# Pesticide removal through wastewater and advanced treatment: full-scale sampling and bench-scale testing

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**Abstract**: Dieldrin and DDx removal through wastewater, ozone, and microfiltration was assessed for a groundwater replenishment reuse project in Monterey, California, USA. Full-scale sampling was conducted at the wastewater treatment plant, and physical wastewater treatment processes, ozonation and microfiltration were tested at the bench-scale. Removals of 84% and 93%, 44% to 63% and 36% to 48%, and 97% to 98% and 92 to 94% were observed through wastewater treatment, ozonation, and microfiltration for dieldrin and DDx, respectively, which were sufficient to meet California Ocean Plan water quality objectives after wastewater treatment alone. Levels in the secondary effluent, ahead of ozonation, microfiltration, reverse osmosis and advanced oxidation in the advanced water purification facility, met drinking water standards.

Removal of dieldrin and DDx through wastewater treatment occurred by physical treatment processes. Removal through the full-scale wastewater treatment plant, which included biological

and physical treatment processes, matched removal through bench-scale, physical wastewater treatment processes. Dieldrin and DDx removal correlated with removal of volatile suspended solids, suggesting that volatile suspended solids could be used as an indicator for pesticide removal through wastewater treatment. Dieldrin and DDx concentrations were highest in the solids contact process, where biomass is accumulated for carbon removal.

**Keywords**: advanced treatment, microfiltration, ozonation, pesticides, potable reuse, wastewater treatment

## Introduction

Effluents of wastewater treatment plants contain constituents that are of interest to human and aquatic health. Among these are two legacy pesticides, dieldrin and DDx, which are of interest for both environmental discharge and potable water consumption. The goals of this study were (1) to quantify the removal of dieldrin and DDx through Monterey Regional Water Pollution Control Agency's (MRWPCA) Regional Treatment Plant (RTP) and bench-scale wastewater treatment, ozonation, and membrane filtration, (2) to compare the effluent levels to environmental and potable benchmarks, and (3) to elucidate treatment mechanisms and monitoring surrogates.

Pending reductions in allowable Carmel River water diversions are spurring the development of new potable water supplies on the Monterey peninsula, in California, USA. The Monterey Peninsula Water Management District (MPWMD) and the Monterey Regional Water Pollution

Control Agency (MRWPCA) are developing the Pure Water Monterey (PWM) project, a groundwater replenishment reuse project, to help address the water shortage. The project includes diversion of additional waters to the Regional Treatment Plant (RTP), which produces both a secondary-treated wastewater and tertiary-treated wastewater. A portion of the secondary effluent will be diverted to the Advanced Water Purification Facility (AWPF), while the remaining secondary effluent is treated at the Salinas Valley Reclamation Plant (SVRP) for non-potable recycled water, or discharged to the Monterey Bay through the ocean outfall.

The RTP has a design capacity of 77.8 cubic meters per minute ($m^3$/min), and the AWPF design capacity is 10.5 $m^3$/min. The main components of the RTP and AWPF treatment train are the following:

- **RTP:** screening, primary clarification, trickling filters/solids contact, and secondary clarification; and,
- **AWPF**: chloramination, ozonation, microfiltration (MF), reverse osmosis (RO), an advanced oxidation process (AOP), and product water stabilization.

The additional raw water sources diverted to the RTP collection system will include agricultural wash water and industrial wastewater from the Salinas Industrial Wastewater Treatment Facility (SIWTF), agricultural tile drainage and runoff waters from the Blanco Drain and Reclamation Ditch, and stormwater from the City of Salinas. Source water monitoring was conducted from July 2013 to June 2014 to characterize the new source waters (Nellor Environmental Associates *et al.* 2016). Two legacy pesticides, dieldrin and 4,4'dichlorodiphenyldichloroethylene (DDE), were detected in the Blanco Drain.

Both dieldrin and DDx (sum of 2,4'dichlorodiphenyltrichloroethane (DDT), 4,4'DDT, 2,4'DDE, 4,4'DDE, 2,4'dichlorodiphenyldichloroethane (DDD), and 4,4'DDD) have water quality objectives in the California Ocean Plan (COP) (State Water Resources Control Board, 2015). The AWPF will produce an RO concentrate that will be discharged through the ocean outfall, along with varying quantities of secondary-treated wastewater. The concentrations of dieldrin and DDx in the secondary effluent and the RO concentrate are of concern due to the potential to exceed COP water quality objectives. Modeling of the AWPF RO concentrate and secondary effluent discharge suggests that removals of 61% to 78% and 58% to 71% for dieldrin and DDx, respectively, would be required through the RTP and/or ozone in order for discharges to comply with the COP objectives (Trussell Technologies 2015, 2016).

The removal of dieldrin and DDx through trickling filter/solids contact wastewater treatment plants has not previously been studied. Removals of 37% to 62% of dieldrin have been observed through primary clarification (Gutierrez *et al.* 1984); dieldrin, DDE, and DDT have been detected in primary sludge, mixed-liquor solids, and/or digested sludge (Dobbs *et al.* 1989; Clarke and Porter 2010; Clarke *et al.* 2010); removals of 30 to 64% for dieldrin and 3 to 65% for DDE were observed through a pilot-scale activated sludge plant (Buisson et al. 1988); removals of 77% and 83% for dieldrin and 4,4'DDT, 4,4'DDE, and 4,4'DDD were observed through a full-scale conventional activated sludge wastewater treatment plant (Katsoyiannis and Samara 2004); and removals of 75% to 81% of dieldrin were observed through wastewater treatment plants with nitrified activated sludge, 2-stage high purity oxygen and chemically enhanced primary treatment, 5-stage Bardenpho, a nitrifying oxidation ditch, and nitrifying sequencing batch reactors (USEPA 2009).

Ozonation studies in drinking water have shown removals of dieldrin and DDx from 10% to 90% and 5% to 79%, respectively (Ormad *et al.* 2008; Ormad *et al.* 2010; Westerhoff *et al.* 2005; Synder *et al.* 2006; Synder *et al.* 2007a); however, the removal of dieldrin and DDx through ozonation in secondary effluents have not been characterized. Removals of more than 85% for DDT have been observed through membrane filtration in a secondary effluent spiked with DDT (Synder *et al.* 2007b), but studies quantifying the removal on ambient dieldrin and DDx in secondary effluents have not previously been conducted.

