

## Pellston Mixtures

# Aquatic Exposures of Chemical Mixtures in Urban Environments: Approaches to Impact Assessment

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**Abstract:** Urban regions of the world are expanding rapidly, placing additional stress on water resources. Urban water bodies serve many purposes, from washing and sources of drinking water to transport and conduits for storm drainage and effluent discharge. These water bodies receive chemical emissions arising from either single or multiple point sources, diffuse sources which can be continuous, intermittent, or seasonal. Thus, aquatic organisms in these water bodies are exposed to temporally and compositionally variable mixtures. We have delineated source-specific signatures of these mixtures for diffuse urban runoff and urban point source exposure scenarios to support risk assessment and management of these mixtures. The first step in a tiered approach to assessing chemical exposure has been developed based on the event mean concentration concept, with chemical concentrations in runoff defined by volumes of water leaving each surface and the chemical exposure mixture profiles for different urban scenarios. Although generalizations can be made about the chemical composition of urban sources and event mean exposure predictions for initial prioritization, such modeling needs to be complemented with biological monitoring data. It is highly unlikely that the current paradigm of routine regulatory chemical monitoring alone will provide a realistic appraisal of urban aquatic chemical mixture exposures. Future consideration is also needed of the role of nonchemical stressors in such highly modified urban water bodies. *Environ Toxicol Chem* 2018;37:703–714. © 2017 The Authors. Environmental Toxicology and Chemistry published by Wiley Periodicals, Inc. on behalf of SETAC.

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## INTRODUCTION

By 2030 it is estimated that nearly 60% of the world population will live in urban areas (United Nations 2014). Although urbanization is serving as a global agent of environmental

change, the fastest pace of urban growth is expected to occur in Africa and Asia. Given the potential for increased emission frequency and amounts of contaminants from a variety of urban sources, this global trend poses water quality concerns for a growing number of receiving waters that transect these areas (Paul and Meyer 2001). Urban areas are generally located along bodies of water because availability of drinking water and transportation of goods via shipping historically led to settlement and expansion. Although water quality concerns have been voiced for a long time, it is only recently that some default scientific approaches have been proposed and adopted for the preliminary assessment of the magnitude of mixture exposures (e.g., Kortenkamp et al. 2009), allowing for a better

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approximation of mixture impacts than the so far common per-chemical approaches. Among others, mixture risk assessment can be executed based on component-based approaches, in which the chemical composition—in terms of identities and concentrations of the compounds—is used as a starting point. This approach can be used with measured concentrations, but it can also be hypothesized that different forms of land use imply different, but typical, chemical compositions.

Exploring this for urban runoff emissions, there are several major sources of contaminants which can enter watercourses in an urban scenario. For example, infrastructure for collection and treatment of industrial and domestic wastewater is expanding but generally is outstripped by urban growth (Corcoran et al. 2010). Storm water overflows from combined sewer systems are potential sources, particularly in older cities. The growing area of impervious surfaces of the urban environment can represent a direct source of contaminants to surface waters during storm events, unless storm water-management facilities such as retention ponds are present. Urban storm water runoff is considered one of the greatest challenges to ensuring clean water for human and ecological health (National Research Council 2008). Furthermore, the urban scenario has to consider diffuse inputs from dry and wet atmospheric deposition as well as untreated or partially treated point source inputs from industrial origins.

Figure 1 is a schematic of the key chemical pollutant sources and pathways into a freshwater urban water body. The sources include 1) surface runoff from impervious surfaces, such as roads and parking lots, building facades and roofs, as well as paved

areas in parks and gardens; 2) combined sewer overflows from wastewater-treatment plants (WWTPs); 3) untreated domestic discharges through misconnections and leakage; and 4) industrial discharges not subject to wastewater treatment. The former 2 sources are transient and rainfall-dependent, whereas the latter are constant sources.

Pressure to conserve water resources can in itself lead to additional inputs to the urban environment. For example, the reuse of gray water in urban areas, especially for landscape and parkland irrigation (including for median strips and roadside planters) is increasing. Gray water is defined as water from all domestic sewerage excluding wastewater generated by toilets and bidets (Maimon et al. 2010). Its composition is highly variable because of geographic differences in lifestyles, customs, product preferences, washing habits, and the types of plumbing installations. The scale of this heterogeneity has been shown down to the household level, making the use of generic summary composition data and the subsequent assessment of potential environmental risks posed by gray water use challenging (Jefferson et al. 2004). Nevertheless, gray water remains a potential source of contaminants which will have received limited, if any, treatment apart from natural attenuation processes.

Runoff from impervious and semipervious surfaces entering the receiving waters may be a complex mixture of chemicals. Road runoff may contain petrochemicals (oil and grease) and polycyclic aromatic hydrocarbons (PAHs) from vehicle emissions, salts used to melt snow/ice, and various road and tire wear products such as suspended solids, black carbon, nanomaterials,

