The Pharmaceutical use of Permethrin: Sources and Behavior during Municipal Sewage Treatment

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Abstract

Permethrin entered use in the 1970's as an insecticide with a wide range of applications, including agriculture, horticultural and forestry, which have since been restricted. In the twenty first century, the presence of permethrin in the aquatic environment has been attributed to its use as a human and veterinary pharmaceutical, in particular as a pedeculicide, in addition to other uses such as a moth proofing agent. However, as a consequence of its toxicity to fish, sources of permethrin and its fate and behavior during wastewater treatment is a topic of concern. This study has established that high overall removal of permethrin (*c.* 90%) was achieved during wastewater treatment and that this was strongly dependent upon the extent of biological degradation in secondary treatment, with more limited subsequent removal in tertiary treatment processes. Sources of permethrin in the catchment matched well with measured values in crude sewage and indicated that domestic use accounted for over half of the load to the treatment works. However, removal may not be consistent enough to achieve the environmental quality standards now being derived in many countries even where tertiary treatment processes are applied.

Keywords: Wastewater; Permethrin; Adsorption; Sources; Biodegradation; Solids Retention Time

Introduction

A plethora of anthropogenic organic micropollutants have been discharged to sewer for many years (Bedding et al. 1982) from both industrial and domestic sources (Meakins et al. 1994) and surface run-off where combined sewers exist (Bedding et al. 1983, Stangroom et al. 1998). Some of these organic micropollutants are a cause for concern because of their potential detrimental impacts on human health should they enter the food chain or water supply, but such occurrences are very rare and regulation safeguards human health (Fawell et al. 2001). However, many of these compounds can have environmental impacts, some are acutely toxic, whilst others act by more complex mechanisms such as endocrine disruption (Lai et al. 2002a, 2002b, Jones et al. 2003, 2005). Many of these chemicals are insecticides, herbicides, solvents, pharmaceuticals or plasticisers although numerous other generic chemical groups contribute compounds of potential concern (Stangroom et al. 1998). For some of these compounds their environmental impacts are well established and they are included on various lists (EC 2008; OSPAR, 1998; USEPA, 1997). These are categorized as including pharmaceuticals (Jones et al. 2007) and endocrine disrupting chemicals (EDCs) (Lai et al. 2002c, Jones, et al. 2004). Some of these compounds have only recently been developed or found application. However, many emerging contaminants are compounds which have been in use for many years, but recent developments in environmental analysis eliminating problems associated with co-extractives and low detection limits (Buisson et al. 1984, Robertson et al. 1994) have been overcome allowing their environmental fate and behavior to be elucidated, identifying issues which have given rise to concerns (Ternes et al. 2004). The insecticide permethrin, [3-(phenoxy)phenyl] methyl 3-(2,2-dichloro-ethenyl)-2,2-dimethylcyclopropane-1-carboxylate, is one such example developed in 1973, it is a synthetic analogue of the natural permethrins (Baser et al. 2003). The *cis* and *trans* isomers of permethrin have insecticidal properties, the *cis* being the most active, thus the toxicity of a permethrin formulation depends on the ratio of these two isomers (Cox 1998). It is a broad spectrum insecticidal agent which exhibits very low mammalian and avian toxicity (Berger-Prieb 1997, Soderlund et al. 2002), however, it is highly toxic to fish (Bonwick 1995, Baser et al. 2003). In addition, it has been shown to be carcinogenic and it may also bind to the receptors for the male sex hormone (Cox 1998), although this maybe a result of metabolites rather than the parent compound (Tyler *et al.* 2000). As a result of the risk posed to fish, permethrin has been designated a specific pollutant under Annex VIII of the Water Framework Directive and in England and Wales an environmental quality standard (EQS) of 0.01 µg/L applies. Although the predicted no-effect concentration (PNEC) is less than this in freshwaters (0.0015 µg/L), the limitations of analytical methods to monitor at such low concentrations make it impossible to implement a lower EQS (EA 2007). Concerns about the impact of permethrin on the aquatic environment have resulted in it being designated a “Restricted Use Pesticide” in the United States of America (USEPA 2009).

Permethrin has a range of non-agricultural uses, being extensively employed for mothproofing in the textile and carpet manufacturing industries, as a wood preservative and as a veterinary and human pedeculicide (Kupper et al. 2006). It is specifically used for the control of fleas in cats and dogs and head lice and scabies in children (Bonwick et al. 1995, Cox 1998). As an active ingredient in head lice treatments, it is likely to find extensive use, as in the UK, 3 million people each year require treatment for this condition (NHS 1999). Permethrin is also one of the two most commonly used active ingredients for the treatment of scabies, approximately 1 in 1,000 people develop scabies each month in the UK (NHS 2008). Permethrin is used in pet-care products for the control of fleas, in the UK there are some 7 million dogs which will require some form of flea treatment annually (Westgarth et al. 2007). These products, both human and veterinary, are available without prescription (Cox 1988, Westgarth 2006), whilst some non-permethrin based products require prescriptions or are only available from a veterinary surgery. Over the counter availability is very likely to encourage the use of permethrin based products as opposed to alternatives. The use of permethrin as a moth proofing agent is also potentially a significant source of this compound to the aquatic environment particularly from textile factory effluents (Woodhead 1983). Permethrin is mainly used in the production of wool based carpets, some 40 million kg of wool, or wool based carpet yarn, is produced annually in the UK (Shaw 1994) which may contain 58 mg/kg of permethrin (SGS 2006), with the potential for loss to the environment through wear and cleaning. Consequently the major pathway to the environment is via discharge to sewer from industrial and domestic sources (Llewellyn et al. 1996, Esteve-Turrillas et al. 2004).

