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Urban Stormwater: An Overlooked Pathway of Extensive Mixed Contaminants to Surface and Groundwaters in the United States

Jason R. Masoner^{*,†}, Dana W. Kolpin[‡], Isabelle M. Cozzarelli[§], Larry B. Barber^{||}, David S. Burden[⊥], William T. Foreman[¶], Kenneth J. Forshay[⊥], Edward T. Furlong[¶], Justin F. Groves[⊥], Michelle L. Hladik[#], Matthew E. Hopton[⊗], Jeanne B. Jaeschke[§], Steffanie H. Keefe^{||}, David P. Krabbenhoft[×], Richard Lowrance[⊥], Kristin M. Romanok⁺, David L. Rus[§], William R. Selbig[×], Brianna H. Williams⁺, Paul M. Bradley[○]

[†] U.S. Geological Survey, Oklahoma City, Oklahoma 73116, United States

[‡] U.S. Geological Survey, Iowa City, Iowa 52240, United States

[§] U.S. Geological Survey, Reston, Virginia 20192, United States

^{||} U.S. Geological Survey, Boulder, Colorado 80303, United States

[⊥] U.S. Environmental Protection Agency, Ada, Oklahoma 74820, United States

[¶] U.S. Geological Survey, Lakewood, Colorado 80225, United States

[#] U.S. Geological Survey, Sacramento, California 95819, United States

[⊗] U.S. Environmental Protection Agency, Cincinnati, Ohio 45268, United States

[×] U.S. Geological Survey, Madison, Wisconsin 53711, United States

⁺ U.S. Geological Survey, Lawrenceville, New Jersey 08648, United States

[§] U.S. Geological Survey, Lincoln, Nebraska 68512, United States

[○] U.S. Geological Survey, Columbia, South Carolina 29210, United States

Abstract

Increasing global reliance on stormwater control measures to reduce discharge to surface water, increase groundwater recharge, and minimize contaminant delivery to receiving water-bodies necessitates improved understanding of stormwater—contaminant profiles. A multiagency study of organic and inorganic chemicals in urban stormwater from 50 runoff events at 21 sites across

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* **Corresponding Author** jmasoner@usgs.gov.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: [10.1021/acs.est.9b02867](https://doi.org/10.1021/acs.est.9b02867).

Method details, sampling information, and additional sample results ([PDF](#))

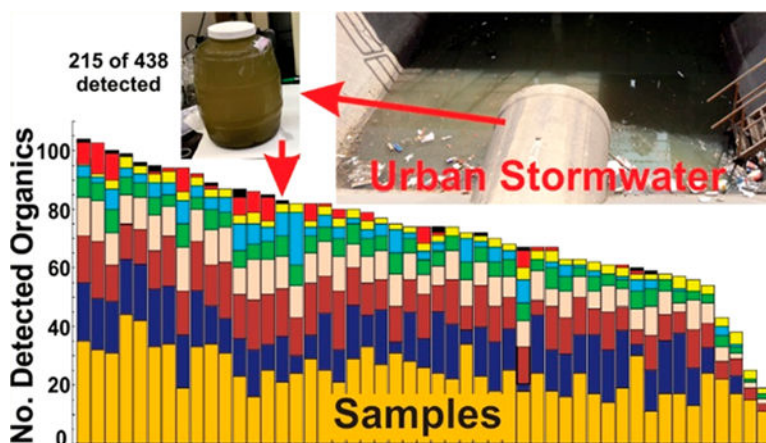
Additional sampling information and characterization data ([XLSX](#))

The authors declare no competing financial interest.

All analytical data are available in the U.S. Geological Survey National Water Information System at <http://dx.doi.org/10.5066/F7P55KJN> or in the associated data releases that follow Public Access Plan.^{50,51}

the United States demonstrated that stormwater transports substantial mixtures of polycyclic aromatic hydrocarbons, bioactive contaminants (pesticides and pharmaceuticals), and other organic chemicals known or suspected to pose environmental health concern. Numerous organic-chemical detections per site (median number of chemicals detected = 73), individual concentrations exceeding 10 000 ng/L, and cumulative concentrations up to 263 000 ng/L suggested concern for potential environmental effects during runoff events. Organic concentrations, loads, and yields were positively correlated with impervious surfaces and highly developed urban catchments. Episodic storm-event organic concentrations and loads were comparable to and often exceeded those of daily wastewater plant discharges. Inorganic chemical concentrations were generally dilute in concentration and did not exceed chronic aquatic life criteria. Methylmercury was measured in 90% of samples with concentrations that ranged from 0.05 to 1.0 ng/L.

Graphical Abstract



INTRODUCTION

Urban stormwater runoff is a recognized contributor to surface water impairment in the United States.^{1,2} Nutrients, heavy metals, bacteria, chlorophenols, and polycyclic aromatic hydrocarbons (PAHs) are commonly reported in stormwater runoff.³⁻¹² Limited research has shown that stormwater also can contain contaminants such as pesticides, pharmaceuticals, personal care products, alkyphenol surfactants, and phthalates.¹³⁻¹⁶ Stormwater runoff is often collected in retention ponds and constructed wetlands where additional contaminants, such as methylmercury (MeHg), can be produced at rates similar to those seen in natural wetlands.¹⁷ Stormwater runoff events discharging into rivers and reservoirs can adversely affect macroinvertebrates,¹⁸ particularly benthic organisms,¹⁹⁻²¹ and may pose a risk to human health through recreational exposures or possible harvesting of aquatic or terrestrial organisms.^{10,18,20-25}

Municipalities and water-management agencies worldwide are increasingly using stormwater control measures (SCMs) at various scales to minimize contaminant transport to receiving waterbodies, reduce stormwater volumes, collect stormwater for reuse, and increase groundwater recharge.²⁶⁻³⁴ Current storm-water reuse applications range from

indirect potable reuse through enhanced aquifer recharge to creation of stormwater-retention wetlands/ponds/lakes that provide aquatic habitats and serve as recreational locations in urban settings or are used as a water source for irrigation in urban and agricultural landscapes. A recent review of >100 studies indicated that SCMs can be an effective approach for reducing concentrations of select contaminants, including total suspended solids, nutrients, copper, and zinc.³⁵ At the national scale, however, little is known about the potential chemical exposures resulting from organic and inorganic contaminants in urban stormwater runoff or the potential effects on groundwater/surface water quality or ecosystem health.

To address this nationwide data gap, the U.S. Geological Survey and U.S. Environmental Protection Agency, in collaboration with municipalities, conducted a national-scale study of 438 organic (e.g., biogenic hormones, halogenated chemicals, household/industrial chemicals, methylmercury, pesticides, pharmaceuticals, and semivolatiles) and 62 inorganic (e.g., anions, cations, rare-earth elements, trace metals, and total mercury) chemicals in urban stormwater. This article analyzes results from 50 storm events at 21 sites across the U.S. to better understand the contaminant contribution of stormwater to surface water, groundwater, and the potential contaminant-exposures to sensitive organic receptors. In addition, correlations between select ancillary stormwater/catchment characteristics and the less understood organic chemicals were analyzed to better understand the factors that control organic-chemical concentrations. This research provides a foundation for future investigations of fate, exposure, toxicity, and risk from stormwater-contaminant mixtures discharged to surface waterbodies or infiltrated to groundwater.

MATERIALS AND METHODS

Urban Stormwater Runoff Sites.

From August 2016 to December 2017, 50 stormwater samples and 7 field quality-assurance samples were collected across 21 sites in 17 states (Figure SI-1 and Table SI-1). Sample sites were in stormwater conveyance infrastructure that discharged mixed stormwater runoff from buildings, parking lots, roads, and other infra-structure in residential, commercial, and industrial landscapes prior to surface water discharge or groundwater infiltration. Samples were collected in conveyance infrastructure constructed of concrete culverts that were buried underground, open concrete canals, or open dirt channels (Table SI-1). Catchment areas ranged from 0.1 to 1 000 km² (Figure SI-2A). A total of 18 of 21 sites were characterized by >90% developed (cumulative developed low-medium-high intensity and urban open space) land-use/land-cover based on the 2011 National Land Cover Data set (LULC, Figure SI-2B).³⁶ In total, 13 (62%) of the 21 sample sites discharged to surface water, whereas the remainder infiltrated stormwater to groundwater. State abbreviations were used as field names with concatenated “-I” to indicate sites that infiltrated stormwater to groundwater. For all sites, sampling occurred in conveyance infrastructure at or near outfalls before discharge to urban surface water networks or upstream of SCMs prior to treatment and infiltration.

Sampling Protocols.

Sampling equipment, tubing, and composite-sample containers used to collect stormwater were (1) cleaned using tap water and anionic detergent and thoroughly rinsed with tap water followed by deionized water, (2) soaked overnight in a 5% hydrochloric acid bath, (3) rinsed with pesticide-free methanol, and (4) air-dried and placed in clean reclosable plastic bags.³⁷ In total, 43 flow-weighted composite samples were collected at 14 sites using refrigerated-automated samplers (Teledyne, Thousand Oaks, CA) and 7 time-weighted composite samples were collected manually (1000 mL collected every 10 min at the beginning of the runoff event) using a polytetrafluoroethylene DH-81 isokinetic water-quality sampler (Table SI-1).³⁷ Both automated and manual sampling approaches targeted a 10-L composite sample (consisting of 10–30 subsamples of 250–1000 mL each) collected across the storm-runoff hydrograph (Figure SI-3).

Automated samplers were equipped with polytetrafluoro-ethylene tubing and intake screens, 30 cm in length silicone peristaltic-pump tubing, and a 10-L glass container. Four sampling sites (AZ1, AZ2, CA1, and CA2-I) with ongoing automated-sampler monitoring efforts had dedicated poly-ethylene tubing. Automated samplers were programmed to perform a field rinse of the sample tubing from the intake screen to the peristaltic pump head upon initiation and prior to collection of each subsample. Retrieval of composite samples occurred within 48 h of sample collection. Composite samples were labeled, double bagged, and shipped overnight on ice to the laboratory for processing and splitting into subsamples for analyses. A 14-L polytetrafluoroethylene churn-splitter was used to split composite samples into subsamples for specific chemical analyses with all subsamples analyzed at U.S. Geological Survey laboratories using published methods (Table SI-2). Additional information on the calculation of storm-event discharges, organic-chemical loads and yields, and statistical analysis are provided in the Supporting Information.

Analytical Methods.

