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

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GC/MS Halogenated Chemicals Method.
This GC/MS halogenated chemicals method is currently unpublished and is therefore summarized herein. This method determines the concentrations for 62 halogenated chemicals (Table SI-3) and analysis was performed at the U.S. Geological Survey National Water Quality Laboratory in Denver, CO. Unfiltered water samples, typically of about 450-milliliter (mL) volume, were fortified with 1 nanogram (ng) of surrogate compounds 4,4'-dibromooctafluorobiphenyl and PCB-202-$^{13}C_{12}$, and 10 ng of 4,4'-DDT-d_8. The samples were extracted by passing the water through 1-gram (g) Oasis® hydrophilic-lipophilic-balanced (HLB) solid-phase extraction (SPE) cartridges (Waters Corp., Milford, MA) at about 10 milliliters per minute flow rate by application of minimal head pressure using nitrogen gas. Each sample bottle was rinsed to remove residual sample water and settled sediment material with 35 milliliters (mL) of potassium phosphate monobasic/dibasic buffer solution (pH 7.0) and passed through the HLB cartridge.

Residual water in the HLB cartridge sorbent was displaced with nitrogen (4 minutes at 13.8 kilopascals). Method compounds were eluted from the HLB cartridge and passed through a 2-g Florisil® SPE cartridge (Biotage, LLC, Charlotte, NC) overlain with sodium sulfate by using 5 mL of hexane, followed by addition of a 10-mL rinse of the sample bottle with a mixture of dichloromethane (DCM) and diethyl ether (DEE) (80:20, v/v), and finally by addition of another 30 mL of this DCM/DEE eluent directly to the HLB/Florisil solvent reservoir. The resultant

collected eluent (extract) was concentrated using nitrogen on an Organomation N-Evap at ambient temperature to a final volume of 1 mL and transferred to a vial containing 2 ng of injection internal standard compounds PCB-141-$^{13}C_{12}$ and PCB-209-$^{13}C_{12}$ in preparation for analysis.

Method compounds were determined by injection of 10 microliters of sample extract using a programmed-temperature vaporization (PTV) inlet (flash heated from 50–320 ºC) into a model 6890 gas chromatograph with model 5975 mass spectrometer operated in the electron-capture negative ionization mode (GC/ECNIMS; Agilent Technologies, Santa Clara, CA) using ammonia reagent gas. Compounds were separated using a 30-meter by 0.25-millimeter internal diameter DB-35MS Ultra Inert capillary GC column having a 0.25-micrometer stationary phase film thickness (Agilent Technologies). Mass spectral data were obtained using simultaneous selected-ion monitoring (SIM) and full-scan acquisition modes. Analyte identification was established by comparing both chromatographic retention times and the ratios of the quantification ion to the secondary qualification ions in environmental samples to the retention times and ion ratios obtained for the calibration standards. For those samples with high analyte concentrations, the SIM results were confirmed by use of the full-scan spectral results. Full-scan results help deduce whether interferences might be present. The PTV GC inlet was used so that both thermally labile compounds and high molecular weight compounds could be analyzed in the same GC analysis. Method analytes were quantified using multi-concentration (typically 9 levels) calibration standards with quantification relative to an injection internal standard compound. Maintenance of calibration performance throughout the analyses was monitored by use of continuing calibration verification standards. A third party check standard also was analyzed to assess calibration accuracy.

Parameters that were analyzed included 62 chemicals grouped into the following classes: selected polychlorinated biphenyl congeners, halogenated flame retardants, legacy and currently used pesticides and selected pesticide degradates, and several industrial or personal care products and selected degradates. Detection levels were estimated using the spike-based method detection limit procedure of the U.S. Environmental Protection Agency[1] or by using laboratory blank-sample data for four blank-limited compounds (triclosan, PBDE-47, PBDE-99, and PBDE-100). Reporting Levels (RLs) were set at 2 or more times the detection level and range from 0.2 to 10 nanograms per liter (ng/L), with concentrations below the reporting and detection levels reported for identified analytes.

(1) U.S. Environmental Protection Agency, 1986, Guidelines establishing test procedures for the analysis of pollutants (App. B, Part 136, Definition and procedures for the determination of the method detection limit—Revision 1.11; June 30, 1986): U.S. Code of Federal Regulations, Title 40; available at https://www.govinfo.gov/content/pkg/CFR-2014-title40-vol23/pdf/CFR-2014-title40-vol23-part136-appB.pdf; accessed July 2019.

Previous sampling efforts included quality control (QC) samples that were prepared along with a set of typically ten environmental samples that included one laboratory blank and one laboratory spike sample prepared using reagent water matrix. Data for these QC samples were used to censor or qualify reported environmental sample results, if needed. Recoveries of surrogate compounds fortified into each sample provided an indication of sample preparation performance

and were used to qualify results, as needed. Field-requested lab matrix spike samples and field replicate samples were used as additional quality-assurance information.

