



Concentrations and loads of PCBs, dioxins, PAHs, PBDEs, OC pesticides and pyrethroids during storm and low flow conditions in a small urban semi-arid watershed



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HIGHLIGHTS

- Trace organic pollutants were measured in a 100% urban watershed over four years.
- Some rarely reported urban contaminants (dioxins, PBDEs, pyrethroids) were measured.
- Pollutant concentrations generally correlated well with turbidity.
- Loads were estimated for most pollutants using regression with turbidity.
- More than 91% of the load for the measured pollutants was transported during storms.

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ABSTRACT

Urban runoff has been identified in water quality policy documents for San Francisco Bay as a large and potentially controllable source of pollutants. In response, concentrations of suspended sediments and a range of trace organic pollutants were intensively measured in dry weather and storm flow runoff from a 100% urban watershed. Flow in this highly urban watershed responded very quickly to rainfall and varied widely resulting in rapid changes of turbidity, suspended sediments and pollutant concentrations. Concentrations of each organic pollutant class were within similar ranges reported in other studies of urban runoff, however comparison was limited for several of the pollutants given information scarcity. Consistently among PCBs, PBDEs, and PAHs, the more hydrophobic congeners were transported in larger proportions during storm flows relative to low flows. Loads for Water Years 2007–2010 were estimated using regression with turbidity during the monitored months and a flow weighted mean concentration for unmonitored dry season months. More than 91% of the loads for every pollutant measured were transported during storm events, along with 87% of the total discharge. While this dataset fills an important local data gap for highly urban watersheds of San Francisco Bay, the methods, the uniqueness of the analyte list, and the resulting interpretations have applicability for managing pollutant loads in urban watersheds in other parts of the world.

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1. Introduction

San Francisco Bay, the “urbanized estuary” (Conomos, 1979), is a typical example of a system impacted by numerous pollutants. Elevated concentrations of polychlorinated biphenyls (PCBs) in fish have prompted consumption advisories (Davis et al., 2007) and concentrations of polybrominated diphenyl ethers (PBDEs) found in biota are among the highest in the world (She et al., 2002; Oros et al., 2005). The Regional Monitoring Program for Water Quality in San Francisco Bay is coordinating a Strategy team to further investigate dioxins in order to support a policy decision and managers continue to watch

trends in polycyclic aromatic hydrocarbons (PAHs) (Greenfield and Davis, 2005). The San Francisco Bay is encircled by nine counties with a population of 7.15 million people (U.S. Census Bureau, 2011). Although runoff from these nine counties represents only 6% of the total freshwater input to the Bay, pollutant loads from the urban landscape are likely disproportionately large because of the legacy of industrial land use and the historic use of many particle reactive, currently banned or restricted trace organic substances. Based on previous studies that have characterized a wide range of pollutant concentrations and loads to the Bay (e.g. Wenning et al., 1999; She et al., 2002; Greenfield and Davis, 2005; Oros et al., 2005; Davis et al., 2007; Oram et al., 2008; Weston et al., 2009; Weston and Lydy, 2010; David et al., 2015), the San Francisco Bay Regional Water Quality Control Board has specified urban stormwater runoff in the total maximum daily loads reports as

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a large and potentially controllable source of pollutants for enhanced management (e.g. [Water Board, 2008](#)).

Although banned from production since the late 1970's, historic oil and water PCB contamination is still present in industrial centers around the world ([Hwang and Foster, 2008](#)). Runoff of these toxic and persistent chlorinated organic compounds to the local Bay Area tributaries is estimated to comprise a significant portion of the loading ([Davis et al., 2007](#)) estimated >9–15 kg/year was sourced from urban tributaries). PCBs have been relatively well studied in urban runoff in other areas of the world ([Foster et al., 2000a, 2000b](#); [Hwang and Foster, 2008](#); [Rossi et al., 2004](#); [Howell et al., 2011](#); [Zgheib et al., 2011, 2012](#)) and concentrations appear to be the greatest in watersheds with older (pre-1980) industrial areas ([McKee et al., 2012](#)). PCBs have been found to occur dominantly in particulate phase ([Hwang and Foster, 2008](#); [Zgheib et al., 2011](#)) and the degree of partitioning appears to relate to the degree of chlorination ([Tlili et al., 2012](#)). Studies on loads and yields are fewer in number and there is less information on seasonal distributions of loads for analyzing the management potential for selectively treating runoff; information which is especially valuable in watersheds with extremely variable flow such as semi-arid systems.

Organochlorine (OC) pesticides are another class of chlorinated organic compounds that are highly toxic and persistent in the environment. These insecticides were heavily used in the United States up until their regulatory bans in the 1970s and 1980s. Despite the bans decades ago, unaltered chemical forms of DDT are still measured in the environment (e.g. [Zhang et al., 2010](#); [Foster et al., 2000b](#); [Kratzer, 1999](#)). Concentrations of the other commonly used OC pesticides are also still observed (e.g. [Zhang et al., 2010](#); [Foster et al., 2000b](#); [Kratzer, 1999](#); [Connor et al., 2007](#)). Like PCBs, loading data are sparse and little information is available for concentrations and loads found in semi-arid watersheds.