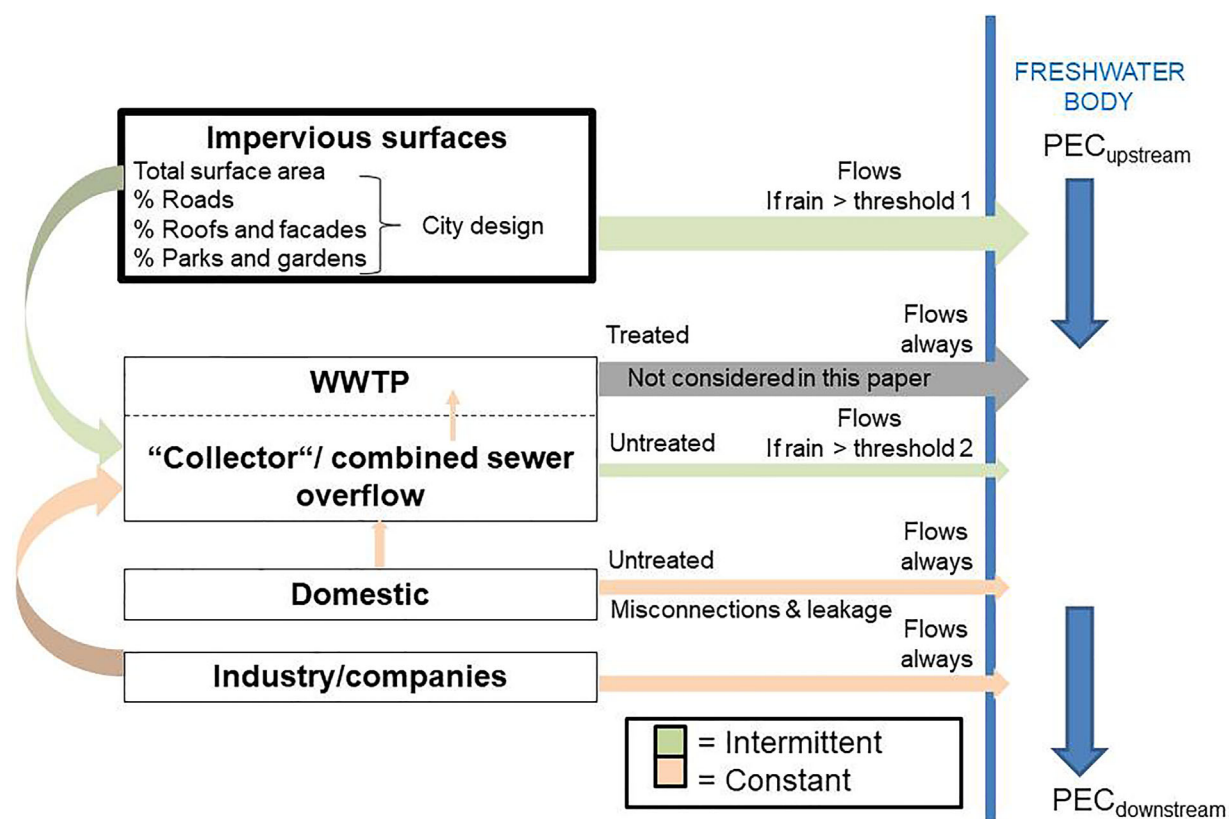


FIGURE 1: Key urban pollutant sources and pathways. PEC = predicted environmental concentration; WWTP = wastewater-treatment plant.

and metals (Göbel et al. 2007; Loganathan et al. 2013). These studies provide a useful overview of the range of contaminants arising from highways and highlight concerns regarding contaminants in particulate form that can lead to high concentrations of metals and organics in river and stream sediments, where they will accumulate and persist but may not be in a bioavailable form. The organic compounds that have been investigated in most detail are the PAHs, and high concentrations of both parent and alkylated PAHs have been observed in sediments.

In buildings and other construction associated with urbanization, structures such as roofing, gutters, facades, decking, cladding, and fencing may weather to release a variety of contaminants. For example, metal objects may leach metals, wooden structures may leach wood preservatives and paint pigments, roofing and sealing materials may leach organics, while plastic building materials may leach plasticizers and flame retardants. In the green space (yards, gardens, fields, forest, boulevards, and parks) and paved urban areas, the use of fertilizers and pesticides may lead to runoff containing a variety of agrochemicals.

The topic of contaminants in urban storm water and other direct emissions to receiving waters is gaining increased attention, as reflected in the recent review by LeFevre et al. (2015). The effect of urbanization on stream ecosystems (hydrology, habitat, chemistry) has also been identified as a research priority in the United States and has been the focus of a recent national-scale study (Coles et al. 2012). That study found that ambient concentrations of nitrogen, chloride, insecticides, and PAHs increased with urban development. Further, loss of sensitive aquatic biota, that is, decrease in abundance of Ephemeroptera (mayflies), Plecoptera (stone flies), and Trichoptera (caddis flies), was observed to be the most consistent biological response to urban development. However, it should be noted that these effects may also be attributed to nonchemical stressors, for example, perturbed flow regimes, temperature increases, high suspended loads, and habitat alterations in addition to multiple chemical stressors.

The present study is an output of a SETAC Pellston workshop<sup>®</sup>, “Simplifying Environmental Mixtures—An Aquatic Exposure-Based Approach Via Exposure Scenarios,” which was held in March 2015 with the aim of looking at 1) whether a simplified scenario-based approach could be used to help determine if mixtures of chemicals posed a risk greater than that identified using single chemical-based approaches, and 2) if so, what might be the magnitude and temporal aspects of the exceedances, so as 3) to determine whether the application of the approach provides insights in mixtures of greatest concern and the compounds dominating those mixtures (prioritization). The aims of the present study were to investigate these questions using standard urban aquatic exposure models and scenarios. Associated articles adopted the same working hypothesis to evaluate the risk of chemical mixtures from 2 other sources: municipal WWTP discharges, which may include both domestic and industrial influents (Diamond et al. 2018) and agriculture-based land sources (Holmes et al. 2018), while a combination of 3 scenarios was generated to evaluate the potential utility of the approach for water systems downstream of combined land uses (Posthuma et al. 2018).

## PREDICTING ECOLOGICAL IMPACT

### *Ecotoxicity and species sensitivity*

Ecosystem integrity is typically assessed by the occurrence of characteristic species, appropriate biodiversity, and proper functioning in terms of nutrient cycling and energy flux. A rather simplistic but widely applied and justifiable paradigm in ecological risk assessment is that an ecosystem is protected when species belonging to that system are able to survive and reproduce (US Environmental Protection Agency 1992, 1998). Thus, ecological risk can be defined as the proportion of species for which well-being is likely impaired. Over the past 40 yr, ecotoxicologists have generated sensitivity data for only a few thousand species in combination with a few thousand chemicals. In most cases, these data were produced by conducting single-species toxicity experiments under controlled conditions in the laboratory. These data show that species differ in sensitivity toward a single toxicant, which may be the result of differences in life history, physiology, morphology, and behavior. This observation led to the use of empirically derived statistical distributions to describe this variation. Species sensitivity distributions (SSDs) now have a prominent role in ecological risk assessment. The basic assumption of the SSD concept is that the sensitivities of a set of species can be described by a defined statistical distribution. The ecotoxicological data are seen as a sample from this distribution and are used to estimate the shape parameters of the SSD. The statistical distribution is used to calculate a concentration that is expected to be safe for most species, which can in turn be used to set an environmental quality standard (EQS). In addition, the SSD can be used to estimate the potentially affected fraction (PAF) of species at any given concentration of a chemical (Posthuma and de Zwart 2014).