Storm Event Discharges, Estimates of Organic-Chemical Loads and Yields, and Statistical Analysis

Stormwater discharge was calculated based on pipe/channel geometry and measurements of velocity and water level recorded in 1-minute or 2-minute increments. Total runoff volumes for the 7 manual time-weighted samples were measured with a handheld Acoustic Doppler Current Profiler (ADCP; NJ-I and NY-I) or estimated following published methods (4 sites: VA, CO, MI, and 2 events at MN-I, (Table SI-1).[2] Single storm-event runoff volumes and cumulative organic-chemical concentrations were used to calculate load and yield estimates for organic chemical classes. At most sites, precipitation was measured with onsite precipitation gauges and logged with the autosamplers. For sites that were manually sampled or instances where a precipitation gauge was not part of the autosampler setup, precipitation data from the nearest U.S. National Weather Service (http://www.weather.gov) site were used to estimate rainfall amounts during sampled stormwater runoff events (Table SI-1). Correlations between site-specific summary contaminant metrics (cumulative detections, concentrations, loads, and yields) and individual drainage-catchment/storm-event characteristics (area, antecedent dry days, precipitation, runoff volume, and LULC metrics) were assessed using the nonparametric Spearman Rank Correlation test in RStudio software (https://www.rstudio.com/).

(2) U.S. Dept. of Agriculture, Soil Conservation Service, E. D. Urban Hydrology for Small Watersheds https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/stelprdb1044171.pdf (accessed Feb 4, 2017).

Supporting Information Tables

Supporting information tables are contained in the associated supporting information spreadsheet "es9b02867_si_002.xlsx". The individual table titles are:

Table SI-1. Site information and hydrologic characteristics for single-event stormwater runoff samples. Sorted by field name then by date.

Table SI-2. Bottle fill sequence, method of analyses, sample container information, preservation, and holding time information for filtered and unfiltered samples.

Table SI-3. Chemicals analyzed in unpublished U.S. Geological Survey GC/MS halogenated chemicals method.

Table SI-4. Laboratory quality-control measurements from organic analyses of reagent-blank samples typically analyzed once every ten field samples. Sorted alphabetically by analytical method then by parameter name.

Table SI-5. Laboratory quality-control recoveries from organic analyses of reagent-spike samples typically analyzed once every ten field samples. Sorted alphabetically by analytical method then by parameter name.

Table SI-6. Field quality-control measurements from organic analyses of three equipment blank samples. Sorted alphabetically by analytical method then by parameter name.

Table SI 7. Summary statistics of relative percent differences (RPDs) calculated between field and replicate samples.

Table SI-8. Organic chemicals summary statistics of recoveries for method reagent-spike samples and isotope-dilution standards (IDSs) and surrogate compounds added to field and quality-assurance samples.

Table SI-9. Concentrations of organic chemicals detected in urban stormwater runoff samples. Sorted alphabetically by analytical method then by parameter name.

Table SI-10. Organic chemicals not detected in urban stormwater runoff samples. Sorted alphabetically by analytical method then by parameter name.

Table SI-11. Drainage areas and proportions of land-use/land-cover (LULC) classes from the 2011 National Land Cover Dataset (NLCD) for sampled stormwater runoff sites.

Table SI-12. Single-event stormwater runoff volumes and organic chemical loads by chemical class. Sorted alphabetically then by date (oldest to newest).

Table SI-13. Single-event stormwater runoff volumes and organic chemical yields by chemical class. Sorted alphabetically then by date (oldest to newest).

Table SI-14. Spearmen rank-order correlation (rho) and significance level (p-value) between cumulative organic chemical detections, storm-event variables, and drainage-catchment variables.

Table SI-15. Spearmen rank-order correlation (rho) and significance level (p-value) between cumulative organic chemical concentrations, storm-event variables, and drainage-catchment variables.

Table SI-16. Spearmen rank-order correlation (rho) and significance level (p-value) between cumulative organic chemical loads, storm-event variables, and drainage-catchment variables.

Table SI-17. Spearmen rank-order correlation (rho) and significance level (p-value) between cumulative organic chemical yields, storm-event variables, and drainage-catchment variables.

Table SI-18. Water properties and measured concentrations of trace metals and rare-earth metals analyzed in urban stormwater samples; methylmercury concentrations in ng/L.