Thus the uses of permethrin will influence the load received at sewage treatment works (STW), where the subsequent fate and behavior during wastewater treatment are critical in determining the discharge of permethrin to the aquatic environment. There is a paucity of information on the fate and behavior of permethrin during municipal wastewater treatment although analyses of sewage sludge has demonstrated the presence of permethrin in urban wastewater systems (Rogers et al. 1989, Plagellate et al. 2004) and sewages (Woodhead 1983). This study was undertaken to establish the sources, fate and behavior of permethrin at a full scale STW, comprising primary sedimentation, secondary biological treatment (trickling filters) and tertiary treatment with biologically aerated flooded filters (BAFF's) and rapid gravity filters (RGFs). Particular attention has been focused on the roles of absorption and biodegradation in determining overall removal.

Materials and Methods

The STW received an average flow of 59 ML per day with an equal split (depending on specific flow conditions) between two influent streams, from high level and low level sewers. The sewage entering from the high level inlet comprised mainly municipal wastewater with a hospital discharge comprising <1% of the flow. Sewage from the lower level inlet again comprised mainly municipal wastewater with trade effluent varying from 5-10% depending on flow conditions. Both 'low level' and 'high level' crude sewage underwent separate primary settlement processes. In addition the 'low level' crude sewage underwent high-rate biological treatment in 'biotowers'. This biotower effluent was subsequently combined with the 'high level' settled sewage to provide the influent to the trickling filters (TF) where it underwent secondary biological treatment. Subsequent tertiary treatment processes included biological aerated flooded filters (BAFFs) and rapid gravity filtration (RGF) prior to final discharge. The backwash from the BAFFs and RGF returned to the head of the works at the 'high level' sewer whilst the sludge liquor returns from the humus tanks, sludge consolidation tanks and centrifuge returned to the head of the works at the 'low level' sewer.

Sewage treatment works and catchment sampling protocol

Sampling occurred during July 2007, and the strategy at the STWs involved taking sewages and effluent samples at four hourly intervals for a period of 96 hours at locations (Table 1) throughout the treatment process resulting in 250 samples from the main wastewater flow stream. The humus sludge and return liquor were sampled once every 24 hours for 96 hours (see Figure 4 in results section). There were eight return / sludge streams, each sampled five times, resulting in 40 samples. Sampling of trade inputs was of one specific industrial activity involving pesticide formulations, where discharges were sampled five times per week (once per day, Monday to Friday) for 10 weeks.

Table 1. A summary of concentrations, flow and the flux of permethrin through the unit processes at the sewage treatment works.

Sample	Conc.[1]. µg/L	Flow ML/day	Flux g/day	Observations
HL crude[a]	0.331	24.3	8.0	
HL crude+rtn	0.356	28.6	10.2	
HL settled	0.269	28.5	7.7	25% removed in HL settling tanks
LL crude+rtn[b]	0.208	28.9	6.5	
LL settled	0.197	31.6	6.1	6% removed in LL settling tanks
BT settled[c]	0.137	31.0	4.2	31% removed in Biotowers
Filter feed	0.282	59.3	16.7	sum of flux through HLSS and BTSS (71%)
BAFF feed[d]	0.031	57.5	1.8	89% removed in trickling filters
RGF feed[e]	0.026	56.7	1.5	17% removed in BAFF
Final effluent	0.016	53.2	0.9	40% removed by RGF 93 % removal overall (load 13.5 g/day)

[1] The average of 25 samples taken. In the final effluent, concentrations ranged from <0.005 –to 0.036 µg/L. Where values were <0.005 half the LOD was used for calculation of the average.

