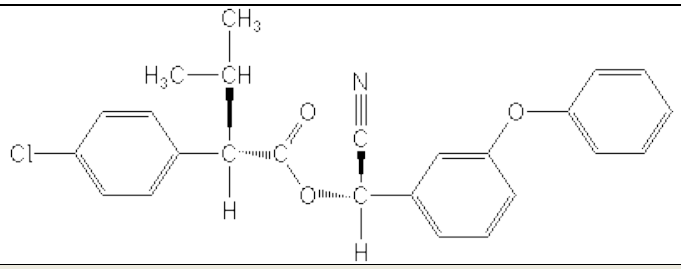
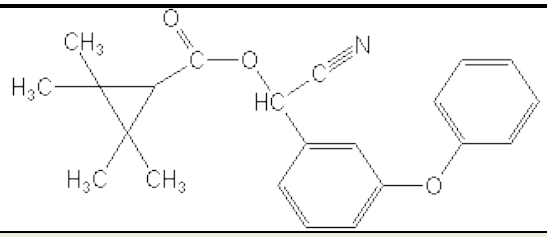
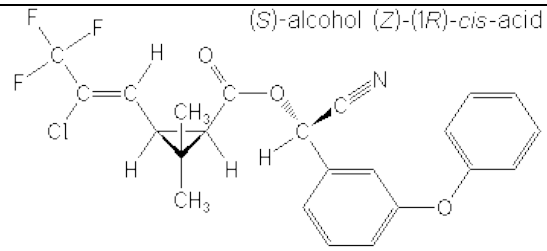
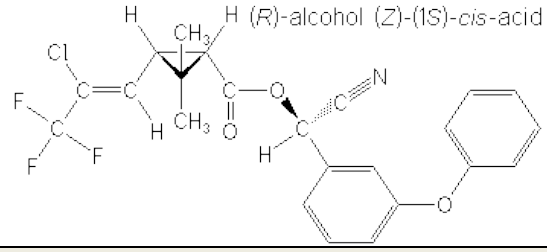
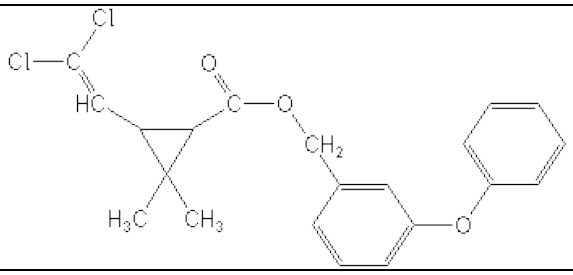
| | |
|---|---|
| **Structure** |  |
| **Common name** | **Deltamethrin.** |
| **IUPAC name** | (S)-α-Cyano-3-phenyoxybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS Name** | 1-[R-[1-α-(S*),3α]]-Cyano(3-phenoxyphenyl)methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS #** | 52918-63-5. |
| **Structure** |   |
| **Common name** | **Esfenvalerate.** |
| **IUPAC name** | (S)-α-Cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate. |
| **CAS Name** | [S-(R*,R*)]-Cyano(3-phenoxyphenyl)methyl 4-chloro-2-(1-methylethyl)benzeneacetate. |
| **CAS #** | 66230-04-4. |
| **Structure** |  |
| **Common name** | **Fenpropathrin.** |
| **IUPAC name** | (RS)-α-Cyano-3-phenoxybenzyl 2,2,3,3,-tetramethylcyclopropancecarboxylate. |
| **CAS Name** | Cyano(3-phenoxyphenyl)methyl 2,2,3,3-tetramethylcyclopropanecarboxylate. |
| **CAS #** | 64257-84-7. |

**TABLE 1.1. Test Compounds Nomenclature[2]**

| | |
|---|---|
| **Structure** |  |
| **Common name** | ***Lambda*-cyhalothrin.** |
| **IUPAC name** | Reaction product of equal quantities of (S)- and (R)- α-cyano-3-phenoxybenzyl (Z)-(1R,3R)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS Name** | [1α(S*),3α(Z)]-(±)-Cyano(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS #** | 91465-08-6. |
| **Structure** |     |
| **Common name** | **Permethrin.** |
| **IUPAC name** | 3-Phenoxybenzyl (1RS,3RS;1RS,3SR)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS Name** | (3-Phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate. |
| **CAS #** | 52645-53-1. |
| **Structure** |  |