Comparison of pollutant concentrations from weekly discrete versus composite samples for residential dry-weather runoff

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Abstract

As urbanization has increased, so has degradation of urban streams. Urban water quality monitoring has focused on storm runoff sampling, but in arid climates, dry-weather runoff is a significant contributor of pollutants to aquatic systems. The majority of dry-weather runoff studies sample a small window of the entire dry-season. For this study constituent concentrations were compared using two sampling protocols. The first protocol repeatedly collected samples on the same day of the week at the same time of day. The second protocol collected samples during two week-long intensive sampling events consisting of sample collection every hour for 24 h for seven consecutive days. The two protocols were compared to determine if sampling at the same time was representative of the entire week. For nitrate, total phosphorous, pronil, permethrin, total organic carbon, and total suspended solids, sampling at the same time was not representative of the weekly mean; however, variability was observed between sites and constituents. For those constituent concentrations with significant differences seen between the two protocols, load adjustment factors (LAF) were determined, using a ratio of treatment means, and employed to adjust dry-season load estimates. Future work should include determining if LAF values can be used at similar sites excluded from the study or for similar constituents from the current sampling sites.

1. Introduction

Water quality in urban streams has degraded due to increased runoff volumes and pollutant loading as a result of the increase in impervious surface cover in urban areas (Klein, 1979). The landmark study documenting runoff water quality was the Nationwide Urban Runoff Program; its results, though dated, are still in use (EPA, 1983). Subsequent runoff quality monitoring studies focused on storm runoff (Makepeace et al., 1995; Oltmann et al., 1987; Smullen et al., 1999). Recently, urban dry-weather runoff research in arid climates has become a research focus. Although sampling of storm events is important, recent studies have shown that dry-weather loading of nutrients, pesticides, and other constituents can be a significant contributor of pollutants to receiving waters and is exacerbated by drought years (McPherson et al., 2002, 2005b; Stein and Ackerman, 2007; Stein and Tiefenthaler, 2005). Some research indicates that dry-weather runoff can have higher concentrations of contaminants than storm runoff because of a lack of dilution (Bay et al., 1996; Schiff and Tiefenthaler, 2003; Weston et al., 2009), possibly causing greater ecological damage because many of these constituents are known to harm aquatic organisms (Bay et al., 1996; Weston et al., 2009).

The majority of dry-weather runoff research has focused on mixed land-use watersheds (McPherson et al., 2002, 2005a; Stein and Ackerman, 2007) with few studies concentrated on pollutant loading from dry-weather runoff derived from single family homes. Within residential watersheds, land cover is characterized by impervious surfaces consisting of sidewalks, driveways, and streets, as well as permeable surfaces of lawns and landscaping. Dry-weather runoff from these areas is primarily from landscape irrigation (Bale et al., 2011; Bay et al., 1996) with a smaller portion from

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automobile washing and other activities. Dry-weather runoff may contain nutrients from fertilizers and pet waste, pesticides from professional or homeowner applications, sediments, and other constituents such as petroleum products and metals from automobiles (Bale et al., 2011; Deffontis et al., 2013; McPherson et al., 2005a, 2005b; Weston et al., 2009).

Protocols for collecting samples during storm events are typically used to obtain a representative sample of runoff from the duration of a storm in order to measure the event mean concentration (EMC) of constituents of interest (Smullen et al., 1999). As most dry-weather residential runoff is from landscape irrigation, it is worthwhile to capture the EMC for irrigation runoff "event"; however unlike storm sampling, it is less clear when the event begins and ends. After dry-season sampling was complete, Bale et al. (2016) determined the occurrence of irrigation runoff events, identified by a daily increase in flow. Since the study was completed prior to analysis of the flows, sampling times could not be adjusted to better capture the irrigation runoff event.

Due to logistical constraints, Bale et al. (2011) collected samples during the same day of the week, usually after flow from irrigation runoff had subsided, and the same day(s) of the week during the dry-season. A more accurate sampling protocol for dry-season load estimation would involve continuous sampling during the entire dry-season or focused sampling on major dry-weather runoff events, i.e. irrigation runoff. This was impractical and costly due to high labor, analytical, and equipment demands.