[a] HL, high level; [b] LL, low level; [c] BT, biotower; [d] BAFF, biological aerated flooded filters; [e] RGF, rapid gravity filter

Analytical methods

The approach used was developed independently, however, it was similar to that reported in January 2007 by Gómez et al. (2007), in that it used SPE extraction for the aqueous phase, and solvent extraction for solids. Permethrin was determined by extraction of 500 ml of sample onto C18 solid phase extraction (SPE) cartridges (Chromabond C18-1000mg, Thames Restek, UK) after filtration with GF/C (1.2 µm) papers (Whatman, UK). On-site, cartridges were conditioned with 5ml of methanol, followed by 5 ml of laboratory grade water (MilliQ, Millipore, UK). Filtered wastewater samples were loaded onto the cartridges using a vacuum manifold at a flow rate of approximately 10 ml/min, and then dried by allowing the vacuum pump to draw air through them. In the laboratory dried SPE cartridges were eluted with 20 ml of diethyl ether which was subsequently evaporated to dryness under a stream of nitrogen gas. The dried extract was reconstituted in 0.5 ml of hexane and transferred to a vial for quantification by gas chromatography with mass spectrometry (GC/MS). The permethrin on the filter papers was extracted by shaking for 40 minutes in 50 ml high density polypropylene tubes with 20 ml of diethyl ether following addition of 5 g of anhydrous sodium sulphate. The ether was decanted into a round bottom flask, and the sample then re-extracted for a further 30 minutes with 10 ml of diethyl ether, which was then combined with the first extract. The combined solvent extracts were then dried under a stream of nitrogen and reconstituted with 0.5 ml of hexane for analysis by GC/MS.

Samples of co-settled and consolidated sludge were frozen on site and then extracted by measuring 2 ml of sample into a 50 ml high density polypropylene centrifuge tube, adding 15 ml of diethyl ether and mixing with a laboratory blender at

2000 rpm for 10 minutes. The sample was centrifuged at 1500 g for 10 minutes and the organic layer transferred to a 50 ml round bottom flask. The sample was then extracted for a second time with 10 ml of diethyl ether, and the extract combined with the first before drying with nitrogen and making to 0.5 ml with hexane for quantification.

Permethrin was quantified by GC/MS using a Perkin-Elmer Clarus 500 system with a programmable split / splitless injector and autosampler. The system was controlled via a PC running Turbomass® software. The cis and trans isomers were quantified using SIR (m/z=163 and 183) with results reported as the sum of both isomers. The performance of the method involving SPE was evaluated by analysing a series of five unspiked and five spiked sub-samples from a single bulk sample of final effluent. Sample volumes of 500 ml were extracted onto the C18 SPE cartridges, with addition of 0.5 ml of 1 µg/mL permethrin standard to spiked samples prior to extraction. The recovery was 102±5%. Recovery from solids on filter papers was calculated by the method of standard addition to five replicate spiked and unspiked samples of settled sewage (post primary tanks). Following filtration, permethrin was quantified in the liquid and solid fraction. Recovery from the aqueous phase by SPE was known to be 102%, and by difference the amount on the solids could be determined. Recoveries from solids were 83±11% and results were corrected for this recovery value. The method detection limit was 0.005 µg/L in wastewater samples, and 0.01 µg/L in trade effluents. This was determined with a three times signal to noise ratio and extrapolating from values determined in the five unspiked samples of final effluent. Data was reported to the detection limit, Biochemical oxygen demand (BOD), suspended solids and ammonia were determined using standard methods (APHA, 1998).

Mass Balance and Source Apportionment Calculations

The mass flux of permethrin across the secondary treatment process was calculated by multiplying the flow velocities (in L/day) by the permethrin concentrations (in µg/L) within the particular process flow-stream and equated to a permethrin loading in g/day. The sludge mass flux was also calculated by multiplying the volume of sludge returned per day (m^3/day) by the concentration of permethrin (µg/L) and equated to a load in g/day. Catchment load assessment and source apportionment were undertaken to assess the possible use of source control to reduce the concentrations of permethrin entering the STW. This used an existing model (UKWIR 2004) to attribute loads to sources designated as domestic, runoff, light industry, consented traders and town centre/commercial, along with values for input concentrations from the literature (Plagellat et al. 2004).

Results and Discussion

The variation in the influent concentrations of permethrin in the ‘high’ and ‘low level’ crude sewages are shown in Figure 1. The concentration of permethrin entering the works in the high level crude sewage averaged 0.331 µg/L, with a maximum input being observed on Wednesday at 22:00 of 0.970 µg/L. There is some evidence of diurnal trends in the concentrations of permethrin entering in the high level flow, with lower concentrations occurring at 06:00 each day. It is also apparent that higher permethrin concentrations occurred from 14:00 on the Wednesday and declined again towards the end of the week (Figure 1a). The samples of ‘low level’ crude plus returns exhibited a lower average concentration of permethrin (0.208 µg/L) with a maximum of 0.416 μg/L being observed on Thursday at 22:00. In contrast to observations in ‘high level crude’, no trends in the concentration of permethrin in the ‘low level’ crude plus return flow was evident (Figure 1b). It is very clear that sources of permethrin were not uniformly distributed throughout the catchment.

