Oil and Grease Measurement in Highway Runoff—Sampling Time and Event Mean Concentrations

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Abstract: An event mean concentration (EMC), usually collected with an automatic, flow-weighted composite sampler, is often used to characterize stormwater pollutants. Automatic samplers are not recommended for collecting oil and grease (O&G) samples due to possible biases associated with interactions with tubing and pumps. To measure the EMC without sampler interferences, a series of grab samples (often over ten samples) must be collected along with the flow measurement to compute the EMC. This paper examines 22 O&G pollutographs from small, impervious highway sites, to determine when a single O&G grab sample most closely approximates a flow-weighted composite sample. Samples collected within the first hour of a storm event overestimated the O&G EMC by 20 mg/L or more, while samples collected toward the end of the event underestimated the EMC. The best time to collect a single grab sample ranged from 1 to 6 h after the beginning of runoff, and was related to site or storm-specific factors. Results obtained from this study also showed that strong correlations ($R^2=0.9$) exist between O&G and other organic constituents, such as chemical oxygen demand (COD) and dissolved organic carbon (DOC). Correlations also exist between O&G EMC, antecedent dry days, and total rainfall. Depending upon site and regulatory specific factors, using COD or DOC EMCs in lieu O&G samples may be a better strategy.

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Introduction

Highway stormwater runoff affects the quality of receiving water bodies by washing contaminants that have accumulated on roadway surfaces to receiving waters. Specifically, stormwater runoff includes suspended solids, nutrients, ionic species, metals, and organic constituents. Oil and grease (O&G), chemical oxygen demand (COD), and dissolved organic carbon (DOC) are frequently used to measure the concentration of organic constituents. Because free O&G can be easily observed as rainbow-colored sheens, it attracts public and regulatory interest. O&G that reaches receiving waters can cause problems, varying from toxicity to aquatic life, depressed dissolved oxygen concentration, odor, unsightly conditions, and loss of use. O&G may contain a wide variety of hydrocarbon compounds, and some, such as polynuclear aromatic hydrocarbons (Eganhouse and Kaplan 1981), are known to be toxic to aquatic life even at very low concentrations.

Land uses that have large numbers of vehicles such as highways are known to discharge more O&G than other land uses such as residential property (Stenstrom et al. 1984). For this reason transportation agencies and others monitor O&G in their stormwater discharges from vehicular-intensive land uses. O&G emissions from vehicles, such as crankcase drippings, and partially combusted fuels, are an important source of hydrocarbons (Duke and Chung 1995). These emissions can be retained on highly impervious surfaces such as highways and are washed off during a runoff event. Hence, managing the discharge of O&G in stormwater runoff from vehicular-intensive land uses such as highways has potential to improve the water quality (Stenstrom et al. 1984).

Most stormwater monitoring programs use automated samplers for collecting flow-weighted composite samples. These samplers generally work well, can be left unattended, and can be triggered automatically to ensure that the very beginning of runoff is sampled. The sampler is programmed to collect many small samples over the entire storm event to insure representativeness. Analysis of a flow-weighted composite sample provides event mean concentration (EMC).

Composite samples are not recommended for analyzing certain constituents, such as O&G (American Public Health Association 1998). The O&G in the sample can adsorb to the collection tubing and sample containers, which will cause the EMC to be underestimated. Subsequent samples can be contaminated by carryover from earlier samples. In the case of toxicity measurements associated with O&G measurement, artifactual toxicity can result from interaction with sampler materials. For some parameters, such as particle size distribution, characteristics can change during the elapsed time in the sample bottle (Li et al. 2005).

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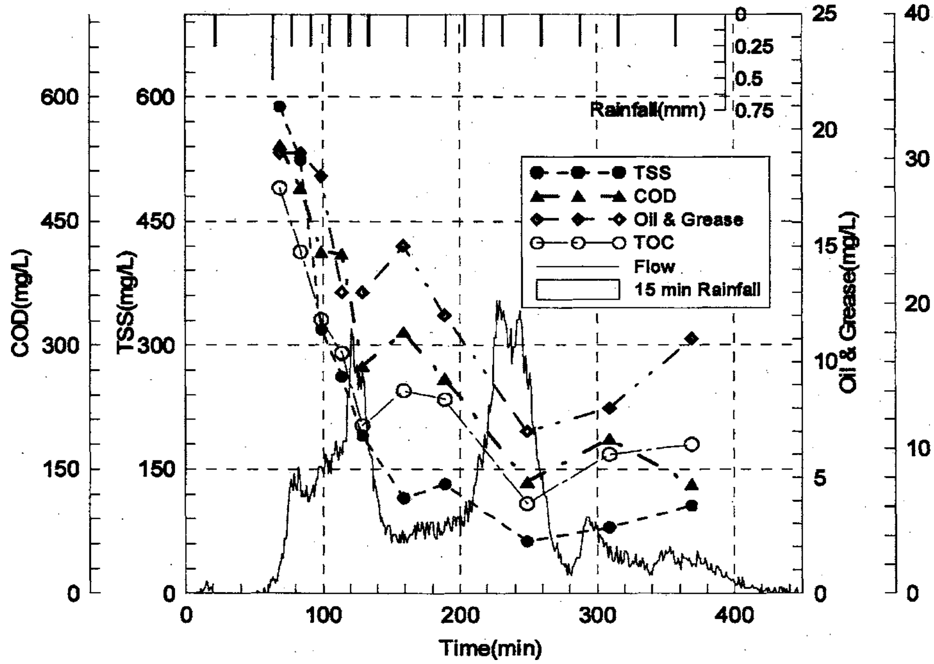