Table SI-19. Measured concentrations of geochemical parameters analyzed in urban stormwater samples.
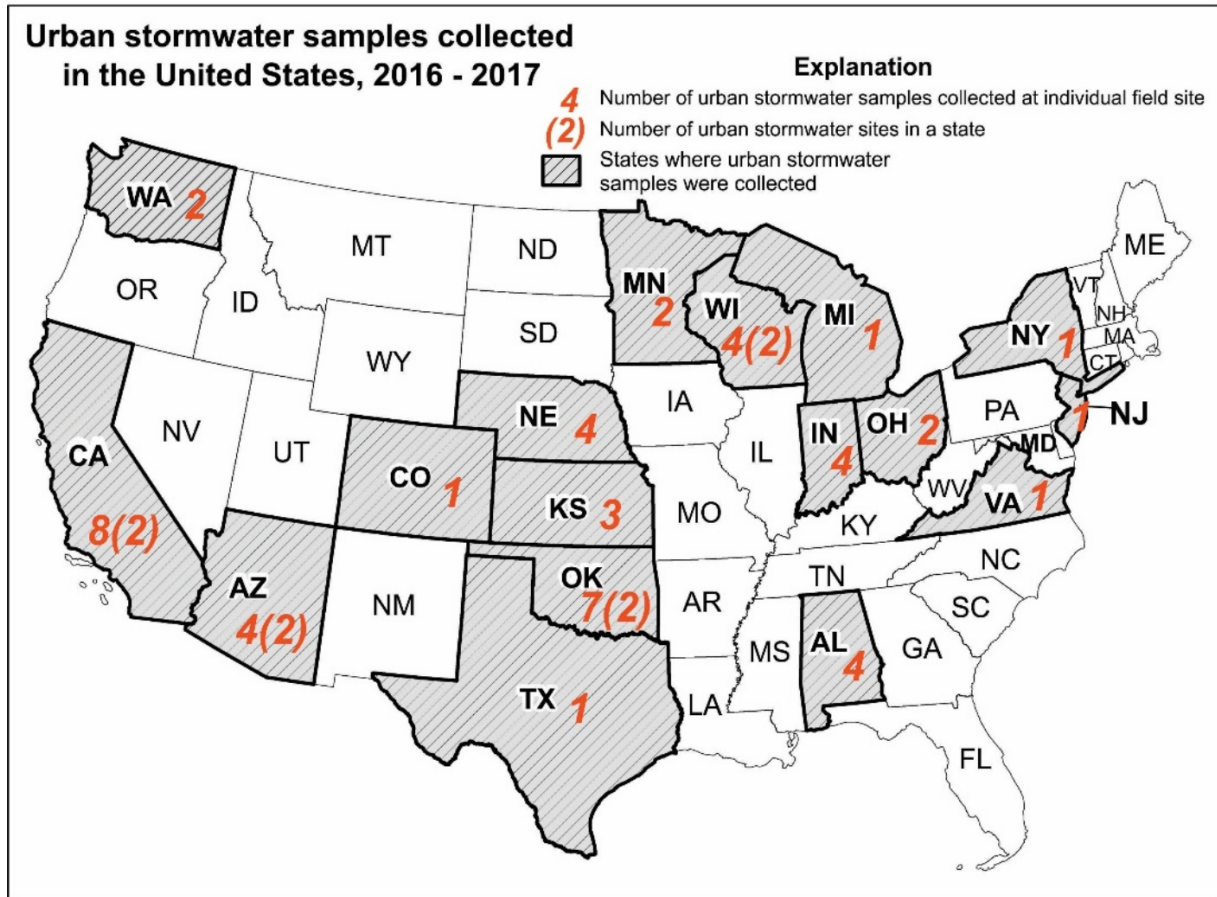

Supporting Information Figures

Figure SI-1. Map showing states where urban stormwater was sampled, and number of environmental samples collected at individual sites across the United States during 2016-2017.

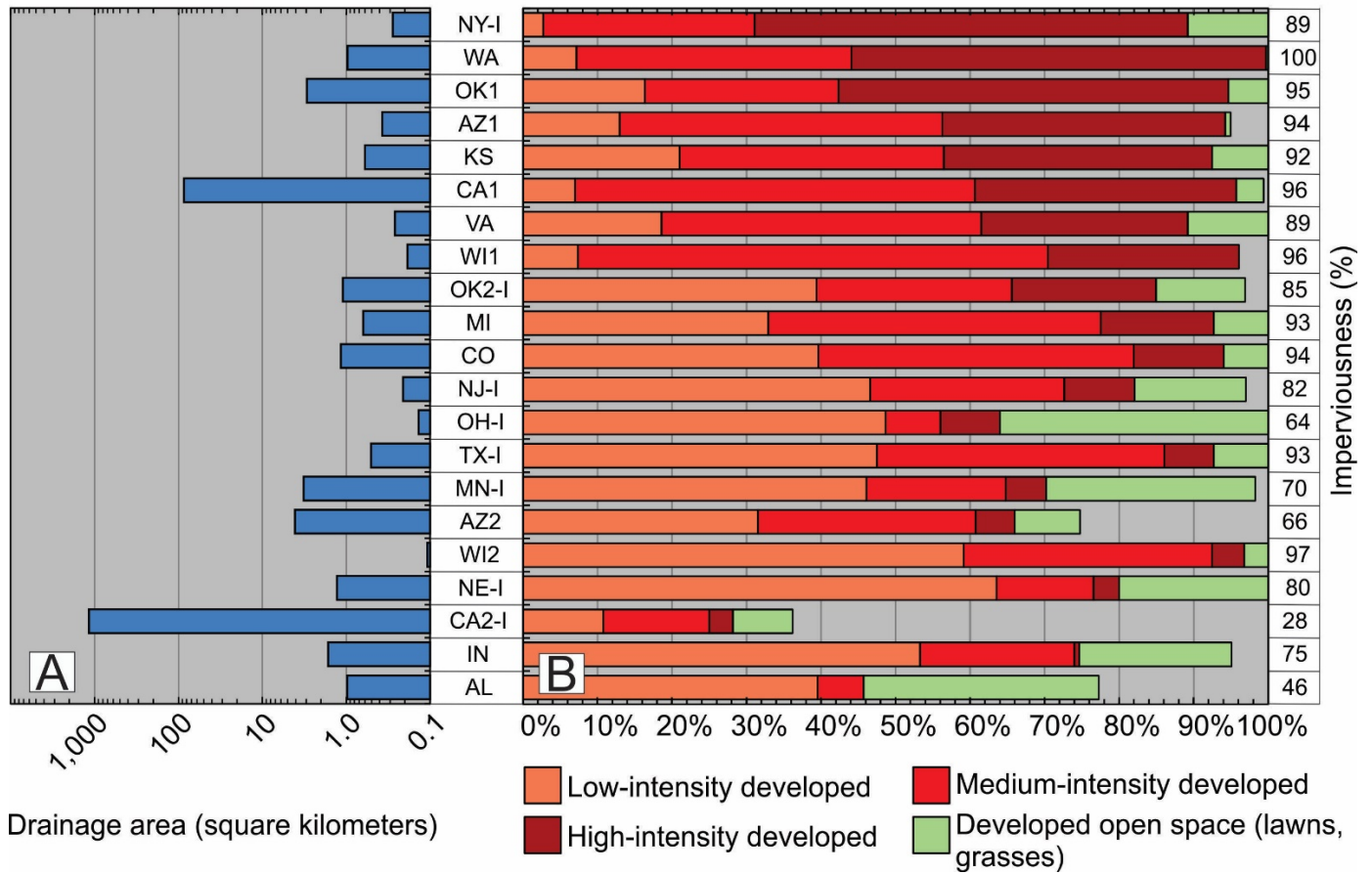**Drainage Areas and Land Use Land Cover for Sampled Sites**

