

# EVALUATION OF POTENTIAL MOLECULAR MARKERS FOR URBAN STORMWATER RUNOFF

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**Abstract.** Source specificity and persistence of several sulfur-polycyclic aromatic hydrocarbons (S-PAHs), nitro-PAHs (N-PAHs), and triphenylene were examined via analyses of stormwater runoff and wastewater effluent samples and spiked samples upon exposure to sunlight. Samples were collected during the 1997/1998 wet weather season from two major storm channels and four major wastewater treatment plants in southern California. Among the target compounds examined, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene/chrysene were detected in storm runoff only. However, 2-(4-morpholinyl)benzothiazole appeared to degrade rapidly in seawater and sediment after sunlight exposure, which might impede its use as a runoff indicator. Dibenzothiophene and triphenylene also degraded quickly in sunlight-exposed seawater samples, but remained fairly abundant in sediments after six months of exposure to sunlight. They are by far the most promising candidates of urban runoff markers based on the criteria of abundance, source specificity, and persistence, although more research efforts are needed to ensure that no other sources would also contribute significantly to their presence in the aquatic environment.

**Keywords:** abundance, molecular marker, persistence, source specificity, southern California, S-PAHs, urban runoff

## 1. Introduction

Urban stormwater runoff has become a significant source of contamination to the coastal marine environment off southern California, as contaminant inputs from major wastewater treatment facilities have steadily declined over the last three decades (Raco-Rands, 2001). Lawn pesticides, petroleum products, and automobile-derived contaminants that are potentially harmful to aquatic organisms can be washed into the ocean via unregulated storm drains during storm events. Tracing where these materials go and discriminating them from other source inputs are important in understanding the impact of urban runoff discharge on the coastal marine ecosystem. Due to heavy mixing of materials from various sources normally occurring in the coastal marine environment, it has been impossible to differentiate runoff-derived contaminants from those of other sources.

To differentiate contaminant inputs of multiple sources, approaches using molecular markers have been widely employed (Takada and Eganhouse, 1998). Molecular markers may not be of environmental concern, but are source specific,



abundant and widespread in the environment, and resistant to chemical and biological degradation. The molecular marker approach in southern California has been used primarily to trace sewage inputs. Linear alkylbenzenes (LABs) are suitable tracers of wastewater discharge in southern California (Eganhouse and Kaplan, 1982; Eganhouse *et al.*, 1988; Zeng *et al.*, 1997; Zeng and Venkatesan, 1999), since they are abundant in wastewater effluents and well preserved in sediments adjacent to sewage outfalls. To our best knowledge, detection of these compounds in other source inputs has not been reported in southern California. Other sewage indicators studied include fecal sterols (Eganhouse *et al.*, 1988; Venkatesan and Santiago, 1989; Venkatesan and Kaplan, 1990; Venkatesan, 1995), trialkylamines (Chaloux *et al.*, 1992), nonylphenols (Chaloux *et al.*, 1992), and silver (Sanudo-Willhelmy and Flegal, 1992), but they have not been as widely utilized as LABs.

The search for urban runoff indicators has been focused on benzothiazole compounds. Benzothiazoles (benzothiazole and its derivatives) are used as vulcanization accelerators in tire and rubber manufacturing processes and as corrosion inhibitors in antifreeze (Brownlee *et al.*, 1981). They have been found in tire manufacturing plant wastewaters, urban stormwater runoff, estuarine sediments, and suspended river particles (Jungclaus *et al.*, 1976; MacKenzie and Hunter, 1979; Brownlee *et al.*, 1981; Spies *et al.*, 1987; Kumata *et al.*, 1996, 2000; Tolosa *et al.*, 1996). Residues of these sulfur-polycyclic aromatic hydrocarbons (S-PAHs) can be deposited on the road surface through traffic activities and, along with other organic contaminants, may be adsorbed by street dust. During storm events, street dust carrying all sorts of chemicals may be washed into storm drains, rivers, streams, and creeks, and eventually transported to the ocean. As a result, benzothiazoles, specifically benzothiazole and 2-(4-morpholinyl)benzothiazole (Spies *et al.*, 1987; Kumata *et al.*, 1997) and recently N-cyclohexyl-2-benzothiazolamine (Kumata *et al.*, 2000, 2002), have been proposed as potential urban runoff markers. However, despite the numerous research efforts on benzothiazoles, their applications in tracing land-derived contaminants in marine environments have not been reported. One of the reasons for this might be lack of understanding on the persistence of these compounds in the environment. In particular, microbial metabolism and photodegradation may greatly reduce the amount of initially discharged benzothiazoles during transportation to sediments.

The goal of this study was to assess the feasibility of the molecular marker approach to trace storm runoff inputs in southern California. Besides a suite of S-PAHs, we also included several nitro-PAHs (N-PAHs) and triphenylene in the evaluation (Table I). Dibenzothiophene and thionaphthene can be released from diesel fuel and motor oil (MacKenzie and Hunter, 1979; Takada *et al.*, 1991; Williams and Bottrill, 1995). 1-Nitropyrene, 9-nitroanthracene, and 2-nitrofluorene have been detected in extracts from vehicle particulate emissions (Newton *et al.*, 1982; Gorse *et al.*, 1983; LaCourse and Jensen, 1986; Robbat *et al.*, 1986; Scheepers *et al.*, 1994). Triphenylene, although not a S-PAH or N-PAH compound, was found in tire wear and brake lining particles (Rogge *et al.*, 1993). All these compounds may

TABLE I  
Target analytes considered as potential stormwater runoff markers<sup>a</sup>

Compound	Possible source(s)	Quantitation ion (m/z)
Benzothiazole	Tire particles/antifreezer	135
2-Mercaptobenzothiazole	Rubber tires	167
2-(Methylthio)benzothiazole	Rubber tires	148
2-(4-Morpholinyl)benzothiazole	Vulcanization accelerators	220
Dibenzothiophene	Tire/asphalt/diesel fuel/motor oil	184
Thionaphthene	Tire/asphalt/diesel fuel/motor oil	134
1-Nitropyrene	Diesel exhausts	201
2-Nitrofluorene	Diesel exhausts	165
9-Nitroanthracene	Diesel exhausts	176
Triphenylene	Tire particles/break lining/asphalt	228

<sup>a</sup> 2-Mercaptobenzothiazole was also included in the initial evaluation, but its response to GC/MS was extremely low probably due to its rapid degradation. It was therefore excluded from subsequent investigations.

potentially be washed off road surface during storm events and into storm channels along with benzothiazoles. Our approaches were: (1) collecting samples of storm water runoff and wastewater effluent during various storm events; (2) analyzing the samples to determine whether the target compounds were abundantly present in storm runoff only; and (3) examining the persistence of the target compounds without and upon exposure to sunlight.

