Chemosphere 369 (2024) 143806

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Pollutants in urban runoff: Scientific evidence on toxicity and impacts on freshwater ecosystems

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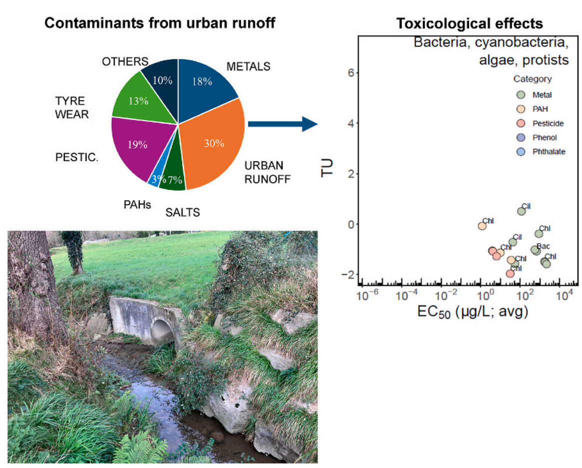
HIGHLIGHTS

- We collect evidence on the occurrence and toxic effects of urban runoff in aquatic organisms.
- Highest risk is associated to metals, polycyclic aromatic hydrocarbons (PAHs), pesticides, and phthalates.
- Toxicity is more intense on the basal components of the food web, less on invertebrates and vertebrates.
- The risks of urban runoff to freshwater ecosystems may be underestimated or overlooked.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Toxic unit (TU)s
EC50

ABSTRACT

Urban runoff effluents transport multiple pollutants collected from urban surfaces. which ultimately reach freshwater ecosystems. We here collect the existing scientific evidence on the urban runoff impacts on aquatic

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https://doi.org/10.1016/j.chemosphere.2024.143806
Received 11 September 2024; Received in revised form 10 November 2024; Accepted 22 November 2024
Available online 28 November 2024

Emergent pollutants
Metals
Algae
Bacteria
Invertebrates
Vertebrates
River ecosystem functions
Urban rivers

organisms and ecosystem functions, assessed the potential toxicity of the most common pollutants present in urban runoff, and characterized the ecotoxicological risk for freshwaters. We used the Toxic Units models to estimate the toxicity of individual chemicals to freshwater biota and observed that the highest ecotoxicological risk of urban runoff was associated to metals, polycyclic aromatic hydrocarbons (PAHs) and pesticides and, in a few cases, to phthalates. The potential risk was highest for copper and zinc, as well as for anthracene, fluoranthene, Di(2-ethylhexyl) phthlate (DEHP), imidacloprid, cadmium, mercury, and chromium. These pollutants had contrasting effects on freshwater biological groups, though the risk overall decreased from basal to upper trophic levels. Our analysis evidenced a lack of data on ecotoxicological effects of several pollutants present in urban runoff effluents, caused by lack of toxicity data and by the inadequate representation of biological groups in the ecotoxicological databases. Nevertheless, evidence indicates that urban runoff presents ecotoxicological risk for freshwater biota, which might increase if hydrological patterns become extreme, such as long dry periods and floods. Our study highlights the importance of considering both the acute and chronic toxicity of urban effluent pollutants, as well as recognizing the interplay with other environmental stressors, to design adequate environmental management strategies on urban freshwater ecosystems receiving urban runoff.

1. Introduction

Drainage sewer schemes are designed to collect urban runoff during rainfall events and to prevent destructive floods. Some cities have combined sewer overflows, where urban runoff is mixed with sewage waters (Perry et al., 2024), though modern schemes feature separated sewage and runoff networks (Shishegar et al., 2018). While these latter schemes may decrease the overall pollutant loads, the impact of urban runoff may still be high regarding the contaminants they transport as well as the large pulse inputs which may be discharged in surface waters such as rivers or lakes. As an example, 70% of the stormwater in Berlin is directly discharged into surface waters surrounding the city (Wicke et al., 2021). Although it has been long suspected that stormwaters cause significant environmental impacts, we still lack systematic knowledge about the effects of the pollutants they release to freshwater ecosystems.

Urban runoff effluents may release a large diversity of pollutants (Awonaike et al., 2021) after washing surfaces and infrastructures, including roads, pavements, residential, industrial areas, or green spaces. Pollutants include metals (Brown and Peake, 2006; Zhao and Li, 2013), salt, dust, plastics, and multiple organic pollutants (Beom et al., 2020; Johannessen and Metcalfe, 2022). Despite recent advances, significant gaps remain in understanding the full chemical composition of urban runoffs, especially as new materials and chemicals used in daily life release additional, yet scarcely studied, pollutants. Many of these are emerging micropollutants (EMPs) that occur at concentrations of ng L^{-1} to μg L^{-1}, including polycyclic aromatic hydrocarbons (PAH), plasticizers, flame retardants, corrosion inhibitors, wood preservatives, pesticides, veterinary drugs, surfactants and tire-related compounds (Bodus et al., 2023; Mutzner et al., 2022). Although the toxicological profile of some of these pollutants is not well characterized, some EMPs are active even at very low concentrations, potentially harming non-target organisms (Isidori et al., 2005), and some, such as the perfluorinated compounds (PFAS), are persistent in the environment and accumulate in organisms (Lewis et al., 2022). The mobilization of EMPs from urban areas may change seasonally according to their chemical characteristics. For instance, the release of phthalates (plasticizers) from surfaces is temperature-dependent, their concentrations peaking during summer rains (Markiewicz et al., 2017). Many EMPs undergo biotic and abiotic transformations in the environment (Yang et al., 2024) or make part of complex mixtures of unknown ecotoxicological risk (Richardson and Ternes, 2014). Finally, although many of the compounds found commonly are not acutely toxic, their frequent inputs may cause long-term effects through unexpected "cocktail" effects (González-Gaya et al., 2021), which makes difficult to forecast their ecotoxicological risk.

The ecotoxicological consequences of urban runoff effluents also depend on the type of biological communities. Some biological groups are more sensitive than others, although this sensitivity also depends on the specific pollutants or mixtures (Beketov et al., 2009; Wood et al., 2019). An interesting tool for the assessment of ecotoxicological risks are the Toxic Units (TU) (Owsianiak et al., 2023). The TU computes the ecotoxicological risk of a pollutant by comparing its concentration in the environment to the effective concentration affecting 50% of a given endpoint (EC50). TUs are thus useful to estimate the potential toxicity of pollutants across species (Ginebreda et al., 2014). We calculated TUs for the most frequent pollutants recorded in urban runoff effluents, including all biological groups for which ecotoxicological data were available.