### *Mixture toxicity*

Most ecotoxicological studies focus on exposure and effects of single substances. However, it is well recognized that organisms in a polluted environment are generally exposed to many pollutants. Most regulatory methods for the management of chemicals are based on single-substance risk evaluations, in combination with some basic toxicological models to predict the joint effect of chemical mixtures on single species.

Methods for estimating mixture toxicity have recently been evaluated by the European Commission (Scientific Committee on Health and Environmental Risks 2012). Under the assumption of concentration additivity, the model of toxic units is frequently used in ecotoxicology for mixtures of similarly acting chemicals. It represents the ratio between the concentration of a component in a mixture and its toxicological acute (e.g., median lethal concentration) or chronic (e.g., long-term no-observed-effect concentration or 10% effect concentration [EC10]) endpoint. The aggregated toxic unit of a mixture is the sum of toxic units of individual chemicals ( $\Sigma$ toxic unit) and represents a metric for potential mixture effects. For mixtures of chemicals with different modes of action, the effects on different endpoints and/or different target organs can be estimated directly from the

probability of responses to the individual components (response additivity). Both the concentration and response addition concepts are based on the assumption that chemicals in a mixture do not influence each other's toxicity; that is, they do not interact with each other at the biological target site. Both concepts have been suggested as default approaches (e.g., Scientific Committee on Health and Environmental Risks 2012) or reference points (Könemann 1981) in regulatory risk assessment of chemical mixtures. Predicting the toxicity of a mixture of toxicants could build on observations that both concentration and response addition could be useful to predict the overall response, depending on the assumed toxic mode of action of the mixture constituents (Altenburger et al. 2000; Faust et al. 2003). In reality, however, chemical mixtures are rarely composed of only similarly or of only dissimilarly acting substances. The proposed protocol for predicting the toxicity of complex mixtures consists of a mixed 2-step approach (de Zwart and Posthuma 2005). In the first step, the protocol requires evaluation of the concentration addition responses to groups of substances with similar toxic mode of action. In the second step, the protocol requires evaluation of the response additive effect of all of these groups with different toxic mode of action. The method to derive mixed-model estimates of ecological mixture impacts—expanding on derivation of toxic pressures from concentrations via SSDs—is described in detail in de Zwart and Posthuma (2005). For the present study, the overall toxic pressures of environmental mixtures are evaluated according to both the concentration addition model for all compounds ( $\Sigma$ toxic unit) as well as the mixed model requiring information on the mode of toxic action (multisubstance PAF of species [msPAF]).

## CHEMICAL SIGNATURES

### General description of urban pollution sources and processes

Storm water runoff, combined sewer overflows, WWTPs, and increased presence of industry, hospitals, and modified receiving waters (channelization, controlled erosion, low-head dams, etc.) all result in unique chemical and water flow signatures that are quite different from the agricultural and domestic mixture scenarios. In the urban environment nearly all receiving water bodies are highly human-modified. The diverse nature of all of the typically urban sources of exposure makes it very hard to distinguish a generally applicable common denominator in the urban discharge scenario. Intuitively, however, urban discharges will be dependent on a number of socioeconomic factors: 1) human population density, 2) economic status, 3) main economic activities (urban agriculture, commercial, industrial, service-oriented), 4) infrastructural quantity (particularly wastewater collection and treatment systems), and 5) infrastructural quality (age, maintenance, technical design). In parallel to socioeconomic factors, urban discharges will also be strongly influenced by geographical factors: 6) surface area, 7) climate, 8) terrain slope and soil permeability (runoff vs infiltration), and 9) ratio of open versus impervious area. Finally, regulations such as restrictions on the type and amount of pesticide usage on buildings and agricultural areas, ban of compounds such as lead

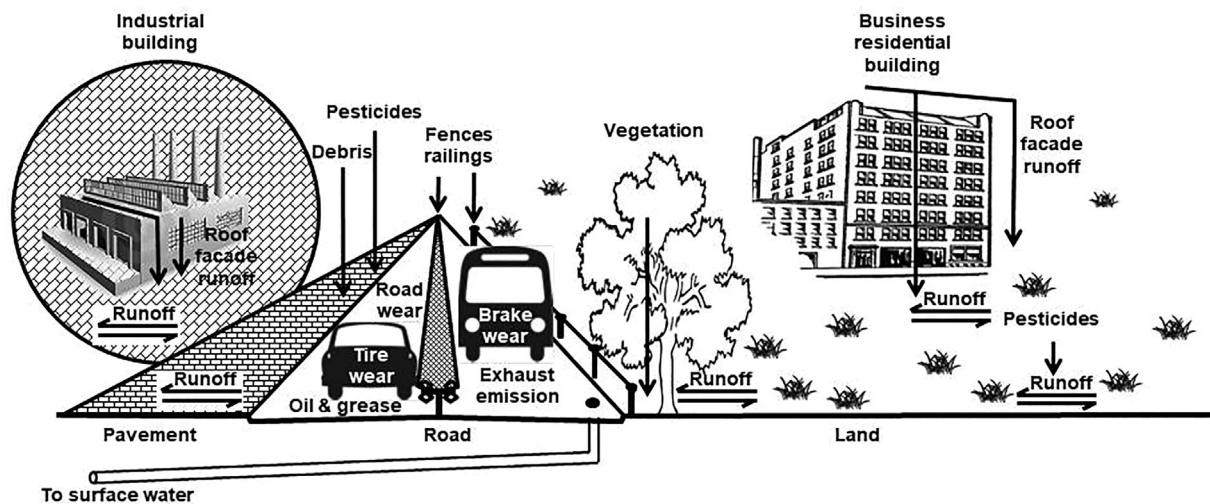
in petrol, and stricter chemical controls can modulate the composition in different countries. Such factors can be visualized and taken into account by analyzing multiple layers of geographic information system data (Kapo et al. 2014).