Eight analytical methods were used to determine concentrations of 438 organic chemicals in urban stormwater samples, including 109 liquid chromatography-tandem mass spectrometry (LC-MS/MS) pharmaceuticals and related chemicals,³⁸ 21 gas chromatography-tandem mass spectrometry (GC-MS/MS) hormones and related chemicals,³⁹ 67 GC-MS household and industrial chemicals,⁴⁰ 147 GC-MS and LC-MS/MS pesticides,^{41,42} 56 GC-MS semivolatiles, ⁴³ methylmercury,⁴⁴ and 60 GC-MS halogenated chemicals (Table SI-3; method details in the Supporting Information). Samples were analyzed for 62 inorganic chemicals/parameters, including alkalinity, concentrations of anions and cations,⁴⁵ trace elements and rare-earth elements,⁴⁶ total mercury,⁴⁷ and stable isotopes of oxygen and hydrogen.^{48,49}

All analytical data are available in the U.S. Geological Survey National Water Information System at <http://dx.doi.org/10.5066/F7P55KJN> or in the associated data releases that follow the Public Access Plan.^{50,51}

Quality Assurance.

Quality-assurance (QA) samples typically consisted of 10% laboratory reagent water blanks and reagent water spikes, three field equipment blanks, and four field replicates (Tables SI-4–SI-8). Equipment blanks were prepared in the field and the laboratory by processing certified organic and inorganic blank water through the sampling equipment in the same manner that field samples were collected and processed (Table SI-6). In addition, isotope-dilution standards (iDSs) or surrogate compounds were added to all organic samples prior to extraction or analyses. Chemical concentrations falling outside the calibration range for each method (i.e., exceeding the analytical calibration curve or falling between the limit of quantitation (LOQ) and long-term method detection limit (LT-MDL)) were considered estimated detections with reduced precision and accuracy and included as is herein. Of the 3 563 total detections, approximately 25% exceeded the highest-calibration point and approximately 27% were estimated between the LOQ and LT-MDL. Field detections less than blank sample concentrations were reported as nondetections, and the LOQ was raised to the concentration of the blank sample. Only *N,N*-diethyl-*meta*-toluamide (DEET) and phenol had field blank concentrations exceeding their LOQ (40 and 160 ng/L, respectively). All DEET and phenol data were retained in this paper, but the LOQ were raised (47 ng/L and 511 ng/L, respectively) and 38 concentrations of DEET and 10 concentrations of phenol that were <10 times the blank concentration were coded “V” (but used in interpretations) to indicate that the reported concentration may be influenced by contribution occurring during collection or analysis.

Median relative percent differences (RPDs) for replicate samples of organic chemicals ranged from 4% for GC-MS/MS biogenic hormones, GC-MS pesticides, and LC-MS/MS pesticides to 18% for GC-MS household and industrial chemicals (Table SI-7). Median RPDs were 1–5% for total mercury, alkalinity, anions, trace elements, and methylmercury (Table SI-7). Larger RPDs generally occurred in low-concentration samples. Overall median recoveries for laboratory reagent-spike samples ranged from 77 to 100% for organic methods (Table SI-8). Median recoveries for IDS and surrogate standards ranged 72–106% for 5 of 7 trace organic methods; recoveries for the other two methods, GC-MS halogenated chemicals and GC-MS/MS hormones, were 47% and 61%, respectively (Table SI-8). Additional quality-assurance data for anions, cations, and trace elements can be found in the associated data releases.^{50,51}

RESULTS AND DISCUSSION

Organic Chemical Mixtures in Urban Stormwater Runoff.

Increased implementation of stormwater capture and reuse as a common method of stormwater management underscores the importance of assessing organic contamination in urban stormwater and potential risks to surface water, aquatic organisms, and groundwater. Of the 438 organic chemicals analyzed, 215 (49%) were detected in one or more stormwater samples (Table SI-9) with 223 (51%) not detected in any sample (Table SI-10). The number of organic chemicals detected in a single stormwater sample ranged from 18 to 103 (median = 73; Figure 1A). Pesticides were the most frequently detected chemical group (accounting for 35% of total detections; Figure 1A). Cumulative organic-chemical concentrations of

samples ranged from 4 370 ng/L to 263 000 ng/L (median = 48 500 ng/L); with 7 samples having a total concentration exceeding 100 000 ng/L (Figure 1B). Of the 215 organics detected, 69 (32%) were frequently detected in >50% of samples (Figure 2). The 69 frequently detected organic chemicals accounted for 70% of the cumulative total 3 563 detections (Figure SI-4A) and were composed of 21 pesticides, 16 PAHs, 11 industrial chemicals, 11 household chemicals, 5 nonprescription pharmaceuticals, 3 plant/animal sterols, and 2 prescription pharmaceuticals (Figure 2). The 69 frequently detected organic chemicals that accounted for 70% of the total detections also accounted for 90% of the cumulative organic-chemical concentration (Figure 2 and Figure SI-4A). Concentrations of the 215 detected organic chemicals spanned over 6 orders of magnitude from less than 1.0 to over 100 000 ng/L (Figure 3A).

Eleven organic contaminants were pervasive across all samples (>90% detection): DEET (insect repellent, 98%), nicotine (alkaloid stimulant, 98%), caffeine (psychoactive stimulant, 96%), carbendazim (broad-spectrum fungicide and benomyl metabolite, 94%), methyl-1H-benzotriazole (corrosion inhibitor, 92%), p-cresol (wood preservative, 92%), cotinine (nicotine metabolite, 92%), desulfinyl fipronil (fipronil-insecticide metabolite, 90%), bisphenol A (plastics, paper receipts, and epoxy resin production, 90%), fluoranthene (PAH, 90%), and pyrene (PAH, 90%). Combined results from two recent studies in California and Minnesota have documented similar detection frequencies of these 11 storm-water contaminants.^{13,16} Although pesticides were the most frequently detected chemical group in the current study (accounting for 35% of all detections), they only accounted for 5% of the total organic concentrations, whereas PAHs accounted for 19% of total detections and 33% of total concentrations (Figures 1A and 3B and Figure SI-4B). Of the 16 frequently detected PAHs, benzo[*a*]anthracene, chrysene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and indeno[1,2,3-*cd*]pyrene are designated as probable human carcinogens and 13 are designated priority pollutants.⁵² Six of the frequently detected PAHs had maximum concentrations of >10 000 ng/L, including fluoranthene (36 700 ng/L), pyrene (29 100 ng/L), phenanthrene (28 800 ng/L), benzo[*b*]-fluoranthene (18 500 ng/L), chrysene (14700 ng/L), and benzo[*a*]pyrene (13 500 ng/L) (Figure 2). For two of these PAHs (pyrene and benzo[*a*]pyrene), previous research documented acute biological effects to embryo-larva of the pacific oyster following exposure to concentrations of 5 000 ng/L in the laboratory.⁵³ In addition, PAH concentrations measured for our study were substantially larger (PAHs up to 180 000 ng/L, with 42% of sites >10 000 ng/L) than concentrations in runoff from unsealed-asphalt pavement (PAHs ranged from 160 to 340 ng/L) and similar to concentrations in runoff from parking lots treated with coal-tar and asphalt-emulsion sealcoats (PAHs ranged from 3 800 to 21 000 ng/L).^{10,11} Thus, the frequency and concentrations of PAHs measured in urban stormwater runoff are of concern considering the documented detrimental effects of coal-tar based sealcoats and PAHs on terrestrial and aquatic ecosystems.⁵⁴⁻⁶¹

Concentrations of 21 frequently detected (>50%) pesticides spanned 5 orders of magnitude from <1 to >10 000 ng/L (Figure 2). Detected pesticides with maximum concentrations >1000 ng/L including carbendazim (fungicide, 9 570 n g/L), pentachlorophenol (restricted-use insecticide, 3 500 ng/L), and diuron (urea herbicide, 1 790 n g/L) were measured at substantially larger (>1 magnitude) concentrations than previously reported in stormwater runoff from residential and commercial catchments in Wisconsin and Minnesota.^{13,14}

Carbendazim has been shown to alter gene expression related to oxidative stress, apoptosis, and immune and endocrine disruption in aquatic organisms during larvae development when exposed to concentrations as low as 4 000 ng/L.⁶² Extensively used agricultural herbicides atrazine and metolachlor, dithiopyr (pre-emergent), DCPMU (diuron degradate), along with the insecticides imidacloprid (neonicotinoid) and fipronil (broad-spectrum), generally ranged in concentration from 3 to 300 ng/L (Figure 2). Recent studies also documented similar concentrations for atrazine and metolachlor in storm-water runoff from a residential landscape¹³ and imidacloprid and fipronil concentrations in urban creeks sampled during runoff events.^{13,63} Temporally increasing imidacloprid detection has been reported in urban streams and attributed to increased home and garden use.⁶⁴

In our study, 74% (37) of the detected imidacloprid concentrations exceeded the 10 ng/L U.S. EPA chronic aquatic life benchmark (ALB) for invertebrates, and 44% (22) of detected fipronil concentrations exceeded the 11 ng/L ALB.⁶⁵ The frequently detected banned insecticides, technical chlordane (cis-chlordane, trans-chlordane, trans-nonachlor, cis-nonachlor) and dieldrin, restricted-use insecticide chlorpyrifos, and the pentachlorophenol degradant pentachloroanisole generally ranged in concentration from 0.2 to 14 ng/L. The historical targeted treatment of urban residential and commercial properties with now banned insecticides for uses such as termite control (i.e., technical chlordane, USA banned >30 years) can provide a continuous source of these persistent legacy insecticides.⁶⁶ The frequent detection of such legacy insecticides illustrates the importance of continued monitoring and management of persistent compounds that are no longer used but may still pose aquatic or human health risks.⁶⁷

Urban stormwater is frequently contaminated with human waste via sources such as leaks from aging-sewage infra-structure.⁶⁸ The frequent detection of prescription pharmaceuticals (i.e., metformin 73%) and nonprescription pharmaceuticals (i.e., acetaminophen 84% and lidocaine 69%) in this study also suggests a potential human waste component in stormwater. Although 27 prescription pharmaceuticals were detected at least once in stormwater samples (Table SI-9), only 2 were detected in >50% of samples, metformin and methenamine (Figure 2). Guanylurea (metformin degradate) was detected in 27% of samples. Metformin is a prevalent environmental contaminant⁶⁹⁻⁷¹ with documented health effects to fish.⁷¹⁻⁷³ The median metformin concentration (102 ng/L) in our study (herein, all reference to median values are based on distribution of detected concentrations) distribution was about 7 times higher than from a previous study of urban stormwater.¹³ Two antibiotic concentrations of 6 030 ng/L for sulfamethoxazole and 3 420 ng/L for methenamine were the highest measured prescription pharmaceuticals in stormwater samples. Research has documented negative effects on growth, nitrate reduction activity, and microbial community structure from exposure to sulfamethoxazole at concentrations as low as 1 110 ng/L.^{74,75}

Caffeine and nicotine were the most frequently detected (>96%) nonprescription pharmaceuticals and measured at the highest concentrations (maximum of 32 200 ng/L and 18 300 ng/L, respectively), composing 89% of the total nonprescription pharmaceutical concentration. When including their degradants (dimethylxanthine and cotinine), caffeine and nicotine comprised 96% of the total nonprescription pharmaceutical concentration.