Figure SI-2. Drainage areas (A) and developed land-use/land-cover classes and percent impervious surfaces (B) from the 2011 National Land Cover Dataset (NLCD) for the 21 sampled sites, sorted by decreasing proportion of developed high-intensity land-use/land-cover (LULC).
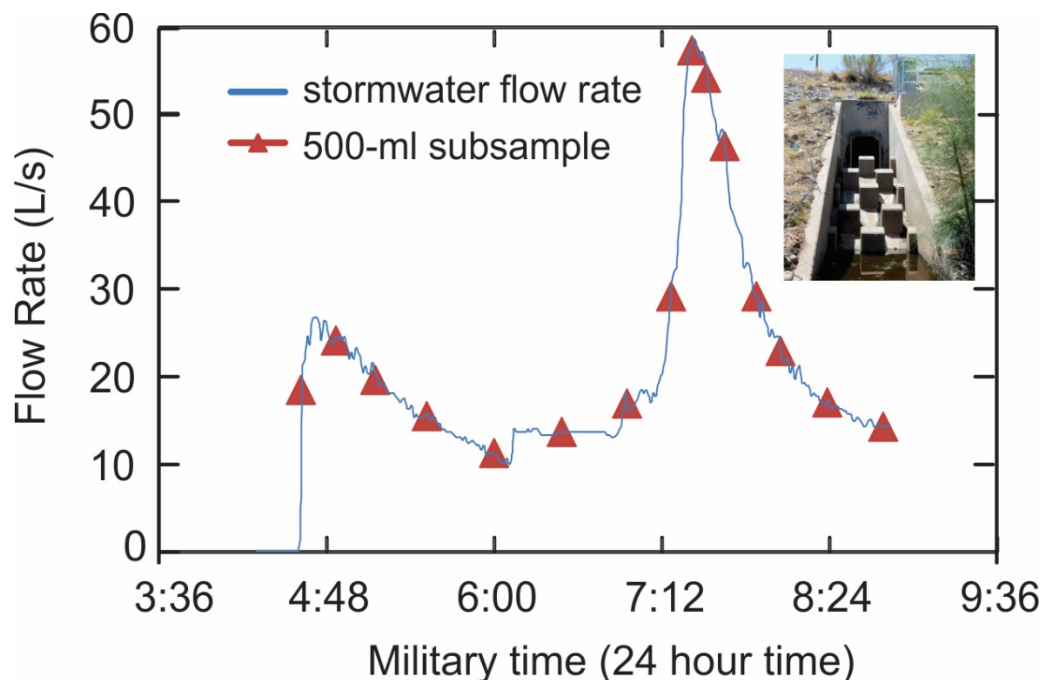
