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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 modelling 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 on the role of non-chemical stressors in such highly modified urban water bodies.

Keywords: mixtures, predictive toxicology, risk assessment, water quality

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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). While 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 related 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, as availability of drinking water and transportation of goods via shipping historically led to settlement and expansion. Although the 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 and others 2009) allowing for a better approximation of mixture impacts than the so far common per-chemical approaches. Amongst 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 starting point. This approach can be utilized using measured concentrations, but it can also be hypothesized that different forms of land-use imply different, but typical, chemical compositions.

Exploring this for urban run-off emissions, there are several major sources of contaminants which can enter water courses 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 and others 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 none 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 Waste Water Treatment Plants (WWTP); (3) untreated domestic discharges through misconnections and leakage; and (4) industrial discharges not subject to wastewater treatment. The former two sources are transient and rainfall-dependent while the later are constant sources.

Pressure to conserve water resources can in itself lead to additional inputs to the urban environment. For example, the re-use of greywater in urban areas, especially for landscape and parkland irrigation (including for median strips and roadside planters) is increasing. Greywater is defined as water from all domestic sewerage excluding wastewater generated by toilets and bidets (Maimon and others 2010). Its composition is highly variable due to 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 greywater use challenging (Jefferson and others 2004).

Nevertheless, greywater remains a potential source of contaminants which will have received limited, if any, treatment apart from natural attenuation processes.

Runoff from impervious and semi pervious 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 tyre wear products such as suspended solids, black carbon, nanomaterials and metals (Göbel and others 2007; Loganathan and others 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 where high concentrations of both parent and alkylated PAHs have been observed in sediments.

In buildings and other construction associated with urbanisation, 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 fertilizers and pesticides may lead to the 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 US and has been the focus of a recent national scale study (Coles and others 2012). This study found that ambient concentrations of nitrogen, chloride, insecticides, and PAHs increased with urban development. Further, loss of sensitive aquatic biota, i.e., decrease in abundance of EPT-taxa (Ephemeroptera - mayflies), Plecoptera - stoneflies, and Trichoptera - caddisflies), 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 non-chemical stressors, e.g., perturbed flow regimes, temperature increases, high suspended loads and habitat alterations in addition to multiple chemical stressors.

This paper is an output of a SETAC Pellston® workshop "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 whether 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 be, 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 this paper were to investigate these questions using standard urban aquatic exposure models and scenarios. Associated manuscripts adopted the same working hypothesis to evaluate the risk of chemical mixtures from two other sources: municipal WWTP discharges which may include both domestic and industrial influents (Diamond and others 2017) and agricultural based land sources (Holmes and others 2017) whilst a combination of three scenarios was generated to evaluate the potential utility of the approach for water systems downstream of combined land uses (Posthuma and others 2017).

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, statement is that an ecosystem is protected when species belonging to that system are able to survive and reproduce (USEPA 1992; 1998). Thus, ecological risk can be defined as the proportion of species for which well-being is likely impaired. Over the past 40 years, 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 towards a single toxicant which may be due to differences in life history, physiology, morphology and behaviour. This observation led to the use of empirically derived statistical distributions to describe this variation. Species sensitivity distributions (SSD) 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 recognised 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 (SCHER 2012). Under the assumption of concentration additivity (CA), the model of toxic units (TUs) 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., LC_{50}) or chronic (e.g. long-term NOEC or EC_{10}) endpoint. The aggregated Toxic Units of a mixture is the sum of TUs of individual chemicals (ΣTU) and represent 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 - RA). Both the CA and RA concepts are based on the assumption that chemicals in a mixture do not influence each other's toxicity, i.e., they do not interact with each other at the biological target site. Both concepts have been suggested as default approaches (e.g., SCHER 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 CA and RA could be useful to predict the overall response, depending on the assumed toxic mode of

action (TMoA) of the mixture constituents (Altenburger and others 2000; Faust and others 2003). In reality, however, chemical mixtures are rarely composed of either only similarly or of only dissimilarly acting substances. The proposed protocol for predicting the toxicity of complex mixtures consists of a mixed two-step approach (2005). In the first step, the protocol requires evaluation of the CA responses to groups of substances with similar TMoA. In the second step, the protocol requires evaluation of the response additive effect of all these groups with different TMoA. 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 paper, the overall toxic pressures of environmental mixtures are evaluated according to both the CA model for all compounds (ΣTU), as well as the mixed model requiring information on the mode of toxic action (multi substance Potentially Affected Fraction of species – msPAF).