### Urban diffuse runoff discharge signature

The urban scenario of diffuse inputs is predominantly related to runoff from impervious surfaces. This also includes storm water overflows from combined and rainwater-only sewer systems (Figure 2). Various types of chemicals can be expected to occur in these diffuse sources to receiving waters. On the basis of the large number of chemicals globally registered, it could be envisaged that there is potential for considerable numbers of chemicals to enter the urban environment. However, to date only a few hundred chemicals have been detected in monitoring of the urban water environment, and these are typically categorized in a few main groups according to their uses and applications, as shown in Table 1.

Although urban storm water monitoring has been conducted for many years (e.g., reviews by LeFevre et al. 2015; Loganathan et al. 2013), only a modest number of studies were identified that have reported detailed contaminant measurements in urban runoff. We were able to obtain a characteristic composition of urban runoff in terms of 90th-centile concentrations for 77 different substances, from a variety of European and United States sources (see Table 2; Supplemental Data, Table S-X1). For these substances we were also able to identify their most likely originating processes/sources and their maximum contribution to runoff toxicity. Our focus was on dissolved pollutants based on the assumption that they are more mobile and bioavailable than particle-borne contaminants (LeFevre et al. 2015). For prioritization of chemical contributions to net toxicity, 90th-percentile concentrations of all 77 individual compounds were converted into 2 metrics for expressing mixture toxicity of the runoff waters. First, results are presented as toxic units calculated using the geometric mean of all acute EC50 values over species, with higher toxic unit values implying higher relative contributions and values exceeding 1 implying acute EC50 effects for more than 50% of the species. Second, results are expressed as mixture toxic pressures, derived using the msPAF procedure described in *Mixture toxicity*.

The present compilation relies heavily on 3 major studies, the United Kingdom Water Industry Research monitoring data set (Comber et al. 2015; WCA Environment 2014) and the studies of urban storm runoff in San Diego (Tetra Tech 2010) and in Sacramento and San Francisco (CA, USA; Ensminger and Kelley 2011). The UK results indicated that urban runoff generally contained high concentrations of nutrients (nitrogen and phosphorus), metals, and PAHs, often at concentrations considerably in excess of their Water Framework Directive adopted EQS values without consideration of dilution in the receiving water. The United Kingdom has recognized that urban runoff is a complex issue and that resolving this problem is complicated for several reasons. Furthermore, there is no established planning methodology for agreeing who needs to do what, where, and when (and who should pay) to clean up



**FIGURE 2:** Schematic illustration of the sources of diffuse urban runoff.

water bodies suffering from urban diffuse water pollution; and a separate strategy to tackle urban diffuse water pollution has not been published (Priestley 2015). The San Diego study focused on a similar suite of metals and PAHs to those of the UK study but also included an extensive list of organochlorine, organophosphorus, and synthetic pyrethroid pesticides (Tetra Tech 2010). Elevated concentrations of copper, zinc, and synthetic pyrethroid pesticides were found in the storm drain system, especially during rain events after prolonged dry weather periods. Ensminger and Kelley (2011) studied pesticides in storm drain outfalls and urban creeks in the Sacramento and San Francisco Bay areas. They also found that “first flush” events after a dry period had the highest pesticide concentrations, with the pyrethroid insecticide bifenthrin having the greatest potential toxicity to sensitive aquatic organisms. Table 2 shows the concentrations in runoff and toxic pressure of those toxicants

**TABLE 1:** Main chemical pollutants observed in the urban water environment (After Göbel and others 2007).

Pollutant group	Substances
Suspended solids	Suspended solids may consist of clay, silt, airborne particulates, colloidal organic particles, plankton and other microscopic organisms
Biodegradable organics	Composed principally of proteins, carbohydrates, and fats, biodegradable organics are measured most commonly in terms of Biological Oxygen Demand
Nutrients	Nitrogen and phosphorus
Priority pollutants	About 100 organic or inorganic compounds selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity or high toxicity
Poorly biodegradable organics	Alkanes, Aromatics, Chlorinated alkanes, Chlorinated aromatics, Polycyclic Aromatic Hydrocarbons (PAH), Substituted PAHs, Pesticides, Phenolic compounds, Petroleum hydrocarbons, Pesticides, Pharmaceuticals
Heavy metals	Copper, Cadmium, Chromium, Lead, Mercury, Nickel, Tin, Zinc
Dissolved inorganics	Salts, Oxygen

where toxic unit  $\geq 1\%$ , which was selected as a criterion to deselect chemicals that may be present but that have only minimal ( $<1\%$ ) contribution to toxicity. Of the 77 substances that are characteristic for urban runoff, only 10 contributed to overall ecotoxicity before the runoff water is diluted in the receiving water body. By far the toxicologically most prominent compounds were copper (probably originating from roofing, gutters, and brake pads) and a number of pyrethroid insecticides. Compounds such as herbicides and pharmaceuticals did not significantly contribute to the overall aquatic toxicity.

The signature of chemicals from urban runoff can also be estimated by use of release estimation techniques from point and diffuse sources, when no direct measurement data of runoff are available. Release estimation is generally done by multiplying the tonnage of a target chemical used by the corresponding emission factors that are expressed as a fraction. Supplemental Data, Table S-X2, summarizes emission factor information available in several documents, which provide some screening estimates of chemical releases from construction materials. Emission scenario documents have summarized release estimation techniques of chemicals from various industrial products (Organisation for Economic Co-operation and Development 2014). Default emission estimates for substances with wide dispersive use are also provided by the European Chemicals Agency (2015).