There are multiple pathways within the urban landscape for caffeine and nicotine (and their degradants) to enter stormwater including the improper disposal of caffeinated products and cigarette butts⁷⁶ and leaking sewage infrastructure.⁶⁸ Median detected concentrations of caffeine (942 ng/L), nicotine (782 ng/L), and acetaminophen (113 ng/L) measured in composite stormwater samples for this study were generally 4 times larger than median concentrations (207, 205, and 23.9 ng/L, respectively) reported in a recent stormwater study (using identical analytical methods) in which grab samples were collected.¹³

Overall, polychlorinated biphenyl/polybrominated diphenyl ethers (PCB/PBDEs) and biogenic hormones were detected less frequently and at lower concentrations than other chemical groups (Figures 1A and 3B), possibly in part from restricted PCB/PBDE use and limited sources of biogenic hormones across the urban landscape. The most frequently detected congeners were PBDE (22%) and PCB 138 (18%). Total PCB/PBDE concentrations in 12 samples from 6 sites ranged from 2 to 84 ng/L, with 6 samples exceeding the 14 ng/L chronic ALB for freshwater species.⁷⁷ *cis*-Androsterone was the most frequently detected (24%) biogenic hormone in this study and had a maximum concentration of 25 ng/L. Effects from exposure to *cis*-androsterone and other biogenic hormones in urban streams at low ng/L (5 ng/L) concentrations have been linked to reproductive and physiological effects in fish.⁷⁸

Results indicate that urban stormwater is transporting an extensive mixture of organic contaminants with highly variable individual-component concentrations (Figures 1–3). The potential environmental effects from exposure to individual chemicals or chemical mixtures in stormwater samples are currently unknown or not well understood.⁷⁹ The organic chemicals detected in stormwater cause concern for aquatic organisms because many of the chemicals persisting in the environment are known carcinogens (PAHs and PCBs), bioactive (pesticides and pharmaceuticals), or hormonally active (biogenic hormones). The multiple detections per site (median of 73 compounds), the ng/L to $\mu\text{g/L}$ individual concentrations, and sites with cumulative mixture concentrations exceeding 100 000 ng/L are concerning as adverse environmental effects have been documented for some individual designed-bioactive contaminants even at low ng/L concentrations.^{72,79–82} This study provides a snapshot of stormwater runoff derived from randomly sampled sites and sampling days from across the U.S. and measured concentrations could vary temporally and spatially.

Influence of Hydrologic and Watershed Characteristics on Organic-Chemical Compositions, Concentrations, Loads, and Yields.

Hydrologic/watershed characteristics (Table SI–1) and LULC metrics from the NLCD³⁶ (Table SI–11) were used to assess relations of these characteristics with cumulative-organic chemical detections, concentrations, loads (Table SI–12, Figure SI–5), and yields (Table SI–13, Figure SI–6). Spearman rank-order correlation identified significant (p -value <0.05) correlations between cumulative detections in storm-water samples and selected hydrologic/watershed characteristics (Table SI–14). There were positive correlations observed between cumulative detections and drainage area (p -value = 0.026, ρ = 0.317), developed high-intensity LULC (p -value <0.001, ρ = 0.492), and impervious LULC (p -value = 0.009, ρ = 0.368). Positive correlations were identified between cumulative concentrations in

stormwater samples and developed high-intensity LULC (p -value = 0.014, ρ = 0.350, Table SI–15) and impervious LULC (p -value = 0.015, ρ = 0.346). Negative correlations were identified between cumulative concentrations and storm-event precipitation (p -value = 0.021, ρ = -0.328) and runoff volumes (p -value = 0.048, ρ = -0.284), emphasizing the importance of precipitation dilution as a potential control on stormwater organic contamination.

Expected positive correlations were observed between organic-chemical loads and site-specific runoff volumes (p -value <0.001, ρ = 0.883), drainage areas (p -value <0.001, ρ = 0.594), and storm event precipitation (p -value = 0.006, ρ = 0.385, Table SI–16). A positive correlation also was observed between organic-chemical loads and duration of antecedent dry days (p -value = 0.009, ρ = 0.368), consistent with previous findings that the duration of antecedent dry days is a driver of stormwater contaminant input.⁸ A negative correlation was present between cumulative stormwater loads and developed low-intensity (*e.g.*, residential) LULC (p -value = 0.008, ρ = -0.376). Positive correlations were identified between cumulative yields (load per unit area) and developed medium-intensity LULC (p -value = 0.014, ρ = 0.350), developed high-intensity LULC (p -value 0.001, ρ = 0.456), and impervious LULC (p -value <0.001, ρ = 0.528, Table SI–17). These results, which were generated using the largest national data set on organic stormwater contaminants to date, are consistent with previous studies with limited sites, geography, and chemical coverage and support the utility of LULC metrics as predictors of mixed-organic-contaminant complexity and the importance of developed LULC and impervious surfaces as stormwater-contaminant sources.^{14,83}

Comparison of Organic Contamination in Urban Stormwater Runoff, Streams, and Treated Wastewater Discharge.

Streams across the U.S. contain a diverse mixture of organic chemicals.^{83–85} How compositions and concentrations of organic chemicals in U.S. streams compare with those in urban stormwater runoff is poorly documented, however. A comparison of results of the present stormwater study with a previous national study of 38 agricultural/developed impacted streams⁸³ (most organic chemicals analyzed using identical analytical methods) revealed many of the same chemicals in both stormwater runoff and agricultural/developed impacted streams with concentrations generally an order of magnitude greater in untreated stormwater runoff assessed in this study. A greater detection frequency (86%) and higher maximum concentrations (331 ng/L) of imidacloprid (agricultural and urban neonicotinoid insecticide) were observed in urban stormwater compared to a previous study of agricultural streams in the Midwestern U.S. following precipitation events (23% and 42.7 ng/L, respectively).⁸⁴

Concentrations and loads observed in urban stormwater samples were compared with those reported in wastewater treatment plant (WWTP) effluent (a source that is systematically monitored and regulated) to assess the relative contribution of untreated stormwater (infrequently monitored and regulated) as an episodic source of organic contamination to surface waters. Such a comparison revealed concentrations of pesticides (*i.e.*, atrazine, carbendazim, diuron, and metolachlor) were generally larger in untreated stormwater

samples compared with previous studies of pesticides in treated effluent from WWTPs.^{86,87} However, the range of imidacloprid concentrations (4.9 to 331 ng/L, mean 48.2 ng/L) in our study were similar to those reported in a study of effluent from 13 WWTPs in the U.S. (20 to 143 ng/L, mean 48.6 ng/L).⁸⁸ Comparison with two previous studies on the occurrence and fate of PAHs in treated wastewater effluent^{89,90} revealed 2 to 3 orders of magnitude greater PAH concentrations in urban stormwater. A global comparison of urban stormwater in our study to WWTP effluent in Asia, North America, Europe, and Italy^{87,91–96} revealed: larger concentrations in urban stormwater for PAHs and bisphenol A; similar measured concentrations for metformin, acetaminophen, caffeine, lidocaine, household chemicals (DEET, tri(2-chloroethyl) phosphate, benzophenone, camphor, and triphenyl phosphate); and generally smaller concentrations in urban stormwater for prescription pharmaceuticals, cotinine, and biogenic hormones compared to WWTP effluent.

The length of the single-event storm durations ranged from 0.3 to 48 h with a median storm-event duration of 5 h (Table SI–1). Single-event total organic-chemical loads observed in urban stormwater spanned 5 orders of magnitude ranging from 4.0 to 104 500 g, with a median of 176 g (Figure SI–5, Table SI–12). By comparison, a study of 42 priority pollutants (including PAHs, industrial chemicals, and PCBs) in treated effluent from a WWTP with a daily treatment capacity of up to 30 million L/day from a highly industrial (44%) sewage grid reported a total load of 825 g/day (industrial chemicals 819 g/day, PAHs = 5.6 g/day, PCBs = <0.1 g/day).⁹⁷ Twenty-eight storm events in our study (median duration of 2.5 h) produced runoff volumes between 1 to 25 million L and contributed total loads up to 725 g for industrial chemicals, 562 g for PAH, and 0.5 g for PCBs. Eight storm events in this study (median duration of 7 h) produced runoff volumes ranging from 0.1 to 2.5 billion L and contributed substantially higher (up to 40 times) total industrial chemical loads (range 165 to 40 100 g, Table SI–12; mean 8 200 g, Figure SI–7).

A previous study of 21 PAHs and 13 PCBs in treated wastewater effluent from a larger-scale WWTP with a daily treatment capacity of 1.3 billion L/day from a domestic (85%) sewage grid reported a total load of 703 g/day (PAHs 700 g/day, PCBs 3 g/day).⁹⁰ In the present study, large single-event (7 h median duration) untreated urban runoff volumes (0.1 to 2.5 billion L) contributed substantially larger total PAH loads that ranged from 9.6 to 2 820 g (mean 822 g, Figure SI–7) and substantially larger total PCBs loads up to 211 g (mean 27.1 g) than daily loads from WWTPs. In a national mass-balance assessment of neonicotinoid insecticides in 13 WWTPs across the U.S., imidacloprid was shown to persist through the wastewater treatment process of one example WWTP (870 million L/day treatment capacity) with loads of 12 g/day to surface waters.⁸⁸ Imidacloprid loads in untreated urban stormwater samples were generally larger and ranged from 2 to 68 g (mean 19 g) in large single-event stormwater runoff volumes (0.1–2.5 billion L). In contrast, a comparison of prescription pharmaceutical and biogenic hormone loadings in the present stormwater study with two comprehensive reviews of WWTP loads^{98,99} suggests generally lower pharmaceutical and biogenic hormone loadings from stormwater.

Organic-chemical concentrations and loads from single-event runoff volumes that were similar to daily treated volumes for WWTPs indicate that untreated urban stormwater potentially contributes (1) substantially larger loads of PAHs, pesticides, and PCBs; (2)

similar loads of household chemicals, industrial chemicals, and nonprescription pharmaceuticals; and (3) generally smaller loads of prescription pharmaceuticals, biogenic hormones, and plant animal sterols. The results indicate untreated stormwater is an important episodic source to surface waters of organic contaminants at levels comparable to and often exceeding those from the well-recognized, persistent treated WWTP effluent sources.

Inorganic Characterization of Urban Stormwater Runoff.