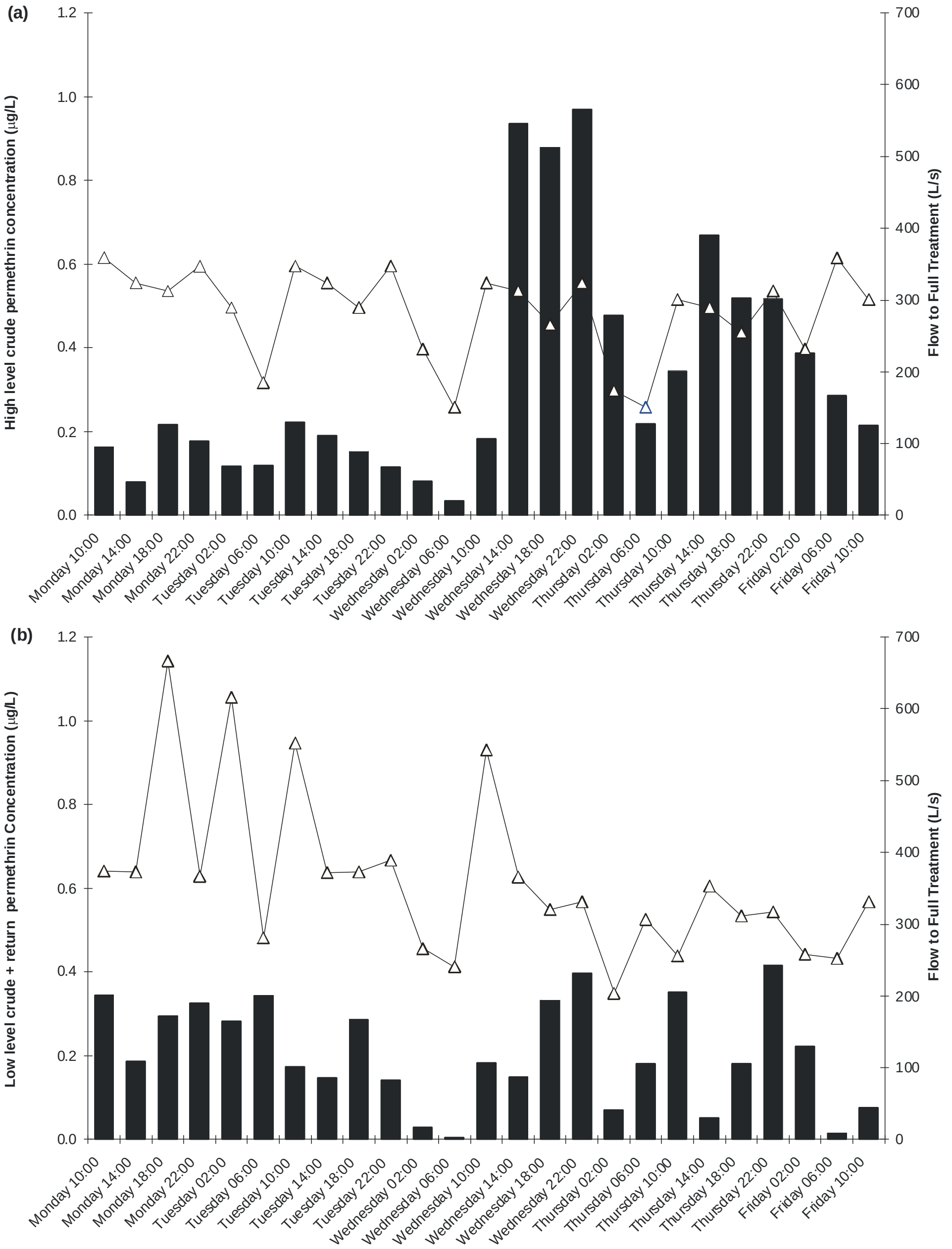

Figure 1 Permethrin concentrations (■) in (a) high level crude and (b) low level crude plus returns at four hourly intervals with flow to full treatment (Δ).

Removal of permethrin during primary sedimentation processes

There was some evidence that limited removal of permethrin occurred during the primary settlement processes. The average concentrations of permethrin across the two primary systems are shown in Figure 2. The average concentration in the 'high level' settled sewage declined, demonstrating a 24% removal in the 'high level' primary tanks with returns included in the influent data. There was evidence of a 5% removal across the 'low level' primary system. Removal of up to 35% of the load of permethrin during primary sedimentation at a Swiss sewage treatment works has been observed (Kupper *et al.* 2006) and attributed to sorption. Overall, the low efficiency of the primary tanks in removing permethrin, which was found to be predominantly associated with solids (70-90%) by analysis of filtered samples, would indicate that the permethrin was associated with fine particles which were not removed in primary treatment.