### Industrial point source discharge signature

One potentially important contributor of chemical stressors to the urban discharge scenario is industrial point sources. These inputs can be either direct or indirect (Figure 1). Direct industrial discharges include industrial process streams as well as runoff collected from industrial sites that are routed to on-site drains. Often, discharges are subject to necessary treatment prior to discharge, to meet regulatory permit requirements. Alternatively, indirect industrial discharges are first routed to an off-site municipal wastewater-treatment works prior to release to

**TABLE 2:** Quantitative measurements of concentrations in runoff for the ranked top 10 of substances with a toxic unit  $\geq 0.01$ , together with a pseudo mode of action indication, geometrically averaged toxicity and derived toxic pressure estimates per substance and for the mixture

Origin	Contaminant group	Contaminant	Pseudo Mode of Action	Concentration 90% ( $\mu\text{g/L}$ )	Avg. EC50 ( $\mu\text{g/L}$ ) (geometric mean)	Toxic pressure (PAF)	Concentration/Average over species	Toxic unit =	% of $\Sigma$ toxic unit	Reference
Brake pads, roofing	Metal	Copper (dissolved)	Cu	33.0	183	20%	0.18	0.18	43%	(WCA 2014)
Galvanized metal structures	Metal	Zinc (dissolved)	Zn	84.0	1903	7%	0.04	0.04	10%	(Tetra Tech 2010)
Garden, park, building	Insecticide	Deltamethrin	Pyrethrin	0.084	2	13.7%	0.04	0.04	10%	(Tetra Tech 2010)
Garden, park, building	Insecticide	Bifenthrin	Pyrethrin	0.03	1	11.4%	0.03	0.03	7%	(Ensminger and Kelley 2011)
Combustion	PAH	Benz(a) anthracene	Non polar narcosis	0.192	10	0.7%	0.02	0.02	5%	(Tetra Tech 2010)
Garden, park, building	Insecticide	Permethrin	Pyrethrin	0.202	12	7.8%	0.02	0.02	4%	(Tetra Tech 2010)
Metal structures	Metal	Iron (dissolved)	Fe	1106.2	66298	0.4%	0.02	0.02	4%	(WCA 2014)
Metal structures	Metal	Aluminum (reactive)	Al	24.2	1925	0.5%	0.01	0.01	3%	(WCA 2014)
Sewage, buildings, surfactants	Plasticiser	Nonylphenol 1 ethoxylate (NP1EO)	Non polar narcosis	4.165	525	0.1%	0.01	0.01	2%	(WCA 2014)
Combustion	PAH	Fluoranthene	Non polar narcosis	0.887	136	0.1%	0.01	0.01	2%	(Tetra Tech 2010)
							$\Sigma$ toxic unit = 0.38		Sum % toxic unit = 100.0%	
							msPAF mixed = 42.5%			

PAF = potentially affected fraction; msPAF = multisubstance potentially affected fraction; PAH = polycyclic aromatic hydrocarbon.

receiving waters. These streams are often required to meet less stringent pretreatment standards that are intended to prevent biological treatment processes from being inhibited by such inputs.

Many point source industrial discharges are characterized by country- or region-specific Pollutant Release and Transfer Registers (PRTRs). A PRTR is a database or inventory of potentially hazardous chemical substances and/or pollutants released to air, water, and soil and transferred off-site for treatment or disposal. A global website is available that provides links to PRTRs for over 30 countries (United Nations Economic Commission for Europe 2015). These databases serve as valuable resources to identify the nature, amount, and geo-spatial characteristics of site-specific, industrial chemical stressor inputs to urban waterways. Further, different industries are typically required to document emissions for certain substances relevant to that sector.

A wide range of target chemicals are reported in national/regional PRTRs; however, there is no common listing (Organisation for Economic Co-operation and Development 2014). The Toxics Release Inventory program of the United States covers the largest number of chemicals (682 chemicals). In total 1084 chemical substances (including some complex mixtures) are covered by whole PRTR in the world. Approximately 100 chemicals are covered by 4 or more of the PRTRs. Guidance has recently been published on elements needed for the design of a global PRTR (Organisation for Economic Co-operation and Development 2014).

Because of the relatively wide coverage of contaminant chemicals compared with other information sources, PRTR could provide potential input information regarding release of chemicals from industrial and, when available, diffuse sources relating to urban discharges.

In the case of the European PRTR, 9 broad industry sectors are identified: 1) energy, 2) production and processing of metals, 3) minerals industry, 4) chemicals industry, 5) waste and wastewater management, 6) paper and wood production and processing, 7) intensive livestock production and aquaculture, 8) animal and vegetable products from the food and beverage sector, and 9) other miscellaneous activities. For each sector, different industry activities are specified with a corresponding list of indicative sector-specific pollutants. Supplemental Data, Table S-X3, provides a summary of all of the water pollutants that are included in the European PRTR. A subset of this list will be reported by different industry sectors when certain activities trigger emission thresholds (European Commission 2006).

To assess the relative importance of various stressors by industry sector, the total emissions released to water for each substance by a given sector can be normalized by the corresponding geometric average EC50 over species. For illustration, this analysis is provided in Supplemental Data, Table S-X4, for the chemical and paper/wood processing sectors using the 2012 European PRTR emission inventory. Results show differences in stressor profiles between these sectors. For example, the chemical industry contributes more chlorinated solvent and hydrocarbons and more metals than the paper industry. Nevertheless, for both sectors, chlorides appear to be

the key stressor. Other contaminants that appear to pose the greatest toxicity concern include fluorides and ammonia. The remaining listed contaminants appear to be much less important in driving risks to aquatic life. This “stressor type” analysis can be applied to other sector-specific emission inventories over time to help define signatures of priority chemical stressors for specific industry sectors. Furthermore, this approach can also be applied on a more local scale using facility-specific data for the receiving water of interest. An example of a European EPTR query that describes wastewater emissions from an urban sewage-treatment works treating industrial wastewaters is described in Supplemental Data, Appendix S1.