In general, the inorganic chemical concentrations in the urban stormwater samples were relatively dilute as suggested by specific conductance values that ranged from 38 to 1 074 $\mu\text{S}/\text{cm}$ (median of 164 $\mu\text{S}/\text{cm}$) and low concentrations of trace elements, anions, and cations (Figure SI-8, Tables SI-18 and SI-19).^{50,51} Chloride (Cl^-) and bicarbonate (HCO_3^- , as alkalinity) were the most abundant anions ranging from 817 to 196 000 $\mu\text{g}/\text{L}$ and 22 700 to 379 000 $\mu\text{g}/\text{L}$, respectively (Table SI-19). By comparison, Cl^- ranged from 46 000 to 199 000 $\mu\text{g}/\text{L}$ in a study of tertiary treated wastewater effluent.¹⁰⁰ No stormwater Cl^- concentrations exceeded the 230 000 $\mu\text{g}/\text{L}$ chronic ALB.⁷⁷ Sulfate (SO_4^{2-}) in stormwater had a maximum of 102 000 $\mu\text{g}/\text{L}$. Fluoride and phosphate (PO_4^{3-}) were both rarely observed in detectable concentrations (each detected in two samples). Dissolved phosphorus (P) was detected in all samples with concentrations that ranged from 4 to 778 $\mu\text{g}/\text{L}$ with a median = 92 $\mu\text{g}/\text{L}$, with 73% of the stormwater samples exceeding the total P criteria of 37 $\mu\text{g}/\text{L}$ for scenic rivers in states developing numeric water-quality criteria for total phosphorus.¹⁰¹ Elevated levels of nutrients, such as P, and PO_4^{3-} can cause water-quality and ecological problems in aquatic systems including fish kills, toxic algal blooms, depleted oxygen, and loss of biodiversity of species important for commerce and recreation.¹⁰² Decreasing P inputs to surface waters is a priority for many stormwater managers and SCM projects.¹⁰³

The major cation composition of urban stormwater was dominated by Na^+ and Ca^{2+} (Table SI-19). The maximum Ca^{2+} concentration of 89 200 $\mu\text{g}/\text{L}$ was measured in the same water as the maximum alkalinity, whereas the maximum Na^+ concentration of 95 900 $\mu\text{g}/\text{L}$ was measured in the same water as the maximum Cl^- concentration. Magnesium (Mg^{2+}) concentrations ranged from 488 to 26 800 $\mu\text{g}/\text{L}$, with the highest concentration found at MN-I, a calcium-carbonate dominated water. Both Ca^{2+} and Mg^{2+} are considered beneficial components of drinking water and provide numerous health benefits.¹⁰⁴ In contrast, there is global concern about the increasing salinization of freshwater from anthropogenic sources, such as road deicing salt,^{105,106} and the costs associated with the loss of ecosystem services, biodiversity, recreational opportunities, and effects on human health.¹⁰⁷ Cl^- and Na^+ concentrations in our national study, which included stormwater samples collected across all seasons and all climates, were substantially smaller than those reported in urban stormwater from sites in cold climates¹⁰⁸ and similar to concentrations in previous stormwater studies.^{106,109}

Dissolved metals measured in the present stormwater study are more likely than particulate-associated metals to infiltrate into groundwater when stormwater is infiltrated into the subsurface.¹¹⁰ According to a recent study, cadmium (Cd), chromium (Cr), lead (Pb), manganese (Mn), aluminum (Al), and iron (Fe) in stormwater can pose human or

recreational health risks even at low concentrations when heavy metals are present as a mixture.²³ Median concentrations for Cd, Cr, Pb, Mn, Al, and Fe in the stormwater samples from this study were lower than the concentrations predicted from previous research to cause negative effects to aquatic organisms (Tables SI–18 and SI–19).²³ Metals such as barium (Ba), copper (Cu), and zinc (Zn) are closely linked to stormwater runoff because of their widespread use in construction and transportation activities.¹¹¹ In this study, the median stormwater concentrations of Ba (16 $\mu\text{g/L}$), Cu (5.5 $\mu\text{g/L}$), and Zn (15 $\mu\text{g/L}$) were lower than median concentrations reported in previous stormwater studies.^{112,113} Other metal concentrations were also generally low in stormwater samples and maximum concentrations for Cd (0.37 $\mu\text{g/L}$), Pb (2.1 $\mu\text{g/L}$), arsenic (As, 3.2 $\mu\text{g/L}$), nickel (Ni, 15 $\mu\text{g/L}$), total mercury (Hg, 0.18 $\mu\text{g/L}$), and Fe (325 $\mu\text{g/L}$) did not exceed chronic ALB (0.72, 2.5, 150, 52.0, 0.77, and 1000 $\mu\text{g/L}$, respectively).⁷⁷

In a recent review, rare earth elements (REEs) were described as an overlooked group of emerging contaminants that pose human and ecological health risks and warrant further assessment of potential impacts on surface water and groundwater systems.^{114,115} The use of REEs is expected to continue to increase due to their importance in many emerging industries, including the alternative energy sector (i.e., wind turbines, electric cars, solar panels). The REEs consist of 14 elements with similar charge and ionic radius and have been widely used as geochemical indicators of hydrogeological processes.^{116,117} Measurements of REEs in stormwater can be especially useful for identifying natural versus anthropogenic sources of contaminants.^{115,118} For example, anthropogenic gadolinium ($\text{Gd}_{\text{anthro}}$) is a synthetic organic Gd complex used in medical diagnostics,^{119,120} and a $\text{Gd}_{\text{anthro}}/\text{Gd}_{\text{background}}$ ratio >1.5 is a useful indicator of municipal wastewater effluent contribution.¹²⁰ Based on ratios from samples in this study, the presence of wastewater was greatest at the CA2-I and IN sites and to a lesser extent at sites NY-I, MI, and AZ1 (Figure SI–9). The analysis of REEs to indicate municipal wastewater coupled with frequent detection of pharmaceutical waste indicators (metformin, acetaminophen, and lidocaine) in the current study supports previous research that stormwater is often contaminated with human waste.⁶⁸

Even though total Hg was measured in stormwater samples at low concentrations that ranged from 0.004 to 0.18 $\mu\text{g/L}$ (well below the 0.77 $\mu\text{g/L}$ chronic ALB), stormwater remains a substantial source of Hg and could pose negative implications for SCMs that favor methylation of inorganic Hg to MeHg (Table SI–18 and Figure SI–10). MeHg is a highly toxic bioaccumulative neurotoxin that is widely recognized as a concern in surface waters, natural wetlands,^{121,122} and more recently in stormwater retention ponds and constructed wetlands.¹⁷ MeHg was measured in 90% of stormwater samples at concentrations that ranged from 0.05 to 1.0 ng/L (Table SI–18, Figure SI–10). The median MeHg concentration for this national study of urban stormwater (0.19 ng/L) was similar to medians reported in a national study of U.S. streams (0.11 ng/L)¹²³ and streams draining abandoned Hg mines (0.04 ng/L).¹²⁴ Total Hg and MeHg concentrations observed in this study suggest that SCMs that incorporate stormwater retention ponds or constructed wetlands should consider the potential exposure implications in these environments.

Implications for Environmental Receptors and Storm-water Reuse.

This national-scale study provides the most comprehensive representative snapshot of the urban storm-water-contaminant profile derived from randomly sampled sites and sampling days from across the U.S. to date. The effects from exposure to complex organic and inorganic contaminant mixtures at low concentrations are poorly understood, and a range of potential mixture effects are possible even when each individual chemical is present in a mixture at low concentrations determined not to have individual effects.^{79,81,82} Many organic and inorganic chemicals detected in the untreated stormwater samples in the present study are known to persist in the environment and, therefore, might be of priority concern for stormwater SCMs or municipal reuse and in terms of potential biological exposures and effects to receiving streams. This study underscores the need for continued assessment of exposures and potential synergistic effects of contaminant mixtures in storm-water, potential contaminant source tracking and mitigation methods, and studies of the fate, transport, and persistence of stormwater contaminants infiltrated to groundwater.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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REFERENCES

- (1). United States Environmental Protection Agency. 2000 National Water Quality Inventory Report to Congress, https://www.epa.gov/sites/production/files/2015-09/documents/2000nationalwater_qualityinventoryreporttocongress.pdf (accessed April 12, 2019).
- (2). Eckley CS; Branfireun B Mercury Mobilization in Urban Stormwater Runoff. *Sci. Total Environ.* 2008, 403, 164–177. [PubMed: 18582918]
- (3). Göbel P; Dierkes C; Coldewey WG Storm Water Runoff Concentration Matrix for Urban Areas. *J. Contam. Hydrol.* 2007, 91 (1–2), 26–42. [PubMed: 17174006]
- (4). Zgheib S; Moilleron R; Chebbo G Priority Pollutants in Urban Stormwater: Part 1 - Case of Separate Storm Sewers. *Water Res.* 2012, 46 (20), 6683–6692. [PubMed: 22209279]
- (5). Zgheib S; Moilleron R; Saad M; Chebbo G Partition of Pollution between Dissolved and Particulate Phases: What about Emerging Substances in Urban Stormwater Catchments? *Water Res.* 2011, 45 (2), 913–925. [PubMed: 20970821]
- (6). Brown JN; Peake BM Sources of Heavy Metals and Polycyclic Aromatic Hydrocarbons in Urban Stormwater Runoff. *Sci. Total Environ.* 2006, 359, 145–155. [PubMed: 16014309]
- (7). Paul MJ; Meyer JL Streams in the Urban Landscape. *Annu. Rev. Ecol. Syst.* 2001, 32 (1), 333–365.
- (8). Pitt R; Field R; Lalor M; Brown M Urban Stormwater Toxic Pollutants: Assessment, Sources, and Treatability. *Water Environ. Res.* 1995, 67 (3), 260–275.