Fig. 1. Example of oil and grease concentration showing first flush and declining concentration

Therefore, a series of grab samples collected at discrete times are recommended to approximate the EMC of specific constituents such as O&G.

Collecting grab samples can be more difficult and less practical during storm events for several reasons: (1) the sampling crew must standby, awaiting the beginning of rainfall and may miss important parts of a storm event if it begins at an inconvenient time; (2) the sampling team may need to travel a great distance in a short time to reach all sampling locations; (3) the sampling team may not have safe access to sampling locations during rainfall; and (4) the cost associated with manually collecting grab samples is high. As a result, often only a single, randomly timed, grab sample is collected, which may not be representative of the EMC. O&G often exhibits a first flush (Lau et al. 2002; Ma et al. 2002), which means samples collected early in the storm will have higher concentrations than those collected later in the storm. Fig. 1 illustrates this phenomenon.

This study was undertaken with the following specific objectives:

1. To determine if there exists a "best time" to collect a single grab sample for O&G from highway land use that most accurately represents the EMC.
2. To develop a mathematical relationship to determine the best time to collect a single O&G grab sample to be more representative of EMC, from site or storm-specific information.
3. To discover mathematical relationships that can be used to accurately correlate the O&G EMC ($EMC_{O\&G}$) from site and storm information and from organic constituents such as COD and DOC that are commonly collected by automatic samplers.

Background

Event mean concentrations are normally used to represent stormwater pollutant concentrations (Huber 1993). The EMC is the flow-weighted average concentration collected over the entire storm event, and is equal to the total mass emission, divided by the total runoff volume. The following equation shows the mathematical definition of EMC (mg/L)

$$\mathrm{EMC} = \frac{M}{V} = \frac{\int_0^T c(t)q(t)dt}{\int_0^T q(t)dt} \qquad (1)$$

where M=total mass of pollutant during the entire runoff (kg); V=total volume of runoff (m^3); $c(t)$=time varying pollutant concentration (mg/L); $q(t)$=time variable flow (L/min); and T=total duration of runoff (min).

In case of a series of grab samples, the flow-weighted EMC is defined using the following equation

$$\mathrm{EMC} = \frac{\sum_{i=1}^{n} C_i V_i}{\sum_{i=1}^{n} V_i} = \frac{C_1V_1 + C_2V_2 + \cdots + C_nV_n}{V_T}$$
$$= W_1C_1 + W_2C_2 + \cdots + W_nC_n \qquad (2)$$

where

$$W_i = \frac{V_i}{V_T} \qquad (3)$$

$$W_1 + W_2 + \cdots + W_n = 1 \qquad (4)$$

where C_i=fractional concentration assigned to the ith grab sample (mg/L); W_i=weight for the ith grab sample (dimensionless); V_i=fractional flow volume assigned to the ith grab sample (L); V_T=total volume of runoff (L); and n=number of grab samples (dimensionless). EMCs are useful because they can be multiplied by total runoff volume to calculate mass discharge, and avoid the high variability that is associated with grab samples (Lee and Stenstrom 2005). They can be correlated to land use (Sartor et al. 1974; Stenstrom et al. 1984; Smullen et al. 1999).

Table 1. Site Characteristics

Site	Location	Highway	Number of events[a]	AREA (ha)	RC	Type of surface	AADT (vehicles/day)
1	Van Nuys	US-101	6	1.28	0.94	Pavement	328,000
2	Getty Center	IS-405	6	1.69	0.71	Pavement	260,000
3	Santa Monica Blvd.	IS-405	10	0.39	0.89	Pavement	322,000

[a]The number of events is the storms used in the analysis.

Methodology

Site Description

Table 1 shows the characteristics of the three sites. These sites were monitored as part of a larger project to determine the characteristics of highway stormwater runoff. The freeways are among the busiest in California, and the construction of the sites is typical of many freeways. The sites are highly impervious. Twenty two events monitored at these sites during the rainy seasons (October–April) of 1999–2000, 2000–2001, and 2001–2002 were used in this analysis. The sites were all close to the UCLA campus so that sampling teams could reach the sites prior to the initiation of runoff.

