Behaviour of selected emerging pollutants in stormwater best management practices (BMPs)

Comportement de certains polluants émergents dans les techniques alternatives (BMPs) des eaux pluviales

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RÉSUMÉ

Certains polluants émergents (EPs) sont maintenant réglementés en tant que substances dangereuses ou prioritaires. Ces pollutions de type diffuses et ponctuelles sont omniprésentes dans les eaux urbaines. La présence dans les eaux urbaines et les origines probables de quatre polluants (diclofenac, perfluoro-octane sulphonic acid ; PFOS, hexabromocyclododecane ; HBCD et dichlorvos ; DDVP) sont discutées dans ce papier. Il y est aussi question de l'importance des événements pluvieux extrêmes et des surcharges des réseaux collectifs dans ce contexte. La méthode utilisée UoP (« unit operating process ») considère les propriétés physico-chimiques de techniques alternatives (BMP) de traitement des eaux et la susceptibilité des polluants a ces propriétés. La méthode permet de quantifier l'efficacité des traitements associées a ces techniques. Même si les niveaux de concentrations observées dans les eaux urbaines restent peu élevés, la méthode permet une première identification des techniques alternatives (BMPs) les plus appropriées par polluants considérés. Des techniques de contrôle a la source de type système d'infiltration, toits enherbes, paves poreux apparaissent comme les mesures les plus efficaces.

ABSTRACT

A range of emerging pollutants (EPs) are now being considered for regulatory designation as potentially hazardous or as priority substances. These EPs occur ubiquitously in urban receiving waters and have both point and non-point sources. The occurrence and likely sources of four selected EPs (diclofenac, perfluoro-octane sulphonic acid; PFOS, hexabromocyclododecane; HBCD and dichlorvos; DDVP) found in urban surface water discharges are discussed with reference to extreme events and CSO discharges. A unit operating process (UoP) methodology is utilised to evaluate primary BMP removal mechanisms and the susceptibility of the individual EPs to be removed by these processes based on their physico-chemical properties. Despite the prevailing low level concentrations encountered in urban runoff, the methodology provides a scientifically underpinned screening framework to identify the most appropriate BMP controls for the pollutant(s) under consideration. True source control approaches such as direct infiltration, green roofs, rain gardens and porous paving would appear to the moist effective management measures.

KEYWORDS

Emerging pollutants, urban runoff, stormwater BMPs, unit operating processes

1 INTRODUCTION

Research into the sources, fate and impacts of emerging pollutants (EP) has exponentially increased over the past decade largely driven by programmes and networks developed in the United States by the USGS (2011) and USEPA (www.water.epa.gov; www.creec.net) as well as similar European networks such as KNAPPE (www.ecologic.eu), POSEIDON, (www.eu-poseidon.com), NORMAN (www.norman-network.net), PHARMAS (www.pharmas-eu.org) etc. However, the large majority of this work has focussed on a limited number of endocrine disruptor chemicals (EDCs), pharmaceutical and personal care products (PPCPs) and persistent organic pollutants (POPs). The USGS studies detected over 100 contender EPs in some 80% of urban receiving water samples (Kolpin *et al.*, 2002) and similar statements on EP incidence in both urban surface waters and groundwater have been expounded for continental Europe (Houtman, 2010; Loos *et al.*, 2009; Musolff *et al.*, 2009) and the UK (Stuart *et al.*, 2011). In the UK study, metabolites were found at higher concentrations than the parent compounds for 60% of all samples with urban groundwater concentrations correlating with wet weather recharge. However it should be noted that relatively few of the samples analysed in these various studies exceeded any regulatory guidelines where these exist, mainly occurring at low levels below 0.1 µg l^{-1}, although as many as 30 – 40 EPs were found as complex mixtures in any single sample.