## 2. Methods

### 2.1. SAMPLE COLLECTION

The sampling locations are depicted in Figure 1. Samples of urban runoff were collected from Ballona Creek (BC) at a bridge on Sawtelle Boulevard near the automated monitoring station operated by the City of Los Angeles Department of Public Works using a one-gallon sampler designed by the Southern California Coastal Water Research Project (SCCWRP, 1986). Three storms were sampled on 13 November 1997, 4 December 1997, and 9 January 1998. Runoff samples were also collected from Santa Ana River (Figure 1) on 9 December 1997. During the 4–9 December 1997 storm event, final effluent samples were also collected from the facilities of the Hyperion Treatment Plant (HTP), Orange County Sanitation District (OCSD), Joint Water Pollution Control Plant (JWPCP), and Point Loma Wastewater Treatment Plant (PLWTP). Samples were acidified with concentrated hydrochloric acid to pH below 2.0 and refrigerated at 4 °C prior to further

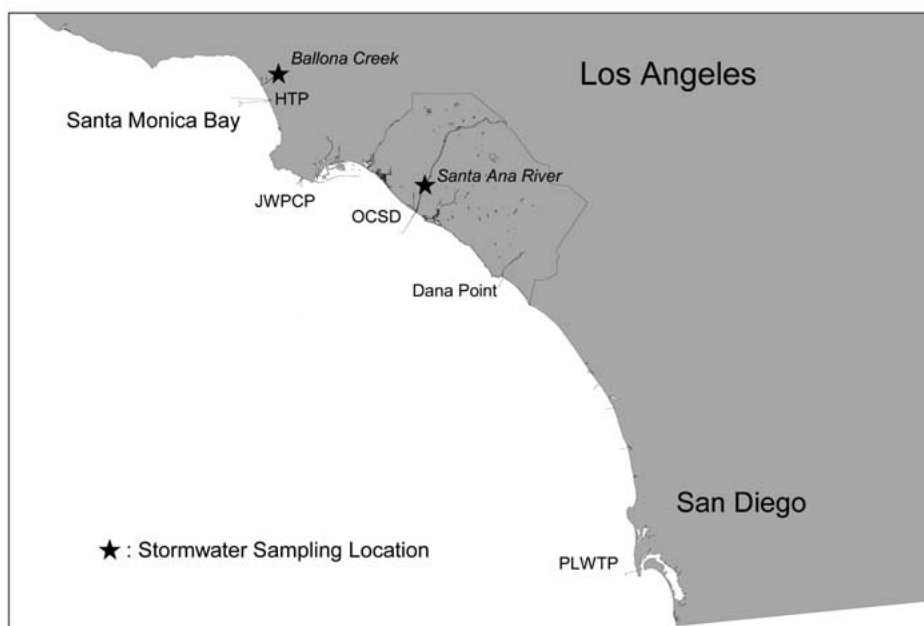


Figure 1. Locations where runoff and wastewater effluent samples were collected. HTP: Hyperion Treatment Plant; CSDOC; County Sanitation District of Orange County; JWPCP; Joint Water Pollution Control Plant; PLWTP: Point Loma Wastewater Treatment Plant.

treatment. In the laboratory, vacuum filtration was subsequently performed using  $0.7 \mu\text{m}$  GF/F glass fiber filters (Whatman International, Maidstone, England), to separate particulates and filtrates for separate chemical analyses.

For the time-series experiments to examine the biodegradability of the target analytes, Sand-filtered sea water was taken from an off-shore intake of Southern California Edison (Redondo Beach, CA, U.S.A.) and clean sediments were collected off Dana Point, CA, U.S.A. (Figure 1).

## 2.2. DEGRADATION EXPERIMENTS

Target compounds (Table I) were spiked into GF/F filtered seawater and clean sediments. Approximately one liter of filtered seawater or 20 g (wet weight) of sediment was used for each spiked sample. For filtered seawater samples, the spiking concentration was  $10 \mu\text{g L}^{-1}$  for benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, thionaphthene, and triphenylene and was  $14 \mu\text{g L}^{-1}$  for 1-nitropyrene, 9-nitroanthracene, and 2-nitrofluorene. For sediment samples, the spiking concentration was  $0.5 \mu\text{g g}^{-1}$  (wet weight) for S-PAHs and triphenylene and  $0.7 \mu\text{g g}^{-1}$  (wet weight) for N-PAHs.

Two sets of degradation experiments were performed. The first set of experiments was designed to test the persistence of the target compounds to photolysis.

The glass-covered samples were submerged in a water bath directly exposed to sunlight. The water bath temperature was maintained at 16–17 °C, mimicking the subsurface temperature in the coastal waters off southern California. In the second set of experiments, samples contained in brown glass bottles were kept in the dark and maintained at 16–17 °C. At various timepoints (weekly from week 0 to week 7 and then at the 6th month), aliquots of the spiked samples were removed and analyzed in triplicate. In addition to the spiked samples, unspiked sediment and filtered seawater samples were also routinely analyzed as part of the QA/QC program.

### 2.3. SAMPLE EXTRACTION

Aqueous samples (20 L each) were extracted using a solid phase extraction method (Zeng and Khan, 1995). Suspended solids retained by GF/F filters and sediment samples (40 g each) were extracted using a roller table method (Zeng and Yu, 1996). Dibenzothiophene- $d_8$  was used as a surrogate. Each extract in hexane was treated with activated copper granules and kept in the dark overnight to remove sulfur. The volume of the extract was reduced to 1 mL using a dry nitrogen stream. An appropriate amount of the extract was introduced onto a 180-mm glass column (11 mm i.d.) packed with alumina:silica gel (2:1). The sample was eluted into three fractions. The first fraction containing mostly aliphatic hydrocarbons was eluted with 10 mL of hexane and discarded. The second fraction containing most target analytes was eluted with 5 mL of hexane, 30 mL of 70/30 hexane/methylene chloride mixture, and finally with 30 mL of methylene chloride. Residual benzothiazoles remaining in the column were eluted into the third fraction using 25 mL of methanol. Twenty five milliliters of distilled water were added to the third fraction and then back extracted three times using 50 mL of methylene chloride each. The second and third fractions were combined and the volume was reduced to 1 mL. Internal standards were added to the extract prior to instrumental analysis.

