Molecular markers in urban stormwater runoff

Kim Tran[1], Diana L. Young, and Eddy Y. Zeng[2]

ABSTRACT

Stormwater runoff contains many pollutants that are potentially toxic to aquatic organisms. To increase our ability to trace land-derived contaminants, we conducted studies to determine whether several compounds, including sulfur-containing polycyclic aromatic hydrocarbons (S-PAHs) (benzothiazole and its derivatives as well as dibenzothiophene), nitro-PAHs (N-PAHs), and triphenylene that are associated with automobile tire residues and exhausts are relatively unique to urban runoff discharges. Samples of stormwater runoff from Ballona Creek (City of Los Angeles) and Santa Ana River (City of Santa Ana), and final effluents from four major wastewater treatment plants, City of Los Angeles Hyperion Treatment Plant (HTP), Orange County Sanitation District (OCSD), County of Los Angeles Joint Water Pollution Control Plant (JWPCP), and City of San Diego Point Loma Wastewater Treatment Plant (PLWTP), were collected during the 1997/1998 wet-weather season. Among the potential marker compounds examined, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene were detected only in the Ballona Creek runoff samples during three storm events, while benzothiazole and 2-(methylthio)benzothiazole were present in both runoff and effluent samples. N-PAHs were absent in both runoff and wastewater samples. Biodegradation experiments indicated that N-PAHs, 2-(mercapto)benzothiazole, and 2-(4-morpholinyl)benzothiazole were degraded rapidly upon exposure to sunlight; hence their use as molecular markers in open environments was deemed doubtful. Dibenzothiophene and triphenylene also degraded quickly in sunlight-exposed seawater samples, but remained abundant in exposed sediments after six months of exposure.

INTRODUCTION

Urban stormwater runoff has become a significant source of contamination to the marine coastal environment off southern California, as the contaminant inputs from wastewater treatment facilities have steadily declined over the last three decades (Raco-Rands 1999). Lawn pesticides, petroleum products, and other chemicals that are potentially harmful to aquatic organisms are 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 almost impossible to differentiate runoff-derived contaminants from those of other sources.

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One approach to tracing contaminants of a specific source is to employ a compound or a group of compounds, which are abundant in the environment, as markers of the

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[1] *Present address: City of Los Angeles, 12000 Vista del Mar, Playa del Rey, CA 90893*

[2] *Present address: Calico Commerce, Inc., 7 Deer Creek Circle, San Jose, CA 95110*

contaminants. These molecular markers must be source specific, conservative in the environment, and to some extent similar in physical and chemical characteristics as the contaminants (Takada *et al.* 1997). Molecular markers may not be of environmental concern, but the co-presence of marker compounds and contaminants of concern allows identification of toxic chemicals from specific sources and therefore effective source control and/or remediation measures can be taken.

Several studies using the molecular marker approach in southern California have focused on sewage inputs. Linear alkyl benzenes (LABs) have been found to be suitable tracers of pollutants derived from wastewater discharge (Eganhouse and Kaplan 1982, Eganhouse *et al.* 1988, Zeng *et al.* 1997, Zeng and Venkatesan 1999). These compounds are abundant in wastewater effluents and sediments adjacent to discharge pipes, although their abundance has steadily declined in both effluents and sediments, probably due to improved treatment methods (Zeng *et al.* 1996). On the other hand, applications of specific markers for tracing land-derived contaminants have not been reported.

A group of S-PAHs and N-PAHs have been identified as potential molecular markers of urban runoff inputs. The presence of S-PAHs in tire manufacturing plant wastewaters, urban stormwater runoff, estuarine sediments, and suspended river particles has been reported (Jungclaus *et al.* 1976, Mackenzie and Hunter 1979, Brownlee *et al.* 1981, Spies *et al.* 1987, Tolosa *et al.* 1996, Kumata *et al.* 1996). Benzothiazoles are used as vulcanization accelerators in tire and rubber manufacturing processes and as corrosion inhibitors in antifreeze (Browlee *et al.* 1981, Spies *et al.* 1987, Kumata *et al.* 1996). N-PAHs such as 1-nitropyrene, 9-nitroanthracene, and 2-nitrofluorene were detected in extracts from vehicle particulate emissions (Newton *et al.* 1982, Gorse *et al.* 1983, Robbart *et al.* 1986, LaCourse and Jensen 1986, Scheeper *et al.* 1994). Dibenzothiophene and thionaphthene were released from diesel fuel and motor oil (MacKenzie and Hunter 1979, Takada *et al.* 1991, Williams and Bottrill 1995). Triphenylene, although not a S-PAH or N-PAH compound, was found in tire wear and brake lining particles (Rogge *et al.* 1993). These compounds 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. Therefore, the compounds mentioned above are potentially markers of contaminants discharged via storm runoff. Specifically, benzothiazole and its derivatives have been proposed as such markers (Spies *et al.* 1987, Kumata *et al.* 1996, Takada *et al.* 1997).