TUs, though, do not reflect the real impact of pollutants on freshwater ecosystems. Impacts are not only due to the direct effect of pollutants, though may be influenced by the chemical composition of the receiving waters and its dilution capacity (Pereda et al., 2020), as well as by the presence of co-occurring stressors (Sabater et al., 2021). The adaptation of the local biota to chronical exposure may reduce the observed effects of urban runoff, as toxicants may eliminate sensitive species, what in turn promotes their replacement by others less sensitive, resulting in a more tolerant community (Blanck, 2002). Species may adjust their physiology and behavior to cope with the presence of pollutants, although this adaptation can come with trade-offs, such as reduced fitness or increased vulnerability to other stressors (Samuel et al., 2023). Also, the effects of urban runoff effluents can become stronger under climate change and water scarcity (Mosley, 2015), when extreme washouts may occur after long dry intervals, and therefore episodic impacts may be expected. There is, therefore, a whole ensemble of accompanying issues that may modulate the potential toxicity of urban effluents. In order to systematize the scientific evidence on the toxicity of pollutants in urban runoff and their actual impacts on freshwater ecosystems, we performed a review on the existing literature, which was later compared with the potential toxicity described by the TUs. These two complementary approaches allowed us to present the potential and realized ecotoxicological risk of urban runoff effluents on freshwater ecosystems, as a way to shed light on the threats they can represent in present as well as future scenarios.

2. Materials and methods

2.1. Data collection

We performed a systematic literature review on the Web of Science (WOS) to determine the main effects of urban runoff pollutants on freshwater biota and ecosystem functions. We included studies considering urban runoff pollution and providing ecological or ecotoxicological data on any biological compartment. We conducted separate searches for the effects on microbes (bacteria, fungi and algae, cyanobacteria and protists), fauna (invertebrates and vertebrates), and ecosystem functions (primary production, decomposition, respiration, nutrient retention). The search query was applied to multiple fields in the WOS database, including the title (TI), topic (TS), abstract (AB) and author keywords (AK). The search included papers published up to April 2024. The sets of Boolean terms used in the search are provided as

Supporting Information (Suppl. Table 1).

2.2. Concentration and toxicity of runoff pollutants

Although the number of pollutants detected in urban runoff effluents is large, we focused on the 48 most frequently detected pollutants in urban runoff. These were selected after the studies by Eriksson et al. (2007), Mutzner et al. (2022) and Wicke et al. (2021) on the basis of being present in over 50% of the sites examined. Once the pollutants were selected, we searched in the literature for their concentration range (Suppl. Table 2). We then retrieved data on their acute and chronic EC50 using the ecotoxicology database of the US Environmental Protection Agency (https://cfpub.epa.gov/ecotox/). The name of each chemical substance was first standardized according to the ECHA (https://echa.europa.eu/es/information-on-chemicals) or the PubChem (2021)database. The EC50 values collected included endpoints such as growth, development, mortality, reproduction, or biochemical and genetic responses. The concerned taxonomic groups were algae, amphibians, crustaceans, fish, fungi, insects/spiders, mammals, mollusks, and other invertebrates, and the data were toxicity tests conducted under both laboratory and field conditions using water as the exposure medium. This search provided a total of 3542 toxicity data points from 611 studies, which represented 329 freshwater species and reduced the initial number from 48 to 40 chemicals. The toxicity data points were assembled in higher taxonomic groups (Cyanobacteria, microalgae, and protists; Invertebrates; and Vertebrates; taxa listed on Suppl. Table 4) to obtain minimum, maximum, and average toxicity values for each taxonomic category and exposure type (data in Suppl. Table 6).

2.3. Toxic units

We calculated the toxic units (TU) of the pollutants in urban runoff following Sprague (1970)and von der Ohe and de Zwart (2013). Toxic units account for the potential toxicity of a pollutant, expressed as the ratio of a compound concentration to a specific toxicity reference value, in this case, EC50 values. The TU of a given chemical *i* was therefore calculated as:

$$TU_i = log_{10}\left(\frac{c_i}{EC50_{i,j}}\right)$$

Where c_i (μg/L) is the measured concentration in urban runoff and $EC50_{i,j}$ (μg/L) the concentration of the *i* compound for the *j* taxonomic group, then estimated separately for microorganisms, invertebrates or vertebrates. As the results spanned over more than 10 orders of magnitude, we expressed the TUs on a logarithmic scale. TUs were calculated based on both the *maximum* and *average* of the occurrence concentration of pollutants, retrieved from the literature (Suppl. Table 1). The application of these concentrations and the minimum or average EC50s defined two exposure scenarios.

(i) *worst-case scenario* (TU_{WC}), where the maximum concentration of the compounds found in urban runoff is considered along with the minimum EC50 values per same compound
(ii) *average scenario* (TU_{ave}), where the average concentration of the compounds is considered together with the average EC50 values per same compound.

Maximum concentrations would indicate episodic short-term exposures that may lead to *acute* toxic effects. In contrast, average concentrations would indicate long-term exposure, potentially resulting in *chronic* toxic effects.

We used the thresholds for acute and chronic effects proposed by Malaj et al. (2014), adapted from Kuzmanovic et al. (2015), to assess the potential impact of chemical pollution on biological communities. TU values higher than −2 indicated acute effects, while aquatic risks of pollutants for freshwater organisms were classified between very low and extremely high, adapting the classification from Bijlsma et al. (2021). Aquatic risk was then defined as very low or insignificant when TUs (in log scale) were lower than −2, low when values were between −1 and −2, moderate when TUs were between −1 and 0, high when TUs were between 0 and 1, and very high or extremely high when TUs were above 1 and 2 respectively. The EC50 values used covered up to 20 taxonomic groups (data in Suppl. Table 6).

3. Results and discussion

3.1. Presence of pollutants in urban runoff

Several pollutants can occur in significant concentrations in urban runoff (Suppl. Table 2, and references therein). Maximal concentrations have been recorded for phthalates (16.7–91.1 μg L^{-1}), PAHs (13.5–26.7 μg L^{-1}), pesticides (72 μg L^{-1} for diuron, 166 μg L^{-1} for simazine), DEET (109 μg L^{-1}), rubber additives (8.8 μg L^{-1}), organophosphates (40 μg L^{-1}), and metals (0.13–30 μg L^{-1}). Most likely, this is a short list among the multiple pollutants that can be found in urban runoff, given the current scarcity of studies. The presence and impacts of many emerging compounds, some in relatively high concentrations in urban runoff, including all their transformation products, remain largely unknown (Badmus et al., 2021; Wang et al., 2024; Yang et al., 2024). Urban runoff also includes multiple dissolved and particulate materials, such as nutrients, salts, sediments or organic matter.