Low levels of dieldrin and DDx biodegradation during wastewater treatment has been reported (Saleh *et al*. 1980; and Katsoyiannis and Samara 2005) and negligible removal through biodegradation is expected compared to removal through adsorption and physical separation (Meakins *et al.* 1994; Byrns 2001; Katsoyiannis *et al*. 2006; Buttiglieri and Knepper 2008; and Margot *et al*. 2015); however, few studies have investigated the mechanism of removal through wastewater treatment plants.

This study reports on (1) removal of ambient dieldrin and DDx through a full-scale trickling filter/solids contact wastewater treatment process, (2) removal through physical wastewater treatment processes on the bench-scale, which elucidates the relative importance of biodegradation and adsorption and physical separation in the removal of dieldrin and DDx through wastewater treatment, and (3) removal of dieldrin and DDx through bench-scale ozonation and membrane filtration. Removal though wastewater treatment and membrane filtration and are compared to removal of other constituents, in order to identify surrogates that can be monitored in place of monitoring pesticides.

## Methods

Testing included the following major components: (1) RTP sampling, (2) RTP bench testing, and (3) AWPF bench testing. Bench testing was conducted on the following blends of grab samples from the RTP and the Blanco Drain, in order to simulate treatment with the new source water through the RTP: (1) primary influent mixture: primary influent sample and Blanco Drain sample, (2) solids contact effluent mixture: solids contact effluent sample and filtered Blanco Drain sample, and (3) secondary effluent (AWPF influent) mixture: secondary effluent sample and filtered Blanco Drain sample.

The filtered Blanco Drain sample was produced by serially filtering the Blanco Drain sample through a 100-micrometer (µm) hydrophilic nylon net filter (Millipore), a 45-µm hydrophobic polypropylene filter (Steriltech), and a 10-µm hydrophobic polypropylene filter (Steriltech), to simulate RTP treatment. The mixtures contained 12% Blanco Drain water, which was the maximum contribution projected for the RTP source water blends.

Samples from the RTP and the Blanco Drain were collected on February 9, 2016. Samples were collected with a pump and tubing, which were flushed prior to filling sample vials. The suction end of the tubing was submerged in the process. All samples were stored in 1-L amber glass vials. Samples were chilled to 6°C on ice and shipped overnight to the laboratories where the dieldrin and DDx analytical analyses and bench-scale testing were performed, or retained for volatile suspended solids (VSS) analysis at the RTP laboratory. The sampling locations are shown in Figure 1.

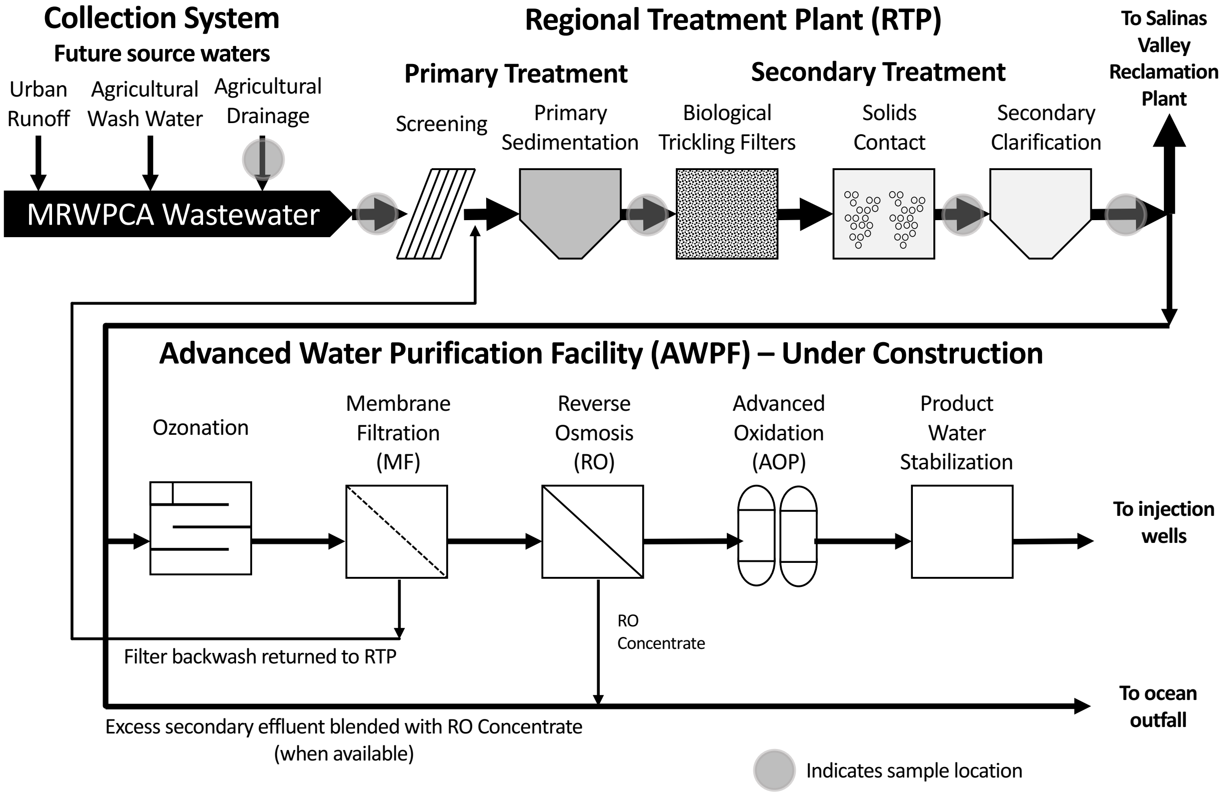

**Figure 1: Process flow schematic of Regional Treatment Plant, the Advanced Water Purification Facility, and the future source waters, with sampling locations indicated**

Bench-scale filtration was used to mimic the physical aspects of primary, secondary, and membrane filtration treatment. For primary and secondary treatment, the samples were serially filtered through the 100-µm filter, the 45-µm filter, and the 10-µm filter. To mimic membrane filtration, either a 0.7-µm glass fiber filter or the 10-µm filter was used to pre-filter the samples, followed by a 0.45-µm hydrophilic nitrocellulose membrane as another pre-filter, and then by a 0.1-µm hydrophilic polyethersulfone membrane filter.

Bench-scale ozone testing was conducted at the Trussell Technologies, Inc. laboratory using the solution ozone test (SOT), based on procedures developed by Rakness (2005). The stock ozone solution concentration was measured using Standard Methods 4500-$O_3$ B Indigo Colorimetric Method (Standard Methods for the Examination of Water and Wastewater 2012). Indigo solution was prepared the day of testing and the ultraviolet absorbance (UVA) at 600 nm was checked to ensure indigo quality.