The objective of this research is to provide an alternative method to load estimate calculation from a limited sampling protocol, i.e. collecting water quality samples repeatedly at the same time of the week. The study presented here relied upon data collected on the same day of the week within the same 4 h time period over three dry-seasons (2007, 2008, and 2010) and two weekend “intensive” (INT) sampling periods where samples were collected every hour for 24 h, each day of the week during two dry-seasons (2008 and 2010) for two sites in California. Using the data collected, the reliability of representing weekly mean constituent concentration from sampling at the same time of day on the same day of the week was evaluated. For those constituent concentrations with significant differences seen between the two protocols, we created load adjustment factors (LAFs) to modify weekly load estimations. The results from this study will help researchers develop better sampling protocols for non-storm runoff monitoring.

2. Materials and methods

2.1. Dry-season defined

For this study, the dry-season is defined as the period after the last storm of the previous wet season and before the first storm of the next wet season. Information on the occurrence of storms collected from on-site rain gauges were used to determine the first and last storm of the wet season.

2.2. Site selection

Two sampling sites were chosen in California consisting of low-density residential areas of single-family homes. Study neighborhoods drained to a single storm drain outfall, so all surface runoff flowed through the sampling site. Sampling sites were selected based on criteria of development age, lot size, assessed value, and viability of sampling site with the latter being the most determining factor. From the above criteria, one site each from Sacramento County and Orange County, California were selected and are the same sites for which load estimates were reported by Bale et al. (2011). Table 1 presents additional information about each site including: outfall pipe diameter, median income, number of parcels, areas, and land cover. The site in the county of Sacramento was located in the city of Folsom (SAC) while the site from Orange County is in the city of Aliso Viejo (OC). SAC is located at 38° 39’ 01.044” N, 121° 08’ 41.93” W. AV is located at 33° 34’ 53.64” N, 117° 44’ 44.70” W.

2.3. Regular sampling procedure (REG)

Grab samples were collected at the end of the storm drain outfall on Tuesdays between 11:00 and 15:00 from SAC and on Wednesdays between 07:00 and 12:00 from OC. Samples were collected weekly in 2007, biweekly in 2008, and monthly in 2010. Two 1-L amber glass bottles (Thermo Fisher Scientific, I-Chem Brand Products, Rockwood, TN) were filled for chemical analysis, stored at 4°C, and transported to the analytical lab at the University of California, Riverside. At OC, an 8.5 L stainless steel bucket was used to collect runoff from the end of the storm drain outfall and distributed between two 1-L amber glass bottles using a Dekaport cone sample splitter (Ricksy Hydrological, Columbus, OH). Those samples originating from SAC were shipped via overnight carrier, while those originating from OC were transported via automobile immediately after they were collected.

Water samples were analyzed for the four most commonly used pesticides (bifenthrin, cypermethrin, fipronil, and permethrin) in both counties during 2007, 2008, 2009, and 2010, based on the California Department of Pesticide Regulation’s Pesticide Use Reports (CDPR, 2010). Pesticide use information from the Structural Pest Control, Landscape Maintenance, and Right-of-Ways reports were evaluated because these are avenues for transport into the drainsheds. The Pesticide Use Report data only includes information on commercial applicator use and does not take into account over-the-counter products that homeowners may be applying because records of homeowner use are not collected by the State of California. Cypermethrin was not included in the data analysis because it was not detected in any samples during the two INT events from either site; this may be due to the fact that some reported pesticide applications are conducted indoors and are unlikely to influence surface water quality.

All reported constituents (nitrate [NO₃⁻], total phosphorous [TP], total suspended solids [TSS], total organic carbon [TOC], bifenthrin, fipronil, cis- and trans-permethrin) were analyzed from every grab sampling event from 2007 to 2010, except NO₃⁻ was not analyzed during 2010. The term “conventional constituents” refers to TSS and TOC. NO₃⁻, TP, TSS, and TOC were measured using EPA methods 9056, 365.4, 160.2, and 9060A with method detection limits (MDL) of 0.01 mg L⁻¹ NO₃⁻-N, 0.05 mg L⁻¹ PO₄-P, 1.0 mg L⁻¹, and 0.1 mg L⁻¹ C respectively. Fipronil was analyzed via the same operating procedure as Lin et al. (2008, 2009). Pyrethroids were analyzed using EPA method 8081A and MDLs for bifenthrin, cis-permethrin, and trans-permethrin were 1.2 ng L⁻¹, 1.7 ng L⁻¹, and 2.9 ng L⁻¹ respectively.

2.4. Intensive sampling procedure (INT)

2.4.1. Autosampler setup

Two Hach Sigma 500 MAX automated samplers (Hach Company, Loveland, CO) were installed at each site; a stainless steel strainer attached at the pickup end of Teflon lined polyethylene tube was submerged in flow at the end of the storm drain outfall pipe. The automated samplers were stored directly above the pipe within a construction box (Greenlee, Rockford, IL).