Sample Collection and Analysis

Both grab and composite samples were collected as part of this study. Grab samples (4 l each) were collected at 15 min intervals during the first hour of runoff and at 1 h intervals over the next 7 h. For those few storms that lasted longer than 8 h, additional grab samples were collected to capture the end of the storm. Grab samples were collected by bailing from a freefall of runoff exiting a discharge pipe. American Sigma (Loveland, Colo.), model 950 equipped with tilting bucket rain gage, and area/velocity flow meter was used for flow-weighted composite samples. The automated composite sampler was allowed to run until the end of runoff. A large suite of water quality constituents were monitored (Lau et al. 2002), but for the purposes of this study, only O&G, COD, and DOC analyses are presented. O&G was measured using the procedure by Lau and Stenstrom (1997); COD was analyzed using U.S. EPA 410.1 and DOC was analyzed using U.S. EPA 415.1, with a Tekmar-Dohrman Model Apollo 9000 analyzer (Mason, Ohio). We are careful to use the term DOC, since instruments such as the Tekmar-Dohrman inject a small sample volume into the furnace, and even if the sample is not filtered, particles larger than 8 μm cannot enter the furnace. The use of a sample boat that can inject a larger volume without using narrow bore tubing is better for total organic carbon measurements.

Timing for Grab Sample Collection

Many constituents exhibit a first flush, which means the concentration declines as the storm progresses (Ma et al. 2002). Best time or time-to-EMC (TEMC) is defined as the time from the beginning of runoff to the point that corresponds to EMC. This assumes concentration is monotonically declining. A grab sample collected too early may overestimate the true EMC because of the first flush effect, and a grab sample collected too late may underestimate the actual EMC as a result of pollutant washoff.

Several best time strategies were evaluated to collect a single grab sample. One strategy was to see if there exists a period in the runoff hydrograph that is routinely more accurate for estimating the EMC. A second strategy was to pick consistent times, such as 3, 4, or 5 h after the beginning of runoff. Another strategy is to determine if rainfall or site characteristics have an impact on the best time, determine if the characteristics can be predicted from weather reports, and then to use a predicted best time to collect a grab sample.

Statistical Analysis

In order to simulate sampling at different points in a storm, it was assumed that the runoff concentrations were piecewise linear functions. Under this assumption it is possible to interpolate between data points to simulate sampling at an arbitrary time. Sampling at a random time was simulated using a random number generator that was programmed to produce random times during the runoff period. O&G concentration was estimated at the random times by interpolating between the measured concentrations that span to random time. Sampling at specific times (1–6 h) after the beginning of runoff was also simulated in this fashion. Analysis was performed using Systat 9 (Richmond, Calif.).

The various events were classified into types based upon concentration and runoff profiles. Next a screening analysis was performed to confirm expected correlations of site and event specific parameters with $EMC_{O\&G}$. From these correlations, further analyses were performed as follows:

1. Strategies to collect a grab sample at timed points in a storm event (i.e., 1, 2, 3 h, etc., after the storm beginning);
2. Strategies to estimate the best time to sample from event and site variables, such as total rainfall (T_RAIN), antecedent dry period, defined here as antecedent dry days (ADD), etc.;
3. Strategies to estimate the $EMC_{O\&G}$ directly from event and site variables, without collecting a grab sample; and
4. Strategies to estimate $EMC_{O\&G}$ from COD and DOC EMC that are collected from automated composite samplers.

Some of the strategies require only parameters known in advance of the storm, such as ADD, annual average daily traffic (AADT), and AREA. Other strategies require parameters related to storm characteristics, and include T_RAIN, duration of runoff (D_RUN), and total runoff (T_RUN). The later parameters must be estimated from weather predictions, which were simulated with three levels of accuracy.

Results and Discussion

The statistical summary of EMCs of relevant constituents is presented in Table 2. The mean EMC values of the contaminants were higher for Site 2 than other sites. Site 3 had the minimum standard deviation of EMCs. Reasons for differences among sites are not known at this time.