In addition to PRTR data, industry-specific monitoring programs may be helpful for characterizing emission profiles and associated risks to aquatic biota. Supplemental Data, Table S-X5, provides a sector-specific example with a compilation of contaminants in 55 European refinery effluents that are discharged to freshwater bodies (CONCAWE 2010). Although the absolute concentrations and associated site-specific risk to aquatic biota will depend on the extent of local dilution, the relative contribution of different components to mixture toxicity can be readily determined using such data. For example, more detailed characterization of the hydrocarbon composition of refinery effluents has been investigated using comprehensive 2-dimensional gas chromatography. This analysis has been used to describe hydrocarbon blocks in effluents, which when coupled to quantitative structure–activity models for aquatic toxicity and site-specific dilution can be used to estimate local risks of these constituents (CONCAWE 2013). Whole-effluent assessment provides a complementary approach to chemical characterization for assessing potential risks posed by industry effluents, but this topic is beyond the scope of the present study.

## METHODS FOR ESTIMATING AN URBAN EXPOSURE SCENARIO

The overview of emission inventories, measured data, and (emission) model approaches combined with 2-effect assessment approaches clearly showed that there is a variety of urban emissions but also a clear option to prioritize chemicals within the emitted mixtures that potentially contribute most to ecotoxic effects. When this is further elaborated in an exposure assessment and effects framework, this may support the establishment of a tiered approach for determining risks associated with the most probable mixtures by which organisms living in an urban water body might be affected. In addition, the method should enable prediction of the potential adverse effect of introducing a new compound to the market into the existing “urban mixture.” For the purposes of demonstrating how a modeling approach might be developed, we describe a simple model to illustrate exposure assessment for both separate and combined sewer systems.

The concept is that rain falling on an urban area will contribute runoff (both flow volume and chemical composition) to a receiving water body depending on the type of urban surface on which it falls. The chemical composition that is delivered to the receiving water is a mass balance in the runoff from these

contributing surfaces. This type of framework has been applied previously in a risk assessment for urban areas (Mitchell et al. 2005) and an urban runoff-management scenario (Ellis et al. 2012). It is based on the event mean concentration concept (EMC; Kayhanian et al. 2007) in which different surface types (e.g., roads, roofs, green spaces) are assumed to have a characteristic mean chemical concentration (for a range of contaminants) that is the same for each runoff event and the mass of each contaminant is determined by the runoff volume of the rainfall event.

In this approach, the mass ( $M$ , in grams) from a particular urban surface type,  $i$ , for compound  $j$  is given by

$$M_i = V_i \times \text{EMC}_{i,j} \quad (1)$$

where  $V_i$  (cubic meters) is the total runoff volume during a rain event from that type of surface and  $\text{EMC}_{i,j}$  (grams per cubic meters) is the event mean concentration (the average concentration of compound  $j$  measured in runoff during rainfall events delivering the compound from this surface type).  $V_i$  is given by

$$V_i = I_i \times P \quad (2)$$

where  $P$  (cubic meters) is the total rainfall volume falling on the urban area and  $I_i$  is a factor quantifying the fraction of that rainfall that will reach the receiving water body (accounts for the different permeabilities of the surfaces). The total flow rate (cubic meters per day) of urban runoff reaching the river system is then the sum of all of the individual flow volumes divided by the duration of the rainfall event. The concentrations of the individual chemicals in the runoff water from the urban surfaces is the average of the EMC values for each surface for each chemical weighted by the volume of water leaving each of those surface types. This defines the expected mean exposure mixture profile for urban runoff.

The concentration of the chemicals in the receiving water ( $RC$ , grams per cubic meters) coming from all ( $n$ ) urban surface types is given by

$$RC_i = T \times \frac{1}{F} \sum_i^n M_i \quad (3)$$

where  $F$  is the flow rate in the receiving water (equal to the sum of the flow upstream and the volume over the rainfall event during the time period,  $T$ , cubic meters per second) and  $T$  is the duration of the runoff(s). Integrating across all of the compounds from all sources gives the mixture exposure from hard surfaces in urban areas in a receiving water body.

In combined systems, the rainwater runoff from the urban surfaces is routed through the domestic wastewater sewer system, which is addressed in the companion paper (Diamond et al. 2018). However, a fraction of this water will in certain circumstances still enter a water body directly. In that case its chemical profile will reflect the sewer. Urban runoff will only reach the sewage-treatment works during rainfall events, and, as mentioned previously, the volumes relative to domestic sewage input are highly dependent on infrastructure and other factors. If

those rainfall events are of sufficient intensity, the capacity of the works to receive the storm water volume will be exceeded and the resulting mix of chemicals in untreated effluent and urban runoff will enter the receiving water course. The chemical signature of the overflow reaching the receiving water should theoretically be calculable by mass balance. An example for chemical  $j$  is given by

$$CSOC_j = \frac{\sum_i^n M_i + SEF \times SEC_j}{V_T + SEF} \quad (4)$$

where,  $CSOC_j$  is the concentration of chemical  $j$  in the combined flow reaching the river,  $SEF$  is the (dry weather) flow from the sewage-treatment works,  $V_T$  is the total flow from the urban areas, and  $SEC_j$  is the concentration of the chemical  $j$  in sewage-treatment works influent (untreated).