Urban runoff effluents result from rainfall or street washing which transport these materials deposited after multiple human activities (transportation, construction, gardening, littering, or atmospheric deposition). Many of these contaminants are finally collected by sewers and released to surface waters (Müller et al., 2020). The quality of urban runoff differs with the intensity and duration of the rainfall events as well as with the type and extension of the drained area. In particular, the *first flush*, or water that washes urban surfaces at the onset of rainfall episodes (Kayhanian et al., 2008), transports a large proportion of pollutants (Johannessen and Metcalfe, 2022), a single episode sometimes exceeding the daily loads from urban runoff discharges (Masoner et al., 2022). Climate modulates the relevance of these events, so frequent rainfall in wet climates may result in press-type inputs on the receiving ecosystem (Jentsch and White, 2019), whereas intense but infrequent rainfall in dry climates will be more intense and wash areas that accumulated more materials (Hochgenei et al., 2024), therefore contributing to pulse-type inputs (Sabater et al., 2022).

The extent of presence and effects of contaminants from urban runoff was explored through a WoS search. This returned a total of 2194 studies, which were reduced to 103 (list of references in Suppl. Material 5) after the removal of duplicates and the application of the eligibility criteria (Suppl. Fig. 1). This search highlight that our current understanding on the presence and effects of contaminants from urban runoff is uneven, with greater knowledge on metals (18%), pesticides (19%), and urban runoff mixtures (30%), but significantly less on other contaminant classes such as PAHs, salts or phthalates (Fig. 1a). Specifically, 61% of the revised articles were related to a particular category of contaminants, mostly tire wire compounds (mainly 6PPD and its transformation product 6PPD-quinone), pesticides, metals, PAHs, or chloride; 29% studied the effects of (mixed) urban or road stormwater runoff; and the remaining 9% tackled two or more categories of contaminants, such as metals and PAHs, or metals and salinity (Fig. 1a).

3.2. Impacts of pollutants from urban runoff on freshwater biota

Up to 85% of the publications in our search used biomarkers at the individual level (survival, mobility, reproduction and development), and only 20% included the responses of biomarkers at lower organization levels, from biochemical to physiological, histological or morphological endpoints. These studies provided data on the impacts of urban

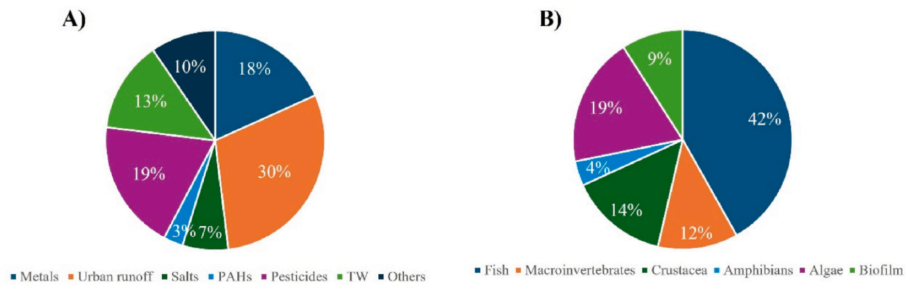

Fig. 1. (A) Proportion of studies dealing with the main groups of chemicals present in urban runoff. PAH: polycyclic aromatic hydrocarbons; TW: tire wear derived compounds. (B). Proportion of the biological groups, calculated after the final selected studies from the published literature, as it is described in Suppl. Fig. 1.

runoff on freshwater biota (Cyanobacteria, microalgae, and protists; Invertebrates; Vertebrates), as well as on functions and on the food web structure of freshwater ecosystems. Overall, 28% of the studies measured impacts on microorganisms, 68% on fish and invertebrates, and only 5.7% on ecosystem functions. Specifically, 42% of the studies focused on fish, 19% on algae or phytoplankton, and 14% on crustaceans. Additionally, 12% examined invertebrates, and 4% amphibians (Fig. 1b). A small number (14%) studied the effects at the community level, from which the majority (9%) studied benthic invertebrates, and the others focused on zooplankton, fish, or oligochaetes in the sediment.

Bacteria, cyanobacteria, algae, and protists. The number of papers studying the impacts of urban runoff on freshwater bacteria (or their associated biofilms) is extremely reduced (9% of papers in the search). Ancion et al. (2010, 2014) exposed bacterial biofilm communities to Zn, Cu and Pb, and observed shifts in its community structure after three days of exposure, which persisted even after 14 days of recovery. Trapped metals continued to influence the bacterial community and were released gradually, being transferred to organisms higher up in the food chain.

Most studies on the impacts of urban runoff effluents or contaminants using algae or cyanobacteria as the target organisms used endpoints such as changes in growth, abundance or biomass, and only a few used biomarkers such as enzymatic activities. The number of studies considering single species (cultures) were similar to those considering communities (phytoplankton or biofilm). Half of the studies in our search examined real urban runoff from highways and industrial areas, mostly characterized by metals, while other studies tested the effect of single pollutants or mixtures (including plasticizers, rare earth elements, used motor oils, or leachates from tires, salts, or cigarette butts).

Urban runoff caused diverse effects on alga and cyanobacteria. The green alga *Scenedesmus subspicatus* showed contrasting effects when exposed to different fractions of stormwater from an industrial log-yard area: whereas the very first flush reduced algal growth by 42–51%, the remaining part of the stormwater promoted it (Kaczala et al., 2011). An analogous pattern was observed when the green alga *Raphidocelis subcapitata* was subject to runoff from a highway: the first 60 min of the storm runoff inhibited growth, whereas subsequent runoff samples stimulated it (Kayhanian et al., 2008). The shift from inhibitory to stimulatory might rely on the toxicity of the pollutants (Kaczala et al., 2011), but also on the shifting balance between toxic substances and nutrients, which can still be important after the first flush (Schiff et al., 2016; Zhao et al., 2022), and thus stimulate algal growth. Beyond that, sensitive algal species (e.g., from oligotrophic sites) experience a higher impact than tolerant species (Babko et al., 2020). Runoff from highway washout changed algal communities from diatom-dominated to green algae (Johnson et al., 2011). Khun et al., 2012 reported a decrease in the effective quantum yield (photosynthetic efficiency) of periphyton after exposure to urban runoff, whereas Roubeau Dumont et al., 2023 reported similar effects in the macrophyte *Lemna minor*, but not in algae, when the two were exposed to chemicals derived from tire wear particles.

Studies focusing on specific pollutants in urban runoff provide more precise ecotoxicological results. Tyre leachates having 100 mg/L of Zn inhibited the growth of the alga *R. subcapitata*. Cigarette butt leachates, which contain plastic-derived short carbon chains and pyridine derivatives, showed initial toxicity on *R. subcapitata* (2.7%–29.6% growth inhibition), which later declined as these compounds degraded. However, leachate toxicity returned during decomposition of the cigarette butts, even after five years (Bonanomi et al., 2020). Used motor oil from automobiles had severe toxic effects on *R. subcapitata* (Ramadass et al., 2015), and increased the activity of antioxidant enzymes such as superoxide dismutase and peroxidase at concentrations of 0.2%. The plasticizer dibutyl phthalate (DBP) had detrimental effects on algae (*Chlorella pyrenoidosa*, *Scenedesmus obliquus* and *Tetradesmus dimorphus*), inhibiting growth, damaging cell structures, reducing photosynthesis and inducing oxidative stress (Gu et al., 2017; Manzi et al., 2022), although lower concentrations of DBP promoted growth (hormesis effect) (Manzi et al., 2022).