Dieldrin and DDx were analyzed by Environmental Protection Agency (USEPA) method 1699 (USEPA 2007), with dieldrin and DDx congener minimum quantification limits of 30 picogram per litre (pg/L) when no interferences are present, and method detection limits (MDLs) ranging from 1 to 5 pg/L. Dieldrin and DDx analysis was conducted by Vista Analytical Laboratories. VSS was measured using Standard Method 2540 E: Fixed and Volatile Solids Ignited at 550°C (Standard Methods for the Examination of Water and Wastewater 2012).

## Results and Discussion

**Regional Treatment Plant Removals:** Dieldrin and DDx were measured in all samples collected from the RTP, allowing for determination of ambient dieldrin and DDx removal (Figure 2). Removals of 84% and 93% were observed for dieldrin and DDx, respectively, which are greater than the required removals for COP compliance.

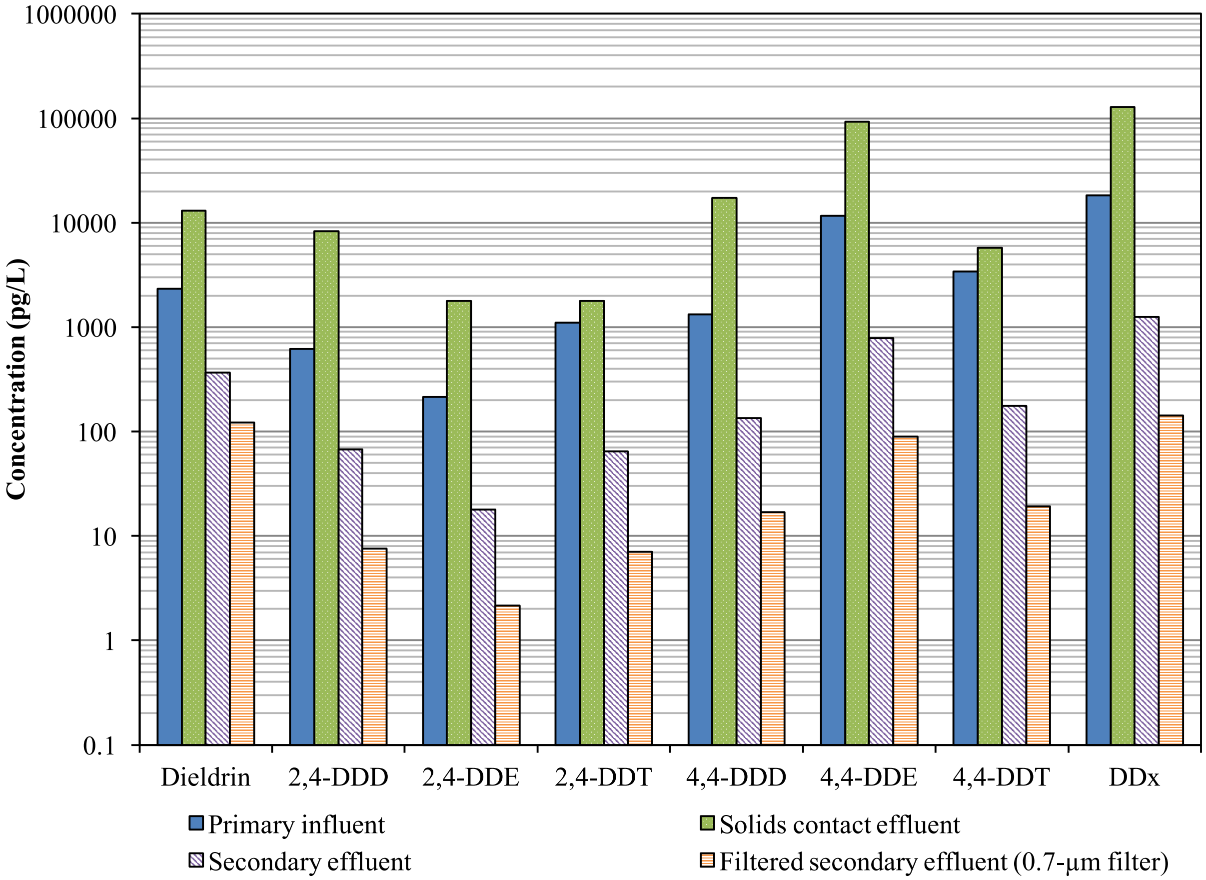

**Figure 2: Regional Treatment Plant dieldrin and DDx sampling results**

**Relationship between Regional Treatment Plant Removals and Volatile Suspended Solids:** Dieldrin and DDx concentrations were correlated with VSS concentrations through the RTP (Figure 3), which suggests that VSS may be used as a surrogate for dieldrin and DDx removal. DDx and dieldrin have a strong affinity to sorb to organics due to their nonpolar structure, minimal hydrogen bonding, and relatively high molecular weight, with log octanol-water partition coefficients of 5.4 to 6.9 (SRC 2017). VSS is comprised of organic matter, such as biological matter in the trickling filter/solids contact, and the correlation suggests that dieldrin and DDx sorb to VSS.