Figure SI-3. Example hydrograph showing time-series flow rates and collection of sub-samples during a storm event at AZ1 site in Arizona on 2-18-2017.
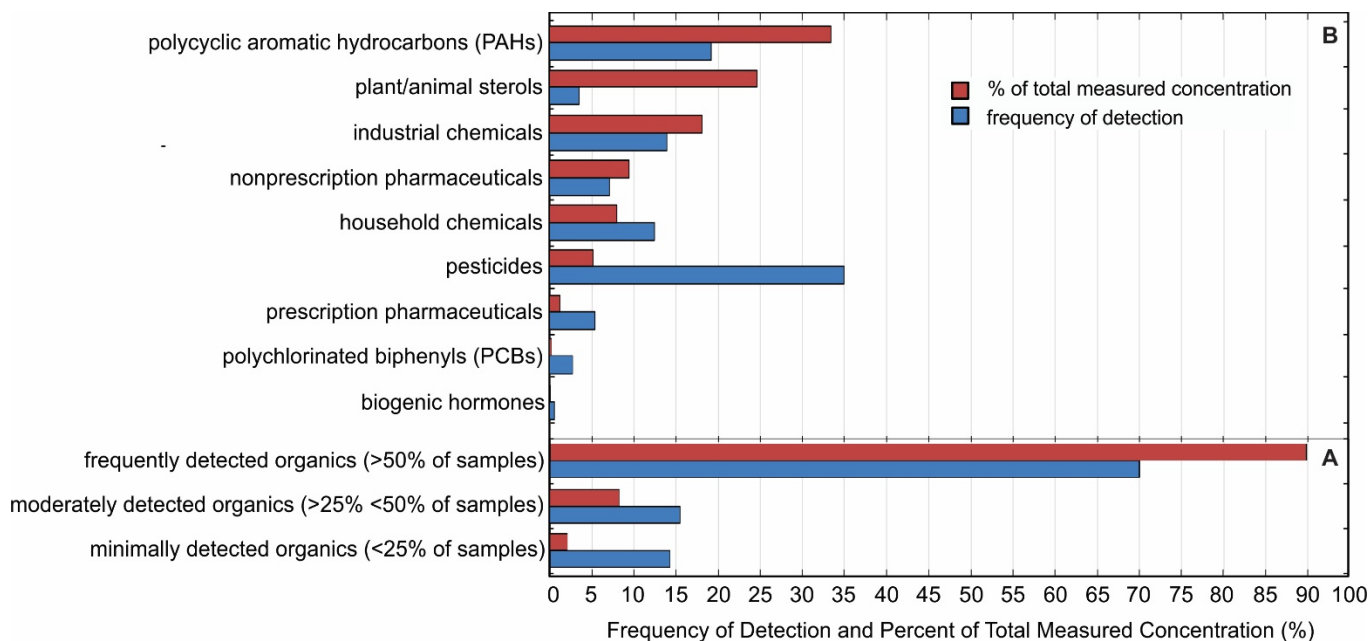
Figure SI-4. Frequency of organic chemicals detected (blue bars) and percent of total measured organic chemicals concentration (red bars) for organics that were minimally detected, moderately detected, and frequently detected (A); and by chemical group (B), sorted from top to bottom by decreasing percent of total measured concentration.
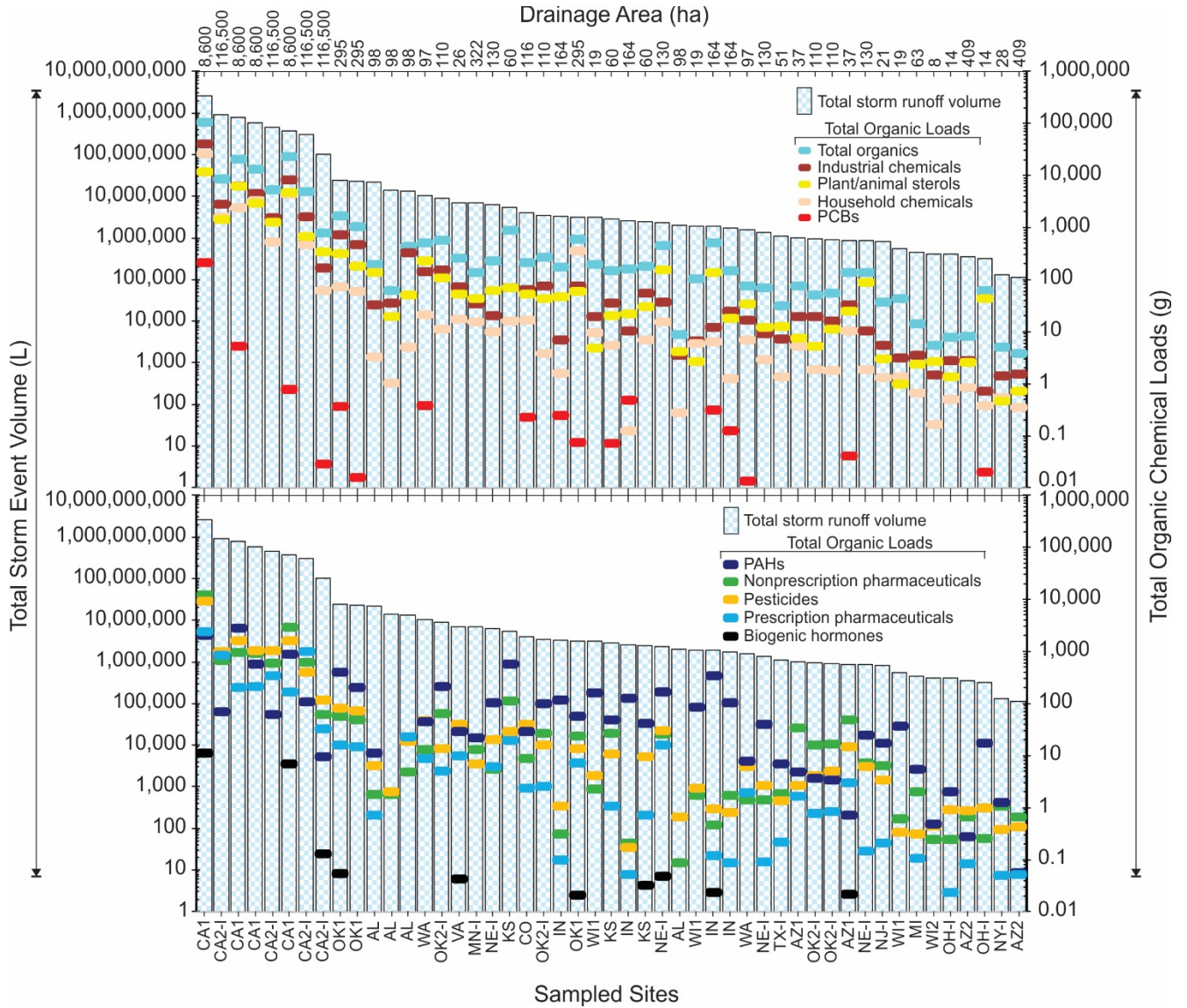
Figure SI-5. Storm runoff volumes in urban stormwater samples and organic chemical loads by chemical class, sorted from left to right by decreasing storm-event volumes.
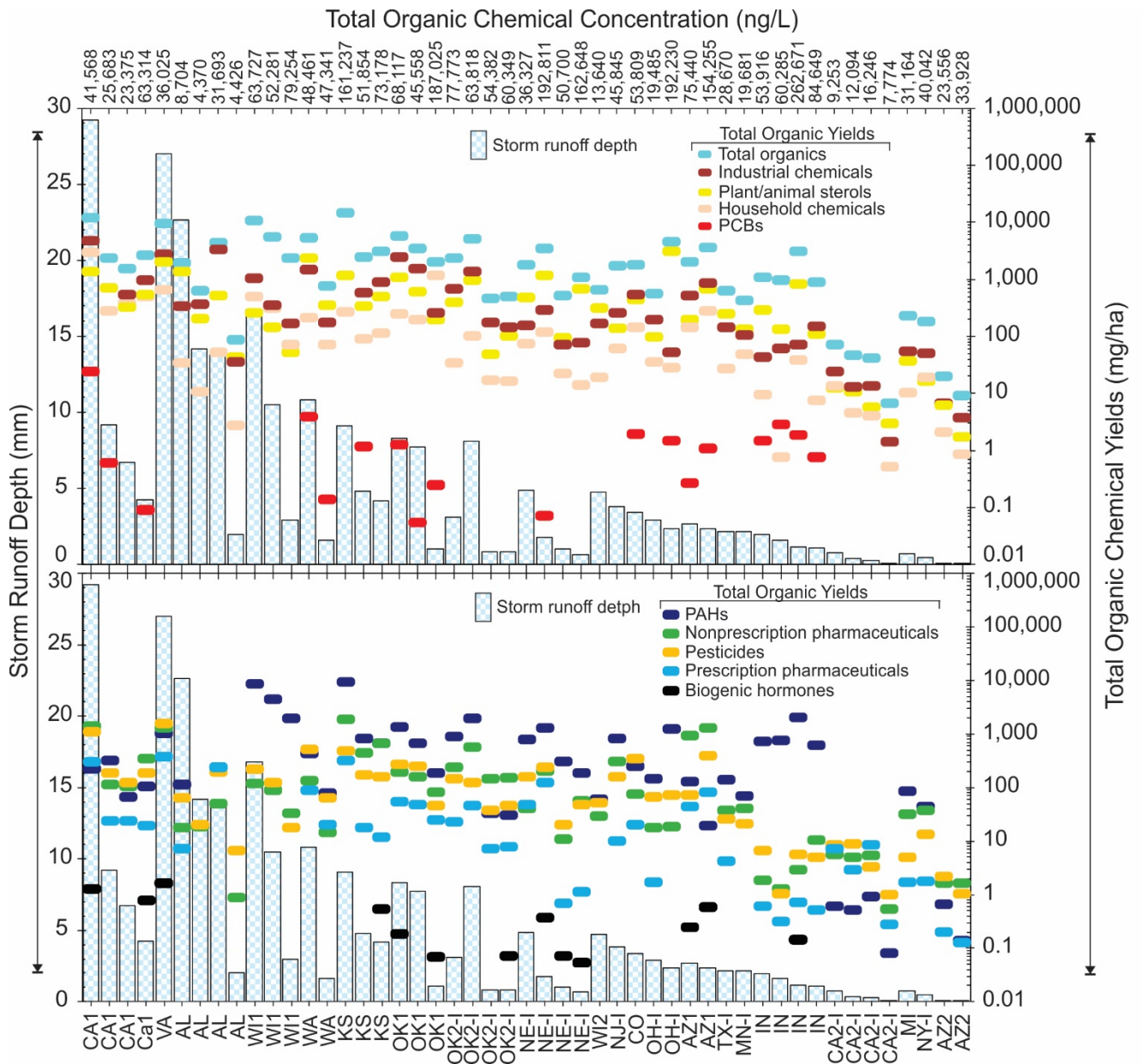