Invertebrates. Nearly 26% of the papers in the search described the impacts of urban runoff on invertebrates (including macroinvertebrates and crustaceans, Fig. 1b), mostly (90%) assessing the effects of contaminants on water, and the rest on sediments. Overall, urban runoff pollutants present in water as well as in sediments had relevant effects on invertebrates. The reported evidence is both at the individual level (e. g., mortality, reproduction, development, behavior) and, less commonly, at lower organization levels (e.g., gene expression).

Overall, pesticides (especially insecticides) present in urban runoff were highly toxic to aquatic invertebrates. Invertebrates exposed to pyrethroid insecticides such as lambda-cyalothrin, deltamethrin, or bifenthrin showed very low LC50 values, in the range of ng L^{-1} (Weston et al., 2009, 2015; Sutton et al., 2019). Organophosphate insecticides (e. g., chlorpyrifos, diazinon, fipronil) (Viant et al., 2006; Sutton et al., 2019) and cadmium (Sutton et al., 2019) can be lethal also at very low concentrations (ng L^{-1}). Sublethal effects of the antioxidant N(1, 3-dimethylbutyl)-N′-phenyl-p-phenylenediamine quinone (6PPD-quinone), a chemical released from tire wear, have been recently observed on invertebrates (De Castro et al. submitted).

The use of salt for winter road de-icing has been reported as another important cause for the decline of invertebrate diversity after stormwater runoff (Allert et al., 2012). Chloride from road salts not only can directly affect the organisms (Haake et al., 2022), but also can increase the mobilization of pollutants, potentially amplifying their toxicological impacts and disrupting the food web (Mayer et al., 2008; Schuler and Relyea, 2018). The abrupt surge caused by urban runoff may mobilize pollutants (e.g. PAHs, metals), not only form urban surfaces, but also from sediments and soils, impacting invertebrates and other biota (Weber et al., 2023). Urban stormwater runoff has been related to the loss of sensitive invertebrate species and to a reduction in functional richness and diversity (Lemes da Silva et al., 2024; Gao et al., 2023b; Padovan et al., 2022). Additionally, urban runoff not only contributes with pollutants but also enhances hydraulic disturbance and thermal changes (Walsh et al., 2005; Müller et al., 2020), which may also affect the invertebrates, and complicates determining the impact of pollutants on them.

Vertebrates and food web structure. Vertebrates are amongst the most studied biological group regarding the effects of urban runoff pollutants (46% of the papers in the search). Fish (42%) are much more studied than amphibians (4%). Survival, mobility, reproduction and development were the most common endpoints considered, although a few studies have also reported the responses of biomarkers at sub individual level (biochemical, physiological, or histological), and only one assessed the effects at community level.

The pollutants most tested on vertebrates have been tire wear compounds, pesticides, metals, and PAHs (60% of the studies in a single contaminant category), while impacts of real runoff waters have not been thoroughly evaluated. In fact, it prevails the analysis of exposure effects to a single pollutant category (e.g., pesticides, metals), or to selected contaminants such as tire wire compounds (mainly 6PPD and its transformation product 6PPD-quinone). A small fraction (10% of the papers in the search) report the effects of the mixture of pollutants in urban runoff in fish, mostly in the water media but also in sediments. A lethal risk has been described for coho salmon (*Oncorhynchus kisutch*) subjected to the tire rubber antioxidant 6PPD-quinone, even at very low concentrations (Greer et al., 2023). Other pyrethroids (i.e., bifenthrin, deltamethrin, lambda-cyalothrin and permethrin) (Beggel et al., 2010; Sutton et al., 2019) and organophosphates (i.e., esfenvalerate, iazinon and chlorpyrifos) (Viant et al., 2006) have also been shown to be lethal for fish, with LC50 values at the μg L^{-1} level. Also, Van Meter and Swan (2014) reported that de-icing salt affected the time to metamorphosis of the ray treefrog tadpole in urban stormwater ponds.

Beyond studies on individual species, there is an extremely low number of studies (2% of the papers in our search), dealing with the effects of urban runoff effluents on vertebrate communities, or considering the different food web compartments.

Ecosystem functioning. Few studies (5.7% of the papers in our search) addressed the impacts of urban runoff on ecosystem functioning. Studies showed contrasting effects of road runoff (including tire wear particles, metals, and nutrients) on primary production (net primary production (NPP) or gross primary production (GPP)) or respiration. Boisson and Perrodin (2006) reported increased periphytic NPP and respiration when exposed to road runoff. However, Johnson et al. (2011) reported unclear patterns in GPP and respiration at different concentrations of road run-off. Studying nutrient retention dynamics, Grimm et al. (2005) reported that nutrient uptake length and uptake rate increased in stream reaches receiving urban runoff, although this effect could not be separated from that associated to the geomorphological simplification of the river channels receiving urban runoff.

3.3. Ecotoxicological effects of pollutants in urban runoff

Toxic Unit estimation. We estimated TUs considering the range of concentrations of pollutants present in urban runoff as well as their potential toxicity (Suppl. Table 6). A high ecotoxicological risk was mostly related to metals, PAHs, and pesticides, and in a few cases also to phthalates, when we considered both the worst-case and the average scenarios (Table 1). The toxicity risk can be related to either the high concentrations in runoff, to their high toxicity (low EC50 values) or to a combination of the two. In the case of copper and zinc, the risk was extremely high as maximum runoff concentrations (in the order of mg L^{-1}) and very low EC50 values (in ng L^{-1}), especially for chlorophytes, crustaceans (i.e., *Daphnia magna*), and Rotifera (Fig. 2, Table 1). Other pollutants detected at levels of tens to hundreds of μg L^{-1}, with EC50 values in the same range, included anthracene, fluoranthene, DEHP, cadmium, mercury, and chromium, all of them with very high risk (TU > 1). The pesticide imidacloprid had a very high risk, not so much related to its high concentrations in urban runoff, but because of its very low EC50 (ng L^{-1}). Other hazardous pollutants were the PAHs benzo[a] pyrene, benzo[a]anthracene, pyrene, and fluorene (high risk, TU > 1), and carbendazim and phenol, which also presented a high risk due to their low EC50 values (few μg L^{-1}) (Fig. 2, Suppl. Table 6). However, phenanthrene, diuron, pentachlorophenol or 2,4-D supposed a moderate risk, since even showing high peak concentrations in urban runoff (tens or hundreds of μg L^{-1}), EC50s were much higher (at the range of μg L^{-1}). Chlorpyrifos had EC50s at the range of ng L^{-1} (Suppl. Table 6), but the measured concentration levels reported in the environment were also very low, making the risk medium or moderate. Pb, glyphosate and butylbenzyl phthalate, reported measured concentrations of few μg L^{-1} but their EC50s were higher (Fig. 2, Suppl. Table 6), which made low the toxic risk.