The principal focus of the EP research effort to date has been on diffuse agricultural runoff (Pal *et al.*, 2010), whilst in terms of urban drainage, the research has almost exclusively addressed wastewater effluents and drinking water with relatively little regard for urban runoff sources and discharges (Ternes and Joss, 2007). Figure 1 shows the principal EP sources, pathways and sinks in urban
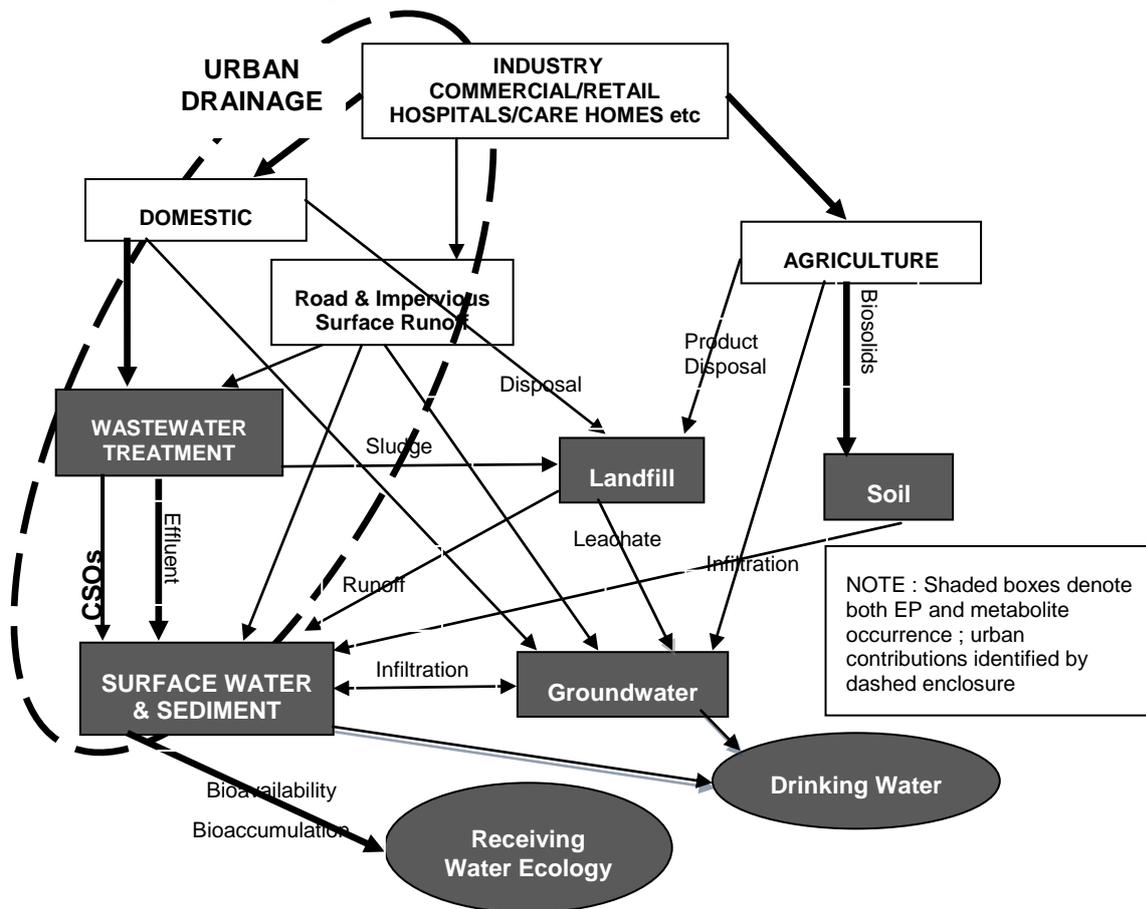

Figure 1. Urban sources, pathways and sinks of emerging pollutants (EPs).

areas and underscores the complexity of EP entry, conveyance, transformation and bioaccumulation mechanisms that can occur within urban drainage networks. It is clear from the literature that there are still fundamental and major gaps in both data and understanding of the occurrence, character and

behaviour of most EPs which make the management and control of their potential toxicity impacts a very challenging issue (Trembley *et al.*, 2011) This renders risk assessment of both individual and multi-generational compounds a highly speculative business in terms of both science and regulation (Ellis 2010; Dietrich *et al.*, 2010). At ultra-trace levels it may no longer be possible to deconvolute imposed EP effects from their incidence as ambient background and it will be difficult to determine the apportionment of EP risk in terms of overall environmental and aquatic concerns. It is certainly clear that the traditional individual substance approach for evaluating risks will not be sustainable in the future given that little environmental or toxicological data is available for the large majority of EPs. This view is confirmed by the growing realisation of the critical importance of multi-generational, simultaneous ecological exposure to individual trace levels of multitudes of chemical stressors. This is particularly true of urban runoff water quality which essentially comprises a "cocktail" of complex mixtures.