Figure SI-6. Storm runoff depths for sampled storm events and organic chemical yields by chemical class, grouped by site and sorted from left to right by decreasing stormwater runoff depth.
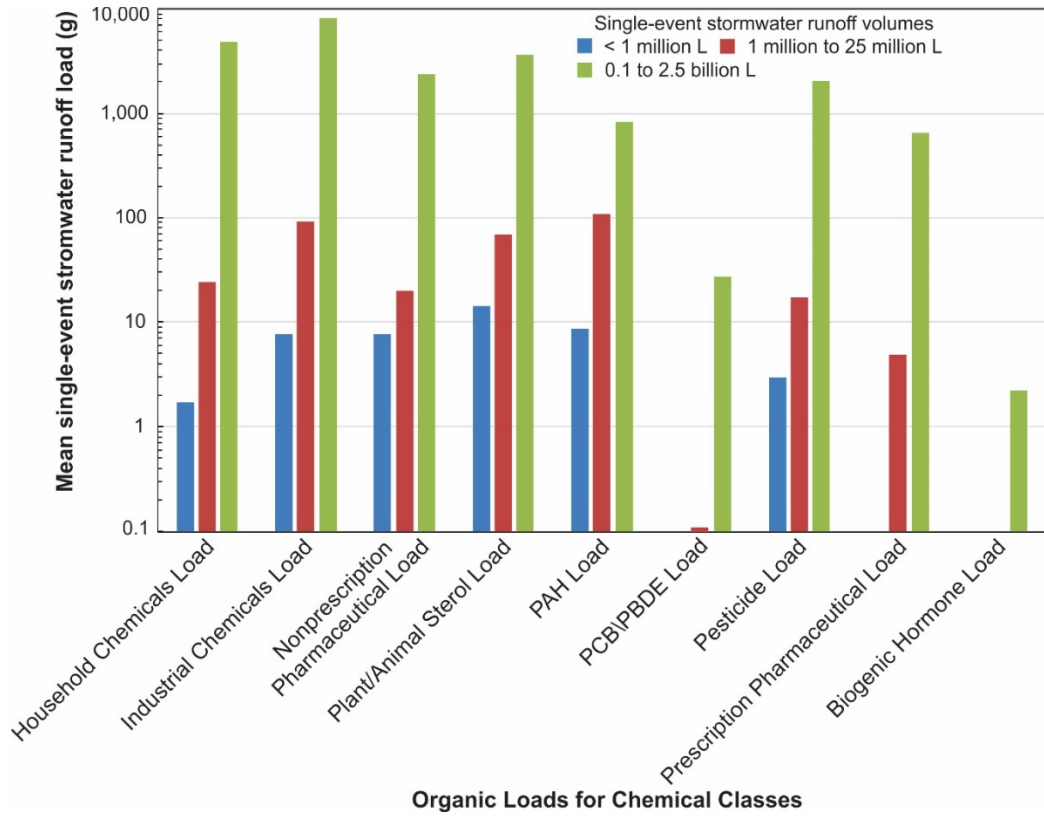
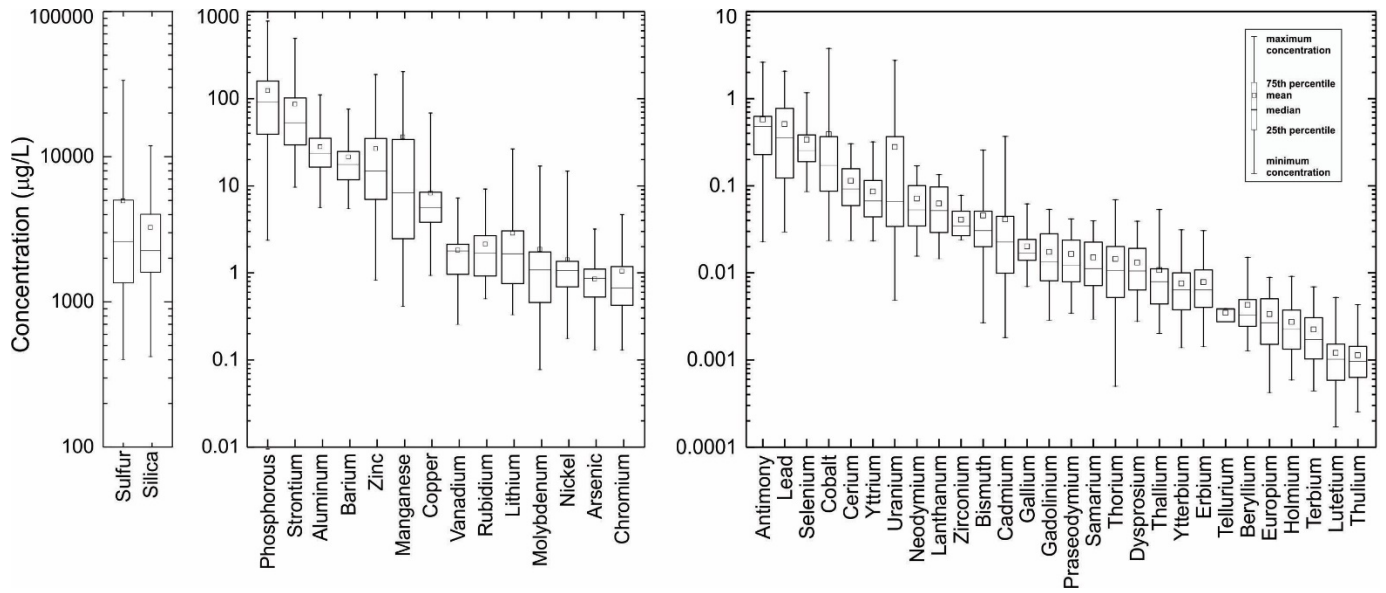**Figure SI-7.** Mean single-event stormwater runoff organic-chemical loads for chemical groups.