### 2.4. INSTRUMENTAL ANALYSIS

Concentrations of target analytes were measured using a Hewlett Packard (HP) 5890 II gas chromatograph (GC) with a 5970 mass selective detector. Chromatographic separation was obtained with a 60 m  $\times$  0.25 mm I.D. (0.25  $\mu$ m film thickness) DB-5 column. The oven temperature was initially set at 70 °C, immediately ramped to 160 °C at 20 °C  $\text{min}^{-1}$  and then to 300 °C at 10 °C  $\text{min}^{-1}$  where it was held for 21.5 min. High purity helium was used as the carrier gas with a flow rate of 2 mL  $\text{min}^{-1}$  at 70 °C. The injector and detector were maintained at 250 °C. Concentrations were determined using the internal calibration technique. Calibration standard solutions were prepared in 0.4, 1, 2, 5, and 10  $\mu\text{g mL}^{-1}$  for benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, thionaphthene, and triphenylene and 4, 5, 6, 7, and 8  $\mu\text{g mL}^{-1}$  for

1-nitropyrene, 2-nitrofluorene, and 9-nitroanthracene. Nitrobenzene-d<sub>5</sub>, fluorobiphenyl, p-terphenyl-d<sub>14</sub>, and dibenzo[a,b]anthracene were used as internal standards at 2  $\mu\text{g mL}^{-1}$ . In addition, dibenzothiophene-d<sub>8</sub> was included as surrogate standard at 0.4, 1, 2, 5, and 10  $\mu\text{g mL}^{-1}$  in the standard solutions. Molecular ions used for quantitation are listed in Table I. The detection limit was 10  $\text{ng L}^{-1}$  for aqueous samples and filtered particles and 10  $\text{ng g}^{-1}$  dry weight for solid samples.

2-Mercaptobenzothiazole initially was also included in the study, but it had an extremely low response to GC/MS. We suspected that it might easily degrade even in standard solutions. It was therefore excluded from further chemical measurements.

## 2.5. QUALITY ASSURANCE

Procedural blanks, spiked blanks, and matrix spiked samples were processed with each batch of samples (<15 samples). No target analytes were detected in procedural blanks. Good to excellent average recoveries in the range of 62.5 (dibenzothiophene) to 97.0% (triphenylene) were obtained for spiked blanks. Similar recoveries were also obtained for the matrix spiked samples. The average recovery of the surrogate standard (dibenzothiophene-d<sub>8</sub>) was  $73.3 \pm 25.7\%$ . Measured concentrations of the target analytes were not corrected for the recoveries of the surrogate standard.

## 2.6. MATERIALS

Benzothiazole, 2-mercaptobenzothiazole, 2-(methylthio)benzothiazole, dibenzothiophene, thionaphthene, 1-nitropyrene, 2-nitrofluorene, 9-nitroanthracene, and triphenylene were acquired from Sigma-Aldrich (St. Louis, MO, U.S.A.), 2-(4-morpholinyl)benzothiazole from Dr. Thomas Dorsey (Department of Chemistry, Bennington College, Bennington, VT, U.S.A.), Dibenzothiophene-d<sub>8</sub> from CDN Isotopes (Ponite-Claire, Quebec, Canada), Nitrobenzene-d<sub>5</sub>, fluorobiphenyl, p-terphenyl-d<sub>14</sub>, and dibenzo[a,b]anthracene from AccuStandard (New Haven, CT, U.S.A.), methylene chloride of HPCL-GC/MS grade from Fisher Scientific (Pittsburgh, PA, U.S.A.), and hexane of pesticide grade from VWR Scientific (West Chester, PA, U.S.A.).

# 3. Results

## 3.1. TARGET COMPOUNDS IN STORMWATER RUNOFF AND WASTEWATER EFFLUENT

Table II summarizes the total concentrations of target compounds in runoff and effluent samples. Benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene/chrysene were found in the Ballona Creek runoff samples (with dibenzothiophene being detectable in the first

storm sample only), but benzothiazole was the lone analyte detected in the Santa Ana River sample. Benzothiazole and 2-(methylthio)benzothiazole were the only target compounds found in wastewater effluent samples. In addition, thionaphthene, 1-nitropyrene, 2-nitrofluorene, and 9-nitroanthracene were not detectable in any of the samples. It is clear that 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene/chrysene were detectable in stormwater runoff but not in wastewater effluent in southern California. It is interesting to note that the concentrations of benzothiazole were substantially higher in stormwater runoff than in wastewater effluent, while those of 2-(methylthio)benzothiazole in effluent were equal to or higher than in runoff samples. Finally, concentrations of detectable target compounds were generally the highest in the first storm sample (from Ballona Creek).

The filtrate and particulate fractions of each water sample were analyzed separately. A comparison was made for the samples collected from Ballona Creek (Table III). Relatively higher concentrations of benzothiazole, 2-(methylthio)benzothiazole, and 2-(4-morpholinyl)benzothiazole were found in the filtrate phase than in the particulate phase. 2-(4-morpholinyl)benzothiazole was detected only in the particulate phase of one runoff sample collected from Ballona Creek on 5 December 1997, but its concentration ( $52 \text{ ng L}^{-1}$ ) was much higher than those ( $0.73\text{--}29 \text{ ng L}^{-1}$ ) obtained by Kumata *et al.* (1996) in samples collected from a storm drain in Tokyo, Japan. Dibenzothiophene partitioned almost equally in the filtrate and particulate phases (detectable in the first stormwater sample only). Triphenylene/chrysene was detected only in the particulate phase, reflecting the relatively strong hydrophobic nature of these compounds.

### 3.2. DEGRADATION OF TARGET COMPOUNDS

Four sets of data were generated from the degradation experiments: recoveries of the target compounds in unexposed seawater samples, sunlight-exposed seawater samples, unexposed sediment samples, and sunlight-exposed sediment samples. Concentrations of the target analytes all declined substantially one week after the experiments were initiated, but the time progressive patterns afterwards were different between the seawater and sediment samples (Figures 4–7).

Most target analytes (except for 2-(methylthio)benzothiazole and 9-nitroanthracene) in the unexposed seawater samples remained abundant (20 to 60% of the original spiking amounts) even after 6 months (Figure 4). In the sunlight-exposed seawater samples, most target analytes were substantially depleted shortly after the exposure was initiated. Only small amounts of benzothiazole and triphenylene (10 and 1.8% of the original amounts, respectively) in sunlight-exposed seawater samples were detected after 6 months (Figure 5).

Target analytes were in low abundance in just one week after the experiments were initiated in both the unexposed and sunlight-exposed sediment samples (from virtually 0 to 38%). At the end of the experiments (after 6 months), both the unex-

TABLE II  
Molecular markers in stormwater runoff and wastewater effluent (both dissolved and particulate phases ( $\text{ng L}^{-1}$ ))

Location <sup>a</sup>	Stormwater runoff					Wastewater effluent				
	BC	BC	BC	SA	PLWTP	HTP	CSDOC	JWPCP	PLWTP	
Date of sampling	11/13/1997	12/5/1997	1/9/1998	12/8/1997	12/9/1997	12/6/1997	12/8/1997	12/6/1997	12/9/1997	
Benzothiazole	555±12	334±300	230±11	86±9	120±5	55±15	87±9	67±5	120±5	
2-(Methylthio)benzothiazole	160±17	93±44	36±1	0	112±53	148±30	329±3	142±72	112±53	
2-(4-Morpholinyl)benzothiazole	215±21	150±213	79±5	0	0	0	0	0	0	
Dibenzothiophene	110±13	0	0	0	0	0	0	0	0	
Thionaphthene	0	0	0	0	0	0	0	0	0	
1-Nitropyrene	0	0	0	0	0	0	0	0	0	
2-Nitrofluorene	0	0	0	0	0	0	0	0	0	
9-Nitroanthracene	0	0	0	0	0	0	0	0	0	
Triphenylene/chrysene <sup>b</sup>	151±7	240±26	76±107	0	0	0	0	0	0	
Total	1191±32	818±530	421±112	86±9	232±58	203±46	416±11	209±77	232±58	

<sup>a</sup> BC: Ballona Creek; SA: Santa Ana River; HTP: Hyperion Treatment Plant; CSDOC: County Sanitation District of Orange County; JWPCP: Joint Water Pollution Control Plant; PLWTP: Point Loma Wastewater Treatment Plant.