Given the apparent ubiquitous occurrence of EPs in urban receiving waters as evidenced by the various US and European studies mentioned previously, there are continuing concerns over their modes of entry into the aquatic environment as well as the characteristics which render them potentially hazardous to the receiving water ecology. In addition, there is an open question as to whether any of the various source control sustainable drainage options provide effective treatment efficiency for EPs in urban runoff, particularly given their low-level concentrations. The purpose of this paper is to explore the characteristics and sources of EPs found in urban runoff and to examine their removal potential under the prevailing processes operating within typical BMP systems.

2   EMERGING POLLUTANTS

2.1   Definitions

A widely used definition for EPs is that they are not currently included in routine monitoring programmes but could pose a significant risk requiring (future) regulation, depending on their potential eco-toxicological and health effects and their levels as found in the aquatic environment. Xenobiotic substances which conform to this definition may be new-to-market "designer" substances (e.g. herbal supplements, non-prescription medicines) or may have for a number of years entered urban receiving water bodies from both natural and anthropogenic sources, but may now be considered "emerging" due to recent awareness of their potential toxicological and human health impacts. They may not have been subject to regulatory checks when first produced and may not be subject to current regulatory receiving water environmental quality standards (EQS). This serves to differentiate them from priority hazardous substances (PHSs) which for example, within the European Community are covered in Article 16 of the Water Framework Directive (WFD; 2000/60/EC) and the associated Priority Substances Directive (2008/105/EC) and Groundwater Daughter Directive (2006/118/EC). Such substances would be covered under the equivalent Contaminant Candidate List (CCL) and Toxic Substance Control Act (Section 6, TSCA) of the Clean Water Act in the US. This means that there is overlap between the EP and PS contaminant suites with current EP organic compounds such as bisphenol A and oestradiol being under review as future designated PSs or PHSs within the Drinking Water Directive (98/83/EC) and having proposed limit values of 0.1 µg l^{-1} and 0.01 µg l^{-1} respectively. The EP triclosan represents an antimicrobial agent which is also under review for future designation as a PS under the EC Priority Substance Directive. As such these EPs represent "stealth" pollutants which have eluded attention to date because they may have been masked, indiscernible, surreptitiously introduced into the environment, difficult or cryptic to detect clearly or may have just previously remained undetected.

2.2 Sources

The presence of POPs in both treated wastewater effluent, CSOs and urban runoff is well known comprising a mix of polyaromatic hydrocarbons (PAHs), EDCs, PPCPs, solvents as well as plasticisers, surfactant breakdown products etc. (Ternes and Joss, 2007). In general terms, assuming a 2% overflow frequency and a 50% dilution, could imply a long term EP substance loss amounting on average to 1% of the total CSO discharge load. As indicated in Figure 1, to this mix could be added landfill leachate (e.g. phthalates, sterols etc) as well as exotic surface-derived substances found in urban runoff such as caffeine, nicotine, cocaine etc.(Rieckermann, 2008) Major potential urban

sources include industrial/commercial and wastewater discharges as well as untreated combined sewer overflows (CSOs) and urban surface water outfalls (SWOs). SWO discharges constitute a major secondary source and derive EPs from a variety of origins:

- Illegal sewer misconnections which allow untreated sewage and greywater to enter and mix with the surface water sewer system. One estimate suggests that between 300,000 to 400,000 such wrong connections (0.6% to 2% of domestic households) exist in England and Wales alone (Defra, 2005). Clearly sanitary wastewater and greywater misconnections to the separate surface water sewer can constitute principal EP sources to urban receiving waters.

- It is estimated that some 1% to 3% of combined sewers (especially in older inner city areas) are subject to exfiltration which could lead to a sewage leakage loss of anything between 26 and 260 m^3 km^{-1} $year^{-1}$ in European cities (Ellis and Bertrand-Krajewski, 2010). A major source of such leakage is believed to be via house connections which are often in a poor structural state (Ternes and Joss, 2007), but unfortunately there are very few studies available to fully confirm this source attribution. The large majority of exfiltration loss will be to urban groundwater but the shallow depth of most surface water pipes means that there will inevitably be some EP return (even if in diluted form) as groundwater flow to urban surface waters as well as resulting from seepage into damaged surface water sewers.

- The flushing of EP substances from impervious urban surfaces during wet weather conditions may also be an important source given the variety of potential everyday materials that contain or sequester xenobiotic pollutants e.g. solvents in wood preservatives, foam retardents, rainfall-runoff flushing of garage service forecourts and industrial yards, discarded recreational drugs, drug syringes and medicants, phthalates leaching from weathered plastic materials etc. (Rieckermann, 2008; Ellis, 2008).