Correlation and Regression Results for Best Time and $EMC_{O\&G}$

Table 3 shows the results as a correlation matrix. As shown, the best time to sample for O&G ($TEMC_{O\&G}$) and $EMC_{O\&G}$ were

Table 2. Statistical Summary of O&G, COD, and DOC EMC Analysis

Constituent	Statistical summary (mg/L) Minimum	Maximum	Median	Mean	SD
O&G					
Site 1	1.84	33.9	6.77	8.95	7.43
Site 2	1.44	80.1	6.37	15.5	19.8
Site 3	1.52	41.6	5.54	8.83	8.63
All sites	1.44	80.1	6.57	11.0	13.2
COD					
Site 1	18.2	258	113	115	73.2
Site 2	31.4	694	105	157	155
Site 3	13.8	418	66.8	103	111
All sites	13.8	694	85.2	124	119
DOC					
Site 1	27.5	820	101	150	176
Site 2	31.3	2,280	76.7	292	522
Site 3	22.0	1,110	70.7	158	228
All sites	22.0	2,280	85.0	199	342

correlated with the eight independent event-specific and site-specific variables chosen. There exists a strong correlation between $EMC_{O\&G}$ and ADD ($R=0.91$), and no strong correlations with other parameters. The time-to-EMC is strongly correlated with D_RUN ($R=0.77$), T_RUN ($R=0.82$), and T_RAIN ($R=0.87$). This was expected since the emission of O&G should occur over the length of runoff, which is related to the total rainfall and its duration. D_RUN, T_RUN, and T_RAIN are highly correlated among themselves, as expected. There is almost no correlation with TEMC and EMC with other site parameters such as RC, AADT, and AREA. CENTROID was poorly correlated with other parameters and the correlations are not reported. AADT would probably not show any correlation in our analysis, since it does not vary greatly among sites. More detailed information on the effects of AADT on water quality can be found in Kayhanian et al. (2003).

Table 4 shows the results of all four strategies for estimating $EMC_{O\&G}$. The results for all methods are placed in one large table to facilitate comparisons. They are divided by the following method: (1) timed samples; (2) samples collected at a specific times determined by regressions of storm characteristics; (3) regressions as a function of event and site characteristics; and (4) regression of $EMC_{O\&G}$ with COD and DOC measured using autosamplers. They are discussed in the following sections.

Best Time for Sample Collection

A simulation was made to determine if specific times for grab sample collection might be a good strategy. Sample collection was simulated by using the pollutograph to determine O&G concentration at specific times, as described previously. Times from 0.25 to 6 h and storm end were evaluated. The results are shown in Table 4. It is useful to compare these results to the results of collecting a random time sample. Root mean square (RMS) error, bias, and number of storms are reported. The number of storms used for analysis decreases at longer sampling times, since not all storms lasted as long as the sampling time. The error and bias are the differences between the EMC calculated from the series of grab samples and the value simulated by the various strategies.

For random timing, the error is 9.4 mg/L with a bias of 1.15 mg/L. Bias is the average difference between the measured EMCs and the EMCs estimated by the various strategies. The RMS error is largest for sampling strategies that are early in the runoff, which is expected since O&G typically shows a first flush. The RMS error is roughly equal for samples collected after 1 h, although the bias decreases to a negative value after 2 h. Therefore sampling at specific times longer than 1 h produces much less error than randomly timed samples, but slightly underestimates the $EMC_{O\&G}$. Sampling at the end of the storm is also a good strategy.

Best Time from Event and Site Variables

The $TEMC_{O\&G}$ is determined by finding the intersection of the O&G pollutograph with the EMC calculated from the grab samples and runoff flow rates. The time where this occurs is defined as $TEMC_{O\&G}$, and is shown in Fig. 2. For monotonically declining concentrations, the O&G concentration equals the EMC value only at a single point. In the case of concentration declines that are not monotone, the O&G concentration might equal the EMC at more than one point, as shown in Fig. 3. For these cases, the first value obtained in the time axis was used to compute the best time for this research. The best times illustrated in Figs. 2 and 3 are 133 and 54 min, respectively. The first occurrence of the EMC was used, although other approaches are possible, such as smoothing the curve or averaging the times.

$TEMC_{O\&G}$ was analyzed as a function of the factors (ADD, D_RUN, and T_RAIN) showing higher correlation. Five forms of equations, namely, linear, power, log, exponential, and inverse were considered for simple and multiple regressions. The linear regression results proved to be better than the nonlinear

Table 3. Correlation Matrix (R) for Dependent and Independent Variables

	$EMC_{O\&G}$	$TEMC_{O\&G}$	ADD	D_RUN	T_RUN	T_RAIN	AADT	RC	AREA
$EMC_{O\&G}$	1.00	—	—	—	—	—	—	—	—
$TEMC_{O\&G}$	−0.38	1.00	—	—	—	—	—	—	—
ADD	0.91	−0.37	1.00	—	—	—	—	—	—
*D*_RUN	−0.30	0.77	−0.22	1.00	—	—	—	—	—
*T*_RUN	−0.26	0.82	−0.22	0.79	1.00	—	—	—	—
*T*_RAIN	−0.29	0.87	−0.25	0.79	0.96	1.00	—	—	—
AADT	0.03	−0.18	0.00	−0.33	−0.43	−0.33	1.00	—	—
RC	−0.17	−0.21	−0.06	−0.12	−0.37	−0.36	0.61	1.00	—
AREA	0.11	0.23	0.07	0.35	0.46	0.25	−0.70	−0.37	1.00