<sup>b</sup> These two compounds coeluted chromatographically under the experimental conditions applied.



TABLE III  
Partitioning of potential marker compounds in stormwater runoff collected from Ballona Creek (concentration in  $\text{ng L}^{-1}$ )

Sampling date	11/13/1997		12/5/1997		1/9/1998	
	Filtrate	Particulate	Filtrate	Particulate	Filtrate	Particulate
Benzothiazole	396±19	159±31	203±188	132±112	189±31	41±20
2-(Methylthio)benzothiazole	119±9	41±8	71±13	22±31	36±1	0
2-(4-Morpholinyl)benzothiazole	215±21	0	98±139	52±74	79±5	0
Dibenzothiophene	48±22	62±9	0	0	0	0
Thionaphthene	0	0	0	0	0	0
1-Nitropyrene	0	0	0	0	0	0
2-Nitrofluorene	0	0	0	0	0	0
-Nitroanthracene	0	0	0	0	0	0
Triphenylene/chrysene <sup>a</sup>	0	151±7	0	240±26	0	76±107
Total	777±71	413±39	372±339	446±191	304±25	117±87

<sup>a</sup> These two compounds coeluted chromatographically under the experimental conditions applied.

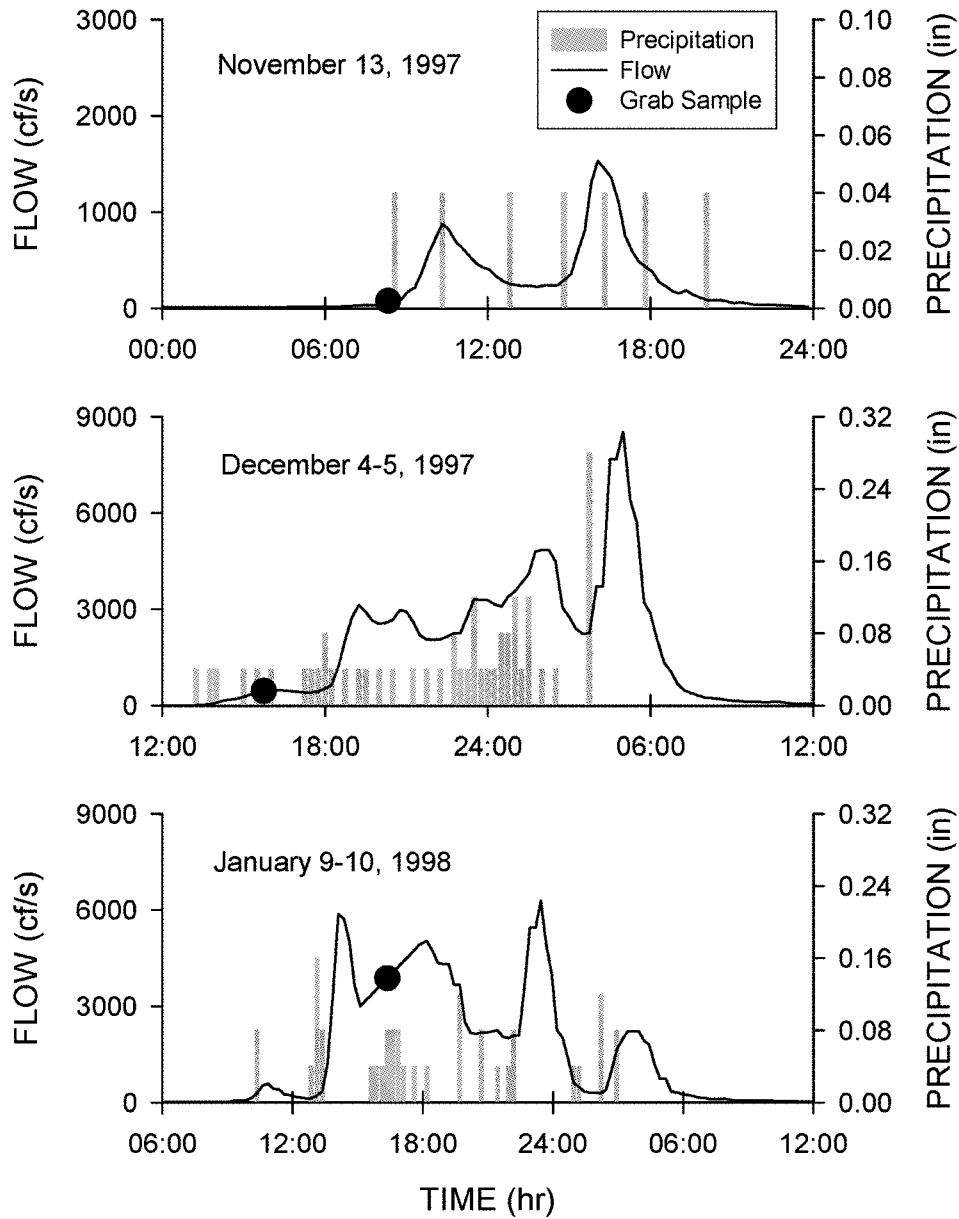


Figure 2. Hydrograph of the storms during which sample were collected from Ballona Creek.

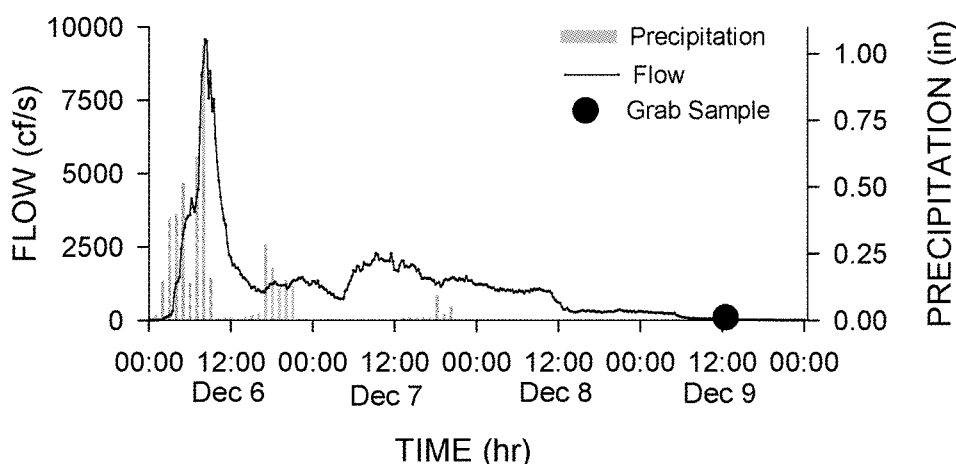


Figure 3. Hydrograph of the storm during which sample was collected from Santa Ana.

posed and sunlight-exposed samples contained approximately the same concentrations of all the target analytes. Benzothiazole, dibenzothiophene, and triphenylene remained abundant in both the unexposed and sunlight exposed sediment samples (about 30% of the original concentrations remaining) after six months (Figures 6 and 7), while they were almost non-detectable in the sunlight-exposed seawater samples (Figure 5).