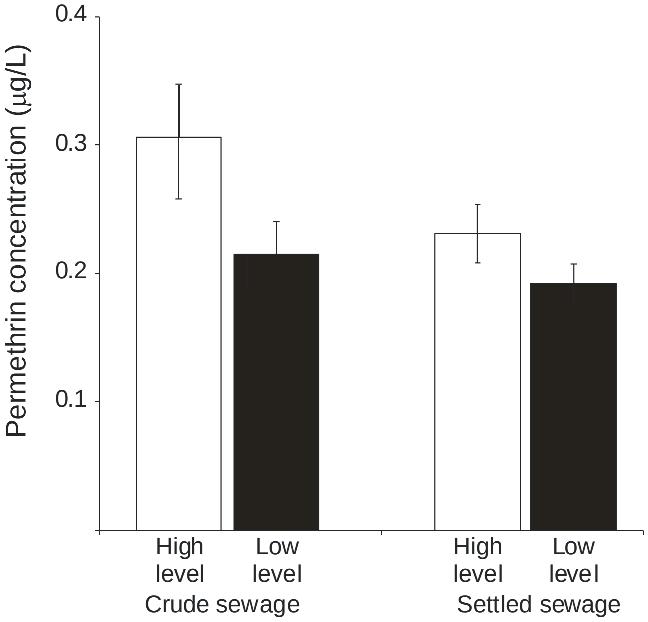

Figure 2. Average concentrations of permethrin across the high level (□) and low level (■) primary systems.

Removal of permethrin during biological filter processes

Following the settling stage the flow from the 'low level' primary tanks underwent treatment in the high rate biological filter and subsequent sedimentation (biotower process). This system was utilized as a roughing filter as a consequence of the very high BOD load entering the 'low level sewer'. The BOD concentration after two primary sedimentation tanks was 272 mg/L and this was reduced to 49 mg/L on average after the biotower process. The biotowers demonstrated a significant, 30% removal of permethrin (Parametric Welch ANOVA statistic due to unequal variances, *p* = <0.05) from 0.197 µg/L to 0.137 µg/L (Figure 3).

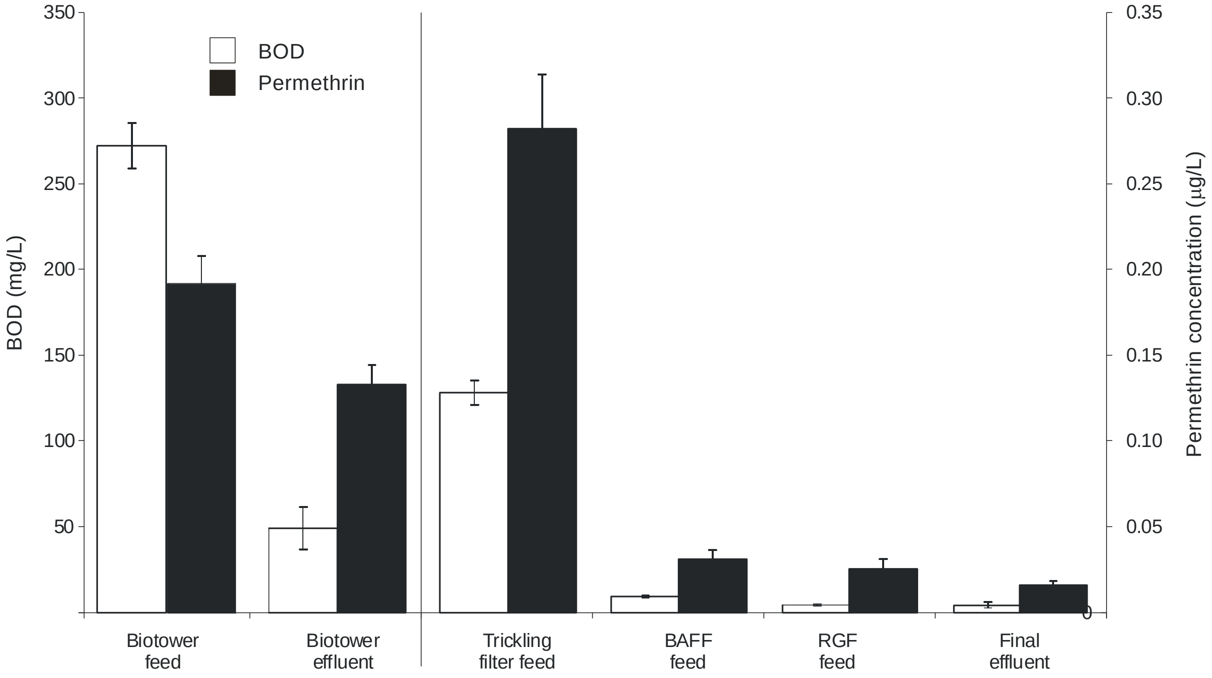

Figure 3. Removal of BOD and permethrin across the biological (biotowers and trickling filters) and the tertiary treatment (BAFF and RGF) processes.