Table 4. Summary of R^2, RMS Error, and Bias Values for Different Methods to Predict $EMC_{O\&G}$

Sampling strategy or regression method	Number of observations	R^2	RMS error (mg/L)	Bias (mg/L)
Random grab sampling time	22	0.54	9.40	1.15
Strategy 1: Timed sample strategies after beginning of runoff				
0.25 h	22		32.4	23.8
1 h	22		3.47	1.39
2 h	22		3.91	−2.07
3 h	18		3.92	−2.54
4 h	15		3.59	−0.88
5 h	14		3.13	−1.21
6 h	9		2.19	−1.38
Storm end	22		3.52	−1.96
Strategy 2: Best sampling time from event and site variables				
Post storm measured parameters				
Total rainfall Eq. (5)	22	0.96	1.99	−0.27
Duration of runoff Eq. (6)	22	0.92	2.64	−0.22
Total rainfall and duration of runoff Eq. (7)	22	0.96	1.96	−0.26
Total rainfall, duration of runoff, and antecedent dry days Eq. (8)	22	0.97	2.72	0.73
Predicted parameters				
Total rainfall Eq. (5)	22	0.89	2.98	0.39
Duration of runoff Eq. (6)	22	0.95	2.22	−0.40
Total rainfall and duration of runoff Eq. (7)	22	0.88	3.19	0.37
Total rainfall, duration of runoff, and antecedent dry days Eq. (8)	22	0.92	3.46	1.18
Strategy 3: EMC of O&G from site and event variables				
Antecedent dry days Eq. (9)	22	0.82	3.84	−0.01
Antecedent dry days and total rainfall Eq. (10)	22	0.83	3.79	0.00
Logarithm of antecedent dry days and total rainfall Eq. (11)	22	0.84	3.60	−0.42
Strategy 4: EMC of O&G from composite COD or DOC measurement				
COD Eq. (12)	22	0.90	2.90	0.07
DOC Eq. (13)	22	0.90	2.84	0.01

regressions. Only the four best results are presented, and are shown in Eqs. (5)–(8), with regression coefficients. Table 5 shows the significance

$$TEMC_{O\&G} = 55.71 + 1.50T\_RAIN \quad R^2 = 0.76 \tag{5}$$

$$TEMC_{O\&G} = 22.29 + 9.12D\_RUN \quad R^2 = 0.59 \tag{6}$$

$$TEMC_{O\&G} = 43.53 + 1.21T\_RAIN + 2.55D\_RUN \quad R^2 = 0.78 \tag{7}$$

$$TEMC_{O\&G} = 52.31 + 1.51T\_RAIN + 2.47D\_RUN - 0.39ADD \quad R^2 = 0.81 \tag{8}$$

The O&G concentrations associated with the different regressions were determined by finding the intersection of the best time and O&G concentration on the pollutograph. Table 4 shows values of R^2, RMS error and bias in EMC concentrations. Note that the R^2 shown in Eqs. (5)–(8) and Table 5 are indicators of how well the best time is predicted. The R^2 shown in Table 4 are indications of how well the O&G concentrations are predicted, using the best times predicted from Eqs. (5)–(8). The estimation is better than timed samples for both RMS error and bias. The RMS error is less than 2.8 mg/L with bias less than $|0.75|$. R^2 values are all above 0.9. Using only the total rainfall provides essentially the best estimate. Adding the D_RUN only marginally improves the estimate, and ADD is not useful for this case. The largest improvement over the timed strategies is the reduced bias, which is

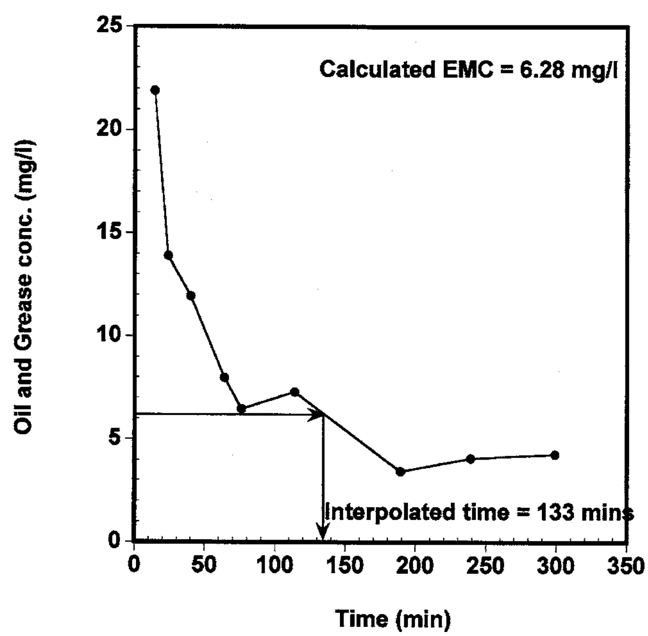

Fig. 2. Example of obtaining interpolated time based on calculated EMC value for monotonically declining oil and grease concentration