CHEMICAL SIGNATURES

General description of urban pollution sources and processes

Storm water runoff, combined sewer overflows, WWTP, increased presence of industry, hospitals, 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 waterbodies are highly human-modified. The diverse nature of all 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 socio-economic factors: 1) Human population density, 2) Economic status 3) Main economic activities (urban agriculture, commercial, industrial, service oriented), 4) Infrastructural quantity

(particularly waste water collection and treatment systems) and 5) Infrastructural quality (age, maintenance, technical design). In parallel to socio-economic factors, urban discharges will also be strongly influenced by geographical factors: 6) Surface area, 7) Climate, 8) Terrain slope and soil permeability (runoff versus 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, or 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 analysing multiple layers of geographic information system (GIS) information (Kapo and others 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. 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 and others 2015; Loganathan and others 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 US sources (see Table 2 and Table S-X1

in Supplementary Information). 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 and others 2015). For prioritization of chemical contributions to net toxicity, 90th-percentile concentrations of all 77 individual compounds were converted into two metrics for expressing mixture toxicity of the runoff waters. First, results are presented as TUs calculated using the geometric mean of all acute EC_{50} values over species, with higher TU-values implying higher relative contributions, and values exceeding 1 implying acute EC_{50}-effects for more than 50% of the species. Second, results are expressed as mixture toxic pressures, derived using the msPAF procedure described earlier.

Our compilation relies heavily on three major studies, the United Kingdom Water Industry Research (UKWIR) monitoring dataset (Comber and others 2015; WCA 2014) and the studies of urban storm runoff in San Diego (CA) (Tetra Tech 2010), Sacramento and San Francisco (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 Environmental Quality Standard (EQS) values without consideration of dilution in the receiving water. The UK has recognized that urban run-off is a complex issue and 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 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 where TU >= 1%, which was selected as criterion to de-select 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 is available. Release estimation is generally done by multiplying the tonnage of target chemical used by the corresponding emission factors that are expressed as a fraction. Table S-X2 summarizes emission factors 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 (OECD 2014). Default emission estimates for substances with wide dispersive use are also provided by ECHA (ECHA 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 the 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 receiving waters. These streams are often required to meet less stringent, pre-treatment 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 (UNECE 2015). These databases serve as valuable resources to identify the nature, amount and geospatial 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 (OECD 2014). The Toxics Release Inventory (TRI) program of the US (http://www2.epa.gov/toxics-release-inventory-tri-program) 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. Around 100 chemicals are covered by four

or more of the PRTRs. Guidance has recently been published on elements needed for the design of an global PRTR (OECD 2014).

Because of the relatively wide coverage of contaminant chemicals compared to 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 nine 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. Table S-X3 (supporting information) provides a summary of all the water pollutants that are included in the European PRTR (EPRTR). A subset of this list will be reported by different industry sectors when certain activities trigger emission thresholds (EC 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 EC_{50} over species. For illustration this analysis is provided in Table S-X4 for the chemical and paper/wood processing sectors using the 2012 EPRTR 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 European EPTR query that describes wastewater emissions form an urban sewage treatment works treating industrial waste waters is described in Supplemental material Appendix S1.

In addition to PRTR data, industry specific monitoring programmes may be helpful for characterizing emission profiles and associated risks to aquatic biota. Table S-X5 provides a sector-specific example providing a compilation of contaminants in 55 European refinery effluents that are discharged to freshwater bodies (CONCAWE 2010). While 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 two-dimensional gas chromatography (GCxGC). 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 (WEA) provides a complimentary approach to chemical characterization for assessing potential risks posed by industry effluents but this topic is beyond the scope of this paper.

METHODS FOR ESTIMATING AN URBAN EXPOSURE SCENARIO

The overview of emission inventories, measured data and (emission) model approaches combined with two 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 to predict the potential adverse effect of introducing a new compound to the market into the existing 'urban mixture'. For the purposes of demonstrating how a modelling 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 and others 2005) and an urban runoff management scenario (Ellis and others 2012). It is based on the Event Mean Concentration concept (EMC - Kayhanian and others 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:

$$M_i = V_i \times EMC_{i,j} \quad [1]$$

Where V_i (m^3) is the total runoff volume during a rain event from that type of surface and $EMC_{i,j}$ (g/m^3) 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 (m^3) 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 (Qrunoff, m^3/day) of urban runoff reaching the river system is then the sum of all 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,* g/m^3) 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,* m^3/s) and T is the duration of the runoff (s). Integrating across all 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 waste water sewer system that is addressed in the companion paper (Diamond et al., 2017). 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 is 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 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:

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

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 RIVPACS-system (River Invertebrate Prediction and Classification System) was established in the UK 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 as they were initially selected for their difference in oxygen requirements. The data for the UK reference sites were first 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 (O/E). This ecological metric can be interpreted as a loss of biodiversity, along with the loss of sensitive EPT-taxa and can be compared against the two metrics of mixture chemical exposure (sum-TU and msPAF).