Overall, the highest TUs were estimated for Chlorophyta, Rotifera and Crustacea, while lower values were observed for vertebrates. The PAH fluoranthene was also detected at high concentrations and supposed a medium to high toxic risk for most of the taxonomic groups. Other pollutants exhibited selective toxicity towards some groups of organisms. For instance, anthracene and benzoanthracene had a high toxic risk for algae and invertebrates but low for vertebrates. Mercury, benzo[a]pyrene, phenanthrene, pentachlorophenol and diuron had acute risk due to their very low EC50 but not because of their high peak concentrations in urban runoff. Phtalates (DEHP) had acute toxicity for crustacea, which has not been reported for bacteria or algae.

TUs on Cyanobacteria, algae, and Protozoa. Metals exhibited the highest toxicity under the worst-case scenario (TU_{wc} from 0.7 to 4). Cu, Ni, Pb, Cd and Cr had toxic effects mostly on Chlorophyta, ciliates, Bacillariophyta and Cyanobacteria (Fig. 2, Table 1). Zn and Cd primarily affected ciliates and Chlorophyta for the average-case scenario (TU_{avg} from −0.7 to 0.5). PAHs as Anthracene, Benzo[a]pyrene, Fluoranthene, Pyrene and Benz[a]anthracene had high risk in the worst case-scenario (TU_{wc} from 0.6 to 2.4), predominantly affecting Chlorophyta and Bacillariophyta. Atrazine and diuron were the pesticides with the higher contribution to acute chemical risk in the two scenarios (TU_{wc} from −1.5 to 2.7 and TU_{avg} from <-2 to −1), affecting Chlorophyta, Cyanobacteria, Prasinophyta, Charophyta, Cryptophyta and Bacillariophyta. Phthalates, phenols, and flame retardants did not exceed the acute risk threshold in any of the component of this biological group.

TUs on Invertebrates. Metals also showed the highest toxicity to invertebrates (Fig. 2). Cu, Zn, Cd, Hg, Cr and Pb showed the highest acute risk in the worst-case scenario (TUwc from −1 to 6), while Cu, Zn, Hg and Cd (not Pb) had the highest risk in the average-case scenario (TU_{avg} from −1 to 1). PAHs also represented a serious risk for the invertebrates, with TUwc ranging from −1 to 2. Anthracene, Fluoranthene, Benzo[a] pyrene, Benz[a]anthracene, Pyrene, Fluorene and Phenanthrene were within the range of acute toxicity, predominantly impacting the phyla Arthropoda and Cnidaria. Fluoranthene, Benzo(a)pyrene and Phenanthrene showed moderate acute risk in the average-case scenario (TU_{avg} from −1 to 0). Pesticides such as Imidacloprid, Carbendazim, Chloropyrifos, Pentachlorophenol, 2.4-D, Diuron and Glyphosate had TUs ranging from −2 to 2 in the worst-case scenario. However, none of them overtook the acute risk threshold in the average-case scenario. Phenol, DEHP and butylbenzyl phatalate showed acute toxicity risk (TUwc from −2 to 2), though only in the worst-case scenario.

TUs on Vertebrates. The greatest risk to vertebrates potentially impacted by urban runoff was associated to metals, followed by PAHs (Table 1, Fig. 2). Zn and Cu induced very high risk in the worst-case scenario (TU_{wc} from 1.7 to 2.2), but low to moderate risk in the average scenario (TU_{avg} from −1.4 to −0.3). Ni, Cd and Hg also reached very high risk for Actinopterygii in the worst-case scenario (TUwc from −0.1 to 1.1). Fluoranthene was the most toxic PAH for vertebrates, showing acute toxicity in the worst-case and average scenarios (TU_{wc} from −0.2 to −0.1 and TU_{avg} from −2 to −1.4), leading to moderate risk in the worst-case scenario (Table 1). Phenanthrene and Benzo[a]pyrene exhibited acute toxicity for Actinopterygii, ranging from very low to moderate risk (TU_{wc} from −2.4 to −0.2). Pesticides, phenols and phthalates exceeded acute effect threshold for vertebrates, mainly in the worst-case scenarios (Table 1). Pentachlorophenol was the pesticide

Table 1
Pollutants commonly occurring in urban runoff, ranked according to their toxicity (logTU > −2) for different taxonomic groups in the *worst-case* and *average* scenarios. Taxonomic groups are ordered from the most affected to the least affected in each pollutant. Asterisks indicate pollutants included in the priority list of the Water Framework Directive (WFD). Triangle indicate pollutants included in the priority list of hazardous substances of the WFD. Suppl. Table 3 accounts for the species included in each Taxonomic group here indicated.

