



**Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, California 95812**

Pyrethroids in Wastewater: Review of Potential Sources, Occurrence, and Fate

Jennifer Teerlink, Ph.D.
August 27, 2014

Introduction

Pyrethroids are active ingredients in a wide range of registered pesticide products for both indoor and outdoor uses. Environmental monitoring studies have identified the presence of pyrethroids in urban surface waters of California at concentrations that exceed US EPA aquatic benchmarks (Amweg et al. 2006, Holmes et al. 2008, Starner 2013, Weston and Lydy 2010). The urban outdoor use of pyrethroids has been the focus of research and subsequent mitigation efforts to reduce loading to surface waters. Numerous studies have been conducted to evaluate the role of product formulation, application, and timing to the off-site transport of pyrethroids from impervious surfaces to stormwater collections systems that enter urban creeks (Jiang et al. 2012, Luo et al. 2013a, Luo et al. 2013b, Trask et al. 2014). In 2012, the California Department of Pesticide Regulation (CDPR) implemented regulations that limit outdoor applications to impervious surfaces to spot and crack-and-crevice applications to reduce runoff to urban water bodies.

The presence of pyrethroids in the effluent of Publically Owned Treatment Works (POTWs) represents a potential discharge-permit compliance issue. Moreover, due to the continuous nature of treated wastewater effluent, pollutants that are insufficiently removed by the treatment process could present a near constant source of stressors to the surface waters to which they discharge. Therefore, there is growing interest in the occurrence, sources, and fate of pyrethroids in POTWs. The objectives of this analysis are to summarize reported values for pyrethroids at various points in wastewater treatment process and identify potential products (particularly those with indoor uses) and pathways that could result in pyrethroids entering wastewater collection systems.

Pyrethroids in Wastewater

There are limited data available regarding the occurrence, distribution and fate of pyrethroids during wastewater treatment. Concentrations of pollutants in wastewater influent can be highly variable (Teerlink et al. 2012). Available studies do not use consistent sampling techniques;

however, all data are included for comparison due to the limited data currently available (Tables 1-3).

Table 1- Reported pyrethroid concentrations and detection frequencies for wastewater effluent.

Pyrethroid	PWG Survey ¹			Weston 2010 ²		Lowest EPA Benchmark ³ (ng/L)
	Average (ng/L)	DF	Max (ng/L)	Max (ng/L)	DF	
Bifenthrin	0.89	82	3.9	6.3	39	1.3
Cyfluthrin	0.60	60	4	1.7	6	7.4
Lambda-Cyhalothrin	0.30	48	1.6	5.5	17	2
Cypermethrin	2.11	81	13	17	6	69
Deltamethrin	0.31	16	1.2	2.7	11	4.1
Esfenvalerate	0.25	32	0.6	3.7	6	17
Fenpropathrin	0.22	3.2	0.8	0	0	64
Permethrin	20	65	170	17.2	33	1.4

PWG = Pyrethroid Working Group

DF = Detection Frequency

Max = Maximum

¹(Markle et al. 2014)

²(Weston and Lydy 2010)

³(EPA 2014)

Table 2- Reported pyrethroid concentration and detection frequencies for wastewater influent.

Pesticide	PWG Survey ¹		
	Average (ng/L)	DF	Max (ng/L)
Bifenthrin	15	96	74
Cyfluthrin	11	88	55
Lambda-Cyhalothrin	5.6	81	72
Cypermethrin	35	81	200
Deltamethrin	8.0	43	210
Esfenvalerate	8.1	46	360
Fenpropathrin	4.6	4.5	130
Permethrin	330	100	3,800

PWG = Pyrethroid Working Group

DF = Detection Frequency

Max = Maximum

¹(Markle et al. 2014)

Table 3- Reported pyrethroid concentrations in biosolids.