- A range of emerging organic pollutants (EOPs) are also associated with wet weather urban runoff from parks, open spaces, gardens, golf courses as well as leachates from local and transport authority applications e.g pesticides such as glyphosate used for weed control.

- Domestic disposal of medications and drugs as well as other abuses of the surface water sewer system e.g. direct disposal to surface water drains of used oil, waste bin washings, unwanted and outdated pesticides/biocides/insecticides, solvents and paints etc.(Daughton and Ruhoy, 2009).

2.3 Classification and Occurrence

As the definition of EPs covers a wide range of compounds, they are often grouped into classes depending on their chemical characteristics or by their mode of action. Table 1 categorises EPs based essentially on their application together with examples of compounds and the concentration ranges of representative compounds (in bold) as consistently detected in urban runoff discharges and receiving waters. Algal toxins and antifouling compounds have been omitted from this list as they have rarely been reported in urban waters. Whilst the median values noted in the table for the four named EP compounds generally confirm that the large majority of EPs are detected at trace levels, one feature is the common occurrence of high magnitude outliers as indicated by the maximum values. One explanation for these might be related to the impact of untreated CSO discharges. Some EPs such as PAHs and bisphenol A can be effectively removed during secondary biological treatment but can substantially increase in concentration within the receiving water during CSO wet weather events as the lack of treatment becomes more important than any in-stream dilution effect. By comparison, POPs and other EPs which are not well removed in STW treatment e.g. carbmazepine and caffeine can be expected to be found at decreasing concentrations due to storm runoff dilution. Fono and Sedlack (2005) have demonstrated the persistent 75% - 90% attenuation of PPCP species such as the PPCP beta-blocker propranolol below CSO discharges which is not explicable by photodegradation or biotransformation mechanisms. Such patterns have been consistently found in many urban receiving water source studies (Phillips and Chalmers, 2009; Ellis, 2008). Some EP species such as the insecticide cypermethrin, have very low solubilities and bind strongly to suspended solids and are therefore likely to accumulate within receiving water sediments adjacent to outfalls. Previous work on PPCPs in urban receiving waters has noted this potential for sediment accumulation as well as possibilities for the development of antimicrobial resistance (Ellis, 2006).

Table 1. Classification and examples of EPs in urban receiving waters together with typical concentration ranges

CLASS	Compound Examples	Concentration Range (ng l^{-1})
PPCPs/ Fragrances	**Diclofenac**, Ibuprofen, Carbamazepine, Diazipane; Camphor, Musk, Parabens	10-(12.6)-85 [1002]
EDCs; Steroid Hormones	Oestradiol, Coprostanol	
Antimicrobials/Virals	Triclosan, Osaltamivir	
Plasticisers	Bisphenol A, Phthalates, Methanone	
Surfactants/ Detergents	**Perfluoro-octane sulphonic acid (PFOS)** Nonylphenols, APEs,	1.3-(3.4)-21.0 [195]
Addictive Drugs	Cocaine, Heroin, Morphine	
Nanoparticles	Silica, Aluminium fibre, Gypsum, Cellulose	
Flame Retardents	**Hexabromochloracyclododecane (HBCD)** Tri (2-chloroethyl) phosphate, PBDEs,	1.0-(2.9)-13.0 [137]
Solvents	Para-Cresol, DNP	
Other POPs (Aromatics, Pesticides, Biocides, Perfluoroalkylated substances etc)	**Dichlorvos (DDVP),** PAHs(Indenopyrene, anthracene, benzofluoranthene etc) Pesticides (Diuron, DEHP, Endosulfan, Glyphosate , Diazinon, Cypermethrin, Perfluoroalkylated Substances Trichloromethane	1.4-(17.8)-40.7 [1552]

NOTE: Concentration range shown as: 25th%ile- (Median) -75th%ile [Maximum] values

3. BMP CONTROL FOR EP DISCHARGES

3.1 Selecting EPs for analysis

The adoption of BMP drainage options for the control and management of urban stormwater runoff has become an integral principle for sustainable urban drainage infrastructure provision. Such BMP devices are seen as providing effective water quality treatment in addition to their primary function of flood control and previous work has shown that the physical, chemical and biological processes operating within such control structures can provide a reliable basis for the assessment of their relative capabilities to remove a variety of micropollutants (Scholes *et al.,* 2008). However, is it feasible to apply a unit operating process methodology to evaluate the removal potential of EPs within BMPs? To explore this question further, a limited number of EP compounds representative of the classes listed in Table 1 have been selected for analysis and are highlighted in bold in the table.