For other geographies it is possible to apply the same RIVPACS-like O/E-methodology to determine the local loss of taxa, after identifying the taxa diversity of suitable reference sites (Hawkins and others 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 and others 2006).

DISCUSSION

Chemical fate / bioavailability

Based on preliminary analysis, Cu and Zn are identified as two substances that rank high on the TU / PAF (risk list) for the urban discharge scenario. Yet, it is well recognized in the literature that physico-chemical characteristics of the receiving water play a great role in modifying their toxicity. Therefore, it should be recognised 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 and others 2008) and thoroughly validated bioavailability correction models exist for metals such as Cu and Zn (Van Sprang and others 2009) are already being used in a regulatory context (European Commission and European Copper Institute 2009).

Site-specific differences in urban sources/chemical signatures

It is very challenging to develop a generic urban exposure scenario as 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 and others 2006), whereas in other countries overflow may be much higher and/or connection to sewers and WWTP is less. It is also important to recognise 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 waste water collection and treatment, poor waste handling, lack of chemical controls and poor environmental awareness.

Runoff from buildings is not only influenced by rain intensity and frequency but also by the age of buildings. Aged materials show approximately one to two order of magnitude lower concentrations in the run-off (Burkhardt and others 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 snap-shot, and are not representative for the whole range of possible runoff situations. There are significant challenges in developing a realistic picture on the concentration dynamics in runoff and receiving rivers. For example, although high-frequency sampling can help resolve some of the issues (Wittmer and others 2011), this is both time-consuming and cost-intensive. Modelling 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 and others 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 and others 2015; Page and others 2014; Roig and

others 2011) and is a promising in-expensive 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 cause adverse effects. However, sampling rates for passive samplers under strongly fluctuating flow regimes need still to be evaluated more rigorously to allow quantitatively assessment (Moschet and others 2015).

Limitation of available analytical methods

Only a limited suite of substances is analysed 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 programmes, including those summarized in the Supplemental Material Tables SX-1, 3, 4 and 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 analysed. 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, UV inhibitors, anti-corrosive agents, surface treatment chemicals, etc. 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 and others 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 modelling based on chemical use data and emission factors as well as biological-based monitoring methods (bioassays as well as diagnostic ecological analyses) should be integrated into site assessments.

Ranking based on TU summation vs 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 sum-TU and msPAF metrics. When comparing the msPAF result with the mixture toxicity prediction based on the TU approach (ΣTU = 0.38 in Table 2, meaning no risk to any species) it becomes obvious that the TU summation based on the geometric mean of the single species EC_{50} values (i.e., the mixture HC_{50} value predicted by CA) give different estimates of the mixture toxicity. While in terms of msPAF the acute $L(E)C_{50}$ is 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 ΣTU. This is a surprising result since CA predictions have been proposed as "reasonable worst case approach" (Berenbaum 1985) usually predicting a slightly higher response than RA 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 for numerically similar predictions with both the RA and CA models predicting the higher toxicity. For the normal distribution model that is usually used for SSD curve fitting, shallow slopes with a standard deviation over 1.0 are prone for CA giving lower mixture toxicity predictions than RA or the mixed model. The slopes of the SSDs for the three pyrethroids in Table 2 are estimated at a TMoA average of 1.25 and also 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 ΣTU 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 and others 2013) who also recommended to be cautious when using CA as a default approach on SSDs with rather shallow slopes. Although two 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 EU REACH framework or standard setting according to the EU technical guidance document (EC 2011) the following minimum validity criteria must be fulfilled:

- at least 10 toxicity values for different species from 8 specified taxonomic groups
- toxicity data need to be log-normally distributed.

The WFD technical guidance document (EC 2011) explicitly strives to harmonize both WFD 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 two (copper and zinc) fulfilled both standard-setting requirements. Fluoranthene fulfils 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 two 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. Since 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 mechanistic-based effect models that are based on mode of action considerations. For example, the recent development of a target lipid model that uses polyparameter linear free energy relationships by Kipka and DiToro (2009) can be broadly used to derive SSDs for a wide range of non-specific 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 is provided to the assessor (Posthuma and others 2016 (in Dutch)).