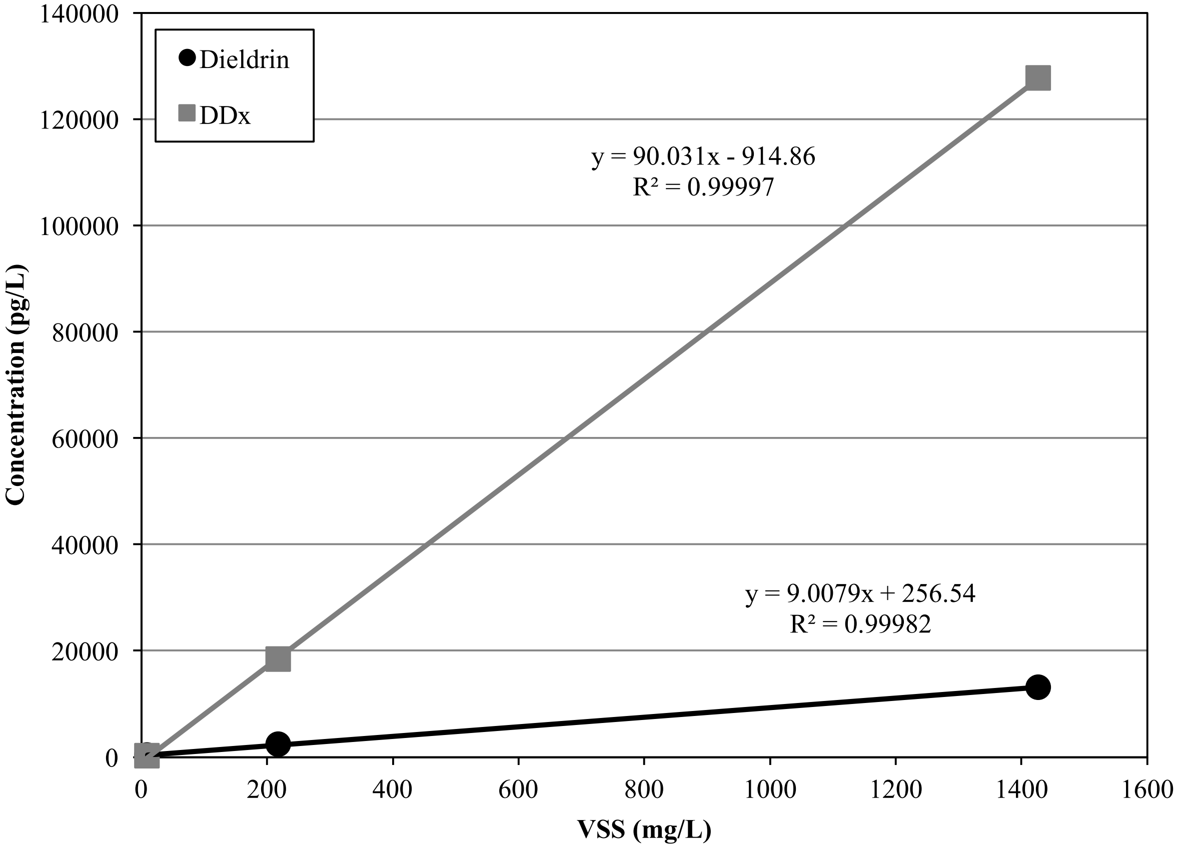

**Figure 3: Relationship between volatile suspended solids and dieldrin and DDx in the Regional Treatment Plant**

Dieldrin and DDx concentrations are higher in the solids contact process where a reserve of biological mass is grown and stored to meet carbon removal and solids retention time (SRT) targets. Subsequent clarification and wasting of waste activated sludge (WAS) removes biological mass, including dieldrin and DDx sorbed to the organic mass. Given the apparent relationship between dieldrin and DDx and VSS, the removal of dieldrin and DDx through wastewater treatment appears to be dependent on secondary clarification removal efficiency.

**Wastewater Treatment Bench-scale Testing:** The removal of dieldrin and DDx through bench-scale testing of RTP processes is shown in Figure 4. The bench-scale removals matched those observed through the RTP, suggesting that biodegradation in the wastewater treatment plant was negligible and that the removal occurs through physical wastewater treatment processes. Concentrations in the primary influent mixture were already lower than the World Health Organization (WHO) dieldrin and DDx drinking water guidelines of 30,000 and 1,000,000 pg/L, respectively. After treatment through the RTP, secondary effluent dieldrin concentrations were below the California State Water Resources Control Board Division of Drinking Water (DDW) Archived Advisory Level for drinking water (AAL) of 2,000 pg/L.

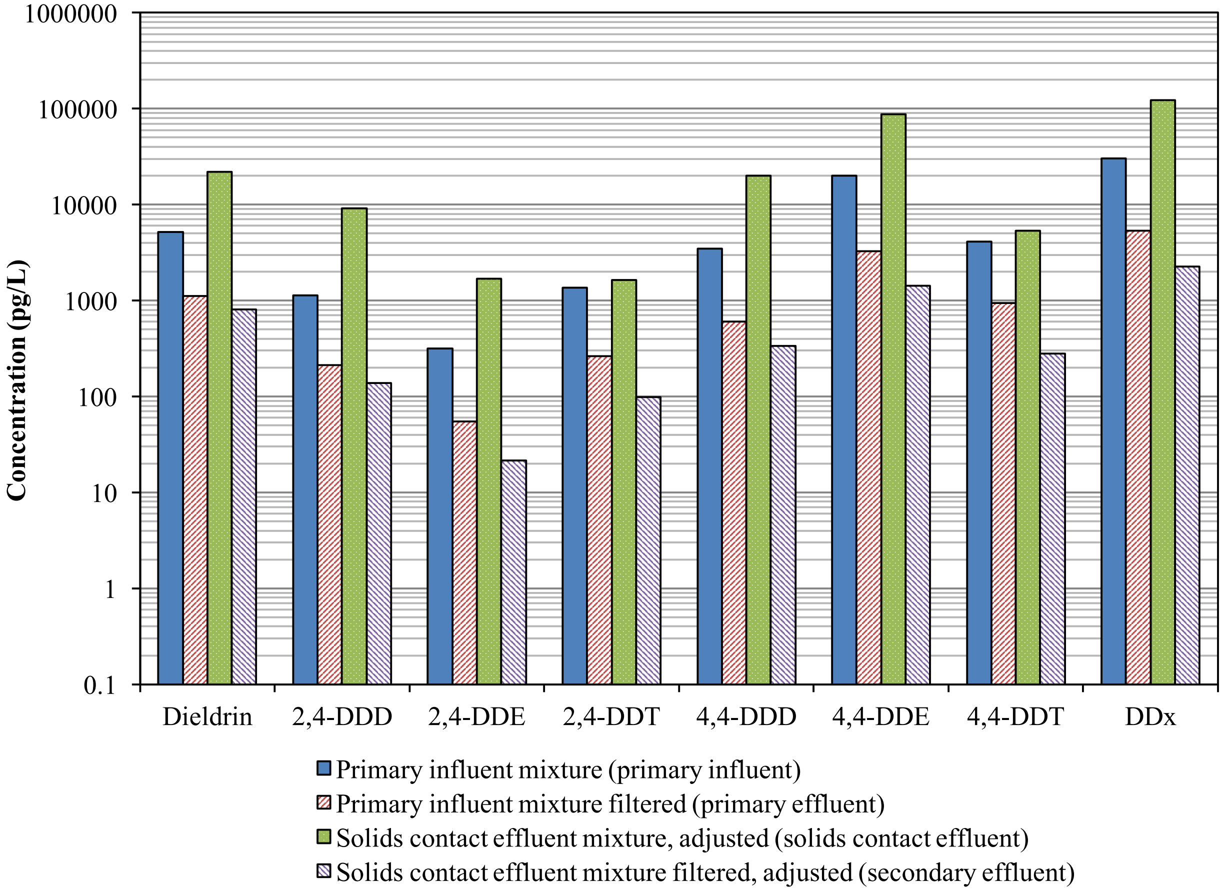

**Figure 4: Removal of dieldrin and DDx through wastewater bench-scale testing**

In order to account for the effect of accumulating dieldrin and DDx from the Blanco Drain through the solids contact process, the measured concentrations of the Blanco Drain were adjusted by the degree of dieldrin and DDx accumulation that was observed during RTP sampling. Removals observed through filtration of the solids contact effluent mixture were applied to the adjusted solids contact effluent mixture to develop the estimate of the secondary effluent concentrations.