Following the biotower process for the low level sewer the flow was combined with the flow from the ‘high level’ primary tanks before flowing over the trickling filters and subsequent treatment stages. The combined sample taken prior to treatment on the trickling filters was described as filter feed, and concentrations of permethrin over the further biological filter treatment stages are also shown in Figure 3. There was a significant (89%) reduction in the concentration of permethrin over the trickling filters from 0.282 µg/L to 0.031 µg/L (Parametric Welch ANOVA statistic due to unequal variances, $p = <0.05$), along with a 97% removal of the BOD from 128 mg/L to 3.5 mg/L. This was followed by further apparent, though not statistically significant, removal of permethrin over the BAFF (18%) and RGF (38%) resulting in an average concentration in the final effluent of 0.016 µg/L. It can be seen from Figure 3 that removal of permethrin was much greater across the trickling filters than it was across the other biological filter processes (biotower and BAFF). There was no further removal of BOD across the tertiary processes, although ammonia was reduced from 4.6 to 0.7 mg/L by the BAFF and suspended solids reduced from 20 mg/L to 15 mg/L over the BAFF and to 9 mg/L after the RGF (in the final effluent).

It has been noted that biological treatment is effective at removing permethrin, with conventional activated sludge ranging from 60 to 99% (Kupper *et al.* 2006), and the trickling filters at this STW performed at the upper end of this range (89%). They were more effective than the removal across an activated sludge plant in Spain, comprising primary sedimentation and conventional activated sludge treatment, where overall removal of 88% was reported (Gomez et al. 2007). There was also a change in the ratio of the ratio of the concentrations of the two isomers over the treatment process. In the influent the cis-isomer was 36% of the total (64% was the trans-isomer), however, in the final effluent the ratio was 50:50. This preferential biotransformation of the trans-isomer was consistent with the results of Lee et al. (2004) and Sharom and Solomon (1981).

Mass balance and fate of permethrin across the sewage treatment works

The average measured load of permethrin to the ‘high level’ inlet with returns was 10.2 g/day, with less (6.5 g/day) in the ‘low level’ crude plus returns (Table 1 and Figure 4). Using removal over the primary process (before the biotower) it was expected that the flux to the sludge would be 2.5 g/day (‘high level’) and 0.4 g/day (‘low level’) primary tanks. Concentrations determined in sludges, with volumetric data from site, indicated a flux of 1.2 g/day from ‘high level’, deemed a good fit, but 9.3 g/day ‘low level’, which was over twenty times above that (0.4 g/day) calculated by difference from the main flow. It is assumed that obtaining representative samples of sludges from the primary and secondary sedimentation tanks, in terms of solids content, and the accuracy of sludge volumetric data, has led to such wide disparity. Fluxes to biotower sludge demonstrated a similar imbalance, with a higher flux (8.9 g/day) calculated from sludge data than removed from the flow stream, of 1.9 g/day (Figure 4). Again, this is attributed to the inherent difficulties in determining the sludge volume as well as those errors associated with representatively sampling the sludge in terms of obtaining a sample with “average” solids content. Therefore percentage removals are more accurate if based on works main flow and calculated by difference in influent and effluent concentrations. Flows through the works are measured accurately for regulatory and process control purposes at a number of points.