Non-chemical 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 and others 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 and others 2016) concluded that, although the mechanisms driving it were complex and interactive, urban storm water delivered to stream by hydraulically efficient drainage systems was identified as a primary large-scale contributor. Storm sewer overflows, waste water treatment works and legacy pollutants also act in these systems and can obscure the direct effect

of the urban runoff (Walsh and others 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 and others 2015). It was postulated that this was because it accounted for both hydrological and water quality stressors.

RECOMMENDATION

This manuscript highlights the need to recognize the variable and intermittent nature of the urban discharge scenario and linkage to landscape attributes. The further use of GIS-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, modelling of chemical exposures, as well as biological-based and effect directed analysis approaches should be used to compliment chemical monitoring efforts (Brack and others 2016). Recent research has explored alternative strategies for ecological risk assessment purposes. A Time-Integrative Passive sampling combined with Toxicity Profiling (TIPTOP) is showing promise as cost-effective effects based approach for water quality assessment (Hamers and others 2016). The primary advantages over existing methods employed under current regulations (such as the EU 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 and others 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, whilst the present effort has focused on chemical stressors potentially impacting urban waterways, further work is needed to understand the role of non-chemical stressors in contributing to ecological risks in urban waterways.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

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Figure 1. Key urban pollutant sources and pathways.

Figure 2. Schematic illustration of the sources of diffuse urban runoff.

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 BOD (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

Table 2 Quantitative measurements of concentrations in runoff for the ranked top 10 of substances with a TU ≥ 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% [µg/L]**	**Avg. EC50 (µg/L) (geometric mean)**	**Toxic pressure (PAF)**	**TU = Concentration/Average EC50 over species**	**% of ΣTU**	**Reference**
Brake pads, roofing	Metal	Copper (dissolved)	Cu	33.0	183	20%	0.18	43%	(WCA 2014)
Galvanized metal structures	Metal	Zinc (dissolved)	Zn	84.0	1903	7%	0.04	10%	(Tetra Tech 2010)
Garden, park, building	Insect-icide	Deltamethrin	Pyreth-rin	0.084	2	13.7%	0.04	10%	(Tetra Tech 2010)
Garden, park, building	Insect-icide	Bifenthrin	Pyreth-rin	0.03	1	11.4%	0.03	7%	(Ensminger and Kelley 2011)
Combustion	PAH	Benz(a) anthracene	Non polar narcosis	0.192	10	0.7%	0.02	5%	(Tetra Tech 2010)
Garden, park, building	Insect-icide	Permethrin	Pyreth-rin	0.202	12	7.8%	0.02	4%	(Tetra Tech 2010)
Metal structures	Metal	Iron (dissolved)	Fe	1106.2	66298	0.4%	0.02	4%	(WCA 2014)
Metal structures	Metal	Aluminum (reactive)	Al	24.2	1925	0.5%	0.01	3%	(WCA 2014)
Sewage, buildings, surfactants	Plasti-ciser	Nonylphenol 1 ethoxylate (NP1EO)	Non polar narcosis	4.165	525	0.1%	0.01	2%	(WCA 2014)
Combus-tion	PAH	Fluoranthene	Non polar narcosis	0.887	136	0.1%	0.01	2%	(Tetra Tech 2010)
						msPAF mixed = 42.5%	**ΣTU = 0.38**	**Sum % TU = 100.0%**	