Both samplers at each site were programmed to collect one 300 mL sample every hour for 24 h. One sampler per site was
programmed to distribute three samples each into 950 mL polyethylene bottles resulting in eight composite samples from different 3 h time periods for nutrient and conventional analysis. The other sampler at each site was programmed to distribute twelve samples each into an I-Chem 3.8-L bottle (Thermo Fisher Scientific, I-Chem Brand Products, Rockwood, TN) resulting in two composite samples from different 12 h time periods for pesticide analysis. Each day before the sampling period, the bottles were packed in each sampler base with ice and a Hobo Pendant temperature logger (Onset Corporation, Bourne, MA). After this, the samplers were programmed for sampling.

After samples were collected, each was weighed to determine if the correct amount had been collected. Two aliquots were taken from each gallon jar, put into separate 1-L amber glass bottles, for a total of four bottles, and transported with ice packs and a temperature logger to University of California, Riverside for pesticide analysis. The 3-h composite samples from SAC were used for laboratory analysis at University of California, Davis. Those 3-h composite samples from OC were analyzed in the laboratory at the South Coast Research and Extension Center in Irvine, CA. The INT procedure was repeated for seven days straight at OC from June 16–23, 2008 and August 9–16, 2010 and at SAC from July 23–30, 2008 and August 24–31, 2010.

2.4.2. Laboratory analysis of INT samples

All TNTplus and Test N’ Tube Reagent sets were from the Hach Company. NO3 concentration was analyzed with TNTplus 835 and 836 with detection ranges between 0.23 - 13.50 and 5.0–35.0 mg L\(^{-1}\) NO3–N, respectively. TP concentration was analyzed with TNTplus 843 and 844 with detection ranges between 0.05 - 1.50 and 0.5–50 mg L\(^{-1}\) PO4–P, respectively. TOC concentration was analyzed with Low Range and Mid Range Test ‘N Tube™ Reagent Set with detection ranges between 0.3 – 20.0 and 15–150 mg L\(^{-1}\) C, respectively. The low range version of a test was used first and if the maximum detection limit was exceeded, the high range test was employed. In several instances the high range test kits were used due to expectations that concentrations would exceed the low range test kit. TSS and pesticide concentrations were analyzed in the same manner as REG.

A blank sample consisting of Barnstead Nanopure water (Thermo Scientific, Rockwood, TN) was included in testing to calibrate the Hach Company DR2800 spectrophotometer to zero before reading the samples. All samples were inserted into the spectrophotometer for reading according to the instrument’s automatic method detection protocol. As per TNTplus 843 sample storage recommendations, samples from SAC to be tested for TP and collected on Aug 28, 2010 after 10:00 until August 29, 2010 before 09:00 were adjusted to pH 2 with concentrated sulfuric acid and stored at 4 °C because there was a shortage of test kits to perform the analysis on the same day samples were collected. The samples were neutralized with sodium hydroxide on August 31, 2010 before testing.

2.5. Statistical analysis

There was no identifiable diurnal pattern seen for any of the constituents, possibly due to consolidating individual 1-h samples into three- or 12-h composites. Compositing was done to reduce time and expense of laboratory analysis but did not allow high enough temporal resolution to detect patterns.

Constituent concentrations below the method detection limit were converted to half the detection limit. Summary statistics for all constituent data except NO3, TP, and TOC at OC were calculated using the “favstats” function in R 3.03.3. Concentration values were logarithmically (base 10) transformed and Analysis of Variance (ANOVA) was performed on each logarithmically transformed constituent, via the R function “oneway.test”, to test for statistical significance between INT and REG.

NO3, TP, and TOC data from INT at OC had right-censored values (i.e., those values above the maximum detection limit), so summary statistics and statistical significance were calculated according to functions as described in Therneau and Grambsch (2000) using the R 3.03.3 (http://www.r-project.org/) package, “Survival analysis, including penalized likelihood.” Mean and median were produced using the “survfit” function and “survdiff” was used to determine statistical significance between REG and INT sampling protocols and is similar to a chi-square goodness-of-fit test.

3. Results and discussion

3.1. Pesticides

Permethrin isomers (cis- and trans-) were analyzed independently in the laboratory and kept separate for statistical analysis and reporting, even though the trend is to sum permethrin isomer concentrations together to get a total permethrin concentration (Weston et al., 2004, 2005). Isolating permethrin isomers within the results was appropriate because loads reported by Bale et al. (2011) were derived from individual isomer concentrations.