TU_{wc}				TU_{avg}		
Pollutant		Most affected taxonomic group	TU	Contaminant	Most affected taxonomic group	TU
Cyanobacteria, algae, and protists						
Metals	Cu	Chlorophyta > Ciliate > Bacillariophyta > Cyanobacteria	0.4 to 4.1	Zn	Ciliate > Chlorophyta	−0.4 to 0.5
	Ni*	Chlorophyta	3.6	Cd*	Ciliate	−0.7
	Zn	Chlorophyta > Ciliate	2.6 to 3.3	Pb*$^{\Delta}$	Chlorophyta	−1
	Pb*$^{\Delta}$	Chlorophyta	2.7	Cu	Bacillariophyta > Chlorophyta > Cyanobacteria > Ciliate	−1.6 to −1.1
	Cd*	Chlorophyta > Ciliate	0.7 to 2.0	Hg*$^{\Delta}$	Chlorophyta	−1.6
	Cr	Bacillariophyta > Chlorophyta	−1.0 to −0.2	Cr		< −2
				Ni*		< −2
PAH	Anthracene*$^{\Delta}$	Chlorophyta	2.4	Benzo[a]pyrene*	Chlorophyta	−0.08
	Benzo[a]pyrene*	Chlorophyta	1.3	Benz[a] Anthracene*$^{\Delta}$	Chlorophyta	−1.1
	Fluoranthene*$^{\Delta}$	Chlorophyta	0.8	Pyrene	Chlorophyta	−1.4
	Pyrene	Chlorophyta	0.6	Anthracene*$^{\Delta}$		< −2
	Benz[a] Anthracene*$^{\Delta}$	Chlorophyta	0.6	Phenanthrene		< −2
	Phenanthrene	Chlorophyta > Bacillariophyta	−1.4 to −1.3	Fluoranthene*$^{\Delta}$		< −2
Pesticides	Atrazine*	Chlorophyta > Cyanobacteria > Prasinophyta > Charophyta > Cryptophycophyta > Bacillariophyta	−1.5 to 2.7	Diuron*	Prasinophyta > Charophyta > Cryptophycophyta > Chlorophyta	−2.0 to −1.0
	Diuron*	Chlorophyta > Cyanobacteria > Prasinophyta > Charophyta > Cryptophycophyta	1.0 to 1.5	Atrazine*		< −2
	Isoproturon*	Bacillariophyta > Chlorophyta > Charophyta	−1.1 to −0.2	Isoproturon*		< −2
	Terbutryn*	Chlorophyta	−1.3	Terbutryn*		< −2
	Pentachloro-phenol*	Ciliate	−1.7	Pentachloro-phenol*		< −2
	Terbuthylazin	Chlorophyta > Cyanobacteria	−1.9 to -1.8	Terbuthylazin		< −2
Invertebrates						
Metals	Cu	Rotifera > Crustacea > Mollusca > Cnidaria > Insecta	2.5 to 6.4	Cu	Cnidaria > Insecta > Mollusca > Crustacea > Rotifera	−1.1 to 1.2
	Zn	Crustacea > Mollusca	2.8 to 2.9	Zn	Mollusca > Crustacea	−0.6 to 0.3
	Cd*	Crustacea > Rotifera	0.3 to 1.4	Hg*$^{\Delta}$	Crustacea > Mollusca	−0.7 to 0
	Hg*$^{\Delta}$	Crustacea > Mollusca	0.4 to 1.3	Cd*	Mollusca > Rotifera > Crustacea	−1.4 to −0.9
	Pb*$^{\Delta}$	Insecta	−1.1	Pb*$^{\Delta}$		< −2
PAH	Anthracene*$^{\Delta}$	Crustacea	1.9	Fluoranthene*$^{\Delta}$	Insecta	−0.1
	Fluoranthene*$^{\Delta}$	Insecta > Crustacea	0.96 to 1.2	Benzo[a]pyrene*	Crustacea	−1.3
	Benzo[a]pyrene*	Crustacea	0.4 to 1.1	Phenanthrene	Cnidaria	−1.9
	Benz[a] Anthracene*$^{\Delta}$	Crurstacea	1	Anthracene*$^{\Delta}$		< −2
	Pyrene	Crustacea	0.8	Benz[a] Anthracene*$^{\Delta}$		< −2
	Fluorene	Crustacea	−0.9 to 0.1	Pyrene		< −2
	Phenanthrene	Crustacea > Cnidaria	−0.5 to −0.1	Fluorene		< −2
Pesticides	Imidacloprid	Insecta > Crustacea	1 to 1.8	Imidacloprid		< −2
	Carbendazim	Crustacea	0.4	Carbendazim		< −2
	Chlorpyrifos*$^{\Delta}$	Crustacea > Insecta	−1 to −0.5	Chlorpyrifos*$^{\Delta}$		< −2
	Pentachloro-phenol*	Crustacea > Insecta > Rotifera	−1.9 to −0.6	Pentachloro-phenol*		< −2
	2.4-D	Crustacea > Rotifera	−1.6 to −0.9	2.4-D		< −2
	Diuron*	Crustacea > Chelicerata	−2 to −1.1	Diuron*		< −2
	Glyphosate	Rotifera	−1.3	Glyphosate		< −2
Phenols	Phenol	Crustacea	0.6	Phenol		< −2
Phthalates	DEHP	Crustacea	1.5	DEHP		< −2

(*continued on next page*)

Table 1 (*continued*)

TU $_{wc}$				TU $_{avg}$		
Pollutant		Most affected taxonomic group	TU	Contaminant	Most affected taxonomic group	TU
	Butylbenzyl phthalate	Crustacea > Cnidaria > Insecta	−1.9 to −1.7	Butylbenzyl phthalate		< −2
Vertebrates						
Metals	Zn	Actinopterygii	2.2	Cu	Amphibia > Actinopterygii	−0.4 to −0.3
	Cu	Actinopterygii > Amphibia	1.7 to 2.2	Zn	Actinopterygii	−1.4
	Ni*	Actinopterygii	1.1	Hg*$^{\Delta}$	Actinopterygii	−1.5
	Cd*	Actinopterygii	−0.7	Ni*		<-2
	Hg*$^{\Delta}$	Actinopterygii	−0.1	Cd*		<-2
PAH	Fluoranthene*$^{\Delta}$	Actinopterygii > Amphibia	−0.2 to −0.1	Fluoranthene*$^{\Delta}$	Actinopterygii > Amphibia	−2 to −1.4
	Phenanthrene	Actinopterygii	−0.2	Phenanthrene	Actinopterygii	−1.7
	Benzo[a]pyrene*	Actinopterygii > Amphibia	−2.4 to −1	Benzo[a]pyrene*		<-2
Pesticide	Pentachloro-phenol*	Amphibia > Actinopterygii	−0.8 to −0.2	Pentachloro-phenol*	Amphibia	−1.8
	Diuron*	Actinopterygii	−1.6	Diuron*		<-2
Phenol	4-tert-Octylphenol	Actinopterygii	−0.4	4-tert-Octylphenol		<-2
	Phenol	Actinopterygii > Amphibia	−1.5 to −0.7	Phenol		<-2
	BPA	Actinopterygii	−1.6	BPA		<-2
Phthalate	DEHP	Actinopterygii	−0.5	DEHP		<-2
	Di-n-butyl phthalate	Actinopterygii	−1.8	Di-n-butyl phthalate		<-2

mostly affecting Actinopterygii and Amphibia, though with moderate risk (TU_{wc} from −0.2 to −0.8). Moreover, the 4-tert-Octylphenol, Phenol and BPA, and the Phtalates DEPH and Di-n-butyl phthalate showed a moderate risk for the Actinopterygii (TU_{wc} from −1.8 to −0.5).

TUs could not be calculated for some flame retardants (e.g., Triphenyl phosphate, tributyl phosphate), metals (e.g., selenium), phthalates (e.g. butylbenzyl phthalate), phenols (e.g., 4-tert-octylphenol), or pesticides (e.g. irgarol). This is a relevant constraint to obtain an accurate risk assessment, and it is limiting for some groups of organisms. As an example, ecotoxicological data for mollusks regarding phthalates, some PAHs (e.g., Benz[a]pyrene, Fluoranthene) and pesticides (e.g., Diuron), are missing. Mollusks play a crucial role in the functioning of freshwater ecosystems as primary consumers and exhibit distinct physiological and ecological traits, which often do not match those characterizing crustaceans or insects. Relying solely on the higher taxonomical category of invertebrates for risk assessment, and not considering the variability within (i.e., mollusks, in this case), may lead to misrepresenting the sensitivities and responses of their components. In fact, the SSD for zinc showed that mollusks were the most sensitive to this pollutant, even more than the basal compartments of the food web such as algae or bacteria. Thus, considering the impacts on the multiple taxa present in freshwaters (Rosner et al., 2024) is essential for a comprehensive understanding of the impact of urban runoff effluents.