Polycyclic aromatic hydrocarbons (PAHs) are a large class of suspected cancer-causing pollutants produced by rapid, incomplete combustion processes (pyrogenic sources) and slower, moderate temperature processes associated with petroleum and coal (petrogenic sources). On the West Coast, where coal combustion and the use of coal tar sealcoat is less common, PAHs are primarily associated with traffic activities in urban areas ([Van Metre and Mahler, 2010](#)). PAH concentrations and loads in urban systems have been relatively well studied but appear to be quite wide ranging ([Ngabe et al., 2000](#); [Hwang and Foster, 2006](#); [Stein et al., 2006](#)). Loads of PAHs in stormwater runoff from these urban areas can be intensely episodic, especially in semi-arid climates where antecedent dry periods allow for greater build-up on the watershed surfaces ([Stein et al., 2006](#)). So although these pollutants have been relatively well studied in urban runoff, data are still not sufficient to accurately characterize concentrations or yields in relation to basic land use and source history characteristics and literature remains relatively sparse for semi-arid systems.

Polybrominated diphenyl ethers were commonly used as flame retardants in a variety of plastics and textiles and although recently banned in California (penta- and octa-formulations in 2006, deca-formulation in 2013), PBDEs are now considered ubiquitous throughout the environment ([Oram et al., 2008](#)). PBDEs have rarely been measured in urban stormwater runoff ([Oram et al., 2008](#); [Tlili et al., 2012](#); [Gasperi et al., 2014](#)). Stormwater runoff measurements from this study, which were collected approximately concurrently with the regulatory bans of this substance in California, will provide an ideal baseline against which to measure trends resulting from the bans.

Dioxins are byproducts of the synthesis or combustion of chlorine-based compounds and include some of the most toxic chemical substances known ([Fisher et al., 1999](#)). This group of substances includes 17 compounds with wide ranging toxicity ([Van den Berg et al., 2006](#)). In the Bay Area, since there are no major local point sources, stormwater runoff has been identified as the greatest source of dioxins to the Bay ([Gervason and Tang, 1998](#)). Despite high toxicity, surprisingly few studies have reported concentrations of dioxins in urban runoff ([Wenning](#)

[et al., 1999](#); [Suarez et al., 2006](#); [Bryant Jr. and Goodbred, 2009](#)). Previous studies have shown that the most toxic compound in this group (2378-TCDD) occurs in relatively lower concentrations than some of the less toxic compounds in the group ([Suarez et al., 2006](#)). Despite inadvertent generation, dioxin compounds appear to be ubiquitous even in watersheds with no local sources ([Wenning et al., 1999](#)). Data on dioxin loadings appears to be relatively rare.

Pyrethroids are toxic insecticides that have largely replaced the use of organophosphate insecticides (e.g., diazinon, chlorpyrifos) in the United States, and although studied frequently in sediments, few studies have been published on pyrethroids in urban stormwater runoff ([Weston et al., 2009](#)). In the few studies to date, concentrations have commonly been detected in direct correlation with the local use patterns of agricultural and urban insecticides ([Weston et al., 2009](#); [Hladik and Kuivila, 2009](#); [Weston and Lydy, 2010](#); [Jorgenson et al., 2013](#)). Estimates of loads and yields from watersheds are rare and relationships between differing land use patterns and individual pyrethroids are likely complex and confounded by the somewhat random availability of products and applicator trends at the local scale. Similar to PBDEs, given ever evolving pesticide use trends and new chemical formulations cycling on and off the market, an improved data set on concentrations and loads in urban areas will provide a useful data set to measure trends in water quality.

Information on concentrations and loads from primary pathways such as stormwater, municipal and industrial wastewater, and atmospheric deposition are needed to determine potential impacts on the overall health of San Francisco Bay. Additionally, even after policy or management decisions are made for an impacted water body using the often minimal information available, improved concentration and loading information can provide confirmation or important information for adaptive management, as was the case for the present study. Although there is a growing data base of urban studies on concentrations and loads of persistent organic compounds as discussed above, studies for some compounds are rare, especially in semi-arid environments which, due to the episodic nature of runoff, may differ from systems with less episodic rainfall and runoff patterns.

The goals of this study were to measure concentrations and loads of PCBs, dioxins, PAHs, PBDEs, pyrethroids and OC pesticides from a small urban watershed with historic and ongoing industrial land use, compare these to findings from urban areas in other parts of the world, and evaluate the proportion of the pollutant loads transported under multiple flow conditions to support design of management actions. High frequency sampling coupled with near real-time measurements of flow and turbidity resulted in an accurate yet cost effective understanding of seasonal concentration, flows, and loads characteristics; important information for stormwater managers in climatically arid regions tasked with finding and abating sources and/or designing treatment solutions. Results from this study can be used to improve our understanding of organic pollutants that are not commonly measured in urban stormwater. Furthermore, correlation of these organic pollutants to turbidity, an easily measured parameter, can facilitate environmental managers in their decision-making process.

2. Methods

2.1. Field sampling

The Zone 4 Line A (Z4LA) channel is an engineered stormwater conveyance which flows directly to the Bay and drains 4.17 km² of relatively flat (average surface slope 0.4%) urban landscape ([Fig. 1](#)). Land use is 19% industrial, 35% commercial, 27% residential, 17% transportation, and 2% open space urban parks. The channel receives no wastewater and no imported water with the exception of minor landscape irrigation overflow and other dry weather discharge of unknown origin. The watershed has a pronounced wet season and receives 95% of its rainfall

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