## VERIFICATION OF PREDICTED ECOLOGICAL IMPACT WITH OBSERVED IMPACT DATA

The River Invertebrate Prediction and Classification System (RIVPACS) was established in the United Kingdom for use in the biological classification of national river pollution surveys. The UK implementation of RIVPACS is based on 85 different taxa taxonomically determined up to the family level. These taxa cannot be assumed to be sensitive to any particular chemical toxicant because they were initially selected for their difference in oxygen requirements. The data for the UK reference sites were established in the early 1970s and are regularly verified. Prediction of the presence or absence of particular taxa in relation to unstressed reference sites allows several metrics to be calculated (Walley and Hawkes 1996). The results of the assessment are often reported as the ratio of locally observed numbers of taxa to expected numbers of taxa derived from otherwise similar reference sites. This ecological metric can be interpreted as a loss of biodiversity, along with the loss of sensitive Ephemeroptera, Plecoptera, and Trichoptera, and can be compared against the 2 metrics of mixture chemical exposure ( $\Sigma$ toxic unit and msPAF).

For other geographies it is possible to apply the same RIVPACS-like observed-to-expected methodology to determine the local loss of taxa, after identifying the taxa diversity of suitable reference sites (Hawkins et al. 2000). These field approaches can be used to verify whether the predicted biological impacts based on exposure to concentrations of multiple chemical stressors are indeed reflected in an observed loss of field biodiversity (de Zwart et al. 2006).

## DISCUSSION

### Chemical fate/bioavailability

Based on preliminary analysis, copper and zinc are identified as 2 substances that rank high on the toxic unit/PAF (risk list) for the urban discharge scenario. Yet, it is well recognized in the literature that physicochemical characteristics of the receiving



water play a great role in modifying toxicity. Therefore, it should be recognized that the ranking calculations in the urban fingerprints are first-tier because these do not take the bioavailable fraction in the water compartment into account. However, higher-tier tools and models are available to refine risk priorities (de Zwart et al. 2008), and thoroughly validated bioavailability correction models exist for metals such as copper and zinc (Van Sprang et al. 2009) and are already being used in a regulatory context (European Commission, European Copper Institute 2009).

### **Site-specific differences in urban sources/chemical signatures**

It is very challenging to develop a generic urban exposure scenario because many parameters vary over different scales (economic status, industrialization, agricultural practice, political regulations, infrastructure type and age, population density, climate, hydrology, soil type). For example, in Switzerland wastewater overflow is estimated to be below 5% (Bürge et al. 2006), whereas in other countries overflow may be much higher and/or connection to sewers and WWTPs is less. It is also important to recognize that in many developing countries a whole host of factors could be leading to a deterioration of urban water quality. These factors include poorly developed infrastructure for wastewater collection and treatment, poor waste handling, lack of chemical controls, and poor environmental awareness.

Runoff from buildings is influenced not only by rain intensity and frequency but also by the age of buildings. Aged materials show approximately 1 to 2 orders of magnitude lower concentrations in the runoff (Burkhardt et al. 2009). Restrictions or prohibition of pesticides in different countries can also have significant influence on urban runoff composition.

As illustrated in Figure 1, runoff occurs mainly after rain events, and the concentrations in the runoff can change considerably over such an event. Accordingly, the concentrations listed in Table 2 represent a snapshot and are not representative of the whole range of possible runoff situations. There are significant challenges in developing a realistic picture of the concentration dynamics in runoff and receiving rivers. For example, although high-frequency sampling can help resolve some of the issues (Wittmer et al. 2011), this is both time-consuming and cost-intensive. Modeling efforts that take release processes and hydrological conditions into account can help overcome this problem and may enable a simulation of various climate conditions (Wittmer et al. 2010), but these require further development.

The use of passive sampling techniques to provide time-averaged, dissolved concentrations in water can provide valuable information on chemicals present in water bodies. This method has been applied in urban environments (Moschet et al. 2015; Page et al. ; Roig et al. 2011) and is a promising, inexpensive advance for use in quantifying urban discharge scenario sources and resulting receiving water exposures. Information gathered from such programs may well extend the list of chemicals detected in water bodies and their potential contribution to adverse effects. However, sampling rates for

passive samplers under strongly fluctuating flow regimes still need to be evaluated more rigorously to allow quantitative assessment (Moschet et al. 2015).

### **Limitation of available analytical methods**

Only a limited suite of substances is analyzed in most urban storm water and industrial effluents. This is a general problem for any chemical aquatic monitoring effort (Muir and Howard 2006). Most monitoring programs, including those summarized in Supplemental Data, Tables SX-1, SX-3, SX-4, and SX-5, have focused on chemicals for which established analytical methods are available; and thus, a suite of metals, unsubstituted PAHs, and widely used pesticides are most commonly analyzed. However, modern societies use many more chemicals in materials exposed to outdoor environments that can also be released and contribute to the toxicity including flame retardants, ultraviolet inhibitors, anticorrosive agents, surface treatment chemicals, and so on. Even for the comparatively well-studied pesticides, monitoring programs usually only get glimpses of the actual contamination in a water body, as reported by Moschet et al. (2014). They demonstrated that only 55 to 65% of the risk could have been detected with a standard set of monitoring analytes. This shows that monitoring data can only be one pillar in a characterization of chemical contamination in surface waters. Therefore, exposure modeling based on chemical use data and emission factors as well as biologically based monitoring methods (bioassays as well as diagnostic ecological analyses) should be integrated into site assessments.

### **Ranking based on toxic unit summation versus ranking based on msPAF**

One of the key notions of the numerical analyses is the clear ranking of the relative contributions of compounds to ecotoxicity within samples. These results were obtained with both  $\Sigma$ toxic unit and msPAF metrics. When comparing the msPAF result with the mixture toxicity prediction based on the toxic unit approach ( $\Sigma$ toxic unit = 0.38 in Table 2, meaning no risk to any species), it becomes obvious that the toxic unit summation based on the geometric mean of the single-species EC50 values (i.e., the mixture 50% hazardous concentration value predicted by concentration addition) give different estimates of the mixture toxicity. Whereas in terms of msPAF the acute median lethal and effect concentrations are exceeded for nearly half of the species in the SSD (42.5%), the mixture concentration would have to be more than doubled to reach the same predicted effect on the community in terms of  $\Sigma$ toxic unit. This is a surprising result because concentration addition predictions have been proposed as a “reasonable worst case approach” (Berenbaum 1985) usually predicting a slightly higher response than response addition or a mixed model. This discrepancy can be explained by the rather shallow slope of the SSD curves. Drescher and Boedeker (1995) have shown that shallow curves are indicative of numerically similar predictions, with both the response and concentration addition models predicting higher toxicity. For the normal distribution model that is usually used for SSD curve