Figure SI-8. Distribution of measured concentrations of trace metals and rare-earth metals analyzed in urban stormwater samples. Grouped by concentration and sorted from left to right by decreasing median concentration.
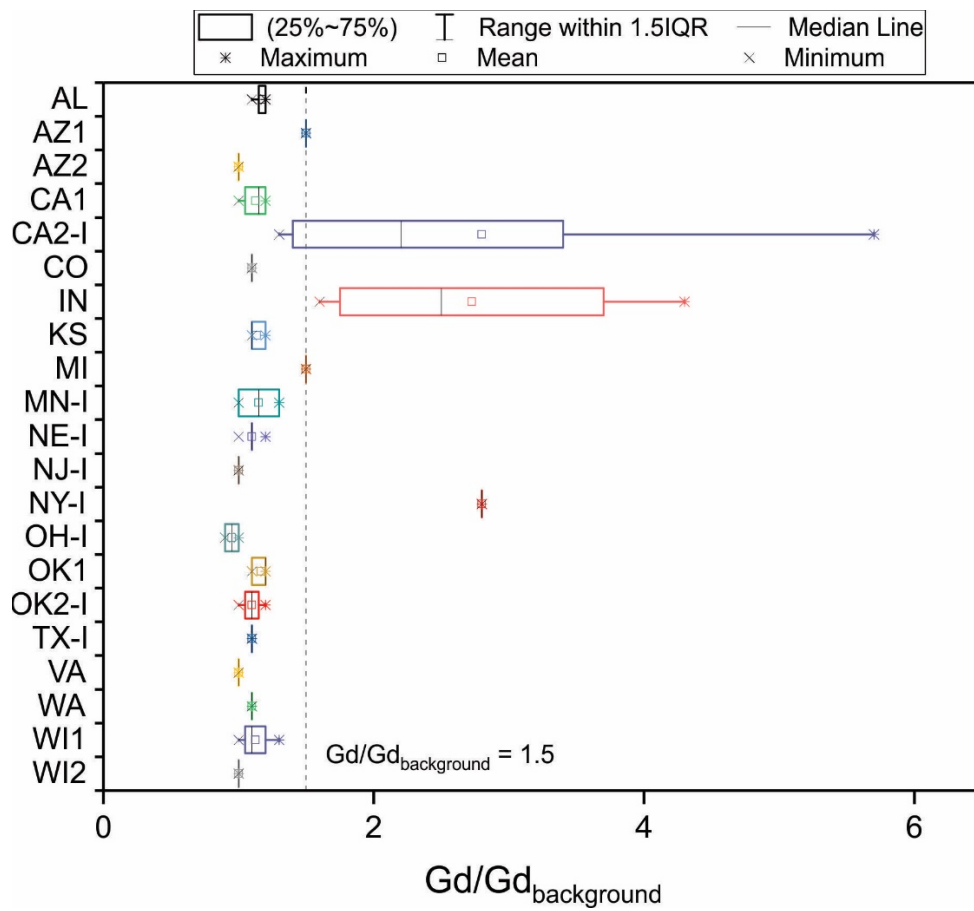
Figure SI-9. Anthropogenic and background gadolinium ratios for urban stormwater runoff samples.
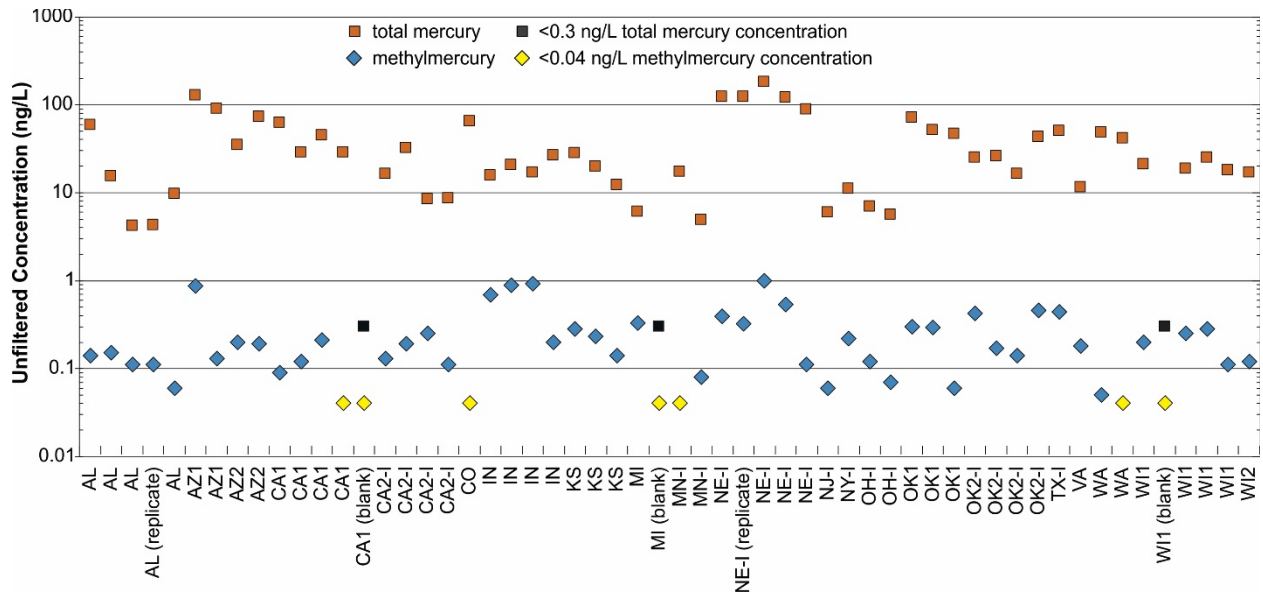
Figure SI-10. Total mercury and methylmercury concentrations in urban stormwater samples. Sorted alphabetically by site then by date (oldest to newest).