- Diclofenac; is a non-steroidal anti-inflammatory PPCP used throughout the world and available as both a prescription and "over-the-counter" drug, with an estimated 151 tonnes per annum used in the UK (Boxall *et al*., 2011) and over 80 tonnes per annum in Germany (Herberer *et al*., 1998). Diclofenac occurs in urban runoff and receiving waters mainly as a result of direct CSO discharges, sewer misconnections and illicit domestic disposal. It has been estimated that up to 50% - 60% of the total observed surface water loads are derived from the two latter sources (Boxall *et al*., 2011). Surveys in UK surface waters indicate a concentration range of 10 – 76.3 ng l^{-1} with a median value of 12.6 ng l^{-1}. Maximum concentrations appear principally associated with wet weather winter periods (Boxall *et al*., 2011). Previous work on urbanised tributaries of the River Thames in metropolitan London has indicated receiving water concentration between10.5 and 85 ng l^{-1} with average concentration of 51 ng l^{-1} being recorded for the River Seine at Orly in metropolitan Paris and 100 ng l^{-1} in Berlin surface waters (Ellis, 2006). In the cited UK studies, sewage treatment plant

discharges of diclofenac were substantially diluted by endogenous concentrations derived from upstream sources primarily fed from diffuse urban inflows. It is known that diclofenac is subject to photolysis and biodegradation with the latter processes having a half-life of about 8 days, although the degradation metabolite products are frequently more toxic than the parent compound (e.g. Lee *et al.,*2012*)*. It is now a designated PS with an EQS value of 0.1 µg l^{-1}.

- Perfluoro-octane sulphonic acid (PFOS); this is a surfactant widely used as a stain repellent and in fire fighting foams as well as in metal plating and photographic processes. PFOS is very resistent to hydrolysis, photolysis and biodegradation and is an exceptionally stable and persistent compound. It is characterised by abundant congeners, all of which are accumulatively adsorbed into internal organs of the receiving water ecology. PFOS became of particular interest in the UK following a major oil terminal fire in Hertfordshire north of London in December 2005 when receiving waters of the Ver and Colne in the urban areas downstream of the fire location recorded PFOS levels between 4.6 and 5.9 µg l^{-1} (Atkinson *et al.*, 2008). Levels of between 8 and 28 µg l^{-1} have also been recorded in surface waters adjacent to airports following fire fighting practice and breakthroughs above 1.0 µg l^{-1} have also been noted in CSO discharges (Atkinson *et al.*, 2008). These reported levels are well in exceedance of the normal quartile range and median values as identified in Table 1 as they represent extreme conditions following exceptional releases. PFOS industrial applications have been limited since 2010 and a 0.2 – 0.3 µg l^{-1} ecosystem threshold risk level has become widely accepted; the compound is now a designated PHS with an annual average EQS value of 0.00065 µg l^{-1}.

- Hexabromocyclododecane (HBCD); this compound is widely used in polystyrene foam insulation boarding and textile coatings as a brominated flame retardant. It is estimated that some 19 kg $year^{-1}$ of HBCD are released into the UK environment of which some 30% is discharged into surface waters (Brookes et al., 2009). It is a persistent, lipophilic organic pollutant having a poor water solubility and low volatility. It becomes strongly adsorbed to suspended solids and sediment and has a low leaching potential (Kohler *et al.*, 2006). There is evidence for trophic magnification particularly in livers of smelt and trout, with a fish to sediment bioconcentration factor of 15:1 (Brooke *et al.*, 2009). HBCD sediment accumulations in the range of 199 – 1680 ng kg^{-1} have been recorded at locations downstream of both CSOs and SWOs in urban receiving waters of N England which could pose long term chronic ecosystem effects. HBCD is now a designated PHS with an annual average EQS value of 0.0016 µg l^{-1}.

- Dichlorvos (DDVP); this is a widely used organophosphorous insecticide and weed killer, which because of its solubility in water possesses a high acute toxicity potential. It has a recommended freshwater EQS of 0.00061 µg l^{-1} which is considerably lower than the maximum 0.02 µg l^{-1} drinking water threshold set by the WHO. DDVP is subject to a combination of volatilisation, hydrolysis and microbial degradation. Few concerns to date have been expressed about its occurrence in urban surface waters and surveys of European rivers have suggested PFOS levels to be generally near the detection limit with a NOEC ecosystem threshold of around 3.4 µg l^{-1}. DDVP has now been designated a PS.