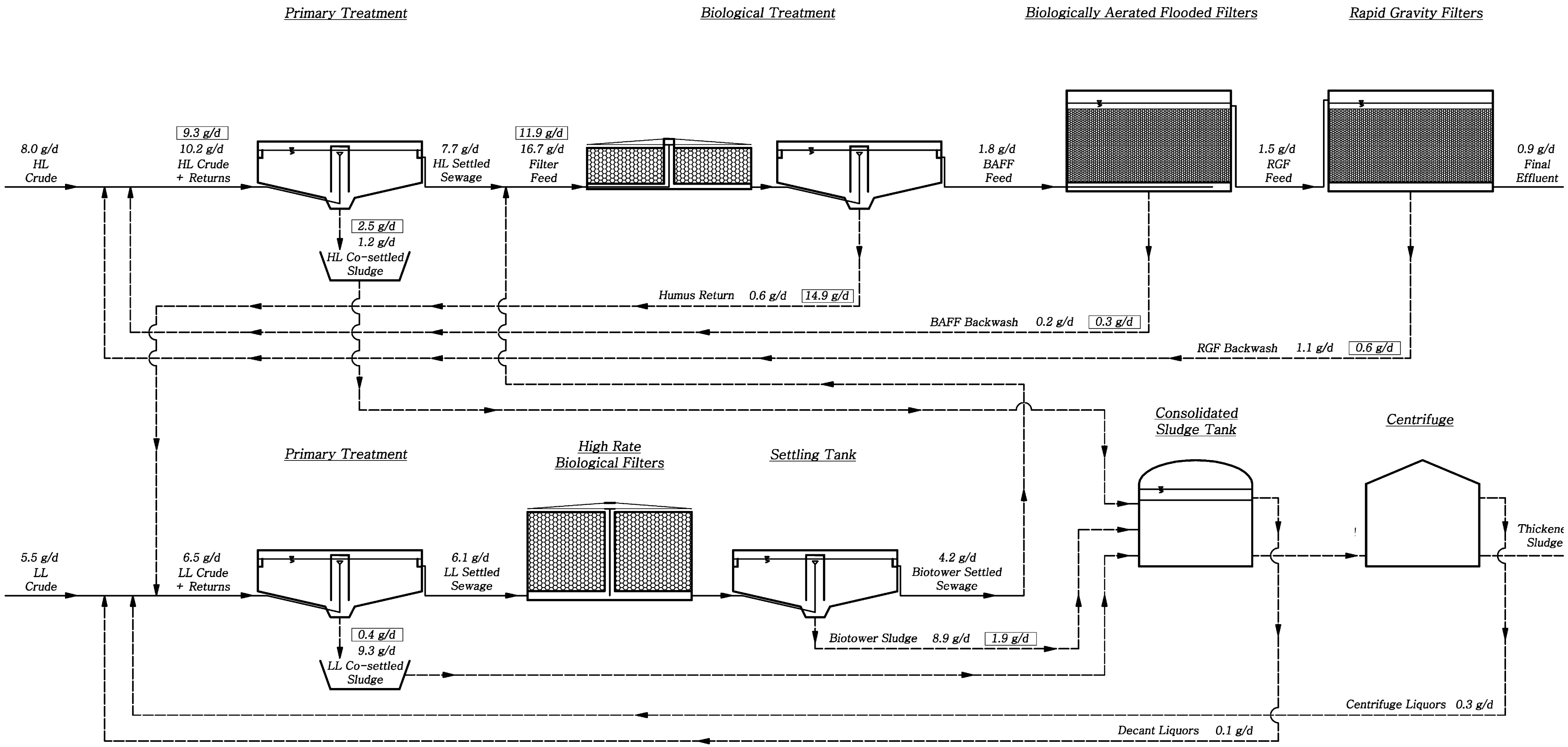

Figure 4 The flux of permethrin (g/day) calculated and measured through the unit treatment processes of the entire sewage treatment works. Open values were calculated from measured concentrations and flows, values in boxes were calculated by the difference between the input to a unit process and output.

A flux of 16.7 g/day (Table 1, Figure 4) was measured entering the trickling filters. The mass balance data indicates efficient removal of permethrin over the trickling filters, with 14.9 g/day removed. There was no evidence of accumulation of permethrin in the humus sludge returned to the ‘low level’ inlet, with concentrations of 0.304 µg/L giving a flux of 0.6 g/day based on volumetric data for the humus returns. Sampling of humus returns, which were flowing continually, was believed to have obtained representative samples in terms of solids content, and flow data from this process stream was of good quality. Therefore the difference between this, and the mass flux of 14.9 g/day obtained by subtracting effluent from influent flux (Figure 4) is most probably due to biodegradation of permethrin on the trickling filters. This biodegradation was observed to be concentration dependent (Figure 5).

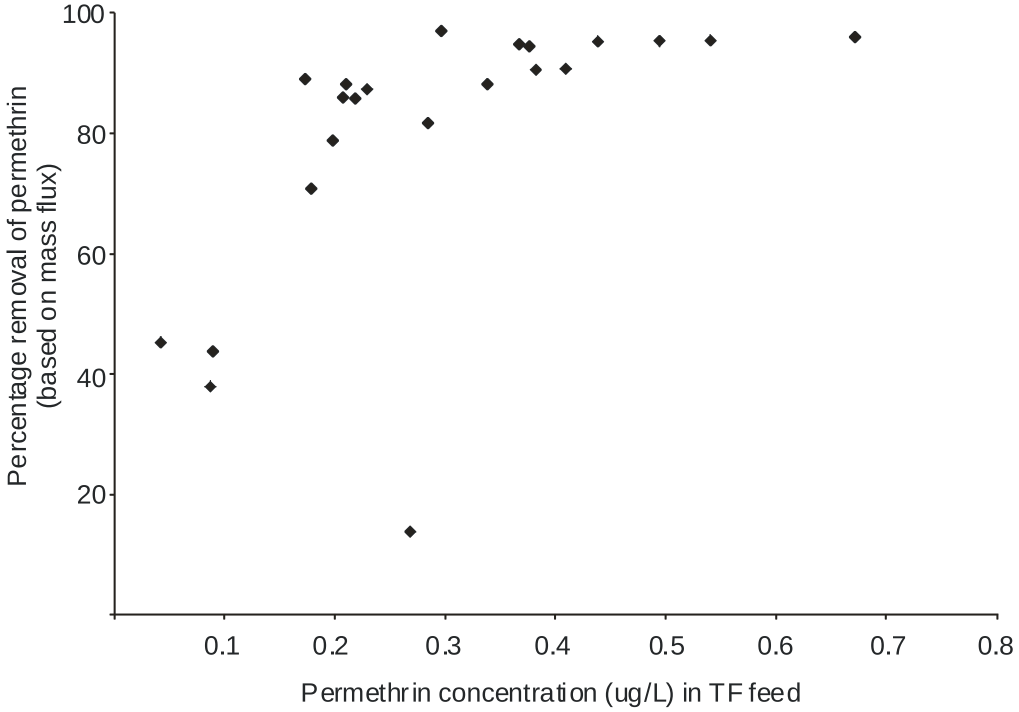

Figure 5 Correlation between permethrin concentration and mass flux percentage removal to examine the impact of concentration on removal efficiency.