Overall, our analysis reflects an unequal knowledge regarding the potential or observed impact on the biological groups present in freshwaters. In general, algae and some invertebrates (i.e., crustacea, insects, mollusks) are the most widely tested groups, while the effect on vertebrates is poorly known. This bias repeats within each of the different biological groups, since many of the studies are related to the response of model species (e.g., *Raphidocelis subcapitata*, *Chlorella vulgaris*, *Daphnia magna*, *Chironomus riparius*, *Danio rerio*), and the effects on whole biological communities are rarely considered (Rosner et al., 2024). Further, many studies target specific biological groups, and only a few consider more than a single group, and hence the impacts on the trophic food web are largely ignored (but see Van Meter and Swan, 2014). The scarcity of studies and derived data is even more shocking in what is concerned to the effects of urban runoff pollutants on the ecosystem functions. Performing a similar search on functions as that done by Peters et al. (2013), we could only find a few studies regarding the ecotoxicological effects of urban runoff on ecosystem functions.

Data on chronic effects of urban runoff pollutants are also scarce, though chronic effects may be highly significant (Kuzmanovic et al., 2015). Freshwater organisms exposed to urban runoff pollutants can suffer chronic effects due to regular episodic exposures, sediment contamination, and bioaccumulation (Brausch and Rand, 2011; Ginebreda et al., 2010). Pollutants such as PAHs, metals, or some pesticides originating in urban runoff may accumulate in sediments, providing a persistent source of exposure to sediment-dwelling organisms, such as invertebrates or epipsammic biofilms, but also may be resuspended during erosive peak flows, then affecting organisms thriving in the water column (Barbosa et al., 2012; Flanagan et al., 2021; Fuchte et al., 2022). The relevance of acute toxicity is closely linked to the occurrence of the first flush and its potential impact on the ecosystem as short-term pulses. Capturing this impact requires identifying the occurrence of the first flush of urban runoff (Gao et al., 2023) and monitoring its potential effect on the freshwater biota and ecosystems. First flushes occur as pollutant mixtures, with unknown additive, synergistic or antagonistic effects (Zhu et al., 2022), which might difficult predicting their effects.

4. Conclusions and implications

Our analysis exposed several limitations, including an insufficient knowledge of chemicals present in urban runoff, as well as the incomplete characterization of their ecotoxicological effects. The effects of other contaminants present in urban runoff effluents might also be relevant to characterize their impact on freshwaters, through the lack of comprehensive toxicological data or their limited detection in urban runoff studies have constrained their inclusion in this study. Future assessments of contaminant impact on freshwater ecosystems need to include them as soon as research data becomes available. Our study aims to lay the groundwork for a systematic methodology that can be expanded to incorporate new contaminants as they emerge. Another relevant limitation is the biased knowledge of biological groups and functions, which highlights the response of invertebrates or fish, while neglecting the impact on ecological functions (primary production, decomposition, or respiration). These overall limitations require acknowledging that the risks of urban runoff to freshwater ecosystems may be underestimated or overlooked.

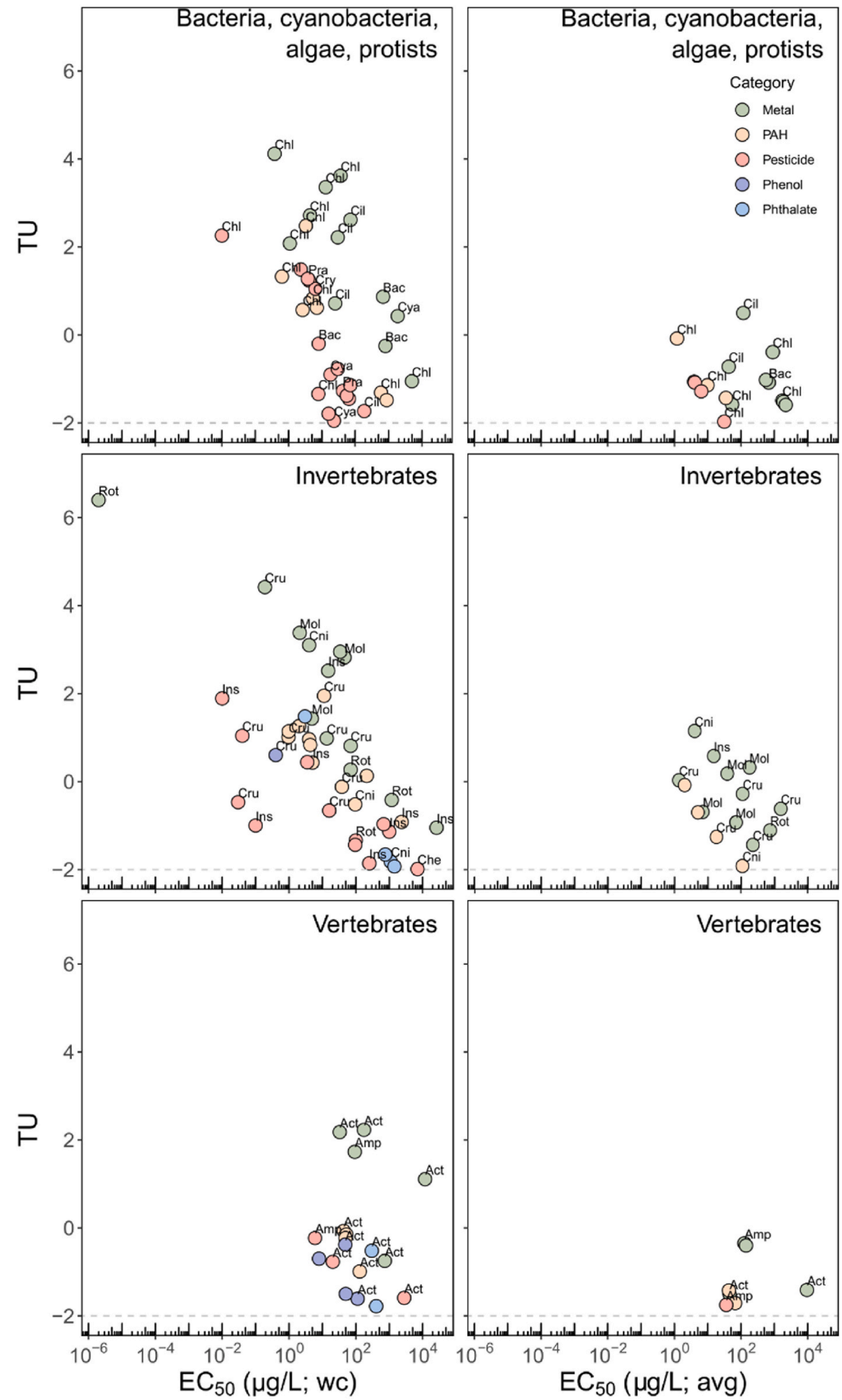

Fig. 2. Pollutant effects for the different taxonomic groups in the worst-case (left) and average (right) scenarios. The contaminants are the most commonly occurring in urban runoff, the different contaminant categories identified by respective colors. The plots relate the two descriptors of their toxicity (EC50 and TU > −2). Abbreviations refer to: Act = Actinopterygii, Amp = Amphibia, Bac = Bacillariophyta, Che = Chelicerata, Chl = Chlorophyta, Cil = Ciliophora, Cni = Cnidaria, Cru = Crustacea, Cry = Cryptophycophyta, Cya = Cyanophycota, Ins = Insecta, Mol = Mollusca, Pra = Prasinophyta and Rot = Rotifera.