3.2 BMP unit operating processes (UoPs) for EPs

Field data on the different environmental behaviours and fates of many of the generic stormwater pollutants within structural BMPs are scarce. In an attempt to overcome this deficiency, a systematic methodology based on unit operating processes (UoPs) to provide a comparative assessment of pollutant removal potentials has been developed by Scholes *et al.*,(2008). The methodology is based on a mixed quantitative/qualitative consideration of primary removal processes (biological, chemical and physical) associated with the different identified BMPs. The susceptibility of individual pollutant species to be influenced by the UoPs is then considered separately. The two sets of data are then combined to derive an overall value for the removal potential of each BMP option for each considered pollutant enabling pollutant specific ranked orders of preference to be generated. Full details of the methodological approach and its application can be found elsewhere (Scholes *et al.*, 2008). In this paper we have added green roofs to the previous list of 15 different BMPs. An additional modification is that in order to ensure that the potential removal characteristics of the EPs are fully considered, the susceptibility to hydrolysis has been included and incorporated together with photolysis in a category identified as abiotic degradation. This is allocated an equal weighting to the other potential mechanisms for pollutant removal during BMP treatment (Table 3).

The methodology to date has been applied to generic pollutants commonly included in the large

Table 2. Indirect/direct removal processes in BMPs

	Removal Process	Relevant measurements and units
Indirect removal process	Adsorption to suspended solids	K_{oc} (L/g).
	Precipitation	Water solubility (mg/l)
Direct removal processes	Settling	Settling velocity (m/s)
	Adsorption to substrate	K_{oc} (L/g)
	Microbial degradation	Rate of aerobic and anaerobic biodegradation ($^1/_2$ life in days)
	Filtration	Function of K_{oc} (L/g) and precipitation (mg/l)
	Volatilisation	K_h (atm-m^3/mole)
	Photolysis	Rate of photodegradation ($^1/_2$ life in days)
	Hydrolysis	Susceptibility to hydrolysis under neutral conditions based on functional groups present
	Plant uptake	K_{ow}; bioaccumulation concentration factor (BCF)

Key: K_{oc} = organic carbon adsorption coefficient = partitioning of a substance between the solid and dissolved phases at equilibrium expressed on an organic carbon basis

K_h = Henry's Law constant (based on the relationship that at a constant temperature the mass of gas dissolved in a liquid at equilibrium is proportional to the partial pressure of the gas)

K_{ow} = octanol-water partition coefficient = a measure of the potential for organic compounds to accumulate in lipids = ratio of the concentration of a pollutant in octanol to that in water at equilibrium

Table 3. Removal processes within BMPs together with their potentials to occur for four emerging pollutants

UoPs	Properties	Diclofenac	Perfluoro-sulphonic acid (PFOS)	Hexabromocyclo dodecane (HBCD)	Dichlorvos (DDVP)
Adsorption	K_{oc} values	405-830	2,562-71,680	1.76-5.2x10^6	27.5-151
	Potential for removal	Low/Medium	Medium/High	High	Low
Precipitation	Solubility (mg/l)*	2.37-4.52	0.104	0.034-0.086	2,044-8,000
	Potential for removal	High	High	High	Medium
Settling & filtration	Potential resulting from adsorption & precipitation potentials	Medium	High	High	Low/Medium
Aerobic biodegradation	Susceptibility or half life (days)	37 – 170d Negligible ;Low	No experimental evidence for aerobic or anaerobic degradation	11-32 ; Medium/High	< 1; High
Anaerobic biodegradation	Susceptibility or half life (days)	Negligible Low		1.1-6.9 ; High	3.5 ; High
Overall biodegradation	Potential for removal	Low	Low	High	High
Volatilisation	K_h values	4.7x10^{-12} – 5.3x10^{-9}	9.34 x 10^{-7}	1.7x10^{-6}-1.2x10^{-4}	5.7-8.6x10^{-7}
	Potential for removal	Low	Low/Medium	Medium	Low/Medium
Photolysis	Half-life (hours)	192 hours ; Low	Resistant to photolysis ; Low	Resistant to photolysis ; Low	Some susceptibility to photolysis ; Medium
Hydrolysis	Susceptibility	Low	Resistant to hydrolysis ; Low	Resistant to hydrolysis ; Low	Half life of 2.5 – 4.0 days at pH7 ;Medium
	Potential for abiotic degradation	Low	Low	Low	Medium
Plant uptake	K_{ow}	10,471-32,359 ; Medium	30,900 ; Medium	5.5x10^7 ; High	3.98-26.9 ;Low
	Potential for bioaccumulation ; BCF value	3.162 ; Low	56 ;Medium	8,800-18,000 ; High	0.6-3.13 ; Low
	Potential for removal	Low/Medium	Medium	High	Low