#### 4. Discussion

##### 4.1. ABUNDANCE AND SOURCE SPECIFICITY OF TARGET COMPOUNDS

The concentrations of benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, and triphenylene/chrysene in urban runoff samples collected from Ballona Creek generally decreased as the storm season progressed. Dibenzothiophene was found only in the first runoff sample from Ballona Creek and most target analytes were not detectable in the runoff sample from Santa Ana River (Table II). These results were consistent with the characteristics of storm events responsible for removing road dust from street surfaces into storm drains as discussed below.

The target compounds found in the stormwater runoff samples were likely derived from vehicle emissions (tire tread debris, exhaust, motor oil, brake linings, etc.). In a coastal city such as Los Angeles, the majority of road dust entering the stormwater channels would eventually be transported to the ocean. During a persistent storm with sporadic, low precipitations, road dust containing a variety of pollutants may be washed to the storm drains over an extended period of time. However, if substantial rainfall occurs at the beginning of a storm, the majority of

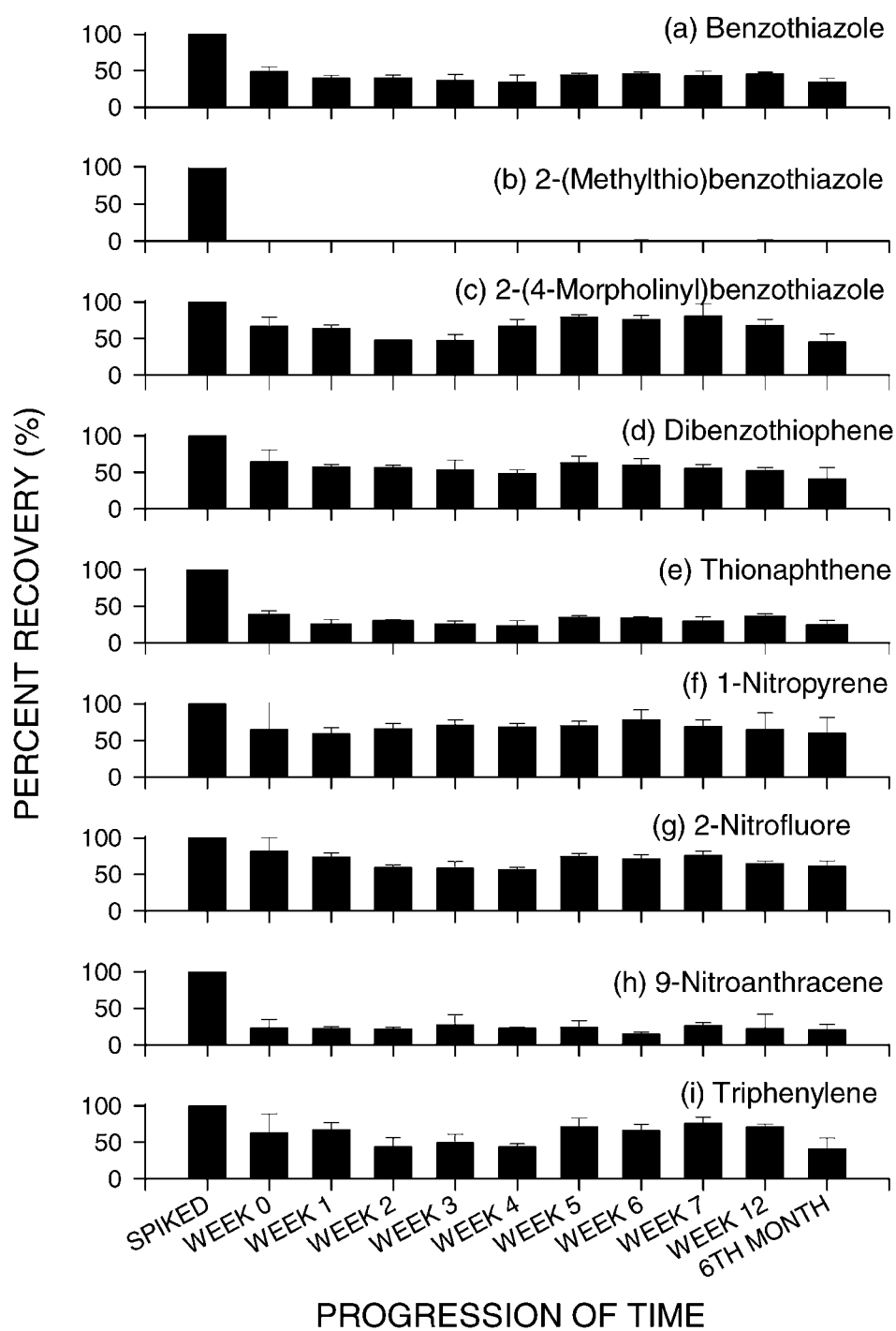


Figure 4. Time-dependent recoveries of target compounds from spiked filtered seawater samples maintained in the dark at 16–17 °C.