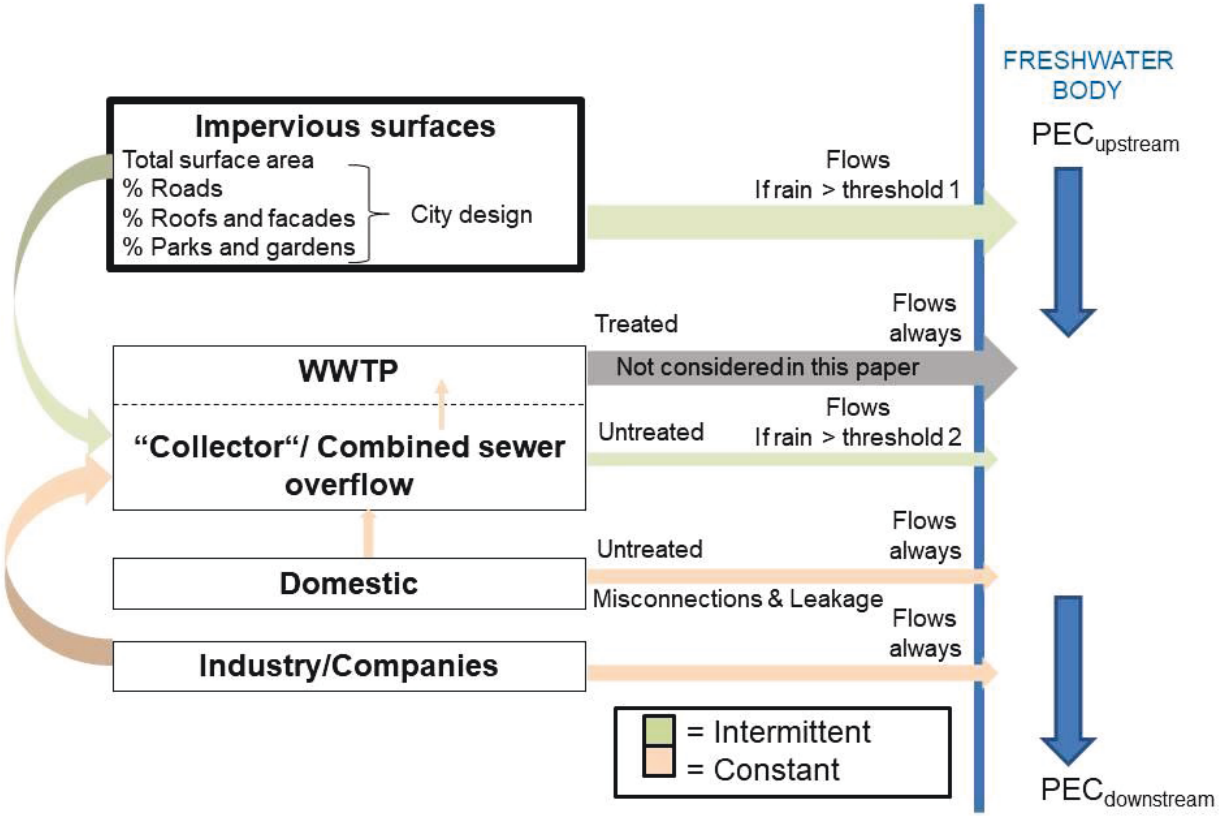

Figure 1

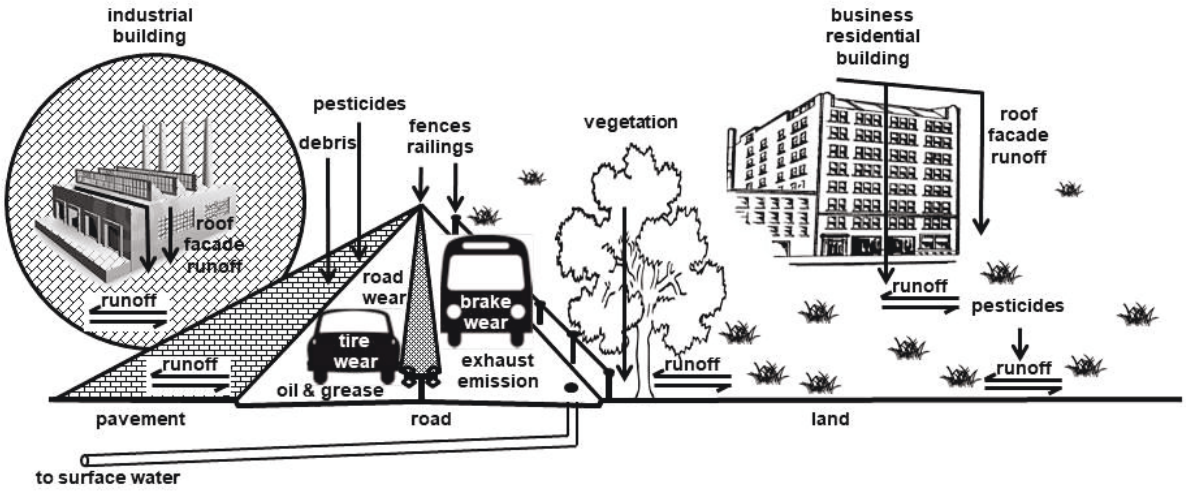

Figure 2