- (9). Tedoldi D; Chebbo G; Pierlot D; Branchu P; Kovacs Y; Gromaire MC Spatial Distribution of Heavy Metals in the Surface Soil of Source-Control Stormwater Infiltration Devices — Inter-Site Comparison. *Sci. Total Environ.* 2017, 579, SS1–892.
- (10). Mahler BJ; Van Metre PC; Crane JL; Watts AW; Scoggins M; Williams ES Coal-Tar-Based Pavement Sealcoat and PAHs: Implications for the Environment, Human Health, and Stormwater Management. *Environ. Sci. Technol.* 2012, 46 (6), 3039–3045. [PubMed: 22296333]
- (11). Mahler BJ; Van Metre PC; Bashara TJ; Wilson JT; Johns DA Parking Lot Sealcoat: An Unrecognized Source of Urban Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol.* 2005, 39 (15), 5560–5566. [PubMed: 16124287]
- (12). Van Metre PC; Mahler BJ; Furlong ET Urban Sprawl Leaves Its PAH Signature. *Environ. Sci. Technol.* 2000, 34 (19), 4064–4070.
- (13). Fairbairn DJ; Elliott SM; Kiesling RL; Schoenfuss HL; Ferrey ML; Westerhoff BM Contaminants of Emerging Concern in Urban Stormwater: Spatiotemporal Patterns and Removal by Iron-Enhanced Sand Filters (IESFs). *Water Res.* 2018, 145, 332–345. [PubMed: 30165318]
- (14). Burant A; Selbig W; Furlong ET; Higgins CP Trace Organic Contaminants in Urban Runoff: Associations with Urban Land-Use. *Environ. Pollut.* 2018, 242, 2068–2077. [PubMed: 30076053]
- (15). Eriksson E; Baun A; Mikkelsen PS; Ledin A Risk Assessment of Xenobiotics in Stormwater Discharged to Harrestrup Å Denmark. *Desalination* 2007, 215 (1–3), 187–197.
- (16). Gan J; Bondarenko S; Oki L; Haver D; Li JX Occurrence of Fipronil and Its Biologically Active Derivatives in Urban Residential Runoff. *Environ. Sci. Technol.* 2012, 46 (3), 1489–1495. [PubMed: 22242791]
- (17). Strickman RJ; Mitchell CPJ Methylmercury Production and Accumulation in Urban Stormwater Ponds and Habitat Wetlands. *Environ. Pollut.* 2017, 221, 326–334. [PubMed: 27939209]
- (18). Chong MN; Sidhu J; Aryal R; Tang J; Gernjak W; Escher B Toze, S. Urban Stormwater Harvesting and Reuse: A Probe into the Chemical, Toxicology and Microbiological Contaminants in Water Quality. *Environ. Monit. Assess.* 2013, 185 (8), 6645–6652. [PubMed: 23264062]
- (19). Goldyn R; Szpakowska B; Swierk D; Domek P; Buxakowski J; Dondajewska R; Baralkiewicz D; Sajnog A Influence of Stormwater Runoff on Macroinvertebrates in a Small Urban River and a Reservoir. *Sci. Total Environ.* 2018, 625, 743–751. [PubMed: 29306163]
- (20). Pratt JM; Coler RA; Godfrey PJ Ecological Effects of Urban Stormwater Runoff on Benthic Macroinvertebrates Inhabiting the Green River, Massachusetts. *Hydrobiologia* 1981, 83, 29–42.
- (21). Ma Y; Liu A; Egodawatta P; McGree J; Goonetilleke A Assessment and Management of Human Health Risk from Toxic Metals and Polycyclic Aromatic Hydrocarbons in Urban Stormwater Arising from Anthropogenic Activities and Traffic Congestion. *Sci. Total Environ.* 2017, 579, 202–211. [PubMed: 27847187]
- (22). Haile RW; Witte JS; Gold M; Cressey R; McGee C; Millikan RC; Glasser A; Harawa N; Ervin C; Harmon P; et al. The Health Effects of Swimming in Ocean Water Contaminated by Storm Drain Runoff. *Epidemiology* 1999, 10 (4), 355–363. [PubMed: 10401868]
- (23). Ma Y; Egodawatta P; McGree J; Liu A; Goonetilleke A Human Health Risk Assessment of Heavy Metals in Urban Stormwater. *Sci. Total Environ.* 2016, 557–558, 764–772.
- (24). Soller J; Bartrand T; Ravenscroft J; Molina M; Whelan G; Schoen M; Ashbolt N Estimated Human Health Risks from Recreational Exposures to Stormwater Runoff Containing Animal Faecal Material. *Environ. Model. Softw.* 2015, 72, 21–32.
- (25). Young A; Kochenkov V; McIntyre JK; Stark JD; Coffin AB Urban Stormwater Runoff Negatively Impacts Lateral Line Development in Larval Zebrafish and Salmon Embryos. *Sci. Rep.* 2018, 8, 2830. [PubMed: 29434264]
- (26). Datry T; Malard F; Gibert J Dynamics of Solutes and Dissolved Oxygen in Shallow Urban Groundwater below a Stormwater Infiltration Basin. *Sci. Total Environ.* 2004, 329 (1–3), 215–229. [PubMed: 15262168]
- (27). Edwards EC; Harter T; Fogg GE; Washburn B; Hamad H Assessing the Effectiveness of Drywells as Tools for Stormwater Management and Aquifer Recharge and Their Groundwater Contamination Potential. *J. Hydrol* 2016, 539, 539–553.

- (28). Fischer D; Charles EG; Baehr AL Effects of Stormwater Infiltration on Quality of Groundwater Beneath Retention and Detention Basins. *J. Environ. Eng.* 2003, 129 (5), 464–471.
- (29). Lewellyn C; Lyons CE; Traver RG; Wadzuk BM Evaluation of Seasonal and Large Storm Runoff Volume Capture of an Infiltration Green Infrastructure System. *J. Hydrol. Eng.* 2016, 21 (1), No. 04015047.
- (30). Mrowiec M Road Runoff Management Using Improved Infiltration Ponds. *Transp. Res. Procedia* 2016, 14, 2659–2667.
- (31). Pitt R; Clark S; Field R Groundwater Contamination Potential from Stormwater Infiltration Practices. *Urban Water* 1999, 1 (3), 217–236.
- (32). Tedoldi D; Chebbo G; Pierlot D; Branchu P; Kovacs Y; Gromaire MC Spatial Distribution of Heavy Metals in the Surface Soil of Source-Control Stormwater Infiltration Devices - Inter-Site Comparison. *Sci. Total Environ.* 2017, 579, 881–892. [PubMed: 27884529]
- (33). Tedoldi D; Chebbo G; Pierlot D; Kovacs Y; Gromaire MC Impact of Runoff Infiltration on Contaminant Accumulation and Transport in the Soil/Filter Media of Sustainable Urban Drainage Systems: A Literature Review. *Sci. Total Environ.* 2016, 569–570, 904–926.
- (34). Luthy RG; Sharvelle S; Dillon P Urban Stormwater to Enhance Water Supply. *Environ. Sci. Technol* 2019, 53, 5534. [PubMed: 30807122]
- (35). Center for Watershed Protection. National Pollutant Removal Performance Database, <http://www.stormwaterok.net/CWP%20Documents/CWP-07%20Nat%20Pollutant%20Removal%20Perform%20Database.pdf> (accessed September 20, 2018).
- (36). Homer C; Dewitz J; Yang L; Jin S; Danielson P; Xian G; Coulston JW; Herold N; Wickham J; Megown K Completion of the 2011 National Land Cover Database for the Conterminous United States - Representing a Decade of Land Cover Change Information. *Photogramm. Eng. Remote Sensing* 2015, 81, 345–354.
- (37). Wilde FD, Radtke DB, Gibs J, Iwatsubo RT, Eds. Processing of Water Samples (ver. 2.2) In U.S. Geological Survey Techniques for Water Resources Investigations, Book 9, Section A, Chapter A5; U.S Geological Survey, 2002; p 166.
- (38). Furlong ET; Kanagy CJ; Kanagy LK; Coffey LJ; Burkhardt MR Determination of Human-Use Pharmaceuticals in Filtered Water by Direct Aqueous Injection-High-Performance Liquid Chromatography/Tandem Mass Spectrometry In U.S. Geological Survey Techniques and Methods; Book 5, Section B, Chapter B10, U.S Geological Survey, 2014; DOI: 10.3133/tm5B10.
- (39). Foreman WT.; Gray JL.; ReVello RC.; Lindley CE.; Losche SA.; Barber LB. Determination of Steroid Hormones and Related Compounds in Filtered and Unfiltered Water by Solid-Phase Extraction, Derivatization, and Gas Chromatography with Tandem Mass Spectrometry In U.S. Geological Survey Techniques and Methods, Book 5, Chapter B9; U.S Geological Survey, 2012; DOI: 10.3133/tm5B9.
- (40). Zaugg SD; Smith SG; Schroeder MP; Barber LB; Burkhardt MR Determination of Wastewater Compounds by Polystyrene-Divinylbenzene Solid-Phase Extraction and Capillary- Column Gas Chromatography/Mass Spectrometry In U.S. Geological Survey Techniques and Methods, Book 5, Chapter B2; U.S Geological Survey, 2006.
- (41). Hladik ML; Smalling KL; Kuivila KM A Multi-Residue Method for the Analysis of Pesticides and Pesticide Degradates in Water Using HLB Solid-Phase Extraction and Gas Chromatography-Ion Trap Mass Spectrometry. *Bull. Environ. Contam. Toxicol.* 2008, 80 (2), 139–144. [PubMed: 18196191]
- (42). Hladik ML; Calhoun D Analysis of the Herbicide Diuron, Three Diuron Degradates, and Six Neonicotinoid Insecticides in Water—Method Details and Application to Two Georgia Streams. U.S. Geological Survey Scientific Investigations Report 2012–5206; U.S. Geological Survey, 2012.
- (43). Fishman MJ Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory; Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments, Open-File Report 93–125, U.S. Geological Survey, 1993.
- (44). De Wild JF; Olson ML; Olund SD Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatographic Separation with Cold Vapor Atomic Fluorescence Detection, Open-File Report 01–445, U.S. Geological Survey, 2002.