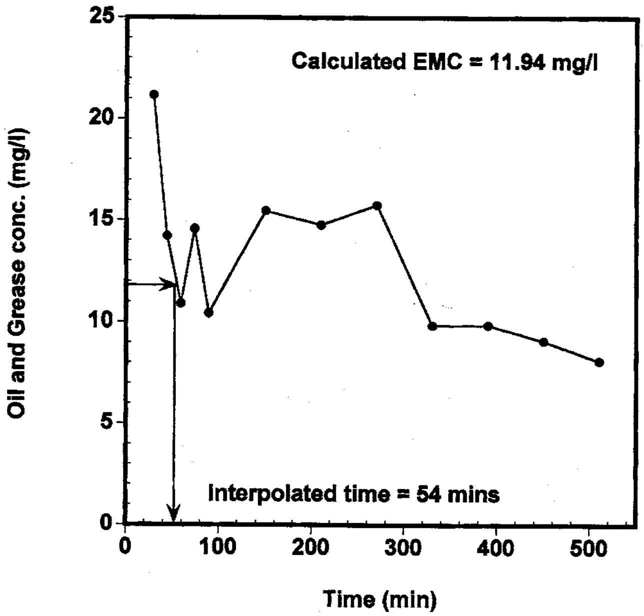

Fig. 3. Example of obtaining interpolated time based on calculated EMC value for nonmonotonically declining oil and grease concentration

essentially within the precision of O&G analysis for the best time strategies.

The problem with this strategy is that some parameters, such as T_RAIN, are not known until after the storm and can only be estimated by weather predictions. To simulate weather prediction, the estimated values of T_RAIN and D_RUN were provided by dividing the post rain data into three categories: low (6 mm and 5 h), medium (13 mm and 7 h), and high (25 mm and 12 h). This assumes that the weather prediction could estimate T_RAIN and D_RUN within this accuracy. These values were substituted into Eqs. (5)–(8). The results are shown in Table 4 under strategy 2, predicted parameters. If weather prediction is able to classify rainfall as small, medium, or large, this best time strategy is superior to timed strategies. This strategy still requires sampling teams to mobilize and travel to the sampling sites at specific times, and this may not be possible for teams with many sites to sample.

The analysis shows that collecting the first flush at the beginning of the storm does not provide a good estimate of the EMC. This means that sampling teams do not need to stand by awaiting the beginning of rainfall to insure collection of the first flush.

$EMC_{O\&G}$ from Event and Site Variables

An analysis was performed to determine if $EMC_{O\&G}$ could be estimated directly from event or site characteristics. This strategy is completely predictive and does not require an O&G sample. Regressions were made between $EMC_{O\&G}$ and the seven previously described parameters using five different models. Simple and multiple regressions were used. Useful results were obtained only when using ADD and T_RAIN. Eq. (9) shows the result for ADD

$$EMC_{O\&G} = 2.64 + 0.38ADD \quad R^2 = 0.82 \tag{9}$$

The p values for the intercept and ADD were 0.03 and 0.00, respectively. This regression provides nearly the same accuracy as the previously described strategies, but its use is limited to type of rainfall events used in this analysis. No event less than 3.8 mm was analyzed; very low rainfall is usually associated with higher $EMC_{O\&G}$.

Although Eq. (9) predicts $EMC_{O\&G}$ reasonably well, it does not include any effects of rainfall or storm duration. There are two primary mechanisms that influence the EMC. The first relates to the buildup phase, which is correlated to ADD and the second is related to the washoff. Eq. (9) considers only the buildup mechanism, which is impacted only by the variables ADD and AADT. The washoff phase can be impacted by other variables: D_RUN, T_RUN, T_RAIN, and RC. A second regression was performed using ADD and T_RAIN, and is shown as Eq. (10). Eq. (10) has slightly better fit (see Table 4) and includes both buildup and washoff mechanisms. In this regression, the significance of the intercept ($p=0.03$) and ADD ($p=0.00$) coefficient remain high, but the significance of T_RAIN or washoff is low ($p=0.50$); therefore, the effect of washoff is either not important or is not estimated by the linear regression

$$EMC_{O\&G} = 3.20 + 0.37ADD - 0.02T\_RAIN \quad R^2 = 0.83 \tag{10}$$

Eq. (11) shows the same regression except using a log transformation of the data

$$\log_{10}(EMC_{O\&G}) = 0.37 + 0.64\log_{10}(ADD) - 0.17\log_{10}(T\_RAIN) \quad R^2 = 0.84 \tag{11}$$

The coefficients are significant with p values of 0.02, 0.00, and 0.09 for the intercept, ADD, and T_RAIN, respectively. Eq. (11) is a more realistic model with the possibility of including two separate effects.