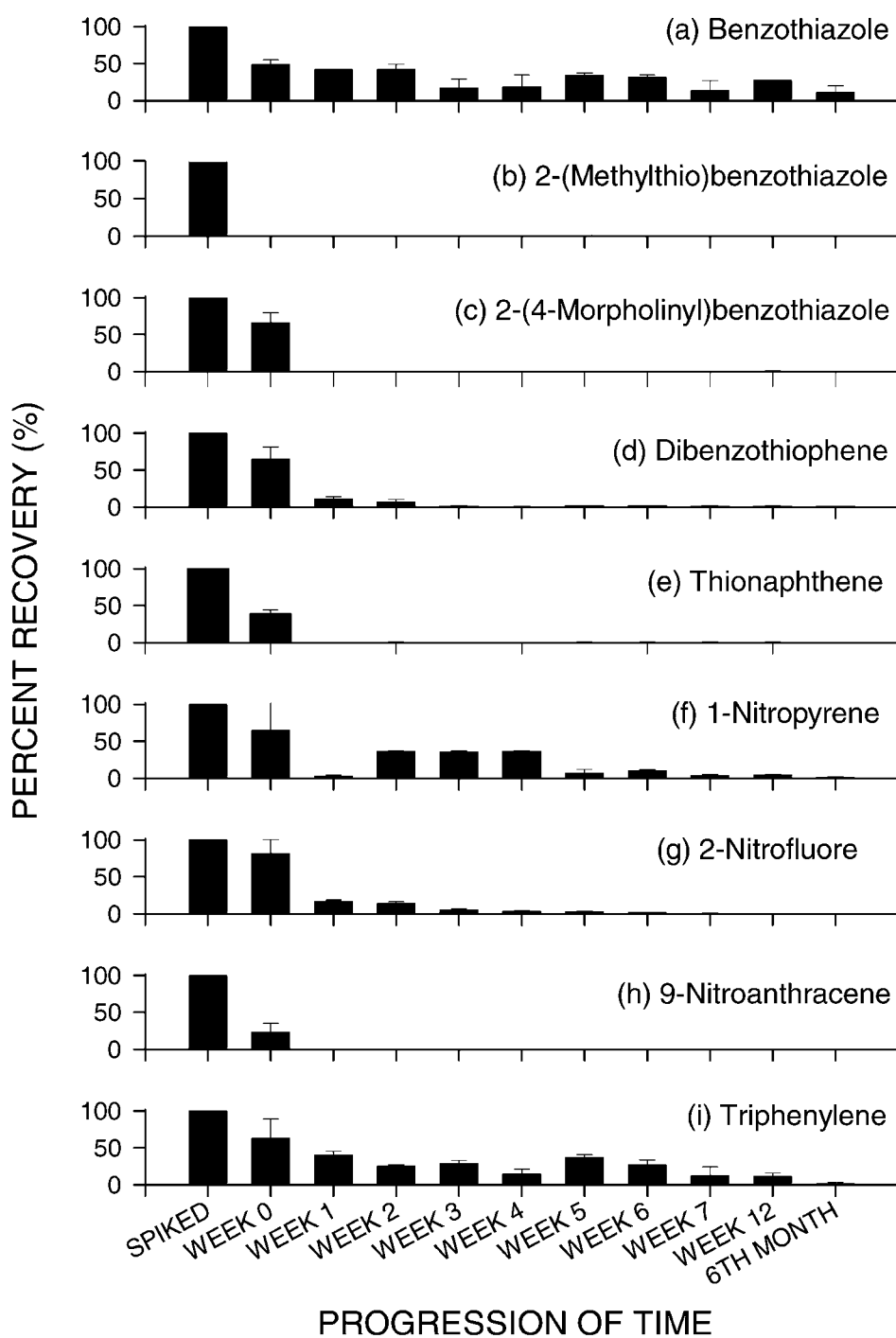


Figure 5. Time-dependent recoveries of target compounds from spiked filtered seawater samples exposed to direct sunlight and maintained at 16–17 °C.

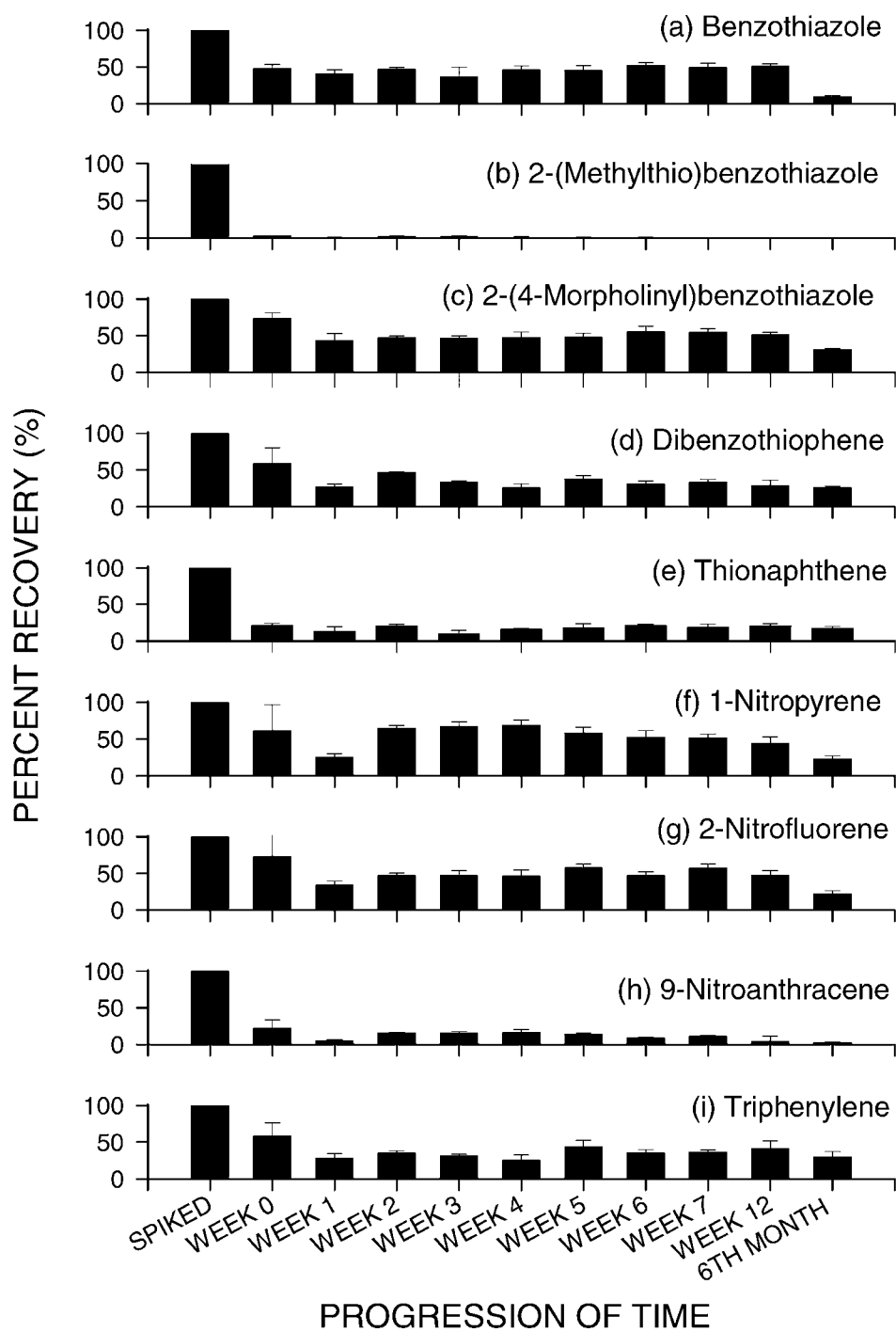


Figure 6. Time-dependent recoveries of target compounds from spiked sediment samples maintained in the dark at 16–17 °C.