Concentrations of permethrin isomers were significantly

<table>
<thead>
<tr>
<th>Name</th>
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<td>Pervious area</td>
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different during INT (years 2008, 2010) and REG (years 2007, 2008, 2010) at both sites (OC cis-, p < 0.001; OC trans-, p = 0.001; SAC cis-, p < 0.001; and SAC trans-, p < 0.001) (Tables 2 and 3). This shows that sampling once weekly was not equivalent to the mean concentration from an entire week of sampling.

Mean bifenthrin concentration was higher for REG than for INT at OC but that was reversed for SAC. In both cases, bifenthrin concentration was not significantly different between INT and REG (OC, p = 0.836; SAC, p = 0.338) (Tables 2 and 3). OC had zero non-detects in both sampling sets while SAC had nine non-detects in INT and six non-detects in REG. In regards to bifenthrin concentrations, it appears that weekly sampling at the same time is representative of the mean weekly concentration. Mean bifenthrin concentration results from other sampling studies are likely an accurate estimation of possible bifenthrin concentrations during the dry-season, assuming a large number of grab samples were collected from a watershed.

Mean fipronil concentration was higher for REG than for INT for both sites (Tables 2 and 3). INT was significantly different than REG for SAC (p < 0.001) and OC (p = 0.019). Detection frequency of fipronil for OC was 100% for both INT and REG while SAC had 18% and 72% detection for INT and REG, respectively. The maximum concentration detected for SAC during REG and INT was and 72% detection for INT and REG, respectively. The maximum concentration detected for SAC during REG and INT was 13.76 and 14.19, respectively and this along with mean and median are indicative of the difference seen between INT and REG data for SAC, with higher concentration values reported for INT than REG for both sites.

3.2. Nutrient and conventional constituents

At OC, both NO₃ and TP mean concentrations are higher for INT than REG and they are significantly different (NO₃, p < 0.001 and TP, p < 0.001) between the two sampling sets (Table 4). In regards to nutrients (NO₃ and TP) weekly sampling at the same time is not representative of the weekly mean concentration. It is unclear what caused the differences seen between INT and REG for NO₃ and TP at OC but the high nutrient concentrations could be attributed to reclaimed wastewater being used for irrigation in a portion of the study area (Occhipinti, 2013). Since reclaimed wastewater can only be applied as irrigation from 21:00–06:00 and REG sampling was performed during normal work hours (after 07:00), it is likely that REG did not capture reclaimed wastewater irrigation in runoff grab samples (Occhipinti, 2013).

At SAC, mean NO₃ concentration for INT and REG was below detection limit and 0.54 mg L⁻¹ NO₃—N, respectively; INT and REG are significantly different (p < 0.001) (Table 5), indicating that weekly sampling at the same time is not representative of the weekly mean concentration for NO₃.

Mean TP concentration at SAC was significantly different between INT and REG (p = 0.034) (Table 5) indicating that the mean TP concentration from weekly sampling at the same time is not representative of dry-season mean concentration. INT had a smaller range of values relative to REG, i.e. REG had greater variability over sampling events. REG had higher detection frequency (90%) than INT (49%).

TOC content was higher in the REG sampling than INT for both sites and were significantly different within each site (OC, p < 0.001; SAC, p = 0.006) (Tables 4 and 5). The mean TOC concentration from weekly sampling at the same time is likely not representative of weekly mean concentration. TOC concentration was highly variable at both sites but SAC had a greater range of values (below detection limit to 400.02). Wet weather urban runoff
studies have shown that TOC concentrations can be highly variable (Helmreich et al., 2010; Sickman et al., 2007) and the data from this study confirms that dry-weather urban runoff has similar variability in TOC concentrations.

Mean TSS concentration was higher for INT sampling than for REG at OC but INT was lower than REG for SAC. TSS results were significantly different between the two sampling protocols for OC (p = 0.013) (Table 4) but were not significantly different for SAC (p = 0.185) (Table 5). The data for OC during both INT and REG and SAC REG is highly variable, but SAC INT was dominated by non-detects. All SAC INT TSS values were consistently low (mean = 0.55 mg/L, median = below detection limit). Unlike storm water samples, which typically have high TSS values (Helmreich et al., 2010), previous research indicates that dry-weather samples are variable (Ackerman and Schiﬀ, 2003; Duke et al., 1999) and the range of TSS concentrations found in this study conﬁrms this. The inconsistency in statistical results between INT and REG for OC and SAC indicates that weekly sampling at the same time may or may not be representative of the weekly mean concentration and could depend on geographical characteristics specific to each site.