The flux data in Table 1 also indicates that there was further removal of permethrin by the BAFF and RGF. The mass balances shown in Figure 4 do indicate that there is a flux of permethrin in the backwash liquors, 0.2 g/day in the BAFF backwash and 1.1 g/day in the RGF backwash. These values demonstrate what is considered to be a good fit with values calculated from removal over the BAFF and RGF of 0.3 and 0.5 g/day respectively. On a mass balance basis, it is possible to calculate the overall removal efficiency of permethrin, with a total load to the works of 8.0 g/day in the high level crude, and 5.5 g/day in the low level crude (when the load in the humus sludge and decant liquors is deducted from the crude plus return load), giving a total load of 13.5 g/day. The flux of permethrin in the final effluent was 0.9 g/day and the overall removal rate was therefore 93% (12.6 g/day).

Sources of permethrin identified by the catchment survey

Samples from the surveyed trader had a concentration of permethrin below the limit of detection (0.01 µg/l). The apportionment of the load of permethrin to the STW generated by the modelling is shown in Table 2. Comparing the predicted permethrin load to the STW to that measured during the sampling exercise shows a very good fit, with 115% of the measured load predicted by the model. The main outputs for this catchment modelling are that predicted domestic inputs of permethrin to the works contribute to 61% of the overall load. Although inputs from town centres and light industry are likely to show spatial and temporal variation, based on a generic value presented in the methodology the average contribution was estimated to be 54% of the total load to the STW. The model predicted that most of the load to the STW is from diffuse sources in the catchment.

Table 2. Predicted sources and average daily loads of permethrin to the STW in comparison to measured values.

Sources	Loads	% of total measured
Domestic inputs		
Population	140365	
Load (µg/person/day)	56	
Calculated load (g/day)	7.846	61%
Industrial discharge		
Volume of effluent to STW (m^3/d)	50	
Concentration in effluent (µg/L)	0.01	
Calculated load (g/day)	0.001	0%
Commercial / light industry		
Load (µg/person/day)	49	
Calculated load (g/day)	6.85	54%
Runoff		
Calculated load (g/day)	0	0%
STW data		
Total flow (annual mean m^3/d)	59058	
Calculated total load (g/day)	14.697	
Calculated concentration (µg/L)	0.249	
Measured concentration at STW (µg/L)	0.216	
Measured load at STW (g/day)	12.773	
Percentage of load predicted by model	115%	

Further analysis of the increase in concentrations observed in the ‘high level’ crude sewage over a period of 12 hours from Wednesday at 14:00 through to 02:00 on the following day, in terms of load and possible source indicated that the flow of crude sewage to the inlet averaged 300 L/s, and the concentration of permethrin was an average of 0.982 µg/L over the this sampling period. This is a flux of 12 g over the

12 hour period. Permethrin is typically present at 1% in lice treatments, and these are applied to dry hair (Chefaro 2010). Treatment may involve application of a complete 59 ml bottle of the 1% solution, which would be 0.59 g of permethrin per person treated, and therefore to generate the flux of 12 g, as few as 20 treatments may have occurred in the catchment over the 12 hour period. A single outbreak of head lice in a school or nursery could, therefore, have resulted in the observed load of permethrin to the STW in the second half of the sampling period.

In England and Wales discharge permits are calculated based on the EQS and the extent to which dilution of the STWs effluent occurs in the receiving water. Sewage treatment works discharges should not result in significant deterioration in water quality, which may be defined by as little as 10% of the standard. With an EQS for permethrin of 0.01 µg/L, and average final effluent concentrations of 0.016 µg/L at this STW, it is apparent that over ten times dilution may be required (10% of 0.01). Hence, although removal of permethrin is effective (93%) at the STW, given the inputs observed during the sampling period, it may not be effective enough to ensure that discharges will be within permitted limits if there is limited dilution. Overall, 24 samples of final effluent were taken, with spot sample concentrations ranging from <0.005 to 0.036 µg/L, and a 95th percentile of 0.035 µg/L, indicating that a percentile based permitting regime, rather than one based on maximum concentrations, would have little impact on the ability of the STW to meet permitted discharges.

Conclusions

The sampling exercise demonstrated that permethrin was present in the wastewater entering the sewage treatment works, and that removal during treatment was predominantly through biodegradation. Although the removal efficiency throughout the treatment works was over 90%, it was apparent that concentrations in the final effluent may be close to any future permitted limits if there is limited dilution in receiving waters. The quantity of permethrin in consumer products, such as formulations for treating head lice, which is effectively all discharged to the sewer, may be significant sources in relation to increasingly stringent environmental quality standards.

Acknowledgements

The authors are grateful to United Utilities PLC for funding the work and for agreement to publish the results

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