- (45). Masoner JR; Kolpin DW; Furlong ET; Cozzarelli IM; Gray JL; Schwab EA Contaminants of Emerging Concern in Fresh Leachate from Landfills in the Conterminous United States. *Environ. Sci. Process. Impacts* 2014, 16 (10), 2335–2354. [PubMed: 25111596]
- (46). Barber LB; Paschke SS; Battaglin WA; Douville C; Fitzgerald KC; Keefe SH; Roth DA; Vajda AM Effects of an Extreme Flood on Trace Elements in River Water—From Urban Stream to Major River Basin. *Environ. Sci. Technol.* 2017, 51, 10344. [PubMed: 28862461]
- (47). EPA US. Method 1631: Mercury in Water by OxidationPurge and Trap, and Cold VaporAtomicFluorescence Spectrometry, Document 821-R-96-012, U.S. Environmental Protection Agency, 2002.
- (48). Revesz K; Coplen TB Determination of the d(18O/16O) of Water: RSIL Lab Code 489 In *Methods of the Reston Stable Isotope Laboratory*, Book 10, Section C, Chapter 2, U.S. Geological Survey; 2008; p 28.
- (49). Revesz K; Coplen TB Determination of the δ (2H/1H) of Water: RSIL Lab Code 1574 In *Methods of the Reston Stable Isotope Laboratory*, Book 10, Section C, Chapter 2, U.S. Geological Survey, 2008; p 27.
- (50). Jaeschke JB; Cozzarelli IM; Masoner JR; Fleger KL Geochemical Composition of Urban Stormwater Runoff Within the Conterminous United States from Samples Collected in 2016–2017, U.S. Geological Survey data release, 2018; DOI: 10.5066/P9Q7MD9J.
- (51). Keefe SH; Barber LB; Roth DA; Masoner JR; Bradley PM; Kolpin DW Survey of Major and Trace Elements in Stormwater Runoff from across the United States 2016 to 2017, U.S. Geological Survey data release, 2018; DOI: 10.5066/P90YU8VB.
- (52). Bojes HK; Pope PG Characterization of EPA's 16 Priority Pollutant Polycyclic Aromatic Hydrocarbons (PAHs) in Tank Bottom Solids and Associated Contaminated Soils at Oil Exploration and Production Sites in Texas. *Regul Toxicol. Pharmacol.* 2007, 47 (3), 288–295. [PubMed: 17291653]
- (53). Lyons BP; Pascoe CK; McFadzen IRB Phototoxicity of Pyrene and Benzo[a]Pyrene to Embryo-Larval Stages of the Pacific Oyster *Crassostrea Gigas*. *Mar. Environ. Res.* 2002, 54 (3), 627–631. [PubMed: 12408628]
- (54). Douben PET PAHs: An Ecotoxicological Perspective; John Wiley & Sons Ltd.: West Sussex, England, 2003.
- (55). Agency for Toxic Substances and Disease Registry. Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs), <https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=122&tid=25> (accessed April 14, 2019).
- (56). van Brummelen TC; van Hattum AGM; Crommentuijn T; Kalf DF Bioavailability and Ecotoxicity of PAHs In *The Handbook of Environmental Chemistry*, Vol. 3, Part J: PAHs and Related Compounds; Springer-Verlag, 1998; pp 203–263.
- (57). Ireland DS; Burton GA Jr.; Hess GG In Situ Toxicity Evaluations of Turbidity and Photoinduction of Polycyclic Aromatic Hydrocarbons. *Environ. Toxicol. Chem.* 1996, 15 (4), 574–581.
- (58). Diamond SA; Milroy NJ; Mattson VR; Heinis LJ; Mount DR Photoactivated Toxicity in Amphipods Collected from Polycyclic Aromatic Hydrocarbon-Contaminated Sites. *Environ. Toxicol. Chem.* 2003, 22, 2752–2760. [PubMed: 14587918]
- (59). Douben PET Assessing Risks from Photoactivated Toxicity of PAHs to Aquatic Organisms In *PAHs: Ecotoxicological Perspective*; Wiley: Hoboken, NJ, 2003; pp 275–296.
- (60). Bryer PJ; Elliott JN; Willingham EJ The Effects of Coal Tar Based Pavement Sealer on Amphibian Development and Metamorphosis. *Ecotoxicology* 2006, 15, 241–247. [PubMed: 16557355]
- (61). Bommarito T; Sparling DW; Halbrook RS Toxicity of CoalTar Pavement Sealants and Ultraviolet Radiation to *Ambystoma Maculatum*. *Ecotoxicology* 2010, 19, 1147–1156. [PubMed: 20440554]
- (62). Jiang J; Wu S; Wang Y; An X; Cai L; Zhao X; Wu C Carbendazim Has the Potential to Induce Oxidative Stress, Apoptosis, Immunotoxicity and Endocrine Disruption during Zebrafish Larvae Development. *Toxicol. In Vitro* 2015, 29 (7), 1473–1481. [PubMed: 26055223]

- (63). Weston DP; Chen D; Lydy MJ Stormwater-Related Transport of the Insecticides Bifenthrin, Fipronil, Imidacloprid, and Chlorpyrifos into a Tidal Wetland, San Francisco Bay, California. *Sci. Total Environ.* 2015, 527–528, 18–25.
- (64). Hladik ML; Kolpin DW First National-Scale Reconnaissance of Neonicotinoid Insecticides in Streams across the USA. *Environ. Chem.* 2016, 13 (1), 12–20.
- (65). United States Environmental Protection Agency. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides, <https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk> (accessed April 9, 2019).
- (66). Gerecke AC; Schärer M; Singer HP; Müller SR; Schwarzenbach RP; Sagesser M; Ochsenbein U; Popow G Sources of Pesticides in Surface Waters in Switzerland: Pesticide Load through Waste Water Treatment Plants--Current Situation and Reduction Potential. *Chemosphere* 2002, 48, 307–315. [PubMed: 12146619]
- (67). Rasmussen JJ; Wiberg-Larsen P; Baatrup-Pedersen A; Cedergreen N; McKnight US; Kreuger J; Jacobsen D; Kristensen DA; Friberg N The Legacy of Pesticide Pollution: An Overlooked Factor in Current Risk Assessments of Freshwater Systems. *Water Res.* 2015, 84, 25–32. [PubMed: 26207877]
- (68). Sidhu JPS; Ahmed W; Gernjak W; Aryal R; McCarthy D; Palmer A; Kolotelo P; Toze S Sewage Pollution in Urban Stormwater Runoff as Evident from the Widespread Presence of Multiple Microbial and Chemical Source Tracking Markers. *Sci. Total Environ.* 2013, 463–464, 488–496. [PubMed: 24300458]
- (69). Oosterhuis M; Sacher F; ter Laak TL Prediction of Concentration Levels of Metformin and Other High Consumption Pharmaceuticals in Wastewater and Regional Surface Water Based on Sales Data. *Sci. Total Environ.* 2013, 442, 380–388. [PubMed: 23183121]
- (70). Tisler S; Zwiener C Formation and Occurrence of Transformation Products of Metformin in Wastewater and Surface Water. *Sci. Total Environ.* 2018, 628–629, 1121–1129.
- (71). Bradley PM; Journey CA; Button DT; Carlisle DM; Clark JM; Mahler BJ; Nakagaki N; Qi SL; Waite IR; Vanmetre PC Metformin and Other Pharmaceuticals Widespread in Wadeable Streams of the Southeastern United States. *Environ. Sci. Technol. Lett.* 2016, 3, 243–249.
- (72). Niemuth NJ; Klaper RD Emerging Wastewater Contaminant Metformin Causes Intersex and Reduced Fecundity in Fish. *Chemosphere* 2015, 135, 38–45. [PubMed: 25898388]
- (73). Bradley PM; Barber LB; Duris JW; Foreman WT; Furlong ET; Hubbard LE; Hutchinson KJ; Keefe SH; Kolpin DW Riverbank Filtration Potential of Pharmaceuticals in a Wastewater-Impacted Stream. *Environ. Pollut.* 2014, 193, 173–180. [PubMed: 25038376]
- (74). Underwood JC.; Harvey RW.; Metge DW.; Repert DA.; Baumgartner LK.; Smith RL.; Roane TM.; Barber LB. Effects of the Antimicrobial Sulfamethoxazole on Groundwater Bacterial Enrichment. *Environ. Sci. Technol.* 2011, 45 (7), 3096–3101. [PubMed: 21384910]
- (75). Haack SK; Metge DW; Fogarty LR; Meyer MT; Barber LB; Harvey RW; LeBlanc DR; Kolpin DW Effects on Groundwater Microbial Communities of an Engineered 30-Day In Situ Exposure to the Antibiotic Sulfamethoxazole. *Environ. Sci. Technol.* 2011, 46 (14), 7478–7486.
- (76). Roder Green AL; Putschew A; Nehls T Littered Cigarette Butts as a Source of Nicotine in Urban Waters. *J. Hydrol* 2014, 519, 3466–3474.
- (77). United States Environmental Protection Agency. National Recommended Water Quality Criteria-Aquatic Life Criteria Table, <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table> (accessed April 18, 2019).
- (78). Barber LB; Brown GK; Nettlesheim TG; Murphy EW; Bartell SE; Schoenfuss HL Effects of Biologically-Active Chemical Mixtures on Fish in a Wastewater-Impacted Urban Stream. *Sci. Total Environ.* 2011, 409 (22), 4720–4728. [PubMed: 21849205]
- (79). Vasquez MI; Lambrianides A; Schneider M; Kummerer K; Fatta-Kassinos D Environmental Side Effects of Pharmaceutical Cocktails: What We Know and What We Should Know. *J. Hazard. Mater.* 2014, 279, 169–189. [PubMed: 25061892]
- (80). Kidd KA; Paterson MJ; Rennie MD; Podemski CL; Findlay DL; Blanchfield PJ; Liber K Direct and Indirect Responses of a Freshwater Food Web to a Potent Synthetic Oestrogen. *Philos. Trans. R. Soc. B* 2014, 369, 20130578.

- (81). Kong L; Kadokami K; Duong HT; Chau HTC Screening of 1300 Organic Micro-Pollutants in Groundwater from Beijing and Tianjin, North China. *Chemosphere* 2016, 165, 221–230. [PubMed: 27657814]
- (82). Futran Fuhrman V; Tal A; Arnon S Why Endocrine Disrupting Chemicals (EDCs) Challenge Traditional Risk Assessment and How to Respond. *J. Hazard. Mater.* 2015, 286, 589–611. [PubMed: 25646754]
- (83). Bradley PM; Journey CA; Romanok KM; Barber LB; Buxton HT; Foreman WT; Furlong ET; Glassmeyer ST; Hladik ML; Iwanowicz LR; et al. Expanded Target-Chemical Analysis Reveals Extensive Mixed-Organic-Contaminant Exposure in US Streams. *Environ. Sci. Technol.* 2017, 51 (9), 4792–4802. [PubMed: 28401767]
- (84). Hladik ML; Kolpin DW; Kuivila KM Widespread Occurrence of Neonicotinoid Insecticides in Streams in a High Corn and Soybean Producing Region, USA. *Environ. Pollut.* 2014, 193, 189–196. [PubMed: 25042208]
- (85). Kolpin DW; Furlong ET; Meyer MT; Thurman EM; Zaugg SD; Barber LB; Buxton HT Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999–2000: A National Reconnaissance. *Environ. Sci. Technol.* 2002, 36 (6), 1202–1211. [PubMed: 11944670]
- (86). Köck-Schulmeyer M; Villagrasa M; López de Alda M; Céspedes-Sánchez R; Ventura F; Barceló D Occurrence and Behavior of Pesticides in Wastewater Treatment Plants and Their Environmental Impact. *Sci. Total Environ.* 2013, 458–460, 466–476. [PubMed: 23410868]
- (87). Margot J; Rossi L; Barry DA; Holliger C A Review of the Fate of Micropollutants in Wastewater Treatment Plants. *Wiley Interdiscip. Rev.: Water* 2015, 2, 457–487.
- (88). Sadaria AM; Supowit SD; Halden RU Mass Balance Assessment for Six Neonicotinoid Insecticides during Conventional Wastewater and Wetland Treatment: Nationwide Reconnaissance in United States Wastewater. *Environ. Sci. Technol.* 2016, 50 (12), 6199–6206. [PubMed: 27196423]
- (89). Sun S; Jia L; Li B; Yuan A; Kong L; Qi H; Ma W; Zhang A; Wu Y The Occurrence and Fate of PAHs over Multiple Years in a Wastewater Treatment Plant of Harbin, Northeast China. *Sci. Total Environ.* 2018, 624, 491–498. [PubMed: 29268221]
- (90). Pham T-T; Proulx S PCBs and PAHs in the Montreal Urban Community (Quebec, Canada) Wastewater Treatment Plant and in the Effluent Plume in the St Lawrence River. *Water Res.* 1997, 31 (8), 1887–1896.
- (91). Castiglioni S; Davoli E; Riva F; Palmiotto M; Camporini P; Manenti A; Zuccato E Mass Balance of Emerging Contaminants in the Water Cycle of a Highly Urbanized and Industrialized Area of Italy. *Water Res.* 2018, 131, 287–298.
- (92). Tran NH; Reinhard M; Gin KYH Occurrence and Fate of Emerging Contaminants in Municipal Wastewater Treatment Plants from Different Geographical Regions—a Review. *Water Res.* 2018, 133, 182–207. [PubMed: 29407700]
- (93). Cabeza Y; Candela L; Ronen D; Teijon G Monitoring the Occurrence of Emerging Contaminants in Treated Wastewater and Groundwater between 2008 and 2010. The Baix Llobregat (Barcelona, Spain). *J. Hazard. Mater.* 2012, 239–240, 32–39.
- (94). Luo Y; Guo W; Ngo HH; Nghiem LD; Hai FI; Zhang J; Liang S; Wang XC A Review on the Occurrence of Micropollutants in the Aquatic Environment and Their Fate and Removal during Wastewater Treatment. *Sci. Total Environ.* 2014, 473–474, 619–641. [PubMed: 24388901]
- (95). Rua-Gomez PC; Puttmann W Impact of Wastewater Treatment Plant Discharge of Lidocaine, Tramadol, Venlafaxine and Their Metabolites on the Quality of Surface Waters and Groundwater. *J. Environ. Monit.* 2012, 14 (5), 1391–1399. [PubMed: 22446514]
- (96). Ratola N; Cincinelli A; Alves A; Katsoyiannis A Occurrence of Organic Microcontaminants in the Wastewater Treatment Process. A Mini Review. *J. Hazard. Mater.* 2012, 239–240, 1–18.
- (97). Sanchez-Avila J; Bonet J; Velasco G; Lacorte S Determination and Occurrence of Phthalates, Alkylphenols, Bisphenol A, PBDEs, PCBs and PAHs in an Industrial Sewage Grid Discharging to a Municipal Wastewater Treatment Plant. *Sci. Total Environ.* 2009, 407 (13), 4157–4167. [PubMed: 19362327]