Table 5. R^2 and p Values for Eqs. (5)–(8)

		p value			
Equation	R^2	Intercept	T_RAIN	D_RUN	ADD
Eq. (5)	0.76	0.00	0.00	—	—
Eq. (6)	0.59	0.14	—	0.00	—
Eq. (7)	0.78	0.00	0.00	0.23	—
Eq. (8)	0.81	0.00	0.00	0.23	0.17

$EMC_{O\&G}$ from Composite COD and DOC Measurement

Another method for estimating $EMC_{O\&G}$ is to correlate the EMC with other parameters measuring organics concentration, such as COD and DOC, or total suspended solids (TSS), which is often used as a surrogate for other water quality parameters in stormwater management. O&G is only a fraction of the compounds that compose COD or DOC and the fraction depends upon land use (Stenstrom et al. 1986; Fam et al. 1987). Highway runoff is all the same land use and we can expect the source of the hydrocarbons to be similar.

There exists a significant correlation between the $EMC_{O\&G}$, EMC_{COD}, and EMC_{DOC} ($R=0.95$). Eqs. (12) and (13) show the regressions between $EMC_{O\&G}$ and EMC_{COD} or EMC_{DOC}. The intercept is not significant for DOC but is still shown in Eq. (13). In both cases the R^2 are 0.90 and the remaining regression parameters are significant ($p<0.02$)

$$EMC_{O\&G} = 3.71 + 0.04EMC_{COD} \quad R^2 = 0.90 \tag{12}$$

Table 6. Basic Statistics for Different Methods to Predict $EMC_{O\&G}$ for Highway Runoff Characterization[a]

Method	Number of cases	Minimum	Maximum	Median	Mean	Standard deviation	COV[b]
Actual values reported	418	1.00	226.00	6.00	10.28	15.00	1.46
Regression with measured constituents							
COD Eq. (12)	102	4.32	19.99	8.89	9.55	3.53	0.37
DOC Eq. (13)	228	1.03	88.53	4.02	5.42	8.49	1.57

[a]Source: Caltrans discharge characterization study report, CTSW-RT-03-065.51.42.

[b]COV=coefficient of variation.

$$EMC_{O\&G} = 0.15 + 0.28 EMC_{DOC} \quad R^2 = 0.90 \qquad (13)$$

TSS and $EMC_{O\&G}$ were not correlated ($R=0.18$). In this case, TSS is not a useful surrogate for O&G.

Practical Applications and Recommendations

Four alternative methods have been presented to estimate $EMC_{O\&G}$: timed samples; estimates of the best time to collect a grab sample, based upon various storm and site specific parameters; regression with storm and site specific parameters; and correlation with COD or DOC. All methods are superior to collecting a randomly timed grab sample and produced RMS errors less than 4 mg/L and R^2 from 0.82 to 0.97. The RMS error associated with a randomly timed sample was 9.4 mg/L. Collecting a sample at the very beginning of a storm event was the worst strategy with RMS error of 32.4 mg/L. Small differences in the performance among the methods were noted. The selection of method should probably be based on considerations in addition to accuracy.

The timed sampling strategies require a sampling team or sampling device to collect a sample at a specific time, which may be inconvenient for teams sampling many sites. Also it may not be possible to know the exact time of the beginning of the storm without local rain gages or flow meters. The best time strategies have the same disadvantage in that a sample must be collected at a specific time, and are more complicated because the sample time must be calculated from a regression and weather prediction.

Regressions with site-specific parameters such as ADD were slightly less accurate than the timed methods, but have the advantage that no sample needs to be collected. Regulatory agencies may not support this strategy, unless the accuracy of the regression is demonstrated.

Correlation of $EMC_{O\&G}$ with EMC_{COD} or EMC_{DOC} is perhaps most promising. It is nearly as accurate as the best of all methods and has no bias. It has the advantage that the result is based upon an actual sample. The sampling team needs to do no extra work, and COD or DOC can be monitored with composite samplers. DOC may be preferable since it is not subject to interferences from inorganic, chemically oxidizable pollutants.

To demonstrate the practical application of methodologies presented in this paper, the data collected as part of the California Department of Transportation (Caltrans) was used for comparison. This data set includes water quality measurements from 1997 to 2002 at 94 highway sites. O&G grab samples were collected for each storm event, as well as flow-weighted composite samples that were analyzed for DOC and COD. The timing for grab sample collection was not controlled, but grab samples were generally collected early in the storm, to ensure that a sample was obtained. Only samples above O&G detection limits were used. The comparison shows the potential difference between O&G estimated from a large number of randomly timed grab samples and correlation to DOC or COD EMC concentrations, using the coefficients developed in this paper.