**Solution Ozone Testing**: Removal of 44% to 63% and 36% to 48% were observed through bench-scale ozonation for dieldrin and DDx, respectively, with higher levels of removal observed with higher ozone doses. The impact of ozone to total organic carbon (TOC) ratios ($O_3$:TOC) on dieldrin and DDx removal is shown in Figure 5. The relationship between removal and $O_3$:TOC ratio was linear under the ranges tested; however, it appears that there may have been an initial rapid removal of dieldrin and DDx at lower ozone doses, prior to the linear range, as the lines fit to the data do not intersect the origin.

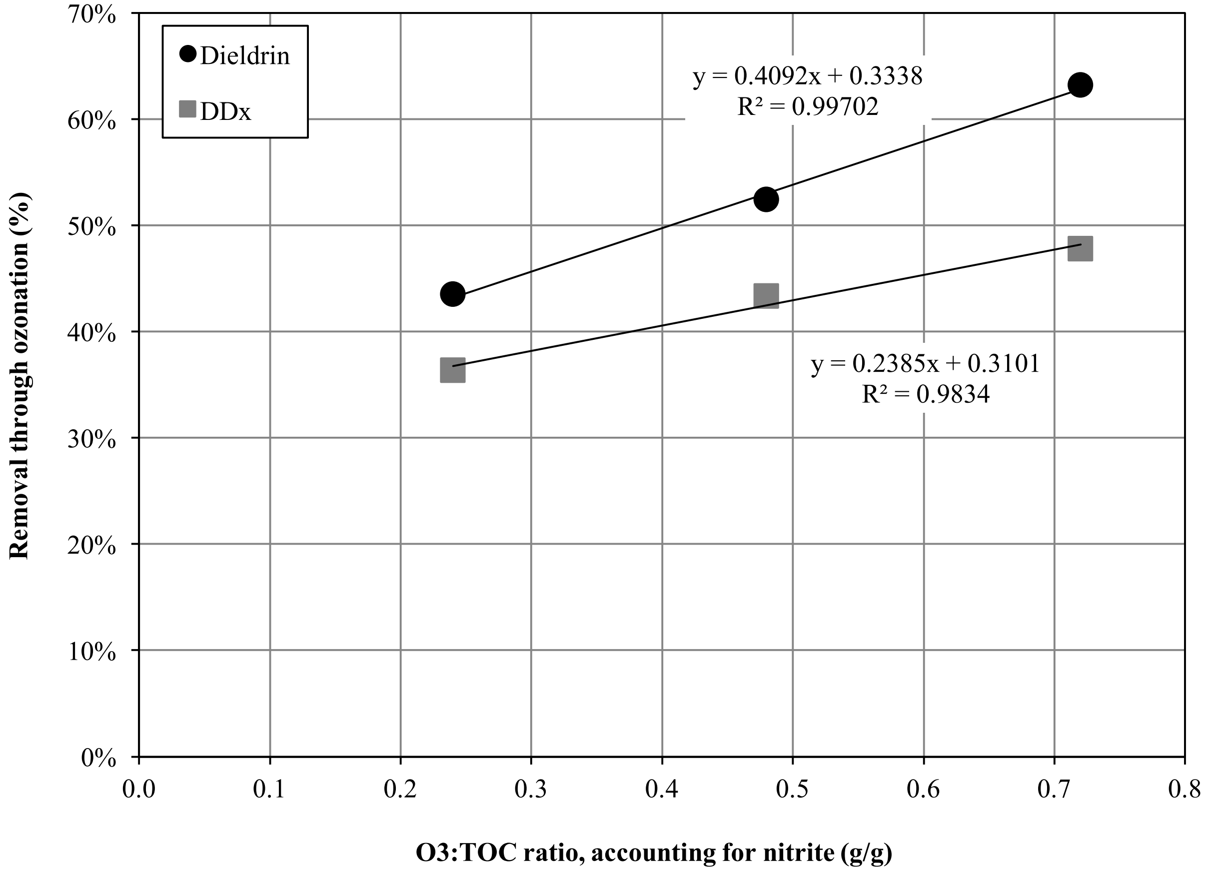

**Figure 5: Impact of ozone to total organic carbon ratio on dieldrin and DDx removal in Blanco Drain-Regional Treatment Plant effluent mixture**

**Microfiltration Bench-scale Testing:** The results from membrane filtration of select ozonated mixtures are shown in Figure 6. Removals of 97% to 98% and 92% to 94% were observed for dieldrin and DDx, respectively.