- (98). Yang Y; Ok YS; Kim KH; Kwon EE; Tsang YF Occurrences and Removal of Pharmaceuticals and Personal Care Products (PPCPs) in Drinking Water and Water/Sewage Treatment Plants: A Review. *Sci. Total Environ.* 2017, 596–597, 303–320. [PubMed: 29272828]
- (99). Verlicchi P; Al Aukidy M; Zambello E Occurrence of Pharmaceutical Compounds in Urban Wastewater: Removal, Mass Load and Environmental Risk after a Secondary Treatment-A Review. *Sci. Total Environ.* 2012, 429, 123–155. [PubMed: 22583809]
- (100). Lubello C; Gori R; Nicese FP; Ferrini F Municipal-Treated Wastewater Reuse for Plant Nurseries Irrigation. *Water Res.* 2004, 38, 2939–2947. [PubMed: 15223289]
- (101). United States Environmental Protection Agency. State Progress Toward Developing Numeric Nutrient Water Quality Criteria for Nitrogen and Phosphorus, <https://www.epa.gov/nutrient-policy-data/state-progress-toward-developing-numeric-nutrient-water-quality-criteria> (accessed April 18, 2019).
- (102). Carpenter SR; Caraco NF; Correll DL; Howarth RW; Sharpley AN; Smith VH Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. *Ecol Appl* 1998, 8 (3), 559–568.
- (103). Selbig W R Evaluation of Leaf Removal as a Means to Reduce Nutrient Concentrations and Loads in Urban Stormwater. *Sci. Total Environ.* 2016, 571, 124–133. [PubMed: 27470671]
- (104). World Health Organization. Calcium and Magnesium in Drinking-Water: Public Health Significance; Cotruvo J, Bartram J, Eds.; World Health Organization Press: Geneva, Switzerland, 2009.
- (105). Marsalek J Road Salts in Urban Stormwater: An Emerging Issue in Stormwater Management in Cold Climates. *Water Sci. Technol* 2003, 48 (9), 61–70.
- (106). Moore J; Bird DL; Dobbis SK; Woodward G Nonpoint Source Contributions Drive Elevated Major Ion and Dissolved Inorganic Carbon Concentrations in Urban Watersheds. *Environ. Sci. Technol. Lett.* 2017, 4 (6), 198–204.
- (107). Schuler MS; Canedo-Arguelles M; Hintz WD; Dyack B; Birk S; Relyea RA Regulations Are Needed to Protect Freshwater Ecosystems from Salinization. *Philos. Trans. R. Soc. j B* 2019, 374, 20180019.
- (108). Taka M; Kokkonen T; Kuoppamaki K; Niemi T; Sillanpaa N; Valtanen M; Warsta L; Setala H Spatio-Temporal Patterns of Major Ions in Urban Stormwater under Cold Climate. *Hydrol Process.* 2017, 31 (8), 1564–1577.
- (109). Corsi SR; De Cicco LA; Lutz MA; Hirsch RM River Chloride Trends in Snow-Affected Urban Watersheds: Increasing Concentrations Outpace Urban Growth Rate and Are Common among All Seasons. *Sci. Total Environ.* 2015, 508, 488–497. [PubMed: 25514764]
- (110). Maniquiz-Redillas MC; Kim L-H Evaluation of the Capability of Low-Impact Development Practices for the Removal of Heavy Metal from Urban Stormwater Runoff. *Environ. Technol.* 2016, 37 (18), 2265–2272. [PubMed: 26862669]
- (111). Barber LB; Paschke SS; Battaglin WA; Douville C; Fitzgerald KC; Keefe H; Roth DA; Vajda AM Effects of an Extreme Flood on Trace Elements in River Water-From Urban Stream to Major River Basin. *Environ. Sci. Technol.* 2017, 51, 10344–10356. [PubMed: 28862461]
- (112). Bay S; Jones BH; Schiff K; Washburn L Water Quality Impacts of Stormwater Discharges to Santa Monica Bay. *Mar. Environ. Res.* 2003, 56 (1), 205–223. [PubMed: 12648956]
- (113). Trowsdale SA; Simcock R Urban Stormwater Treatment Using Bioretention. *J. Hydrol.* 2011, 397 (3), 167–174.
- (114). Gwenzi W; Mangori L; Danha C; Chaukura N; Dunjana N; Sanganyado E Sources, Behaviour, and Environmental and Human Health Risks of High-Technology Rare Earth Elements as Emerging Contaminants. *Sci. Total Environ.* 2018, 636, 299–313. [PubMed: 29709849]
- (115). Lerat-hardy A; Coynel A; Dutruch L; Pereto C; Bossy C; Gil-diaz T; Capdeville M; Blanc G; Schafer J Rare Earth Element Fluxes over 15 Years into a Major European Estuary (Garonne-Gironde, SW France): Hospital Effluents as a Source of Increasing Gadolinium Anomalies. *Sci. Total Environ.* 2019, 656, 409–420. [PubMed: 30513431]
- (116). Haskin LA; Haskin MA; Frey FA; Wildeman T R Relative and Absolute Terrestrial Abundances of the Rare Earths In Origin and Distribution of the Elements; International Series of Monographs in Earth Sciences; Elsevier, 1968; pp 889–912,

- (117). Gromet LP; Haskin LA; Korotev RL.; Dymek RF. The “North American Shale Composite”: Its Compilation, Major and Trace Element Characteristics. *Geochim. Cosmochim. Acta* 1984, 48 (12), 2469–2482.
- (118). Barber LB; Paschke SS; Battaglin WA; Douville C; Fitzgerald KC; Keefe H; Roth DA; Vajda AM Effects of an Extreme Flood on Trace Elements in River Water-From Urban Stream to Major River Basin. *Environ. Sci. Technol.* 2017, 51, 10344–10356. [PubMed: 28862461]
- (119). Verplanck PL; Taylor HE; Nordstrom DK; Barber LB Aqueous Stability of Gadolinium in Surface Waters Receiving Sewage Treatment Plant Effluent, Boulder Creek, Colorado. *Environ. Sci. Technol.* 2005, 39 (18), 6923–6929. [PubMed: 16201612]
- (120). Rabiet M; Togola A; Brissaud F; Seidel J-L; Budzinski H; Elbaz-Poulichet F Consequences of Treated Water Recycling as Regards Pharmaceuticals and Drugs in Surface and Ground Waters of a Medium-Sized Mediterranean Catchment. *Environ. Sci. Technol.* 2006, 40 (17), 5282–5288. [PubMed: 16999100]
- (121). Hall BD; Aiken GR; Krabbenhoft DP; Marvin-DiPasquale M; Swarzenski CM Wetlands as Principal Zones of Methylmercury Production in Southern Louisiana and the Gulf of Mexico Region. *Environ. Pollut.* 2008, 154 (1), 124–134. [PubMed: 18242808]
- (122). Marvin-DiPasquale M; Lutz MA; Brigham ME; Krabbenhoft DP; Aiken GR; Orem WH; Hall BD Mercury Cycling in Stream Ecosystems. 2. Benthic Methylmercury Production and Bed Sediment-Pore Water Partitioning. *Environ. Sci. Technol.* 2009, 43 (8), 2726–2732. [PubMed: 19475941]
- (123). Scudder BC; Chasar LC; Wentz DA; Bauch ME; Moran PW; Krabbenhoft DP Mercury in Fish, Bed Sediment, and Water from Streams Across the United States 1998–2005; Scientific Investigations Report 2009–5109, U.S. Geological Survey, 2009.
- (124). Domagalski JL; Alpers CN; Slotton DG; Suchanek TH; Ayers SM Mercury and Methylmercury Concentrations and Loads in the Cache Creek Watershed, California. *Sci. Total Environ.* 2004, 327, 215–237. [PubMed: 15172583]