fitting, shallow slopes with a standard deviation  $>1.0$  are prone for concentration addition giving lower mixture toxicity predictions than response addition or the mixed model. The slopes of the SSDs for the 3 pyrethroids in Table 2 are estimated at a toxic mode of action average of 1.25, and the remaining substances show slopes that are rather shallow (range 0.8–1.6). This indicates that with rather shallow SSDs a ranking based on contribution to msPAF might be more conservative than the relative contribution to  $\Sigma$ toxic unit when trying to identify the substances with the highest potential for contributing to the mixture toxicity. This is in line with simulations published recently by Gregorio et al. (2013), who also recommended caution when using concentration addition as a default approach on SSDs with rather shallow slopes. Although 2 methods were used for prioritization, both methods resulted in very clear prioritization rankings, which can support risk-management priorities.

### Data gaps for SSD determination

When deriving EQSs based on SSDs within the European Union's Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) framework or standard setting according to the technical guidance document (European Commission 2011), the following minimum validity criteria must be fulfilled: at least 10 toxicity values for different species from 8 specified taxonomic groups, with toxicity data log-normally distributed. The Water Framework Directive technical guidance document (European Commission 2011) explicitly strives to harmonize both Water Framework Directive and REACH regulations in terms of risk calculations and standard setting. These quality criteria have been established to provide a "level playing field" in setting protective, generic concentration standards when evaluating compounds for registration and allowing them to be produced and used. Obviously, the higher the number of data, the more statistically robust an SSD (and its outputs) will be.

Of the 10 substances listed in Table 2, only 2 (copper and zinc) fulfilled both standard-setting requirements. Fluoranthene fulfills the data requirements, but the data failed the test on log-normality. Data on more than enough species were available for deltamethrin and bifenthrin, but they were lacking one and 2 taxonomic groups, respectively. The rest of the substances failed the standard-setting criteria for SSDs because toxicity values were available for fewer than 10 species. Because in our example copper, zinc, deltamethrin, and bifenthrin are the substances with the highest impact on the predicted mixture toxicity as well as the substances with the most robust SSDs, the effect of data gaps for the other substances may have only a minor impact on the analysis. However, the high data requirements might be a recurring issue with predicting mixture toxicity based on SSDs. One solution is to apply mechanistically based effect models that are based on mode of action considerations. For example, the recent development of a target lipid model that uses poly-parameter linear free energy relationships by Kipka and Di Toro (2009) can be broadly used to derive SSDs for a wide range of nonspecific-acting nonpolar and polar organic chemicals.

It should be kept in mind that the assessment of local ecological risk may demand less stringent SSD-derivation

validity criteria than the derivation of globally applicable EQSs. This is particularly true in initial tiers of risk assessment where the use of conservative assumptions may be sufficient to indicate lack of potential risk. This approach has recently been implemented in The Netherlands, where quantitative impact assessments for mixtures of chemicals in water systems is supported by SSD modeling for more than 2000 compounds, whereby the quality and robustness of each of the SSDs are provided to the assessor (Posthuma et al. 2016).

### Nonchemical stressors related to urbanization

Streams that drain urbanized catchments are often degraded in terms of the ecology they support, and this has been termed the "urban stream syndrome" (Meyer et al. 2005). Common characteristics of this syndrome are a flashier hydrograph, elevated concentrations of nutrients and contaminants, altered channel morphology, and an aquatic community with reduced biodiversity that is dominated by more tolerant species. A recent review of the syndrome (Booth et al. 2016) concluded that, although the mechanisms driving it were complex and interactive, urban storm water delivered to streams by hydraulically efficient drainage systems was identified as a primary large-scale contributor. Storm sewer overflows, wastewater-treatment works, and legacy pollutants also act in these systems and can obscure the direct effect of the urban runoff (Walsh et al. 2005). In a recent study it was shown that a landscape measure of connected imperviousness, weighted for proximity to the stream, was a good indicator of biotic health and a better indicator than a suite of hydrological measures (Burns et al. 2015). It was postulated that this was because it accounted for both hydrological and water quality stressors.

## RECOMMENDATION

The present study highlights the need to recognize the variable and intermittent nature of the urban discharge scenario and linkage to landscape attributes. The further use of geographic information system-based analysis tools is encouraged for tackling this challenge at local and regional watershed scales. In addition, use of integrative passive sampling methods offers promise for better defining various urban sources and exposures. However, recognizing the limitations of analytical methods for the wide range of potential contaminants that may occur in urban water bodies, modeling of chemical exposures as well as biologically based and effect-directed analysis approaches should be used to complement chemical monitoring efforts (Brack et al. 2016). Recent research has explored alternative strategies for ecological risk-assessment purposes. Time-integrative passive sampling combined with toxicity profiling is showing promise as a cost-effective effects-based approach for water quality assessment (Hamers et al. 2016). The primary advantage over existing methods employed under current regulations (such as the European Union's Water Framework Directive) is that this provides an opportunity to include the integrated toxic potency of passively sampled

complex mixtures in addition to assessing the chemical and ecological status. Along those lines 10 recommendations including passive sampling and effect-based tools to improve monitoring and to strengthen comprehensive prioritization, to foster consistent assessment, and to support solution-oriented management of surface waters have recently been compiled (Brack et al. 2017). Such approaches, if further validated, could help improve the interpretation of potential effects in urban water bodies. In the meantime, the use of msPAF methodology provides a valuable framework for assessing the relative importance of multiple chemical stressors associated with the urban discharge scenario. Finally, while the present effort has focused on chemical stressors potentially impacting urban waterways, further work is needed to understand the role of nonchemical stressors in contributing to ecological risks in urban waterways.

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