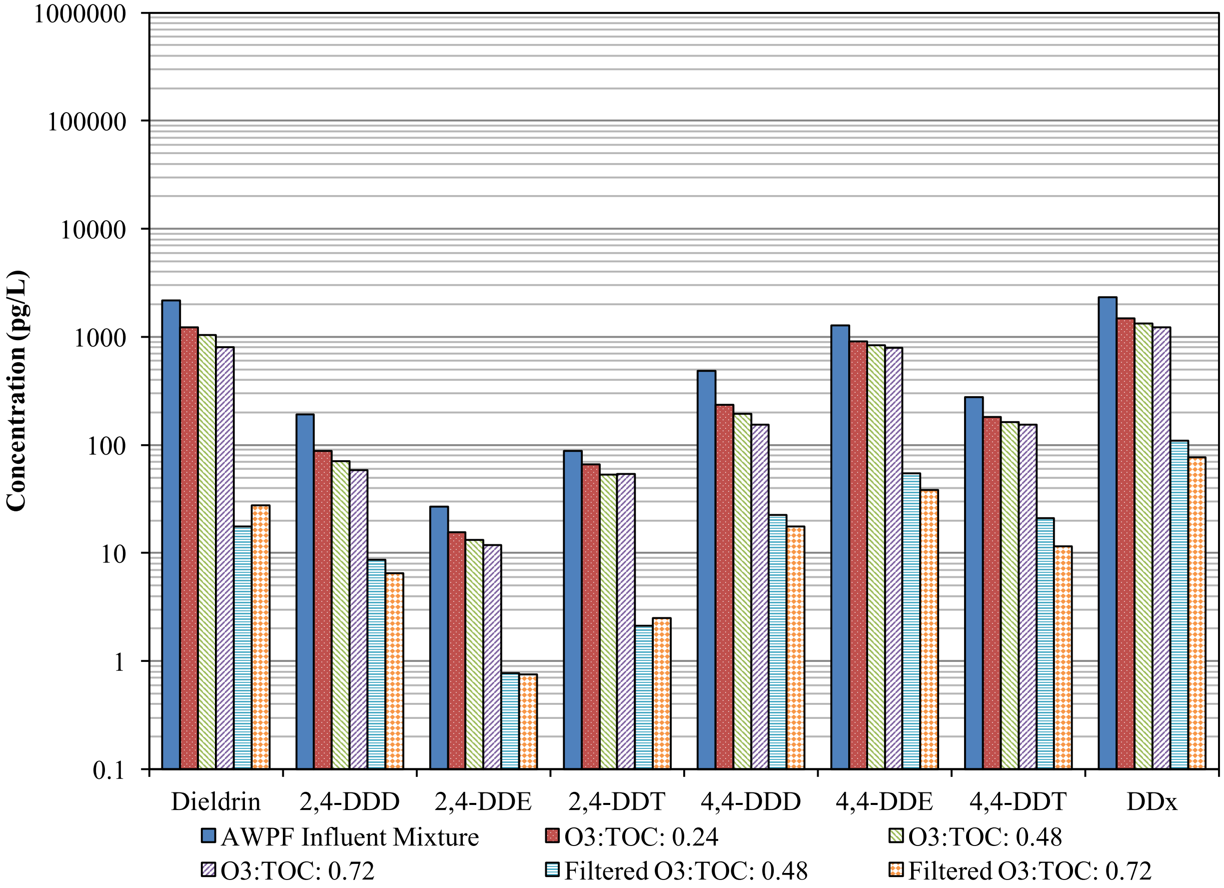

**Figure 6: Dieldrin and DDx removal through membrane filtration of Blanco Drain-Regional Treatment Plant effluent mixture**

Dieldrin and DDx sorbed to organics and particulates that are captured on the MF membrane will be returned to the RTP headworks during regular backwashes, chemical washes, and clean-in-places (CIP) events. This recycling of waste backwash water slightly increases the concentrations of dieldrin and DDx in the RTP influent and may marginally increase concentrations in RTP effluent; however, the overall removal of dieldrin and DDx is projected to increase, as recycling increases the amount of dieldrin and DDx removed through the RTP and the ozone system.

The removal of dieldrin through various size filters for different water qualities is shown in Figure 7. The data exhibit a log-linear relationship between filter size and removal for waters relatively low in solids and/or for filter sizes of 0.7 µm or less.

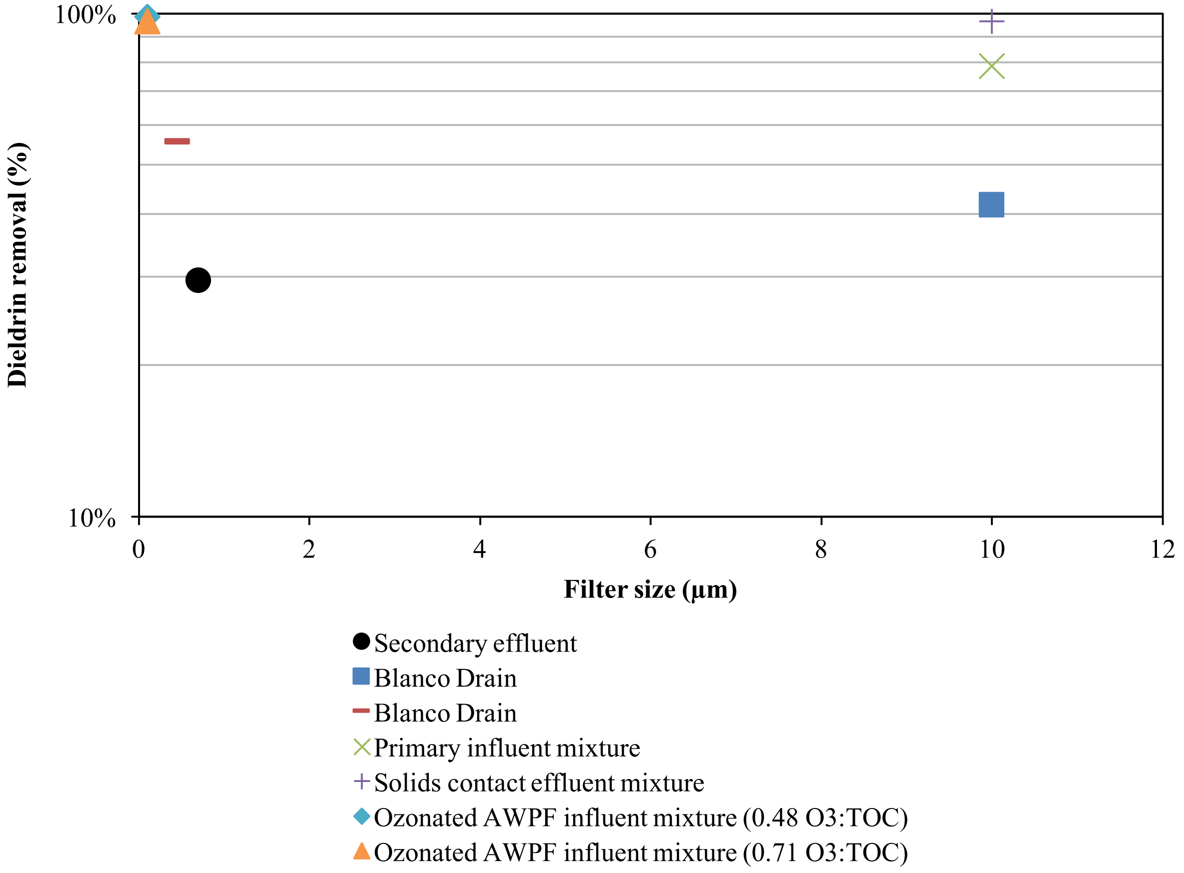

**Figure 7: Dieldrin removal through filtration as function of filter size and water quality**

The data in Figure 7 also suggest that removal was dependent on another variable besides filter size for samples with relatively high concentrations of solids when filtering through the 10-µm filter. Figure 8 shows that more removal was observed for samples with higher solids concentrations.