majority of urban runoff investigations and which occur in readily detectable concentrations as

reflected in the event mean concentration (EMC) distributions recorded in the US EPA nationalstormwater BMP database (www.bmpdatabase.org). EPs on the other hand generally occur at low or ultra-low concentrations and have a minimal evidence database. Whilst ultra-trace concentrations may imply that EP transformation is unlikely to contribute much to microbial growth, enzyme degradation might well make substantial contributions to co-metabolism functions rendering them potentially ecologically hazardous. Table 3 illustrates both quantitative and qualitative process values for each of the four selected EP compounds which form the basis for evaluating their overall removal potentials to the UoPs. Experimental data has been used where this is available but is often subject to wide variations as demonstrated by the ranges of K_{oc} values for PFOS and K_h values for diclofenac and HBCD. However, this has a limited impact on the applied methodological approach as the EP removal potentials are broadly categorised as low, low/medium, medium, medium/high and high as shown in Table 3. Thus HBCD can be seen to be highly susceptible to removal by adsorption to substrate, settling/filtration, microbial degradation and plant uptake but it is resistant to abiotic degradation processes. In contrast, DDVP although biodegradable, is less readily removed by adsorption and precipitation mechanisms and is not susceptible to plant uptake. It is the only one of the four investigated EPs to demonstrate a potential to undergo abiotic degradation. The qualitative assessments for the removal potentials have been converted to numerical values and by combining the values for removal of a specific pollutant by a BMP removal process with the values representing the importance of the primary removal mechanisms within each BMP, the relative rankings for the removal of different EPs within the different BMPs has been established as shown in Figure 2.

4. BMP REMOVAL POTENTIALS
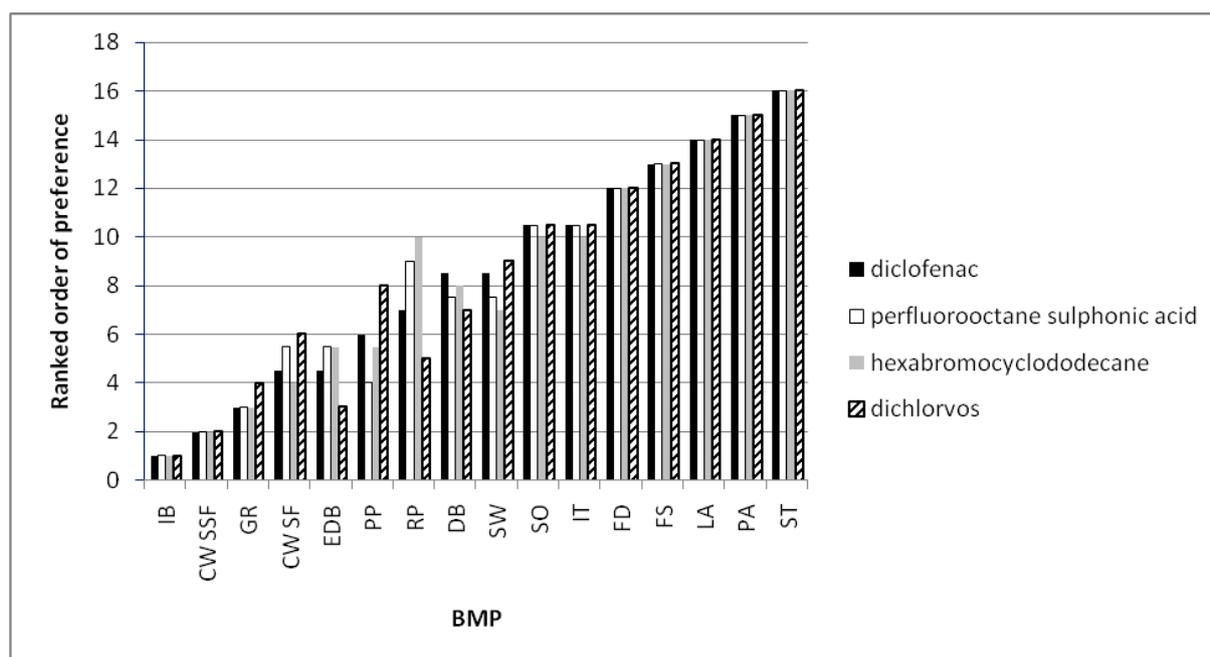
IB=infiltration basin; CWSSF=sub-surface flow constructed wetland; GR=green roof; CWSF=surface flow constructed wetland; EDB=extended detention basin; PP=porous paving; RP=retention pond; DB=detention basin; SW=swale; SO=soakaway; IT=infiltration trench; FD=filter drain; FS=filter strip; LA=lagoon; PA=porous asphalt; ST=sedimentation tank.