Pesticide	PWG Survey ¹		
	Average (ng/g)	DF	Max (ng/g)
Bifenthrin	150	96	1,100
Cyfluthrin	34	87	190
Lambda-Cyhalothrin	29	52	200
Cypermethrin	110	90	1,000
Deltamethrin	28	31	78
Esfenvalerate	15	31	42
Fenpropathrin	12	5.8	71
Permethrin	1,500	92	11,000

PWG = Pyrethroid Working Group

DF = Detection Frequency

Max = Maximum

¹(Markle et al. 2014)

Pyrethroids are characterized by an affinity for organic matter and low water solubility (log K_{ow} between 4 and 7). During the wastewater treatment process, removal is dominated by sorption to particulate organic matter and incorporation into sewage sludge. Weston et al. (2013) utilized flow-weighted 24-hour composite sampling for both influent and effluent samples from the Sacramento Regional County Sanitation District (SRCSD) treatment plant in 2010. This approach was necessary to account for the highly variable influent concentrations (Ort et al. 2010). The timing of effluent sampling helped account for the residence time within the treatment system. Removal efficiencies were typically 80% or greater.

Pilot scale studies revealed some mechanisms responsible for the removal of pyrethroids during wastewater treatment process. Parry and Young (2013) investigated the role of suspended particle size and dissolved organic matter on pyrethroid removal. They found the sorption of pyrethroids to suspended sediment was correlated with the particle surface area. Another pilot scale study investigating the fate of permethrin in wastewater treatment found a solids retention time of greater than 8 days decreases concentration in effluent and that a high mixed liquor suspended solids concentration decreases permethrin concentrations in the final effluent (Santos 2011). However, both studies confirm that even with optimized treatment parameters, pyrethroids were found in the final effluent associated with suspended and dissolved organic matter, which suggests decreasing mass loading to wastewater treatment plants may be a more effective mitigation approach for ultimately reducing effluent pyrethroid concentrations.

Indoor Sources

The characterization of mass loading of indoor sources to the wastewater collection system has not yet been reported for pyrethroids. During the 2010 sampling study of SRCRD treatment

plant, subsamples were taken from interceptors within the larger wastewater collection system. Interceptors represent sub-catchments from newer residential areas where storm and sewer collection systems are separate. Pyrethroid concentrations from these residential interceptors were comparable to concentrations from plant influent suggesting that residential area inputs other than those from irrigation and storm water runoff are important to total mass loading to the wastewater plant (Weston et al. 2013).

Registered uses for pyrethroids include a variety of indoor uses including pet treatments, indoor pest control, and clothing treatment. The presence of pyrethroids on indoor dust has been reported (Julien 2008). Cleaning activities, such as mopping, could represent a pathway for pyrethroids to enter the wastewater collection system. Washing pets treated with pyrethroids could also represent a pathway to the wastewater collection system.

Organophosphates were phased out of residential use in the early 2000s. Pyrethroid products, and increasingly fipronil, have taken their place. A 1996 survey of the Contra Costa County Sanitation District measured chlorpyrifos and diazinon loads entering the wastewater treatment facility from residential and commercial sources (including pest control operators, pet groomers, and kennels). Residential sources were responsible for a greater portion of total mass load to the wastewater treatment plant than commercial sources. Individual samples from pet grooming operation wastewater had the highest pesticide concentrations, however, the largest mass contribution was from residential sources as a result of the much higher associated flow (Singhasemanon et al. 1998). Although the 1996 study involved different products and active ingredients, this study gives some insight into use patterns of insecticide products that enter the wastewater collection system.

Discussion

Pyrethroids are frequently detected in wastewater effluent representing a source of potential toxicity to surface waters to which they discharge. Wastewater treatment operations can be optimized to maximize retention of hydrophobic pyrethroids in biosolids; however, some fraction associated with dissolved and suspended organic matter remains in the final effluent. Sampling of residential wastewater (not influenced by stormwater) suggests indoor uses represent substantial contribution to total mass loading. Source identification for organophosphate pesticides with similar uses identified residential uses as more significant than commercial or industrial sources.