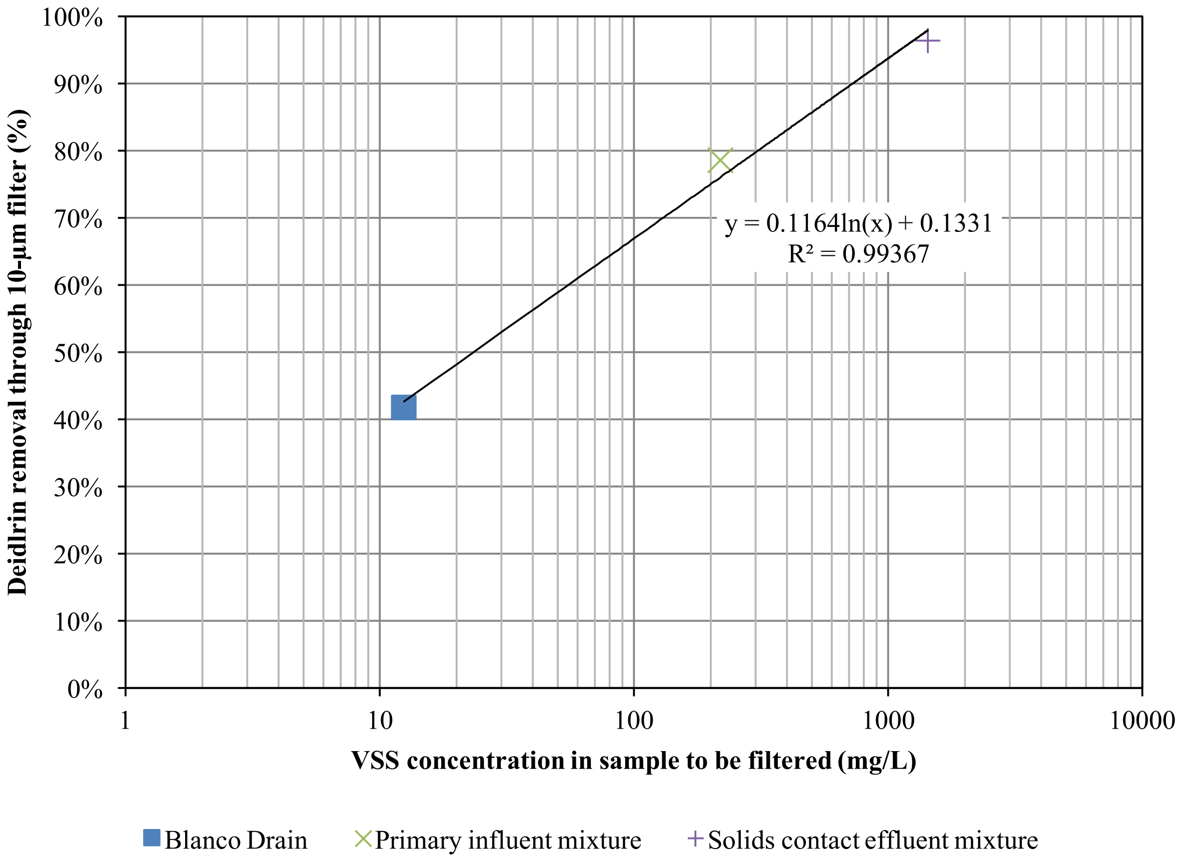

**Figure 8: 10-µm filter removal of dieldrin as a function of volatile suspended solids**

## Conclusions

A summary of removals observed through full-scale sampling of the RTP and bench-scale testing is shown in Table 1.

**Table 1: Summary of dieldrin and DDx removals observed through full-scale sampling and bench-scale testing**

| Process | Test | Removal (%) | |
|---|---|---|---|
| | | Dieldrin | DDx |
| RTP | Full-scale sampling | 84% | 93% |
| RTP | Bench-scale (RTP-Blanco blend) | 84% | 93% |
| Ozone | Bench-scale (RTP-Blanco blend) | 44% - 63% | 36% - 48% |
| Membrane filtration | Bench-scale (RTP-Blanco blend) | 97% - 98% | 92% - 94% |

The following conclusions can be drawn from the sampling and bench-scale testing:

- Significant dieldrin and DDx removal occurred through the RTP, ozonation, and filtration, and removals were similar to those reported in previous studies;
- Removal through the RTP alone was sufficient to meet COP objectives, while removal through ozonation and MF offer additional layers of redundancy and robustness for COP compliance;
- Primary influent dieldrin and DDx concentrations were already below WHO drinking water guidelines, and treatment through the RTP reduced secondary effluent dieldrin concentrations to below DDW's archived advisory level for drinking water, while removal through ozonation, microfiltration, reverse osmosis, advanced oxidation, and aquifer treatment will provide additional layers of protection for the PWM product water;
- Bench-scale wastewater treatment dieldrin and DDx removals matched removals observed during full-scale sampling of the RTP, indicating negligible biodegradation of dieldrin and DDx through wastewater treatment with removal occurring through physical wastewater treatment processes;

- Dieldrin and DDx concentrations through the RTP correlated with volatile suspended solids concentrations, suggesting that volatile suspended solids could be used as an indicator of dieldrin and DDx removal; and
- Dieldrin and DDx removal related to filter size for filters 0.7 µm or less, whereas dieldrin and DDx removal through 10-µm filters correlated with unfiltered volatile suspended solids concentrations.

## References

Buisson, R.S.K., Kirk, P.W.W., and Lester, J.N. 1988. The Behavior of Selected Chlorinated Organic Micropollutants in the Activated Sludge Process: A Pilot Plant Study. *Water, Air, and Soil Pollution*, **37**(3-4), 419-432. DOI: 10.1007/bf00192951.

Buttiglieri, G. and Knepper, T.P. 2008. Removal of Emerging Contaminants in Wastewater Treatment: Conventional Activated Sludge Treatment. In: Handbook of Environmental Chemistry, Barceló, D. and Kostianoy, A.G. (ed.), Springer International Publishing AG, Switzerland.