Still, the collected evidence indicates some consistent emerging patterns. Pollutants from urban runoff may be a major threat to urban freshwater ecosystems, due to the presence of a wide diversity of pollutants, several of them potentially hazardous. This general statement is supported both by our literature search as well as the TUs calculations. Metals, pesticides and PAHs may have the most toxic effects on freshwater organisms, and their toxicity is more intense on the basal components of the food web (bacteria, protists, fungi, algae), less on invertebrates, and even less in vertebrates. Vertebrates become only affected at extremely high concentrations, rarely observed in urban runoff.

The intensity of the urban runoff pulses also interacts with the dilution capacity of the receiving ecosystem, and therefore may be more severe when the dilution is low. Graham et al. (2024) observed that the decreased water volume in the receiving waterbodies (especially during drought periods) caused an increase in water conductivity, lower concentration of total suspended solids, as well as lower dissolved oxygen. Under these circumstances, the biota is already stressed, and the potential impacts of urban runoff pollutants may be significantly magnified beyond anticipated levels, even leading to ecological surprises (Lindenmayer et al., 2010).

Using comprehensive environmental management strategies of the effects of urban runoff effluents requires recognizing the potential toxicity of the pollutants present. Still, only 17 of the most common pollutants in urban runoff (Suppl. Table 2, Suppl. Table 6) are included in the list of Priority Substances of the Water Framework Directive. Fourteen also showed maximum occurrence levels in urban runoff above the maximum environmental quality standards (MaxEQS), and 12 showed average occurrence levels above the annual average EQS (AAEQS). The metals Ni and Cd, the pesticides chlorpyrifos, diuron and pentachlorophenol, and PAHs, exceed both the maximum and average EQS. Anthracene, fluoranthene, Pb, Hg and chlorpyrifos are considered Priority Hazardous substances. In addition, chlorpyrifos, Hg and fluoranthene are also considered uPBT (ubiquitous, persistent, bioaccumulative, and toxic substances). While these thresholds have been estimated for the pollutant levels in surface waters, our toxicological estimations in urban runoff indicate that effects may be relevant when the dilution capacity of the receiving system is low.

Further research steps are required to comprehend the full potential impact of urban runoff on freshwater ecosystems, as well as to develop adequate policies for their proper management. One of these is to identify the full spectrum of pollutants present in urban runoff, including those from novel materials and chemical formulations, by improving the detection methods for low concentration micropollutants and their transformation products. It is also urgent to understand the effects of chemical mixtures which characterize urban runoff effluents. Future research should focus on understanding the additive, synergistic, or antagonistic effects of chemical mixtures on freshwater organisms. The development of mixture toxicity models could significantly improve predictions of ecological risks.

Beyond chemical characterization, more attention is needed on how seasonal changes and climate conditions, such as droughts or intense rainfall events, influence the mobilization, concentration, and ecotoxicological impact of these contaminants. This aspect is crucial to anticipate how climate change may alter the dynamics and impacts of urban runoff pollutants and might be particularly important in the context of water scarcity (Graham et al., 2024). Persistent dry conditions may favor the accumulation of pollutants, intensifying both immediate/acute and long-term ecological risks when get to freshwaters. In fact, understanding the long-term ecotoxicological effects of urban runoff effluents seems imperative. While acute toxicity effects have been relatively well-studied, there is a need to understand the chronic and sub-lethal effects of low-level exposure to contaminants that could lead to pseudo-persistence in freshwaters. Finally, enhancing the current ecotoxicological data sets by incorporating results from multiple species and endpoints, especially for emerging contaminants where data are currently limited, might be critical to improve ecological risk assessment tools such as the Toxic Units (TU) estimates.

Our results emphasize the need for improved prevention and mitigation measures to address the impact of urban runoff contaminants on freshwater systems. By identifying the types and concentrations of contaminants present in urban runoff, targeting specific pollutants is feasible. This is the case of using Granular Activated Carbon (GAC) Adsorption systems for PFAS removal (Cantoni et al., 2021). However, the lack of toxicological data for several contaminants and the potential for long-term effects suggest taking cautionary approaches, such as Nature-Based Solutions (e.g., riparian buffers or natural wetlands) which may help intercepting urban runoff and naturally reduce pollutant entry into waterways. Replacing asphalt surfaces with green urban infrastructure (e.g., green roofs and permeable pavements) can aid in retaining contaminants and reducing levels of pollutants, such as PAHs and metals. Finally, understanding the true impact of urban runoff requires the implementation of long-term monitoring programs to assess contaminant presence and effects, particularly in the most vulnerable urban areas.

CRediT authorship contribution statement

Lorena Cojoc: Writing – review & editing, Writing – original draft, Visualization, Methodology, Data curation, Conceptualization. **Núria de Castro-Català:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Data curation. **Ioar de Guzmán:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Data curation. **Julene González:** Writing – review & editing, Data curation. **Maite Arroita:** Writing – review & editing. **Neus Besolí-Mestres:** Writing – review & editing, Data curation. **Isabel Cadena:** Writing – review & editing, Data curation. **Anna Freixa:** Writing – review & editing, Visualization, Data curation. **Oriol Gutiérrez:** Writing – review & editing. **Aitor Larrañaga:** Writing – review & editing, Investigation, Funding acquisition. **Isabel Muñoz:** Writing – review & editing, Investigation, Funding acquisition. **Arturo Elosegi:** Writing – review & editing, Writing – original draft, Investigation, Funding acquisition. **Mira Petrovic:** Writing – review & editing, Investigation, Funding acquisition. **Sergi Sabater:** Writing – review & editing, Writing – original draft, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This paper was funded by the project “City runoff pollution impacts on river biodiversity under extreme climatic events”, CityPoll (TED2021-129966B-C31, TED2021-129966B–C32, and TED2021-129966B–C33) funded by MCIN/AEI/10.13039/501100011033 and by the European Union NextGeneration EU/PRTR. We thank the Generalitat de Catalunya through the Consolidated Research Group 2021 SGR 01282 (ICRA-ENV). ICRA researchers thank funding from the CERCA institution. LC and JG were funded by the Investigo Programme of the NextGeneration EU.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.143806.

Data availability

All data are provided in Supplementary Inrformation

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