Figure 2. **Predicted order of preference for BMPs to remove diclofenac, perfluorosulphonic acid (PFOS), hexabromocyclododecane (HBCD) and dichlorvos (DDVP).**

The ranking orders displayed in Figure 2 demonstrate identical behaviours by the selected EPs for the two most highly ranked treatment systems (infiltration basins and sub-surface flow constructed wetlands) and for the five least efficient treatment systems (filter drains, filter strips, lagoons, porous asphalt and sedimentation tanks). Although green roofs are mainly employed for water volume retention purposes, the results of this theoretical approach indicate their ability to perform consistently well with regard to the removal of four EPs. Between the identified extremes of the treatment performance rankings there is evidence of discrimination in how the individual pollutants respond to

different BMPs. The greatest variation in performance rankings across the four pollutants occurs for porous paving and retention pond treatment systems. Porous paving has an average ranking of 6 but performs best for perfluorosulphonic acid (ranking 4) due to the combined susceptibility of this pollutant for removal by adsorption and filtration, which are both important removal mechanisms in porous paving systems, particularly where an underlying substrate is present. Dichlorvos possesses the lowest ranking (8) for porous paving as a relatively low K_{oc} value and an increased solubility compared to the other pollutants do not facilitate ready removal by adsorption and filtration. The behaviour of dichlorvos reverses for retention ponds where it demonstrates the highest removal potential (ranking 5 compared to an average ranking of ~8) due to its susceptibility to both aerobic and anaerobic biodegradation in retained water systems. Hexabromocyclododecane behaves least well in retention ponds as two of its major removal mechanisms, adsorption and filtration, do not have high importance in this type of treatment system. The same factors influence the preferential pollutant removal patterns in extended detention basins (average ranking between 4 and 5) and to a lesser extent in detention basins (average ranking ~8) where sedimentation is less important due to the time available for this process.

Sub-surface flow constructed wetlands consistently perform more efficiently than the corresponding surface flow systems due to the greater potential in the former for adsorption, filtration and microbial degradation to occur in both aerobic and anaerobic conditions. Both systems are vegetated but the sub-surface flow version will provide increased contact time between the pollutant and the plant roots as well as an increased possibility of algal uptake. Hexabromocyclododecane is removed most efficiently in those vegetated systems (surface flow constructed wetlands and swales) which exhibit discrimination because of high K_{ow} and BCF values. In contrast, dichlorvos has low values for both these parameters and so tends to perform least well in vegetated systems, as represented by surface flow constructed wetlands and swales. The same characteristics properties also account for dichlorvos performing least well in green roofs.

5. CONCLUSIONS

A UoP methodological approach to evaluate the potential performance efficiency of BMP control structures to remove EPs provides a feasible theoretical framework. The methodology appears to retain discriminatory power for individual compounds even when they are known to occur together as multi-generational complex mixtures as their physic-chemical properties are individually distinctive. This is supported by the prevailing low-level concentrations which limit compound interactions that could affect their characteristic behaviours.   Nevertheless, there is considerable variability in the data values reported for many of the UoP processes noted in Table 3 which inevitably introduces uncertainty into the methodology. This implies that the relative BMP removal rankings illustrated in Figure 2 should be regarded as providing a first-order screening function. However, it is apparent that true source controls such as direct infiltration, rain gardens (pocket-wetlands), green roofs and porous paving offer the most appropriate and effective EP treatment for urban stormwater runoff.

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