Byrns, G. 2001. The Fate of Xenobiotic Organic Compounds in Wastewater Treatment Plants. *Water Research*, **35**(10), 2523-2533. DOI: 10.1016/S0043-1354(00)00529-7.

Clarke, B.O. and Porter, N.A. 2010. Persistent Organic Pollutants in Sewage Sludge: Levels, Sources, and Trends. In: Contaminants of Emerging Concern in the Environment: Ecological and

Human Health Considerations. Halden, R. (ed.) ACS Symposium Series; American Chemical Society: Washington, DC, 2010.

Clarke, B.O., Porter, N.A., Marriott, P.J., Blackbeard, J.R. 2010. Investigating the levels and trends of organochlorine pesticides and 2 polychlorinated biphenyl in sewage sludge. *Environment International,* **36**(4), 323-329.

Dobbs, R.A., Wang, L., Govind, R.1989. Sorption of Toxic Organic Compounds on Wastewater Solids: Correlation with Fundamental Properties. *Environmental Science & Technology*, **23**(9), 1092-1097. DOI: 10.1021/es00067a004.

Gutierrez, A.G., McIntyre, A.E., Perry, R., Lester, J.N. 1984. Behavior of Persistent Organochlorine Micropollutants during Primary Sedimentation of Waste Water. *Science of the Total Environment*, **39**(1-2), 27-47. DOI: 10.1016/0048-9697(84)90022-6.

Katsoyiannis, A. and Samara, C. 2004. Persistent organic pollutants (POPs) in the sewage treatment plant of Thessaloniki, northern Greece: occurrence and removal. *Water Research*, **38**(11), 2685-2698. DOI: 10.1016/j.watres.2004.03.027.

Katsoyiannis, A. Samara, C. 2005. Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: fate and mass balance. *Environmental Research*, **97**(3), 245-257. DOI: 10.1016/j.envres.2004.09.001.

Katsoyiannis, A., Zouboulis, A., and Samara, C. 2006. Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: Model predictions against experimental values. *Chemosphere*, **65**(9), 1634-1641. DOI: 10.101s6/j.chemosphere.2006.02.030.

Margot, J., Rossi, L., Barry, D.A., and Holliger, C. 2015. A review of the fate of micropollutants in wastewater treatment plants. *WIREs Water*, **2**:57–487. DOI: 10.1002/wat2.1090.

Meakins, N.C., Bubb, J.M., and Lester, J.N. 1994. The behavior of the s-triazine herbicides, atrazine, and simazine, during primary and secondary biological wastewater treatment. *Chemosphere*, **28**(9), 1611-1622. DOI: 10.1016/0045-6535(94)90420-0.

Nellor Environmental Associates, Trussell Technologies, and Todd Groundwater 2016. Final Engineering Report: Volume I: Engineering Report prepared for the Pure Water Monterey Groundwater Replenishment Project. September 2016.

Ormad, M.P., Miguel, N., Claver, A., Matesanz, J.M., Ovelleiro, J.L. 2008. Pesticides removal in the process of drinking water production. *Chemosphere*, **71**(1), 97-106. DOI: 10.1016/j.chemosphere.2007.10.006.

Ormad, M.P., Miguel, N., Lanao, M., Mosteo, R., Ovelleiro, J.L. 2010. Effect of Application of Ozone and Ozone Combined with Hydrogen Peroxide and Titanium Dioxide in the Removal of Pesticides from Water. *Ozone: Science & Engineering*, **32**(1), 25-32. DOI: 10.1080/01919510903482764.

Rakness, K. L. (2005). Ozone in Drinking Water Treatment: Process Design, Operation and Optimization. Denver, CO, American Water Works Association.

Salah, F.Y., Lee, G.F., and Wolf, H.W. 1980. Selected Organic Pesticides, Occurrence, Transformation, and Removal from Domestic Wastewater. *Journal Water Pollution Control Federation*, **52**(1), 19-28.

*Standard Methods for the Examination of Water and Wastewater* 2012 22nd edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

State Water Resources Control Board, California Environmental Protection Agency (SWRCB), 2015. *California Ocean Plan: Water Quality Control Plan, Ocean Waters of California*.

SRC 2017. PhysProp Database. Syracuse Research Corporation. Arlington, VA. http://esc.syrres.com/fatepointer/search.asp (accessed 17 June 2017).

Synder, S.A, Wert, E.C., Rexing, D.J., Zegers, R.E., Drury, D.D. 2006. Ozone Oxidation of Endocrine Disruptors and Pharmaceuticals in Surface Water and Wastewater. *Ozone: Science & Engineering*, **28**(6), 445-460. DOI: 10.1080/01919510601039726.

Synder, S.A., Wert, E.C., Lei, H., Westerhoff, P., Yoon, Y. 2007a. Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes. Denver, CO. AWWA Research Foundation/American Water Works Association/IWA Publishing. 2007.

Synder, S.A, Adham, S., Redding, A.M., Cannon, F.S., DeCarolis, J., Oppenheimer, J., Wert, E.C., Yoon, Y. 2007b. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination*, **202**(1-3), 156-181. DOI: 10.1016/j.desal.2005.12.052.

Trussell Technologies, 2015. *Ocean Plan Compliance Assessment for the Pure Water Monterey Groundwater Replenishment Project* in the Draft Environmental Impact Report prepared for the Pure Water Monterey Groundwater Replenishment Project by Denise Duffy & Associates on April 2015. Technical Memorandum. February 2015.

Trussell Technologies, 2016. *Dieldrin and DDx Removal Testing for the Pure Water Monterey Groundwater Replenishment Project* in the Final Engineering Report: Volume II: Appendices for Engineering Report prepared for the Pure Water Monterey Groundwater Replenishment Project by Nellor Environmental, Trussell Technologies and Todd Groundwater on September 2016, Appendix K. Technical Memorandum. January 2016.

USEPA. 2007. Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. EPA-821-R-08-001. Washington, D.C. United States Environmental Protection Agency.

USEPA. 2009. Occurrence of Contaminants of Emerging Concern in Wastewater from Nine Publicly Owned Treatment Works. EPA-821-R-09-009. Washington, D.C. United States Environmental Protection Agency.

Westerhoff, P., Yoon, Y., Synder, S., Wert, E. 2005. Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes. *Environmental Science & Technology*, **39**(17), 6649-6663. DOI: 10.1021/es0484799.