3.3. Load adjustment factors

Pollutant mass load is the product of total ﬂow and constituent concentration data acquired for individual sampling locations (Duke et al., 1999; Stein and Tiefenthaler, 2005). Therefore, it is possible to adjust loads based on supplemental information, such as weekly ﬂuctuations, from either ﬂow or concentration. Load adjustment factors (LAF) were derived from the ratio between mean concentrations from INT and REG sampling protocols, with the LAF values then multiplied by the ﬁnal load estimates, resulting in an adjusted load estimate. LAF values are easily determined for individual constituents by dividing the INT mean by the REG mean. LAF values were created for all the constituents where INT and REG were signiﬁcantly different (p < 0.05). Those constituents that are signiﬁcantly different between INT and REG are NO3, TP, TOC, ﬁpronil, cis-, and trans-permethrin for both sites with the addition of TSS for OC.

The method proposed here is limited to dry-weather runoff of a residential watershed with a single outfall. Potentially, this method could be applied to larger mixed-land use watersheds; however, load adjustment factors are speciﬁc to the site for which they are calculated for SAC could be applied to loading estimates stemming from SAC2. However, it would be recommended that LAF values for SAC2 be conﬁrmed by performing an intensive sampling study.

Not only are LAF values site speciﬁc, but they are constituent speciﬁc also, as evidenced by the different LAFs for TP (2.0645) and NO3 (4.0821) from OC (Table 6). These two sites are different in their topography and are located in different regions of California. Although LAF values are site speciﬁc, potential exists to use them at locations that have similar land traits such as: topography, domestic water source, age of home construction, land cover, etc. There is an outfall site (SAC2) located within 0.5 km of SAC with similar geographic characteristics and homes of the same age. It’s reasonable to assume these two outfalls would have similar LAF values and those calculated for SAC could be applied to loading estimates stemming from SAC2. However, it would be recommended that LAF values for SAC2 be conﬁrmed by performing an intensive sampling study.
3.4. Load adjustments

As part of this study, load estimates were compiled for a report to the State Water Resources Control Board from the sampling sites (Bale et al., 2011). LAF values were applied to the load estimations to get an adjusted load for those constituents where REG was significantly different (p < 0.05) from INT. All loads presented here are estimations and for policy purposes it makes sense to consider the Bale et al. (2011) loads and adjusted loads as a range within which the true load falls.

In regards to pesticide loads, adjusted loads of permethrin isomers from both sites were higher at OC (20,493 and 21,137 mg km$^{-2}$ yr$^{-1}$), cis- and trans-permethrin, respectively) and SAC (62 and 47 mg km$^{-2}$ yr$^{-1}$, cis- and trans-permethrin, respectively) than reported in Bale et al. (2011). Adjusted fipronil loads were lower at SAC and OC (Table 6), 48,372 and 1.59 mg km$^{-2}$ yr$^{-1}$, respectively than reported by Bale et al. (2011). The LAF for fipronil at SAC is less than 1.0 because INT had a high percentage of non-detects (82%) versus REG (28%) (Table 3). However, the other adjusted pesticide loads, cis- and trans-permethrins for OC and SAC, included a higher percentage of non-detects in the REG (49–84%) than the INT sampling data (4–50%) (Tables 2 and 3). Left-censored values effectively decrease the mean of the data resulting in the sampling set with more non-detects having a lower mean. With regards to fipronil at OC, REG had consistently higher fipronil concentrations than INT.

Based on LAF values, nutrient and conventional loads at SAC were overestimated using Bale et al. (2011) load calculations (Table 7). Constituent concentrations were two to eight times higher during the REG weekly sampling as evidenced by the LAF values. It is unclear what is occurring at SAC during the REG sampling time that is elevating the concentrations as compared to the INT timeframe. But the large spikes in TOC concentration (max concentration = 400.02 mg L$^{-1}$) during REG (Table 6) contributes to the difference seen within these data because the high values were not present during INT.

Future research focusing upon sample collection of dry-weather runoff throughout the week or on major dry-weather runoff events may result in more accurate loading models. However, if the recommended sample collection methods are not practical, developing load adjustment factors based on weeklong intensive sampling procedures in conjunction with repeated sampling at the same time of day and same day of the week are a viable alternative to high frequency sampling protocols for dry-weather runoff from a residential watershed. Although the method presented here is for residential drainages, it could be applied to industrial or mixed-land use areas and should give valuable information to the scientific community, policymakers and regulators.
Acknowledgements

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