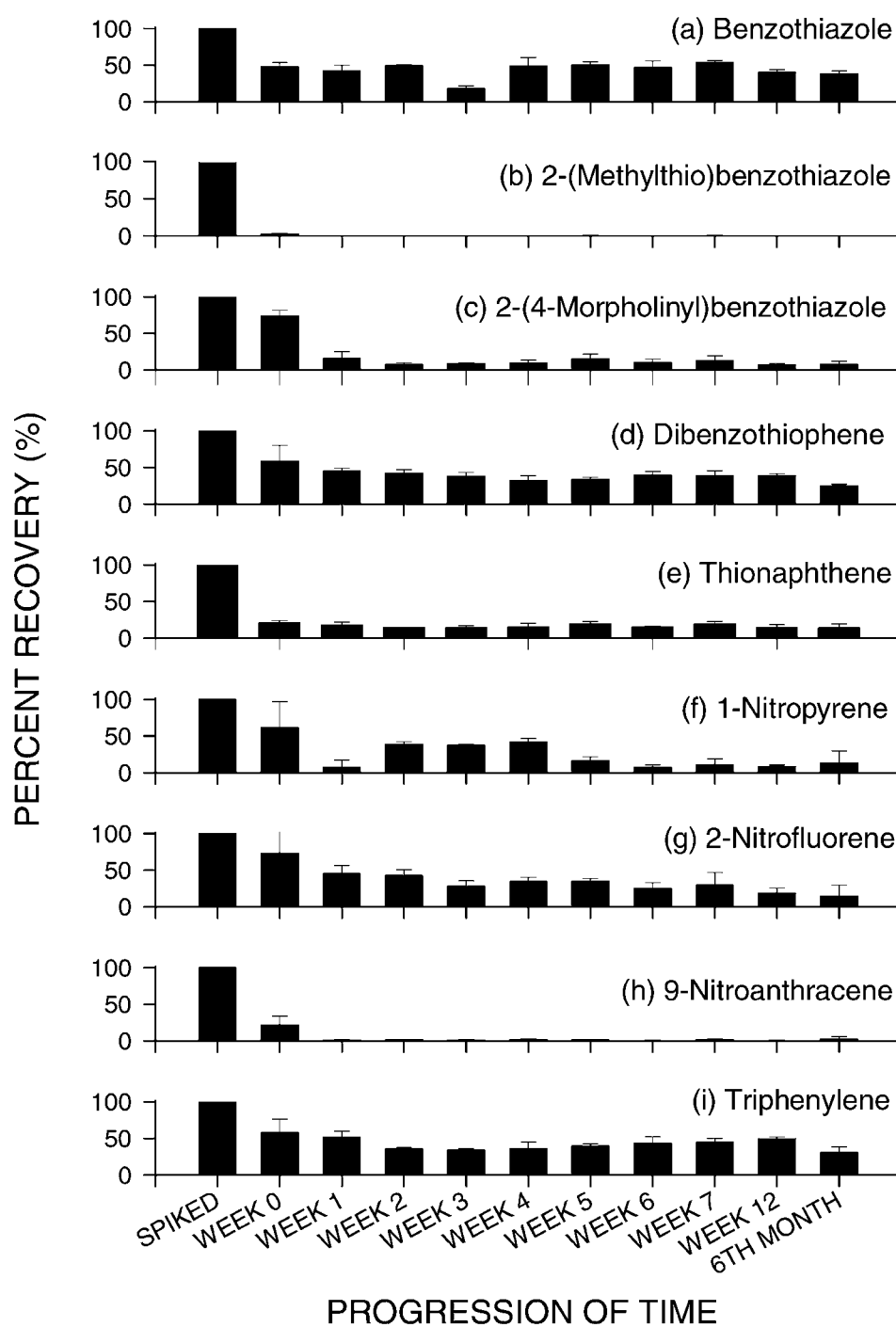


Figure 7. Time-dependent recoveries of target compounds from spiked sediment samples exposed to direct sunlight and maintained at 16–17 °C.

road dust along with other debris may be well washed off the street surface during the early stage of the storm. The ability to detect target compounds in stormwater runoff thus may vary with time when the samples are collected. In addition, the antecedent dry period in the study area also affects the level of road dust accumulated on the street. A relatively short interval between two consecutive storms would likely reduce the amount of road particles entering the storm drains during the subsequent storm. Finally and obviously, the first storm of a rainy season would carry the largest amount of street materials into storm drains and to the ocean.

During the 1997/1998 wet weather season, the 'El Niño' phenomenon was strongly experienced in southern California. As a consequence, a greater number of rainstorms than normal occurred. The first sample, collected from Ballona Creek on 13 November 1997 during the first storm event of the season, was part of the 'first flush' and was collected at the early stage of the storm (Figure 2). Therefore, most target analytes in this sample were detected with the highest abundances among all the runoff samples. The third sample (9 January 1998) that was not collected at the beginning of the storm contained the lowest concentrations of the target analytes (Table II). In addition, the relatively high flow at the Ballona Creek prior to sampling effectively diluted the concentrations of most compounds. All these reduced the chance for the target analytes to be detected. The runoff sample from Santa Ana River, collected at the end of the storm on 9 December 1997 (Figure 3), was free of most target analytes (Table II). By comparison, Kumata *et al.* (1997) reported that the concentration of 2-(4-morpholinyl)benzothiazole in the runoff particles was reduced from 215 to 150 ng g<sup>-1</sup> and then to 1.2 ng g<sup>-1</sup> in samples collected at the initial, middle, and final stage, respectively, of a 1989 storm event in Tokyo.

Despite the concentration variation, the results from this study confirmed the presence of some target analytes in storm runoff discharged into the coastal waters off southern California. The abundances of most detectable target analytes appeared adequate in particulate and/or dissolved phases to be detected in environmental samples (Table III). Since wastewater discharge is a major source of contamination to the Southern California Bight, potential markers for runoff inputs have to be source specific or free of interferences from wastewater discharge.

The concentrations of benzothiazole and 2-(methylthio)benzothiazole in the effluent samples, collected at or near the peak flows during the 6–9 December 1997 storm from four southern California major wastewater treatment plants, were comparable to those in the runoff samples (Table II). The possible scenario for this to occur was that effluent from local tire manufacturing plants and other rubber industries entered the municipal wastewater treatment plants before being discharged to the coastal environment. During a heavy rainfall, storm water typically overflows via manholes into sewage systems and is treated along with domestic wastewater. Some compounds residing on road dust thus exist in wastewater effluent. Previous studies also found similar compounds in wastewater effluent. Jungclaus *et al.* (1976) reported relatively high concentrations of benzothiazole and



2-(methylthio)benzothiazole in wastewater discharged from two tire manufacturing plants. Jop *et al.* (1991) reported the presence of 2-(4-morpholinyl)benzothiazole in a chemical plant effluent. Although 2-(4-morpholinyl)benzothiazole and triphenylene/chrysene were absent in the effluent samples collected from the nearby Hyperion Treatment Plant or other treatment facilities (Table II), it could be due to breakdowns of these compounds during the transport processes.