Table 6 shows the result of this comparison. The median value of the O&G estimate from correlating to COD would have been 2.9 mg/L higher, while the median value of the O&G estimate correlated to DOC would have been 2.0 mg/L lower. The mean values for O&G correlated to DOC and COD were both lower than the estimate from grab samples. The concentrations associated with the grab samples, which were generally collected early in the rainfall event, are consistent with the observations at the three highway sites discussed earlier in the paper.

This exercise suggests that O&G estimates from grab samples may slightly overestimate the actual EMCs. The new methods produced less variable results and can be performed without collecting grab samples, which should result in substantial cost savings. The approach used in the paper might also be useful for other parameters that require grab samples or are difficult to sample with automated composite samplers.

We caution the use of the O&G/DOC correlations developed in this paper for other types of land uses. The source of the O&G impacts its characteristics (Fam et al. 1987; Duke and Chung 1995), who showed that nontransportation land uses can produce more oil and grease containing a higher fraction of fatty acids, which can have a different COD/O&G ratio. The methodology may be applicable to sites with different sources of O&G, but new regressions and correlations should be performed.

Conclusions

This paper addresses the question of when to collect a grab sample for O&G to best approximate the EMC for an entire storm event. Twenty two storm events using three sites during the rainy seasons (October–April) of 1999–2002 were used to determine if there exists a point in the pollutograph that best approximates the O&G EMC $EMC_{O\&G}$. Regression analyses were performed to determine if $EMC_{O\&G}$ and best sampling time could be related to storm-specific parameters such as total rainfall, or site-specific parameters, such as antecedent dry days (ADDs). Finally, correlations were made between other organic parameters, such as COD and DOC, to determine if using a correlation to estimate $EMC_{O\&G}$ is a viable strategy. The paper provides quantitative relations that support the following conclusions:

1. Collecting a single grab sample at no specific time is a poor strategy for estimating $EMC_{O\&G}$.
2. If a single O&G grab sample is to be collected to characterize the storm event, it should be collected several hours into the storm. Samples collected at the beginning of the storm event (~15 min) can overestimate the $EMC_{O\&G}$ by 20 mg/L or more. Samples collected after 1 h generally had root mean square errors under 4 mg/L, when compared to the EMC.

Samples collected toward the end of the storm may underestimate the EMC, but only by 1–2 mg/L.

3. There exists a best time to sample for O&G which is related to storm characteristics such as total rainfall (T_RAIN). Greater T_RAIN or storm duration delays the best time to collect a sample.
4. The $EMCs_{O\&G}$ were well correlated to site-specific storm conditions such as antecedent dry days and T_RAIN.
5. There exists a strong correlation ($R^2 \sim 0.9$) between $EMC_{O\&G}$ and COD or DOC. Using the correlation with EMC_{COD} or EMC_{DOC} is a viable strategy for estimating $EMC_{O\&G}$ for highway runoff. This correlation is specific for the types of oil and grease discharged from highway land use and should be confirmed for other types of land use.
6. $EMC_{O\&G}$ was not well correlated to total suspended solids EMC ($R^2 \sim 0.2$).
7. A comparison of the methods presented here with a large California, statewide stormwater monitoring program suggests that the new methods will have less variability and will, on average, produce O&G concentrations that are 2 mg/L less than those obtained with grab samples.

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Notation

The following symbols are used in this paper:

AADT = annual average daily traffic;
ADD = antecedent dry days (day);
AREA = catchment area (ha);
C_i = fractional concentration assigned to *i*th grab sample ($mg\,L^{-1}$);
$c(t)$ = time varying pollutant concentration ($mg\,L^{-1}$);
D_RUN = duration of runoff total runoff (h);
EMC = event mean concentration ($mg\,L^{-1}$);
M = total mass of pollutant during entire runoff (kg);
n = number of grab samples;
O&G = oil and grease;
p = probability value;
q(t) = time variable flow ($L\,min^{-1}$);
R = correlation coefficient;
RC = rational runoff coefficient;
T = total duration of runoff (min);
TEMC = best time to sample from beginning of runoff (min);
T_RAIN = total rainfall (mm);
T_RUN = total runoff volume (L);
TSS = total suspended solids ($mg\,L^{-1}$);
U = unit loading rate ($kg\,ha^{-1}\,mm^{-1}$);
V = total volume of runoff (m^3);
V_i = fractional flow volume assigned to *i*th grab sample (L);
V_T = total volume of runoff (L); and
W_i = weight for *i*th grab sample.

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