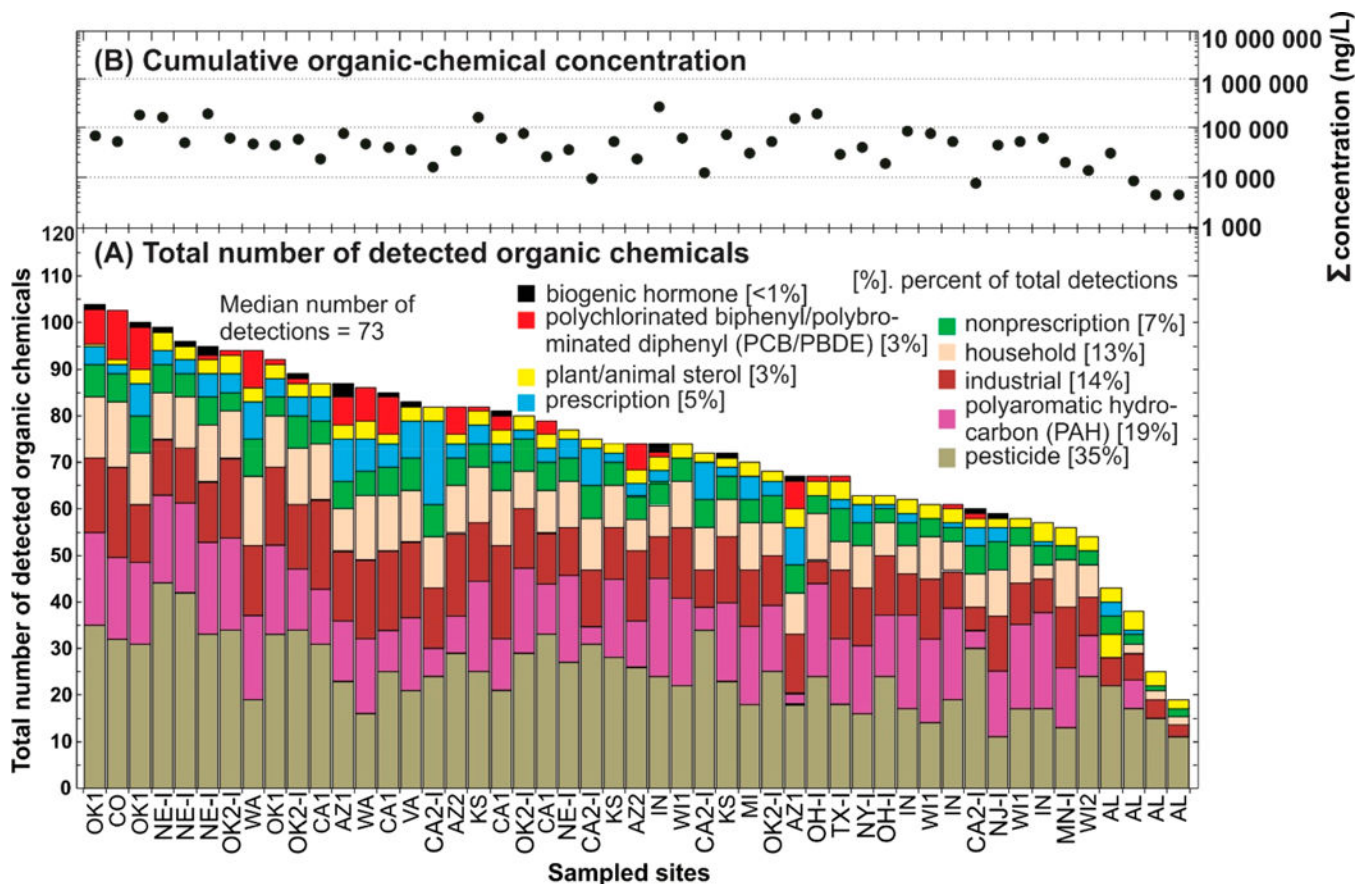


Figure 1. Total number of detected organic chemicals for sampled sites, sorted from left to right by decreasing number of detections (A) and total measured organic-chemical concentration for sampled sites (B).

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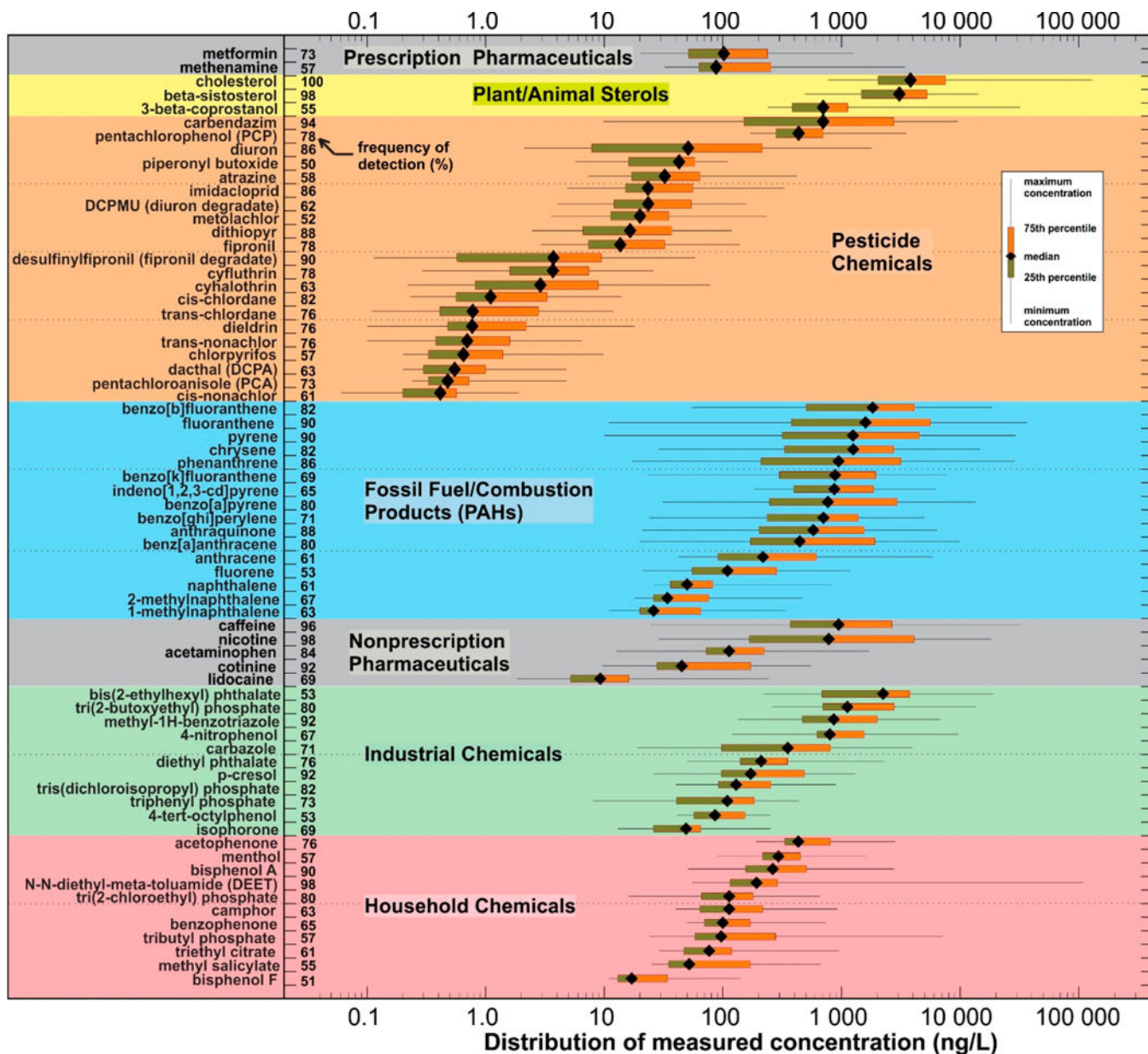


Figure 2. Box-plot distributions of measured concentrations for the 69 organic chemicals detected in 50% or more of 49 urban stormwater samples. Sorted alphabetically from top to bottom by chemical class and decreasing median concentrations.

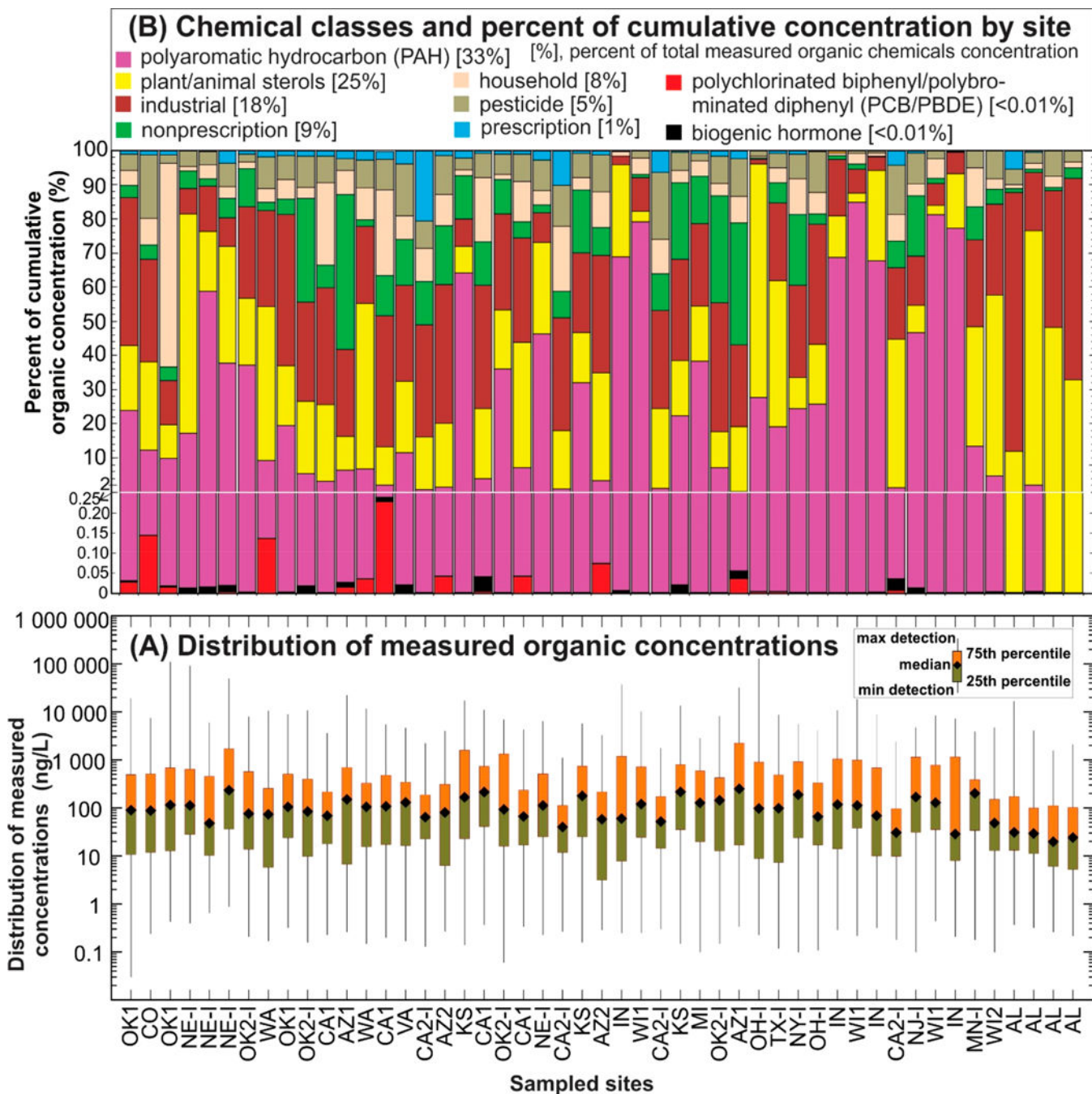


Figure 3. Box plot distributions of measured concentrations for organic chemicals in urban stormwater samples (A) and percent of total measured organic chemicals concentration by chemical class (B). Sorted from left to right by decreasing number of detections.