References

- Amweg, E.L., Weston, D.P., You, J. and Lydy, M.J. (2006) Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. *Environmental Science & Technology* 40(5), 1700-1706.
- EPA, U. (2014) Office of Pesticide Program's Aquatic Life Benchmarks.

- Holmes, R.W., Anderson, B.S., Phillips, B.M., Hunt, J.W., Crane, D.B., Mekebri, A. and Connor, V. (2008) Statewide Investigation of the Role of Pyrethroid Pesticides in Sediment Toxicity in California's Urban Waterways. *Environmental Science & Technology* 42(18), 7003-7009.
- Jiang, W., Haver, D., Rust, M. and Gan, J. (2012) Runoff of pyrethroid insecticides from concrete surfaces following simulated and natural rainfalls. *Water Research* 46(3), 645-652.
- Julien, R.A., Levy, J.I., Bennett, D., Nishioka, M., and Spengler, J.D. (2008) Pesticide loadings of select organophosphate and pyrethroid pesticides in urban public housing. *Journal of Exposure Science and Environmental Epidemiology* 18, 167-174.
- Luo, Y., Jorgenson, B.C., Thuyet, D.Q., Young, T.M., Spurlock, F. and Goh, K.S. (2013a) Insecticide Washoff from Concrete Surfaces: Characterization and Prediction. *Environmental Science & Technology* 48(1), 234-243.
- Luo, Y.Z., Spurlock, F., Jiang, W.Y., Jorgenson, B.C., Young, T.M., Gan, J., Gill, S. and Goh, K.S. (2013b) Pesticide washoff from concrete surfaces: Literature review and a new modeling approach. *Water Research* 47(9), 3163-3172.
- Markle, J.C., van Buuren, B.H., Moran, K.D. and Barefoot, A.C. (2014) Pyrethroid pesticides in municipal wastewater: A baseline survey of publicly owned treatment works facilities in California in 2013, Pyrethroid Working Group.
- Ort, C., Lawrence, M.G., Reungoat, J. and Mueller, J.F. (2010) Sampling for PPCPs in Wastewater Systems: Comparison of Different Sampling Modes and Optimization Strategies. *Environmental Science & Technology* 44(16), 6289-6296.
- Parry, E. and Young, T.M. (2013) Distribution of Pyrethroid Insecticides in Secondary Wastewater Effluent *Environmental Toxicology and Chemistry* 32(12), 2686-2694.
- Santos, A., Reif, R., Hillis, P., Judd, S.J. (2011) Fate and removal of permethrin by conventional activated sludge treatment. *Environmental Technology* 32(11-12), 1367-1373.
- Singhasemanon, N., Nordmark, C. and Barry, T. (1998) Diazinon and Chlorpyrifos in the Central Contra Costa Sanitary District Sewer System, Summer 1996, California Department of Pesticide Regulation.
- Starner, K.a.Z., X. (2013) Analysis of Pesticide Detections in California Surface Waters, 1991-2010: Identification of detections exceeding US EPA Aquatic Life Benchmarks, California Department of Pesticide Regulation.

Teerlink, J., Hering, A.S., Higgins, C.P. and Drewes, J.E. (2012) Variability of trace organic chemical concentrations in raw wastewater at three distinct sewershed scales. *Water Research* 46(10), 3261-3271.

Trask, J.R., Harbourt, C.M., Miller, P., Cox, M., Jones, R., Hendley, P. and Lam, C. (2014) Washoff of Cypermethrin Residues from Slabs of External Building Material Surfaces Using Simulated Rainfall *Environmental Toxicology and Chemistry* 33(2), 302-307.

Weston, D.P. and Lydy, M.J. (2010) Urban and Agricultural Sources of Pyrethroid Insecticides to the Sacramento-San Joaquin Delta of California. *Environmental Science & Technology* 44(5), 1833-1840.

Weston, D.P., Ramil, H.L. and Lydy, M.J. (2013) Pyrethroid Insecticides in Municipal Wastewater. *Environmental Toxicology and Chemistry* 32(11), 2460-2468.