#### 4.2. PERSISTENCE OF TARGET ANALYTES

Another issue that needs to be resolved before a molecular marker can be validated is the persistence or stability of the compound in the open environment. One factor that can affect the proportion of potential marker compounds is their solubility. The water solubility at 24 °C for benzothiazole and 2-(methylthio)benzothiazole were reportedly 3000 and 125 mg L<sup>-1</sup>, respectively (Brownlee *et al.*, 1992). Benzothiazoles are thus more soluble in water than many other organic contaminants such as DDTs or PCBs. Triphenylene, however, is much less soluble in water. These facts are consistent with the data presented in Table III. Most detectable benzothiazoles were more abundant in the filtrates than in the particulates. Meanwhile, triphenylene/chrysene was detected only in the particulate samples. Benzothiazoles are thus likely to be transported to a great distance and unlikely to incorporate into the bottom sediments near the discharge area, while triphenylene/chrysene may have a strong tendency to settle close to shore.

Degradation is another factor that can affect the persistence of potential marker compounds in the aquatic environment. The two most common degradation pathways are photolysis and microbial reaction. For instance, 2-mercaptobenzothiazole was so unstable that it was hardly detected even in calibration standards. This was consistent with the relatively high rates of degradation (>99% in 4 days) for 2-mercaptobenzothiazole in Canagagigue Creek water obtained by Brownlee *et al.* (1992). This also explained why 2-mercaptobenzothiazole has been most widely used in rubber tire industry among benzothiazoles (Brownlee *et al.*, 1981).

The effects of photolysis were evident by the markedly different results obtained from the sunlight-exposed and unexposed samples. Most target analytes were photodegraded by more than 50% of the spiked amount after the first month of sunlight exposure (Figures 5 and 7). Target analytes experienced less degradation in unexposed samples, particularly in unexposed seawater samples (Figures 4 and 6). Compounds having high water solubility might be effectively eradicated by photochemical reactions in a relatively short period of time. It should also be noted that benzothiazole was reported as a photolysis product of 2-mercaptobenzothiazole (Brownlee *et al.*, 1992). The chemical structure of 2-(4-morpholinyl)benzothiazole suggests that its degradation products also include the parent compound benzothiazole (Kumata *et al.*, 1996). Benzothiazole remained detectable in the sunlight-exposed seawater samples over the entire course of this study (Figure 5). N-PAHs were degraded substantially in less than one month after sunlight exposure

(Figures 5 and 7). This may explain why these compounds were not detected in any of the runoff and wastewater samples (Table II).

The sediment spiking experiments were intended to evaluate the stability of the target compounds in suspended particulate matter or sediments. While 2-(methylthio)benzothiazole degraded rapidly even without sunlight exposure, other potential marker compounds remained fairly stable in unexposed sediments (Figure 6). Degradation of most compounds was notably enhanced when results from sunlight-exposed and unexposed sediments were compared (Figures 6 and 7). Benzothiazole remained relatively abundant in the sunlight-exposed sediments 6 months after exposure was initiated (Figure 7). This was probably resulted from the extra amount of benzothiazole produced via the degradation of 2-mercaptobenzothiazole and 2-(4-morpholinyl)benzothiazole (Brownlee *et al.*, 1992). Dibenzothiophene and triphenylene remained easily detectable in both sunlight-exposed and unexposed sediment samples (Figures 6 and 7), as opposed to their low abundances in sunlight-exposed seawater samples (Figure 5).

#### 4.3. ASSESSMENT OF TARGET ANALYTES AS MARKERS OF RUNOFF INPUTS

Several target compounds including benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene/chrysene were detected in the stormwater runoff samples collected during the 1997–1998 storm season from Ballona Creek and Santa Ana River. Among them, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene/chrysene were absent in the effluent samples collected from four major wastewater treatment plants in southern California (Table II). These compounds appeared to be specific to storm runoff inputs.

Further assessment can be made in conjunction with a previous study that sampled sediments at five stations (25 m water depth) about 2.5 km offshore Ballona Creek following the 13 November 1997 storm (Bay *et al.*, 1998). This study found that none of the target analytes mentioned above were detectable ( $<10 \text{ ng g}^{-1}$  dry weight) in the sediment samples (analyzed by the same laboratory that was responsible for the sample analysis in this paper). It was unclear what caused this to happen, but the same study also found that even PAH compounds were absent ( $<10 \text{ ng g}^{-1}$  dry weight) in the same samples) (Bay *et al.*, 1998).

2-(4-Morpholinyl)benzothiazole has been proposed as a urban runoff marker due to its presence in both street runoff and sediments adjacent to the runoff channels (Spies *et al.*, 1987; Kumata *et al.*, 1997). The findings in the present study further confirmed the source specificity of 2-(4-morpholinyl)benzothiazole. However, our degradation experiments suggested that 2-(4-morpholinyl)benzothiazole degraded rapidly in sunlight-exposed seawater and to a slightly less extent in sediment samples (Figures 5 and 7). This compound was measured in the study of Bay *et al.* (1998) and absent ( $<10 \text{ ng g}^{-1}$  dry weight) from the sediment samples. The concentrations of 2-(4-morpholinyl)benzothiazole in San Francisco Bay sediments

ranged from 49 to 360 ng g<sup>-1</sup> (Spies *et al.*, 1987), but the samples were taken at least ten years earlier than the ones taken in Bay *et al.* (1998). The more recent sampling of river sediments in Tokyo (Kumata *et al.*, 1997) yielded concentrations of 2-(4-morpholinyl)benzothiazole to be 2.5±1.5 and 5.1±2.3 ng g<sup>-1</sup> in two types of sediment, which were below the detect limit (10 ng g<sup>-1</sup>) used by Bay *et al.* (1998). The seemingly low abundance of 2-(4-morpholinyl)benzothiazole in marine sediments can be largely attributed to: (1) its strong affinity to the aqueous phase (Table III) that prevents it from depositing into nearshore sediments and (2) rapid degradation during transport to the open environment. We believe that use of 2-(4-morpholinyl)benzothiazole as an urban runoff marker would be analytically challenging if not impossible.

Both dibenzothiophene and triphenylene could be degraded rapidly (with less extent compared to 2-(4-morpholinyl)benzothiazole) in sunlight-exposed seawater samples (Figure 5), but remained abundant in sunlight-exposed sediments after six months of exposure (Figure 7). It should be noted that dibenzothiophene was detected only in one of the three storms sampled (Table II) and both of them were not detectable in the nearshore sediments (Bay *et al.*, 1998). In addition, triphenylene normally coelutes with chrysene in chromatographic analysis, and the sole presence of triphenylene in field samples therefore needs to be confirmed with a separate methodology. Nevertheless, these two compounds by far appear to be the most promising candidate as urban runoff markers based on the criteria of abundance, source specificity, and persistence. Since only runoff and wastewater samples were examined in the present study, the source specificity and environmental abundance of these compounds need to be further investigated with samples from other sources.

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