An important aspect of using molecular markers is the persistence of these compounds in the environment. Before deposition to the sediments, marker compounds may have been subjected to many different physical, chemical, and biological alterations. Particularly, microbial metabolism and photodegradation are two important mechanisms determining the amounts of the initially discharged material reaching the sediments. Once deposited on the sediments, marker compounds may continue to undergo further degradation. Knowledge regarding the effects of photochemical and microbial processes is thus of importance in determining the validity of the molecular marker approach.

To explore the possibility of using the molecular marker approach to trace storm runoff inputs, we examined the abundance, source specificity, and stability of selected S-PAHs, N-PAHs, and triphenylene (Table 1). Specifically, samples of storm- water runoff and wastewater effluents collected during various time periods were analyzed to determine whether these compounds were abundantly present in environmental samples derived from storm runoff only. The persistence of these compounds without and upon exposure to sunlight was then examined.

METHODS

Sample Collection

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

TABLE 1. Potential molecular markers of stormwater runoff.

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

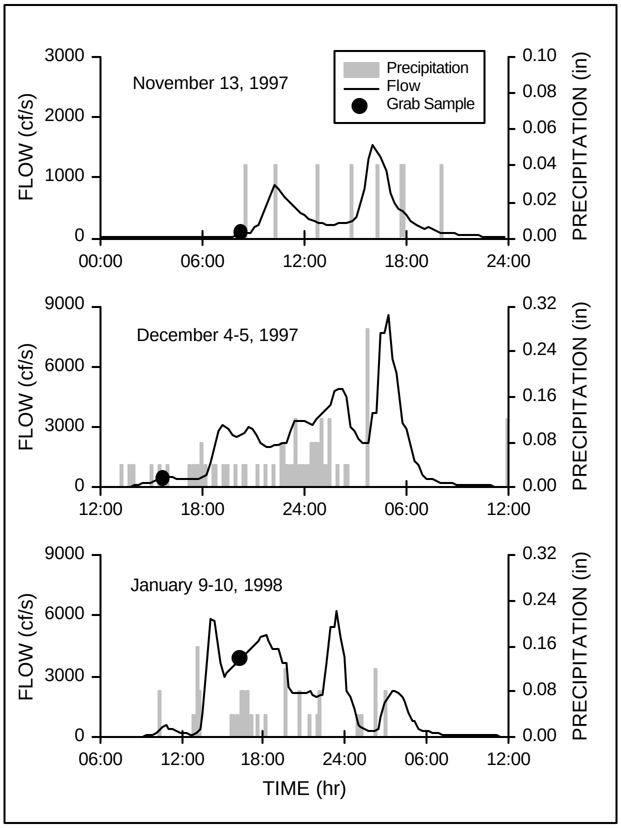


FIGURE 1. Hydrograph of the storms during which samples were collected from Ballona Creek.

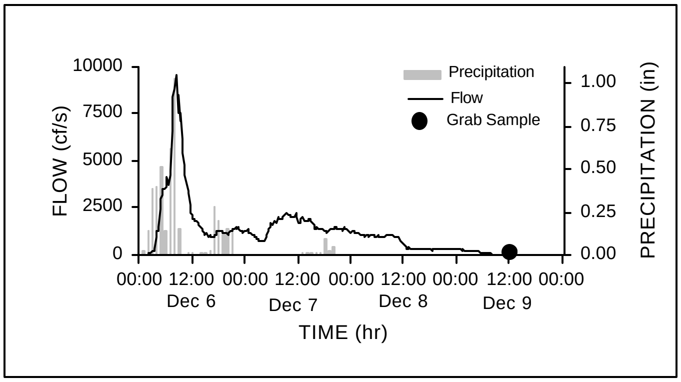


Figure 2. Hydrograph of the storm during which sample was collected from Santa Ana.

Angeles Department of Public Works using a one-gallon sampler designed by SCCWRP (1986). Three storms were sampled on November 13th and December 5, 1997 and January 9, 1998 (Figure 1). Runoff samples were also collected from Santa Ana River on December 9, 1997 (Figure 2). During the December 4, – 9, 1997, storm event, final effluents 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 Water Treatment Plant (PLWTP). Samples were acidified with concentrated hydrochloric acid to pH below 2.0 and refrigerated at 4° C. Vacuum filtration was subsequently performed using GF/F filters (0.7 µm pore size) to separate particulates and filtrates for separate chemical analyses.

Biodegradation Experiments

Target compounds (Table 1) were spiked into GF/F filtered seawater and clean sediments collected off Dana Point, California. 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 mg/L for S-PAHs, including benzothiazole, 2-(4-morpholinyl)benzothiazole, 2-mercaptobenzothiazole, thionaphthene, and dibenzothiophene, as well as triphenylene. The spiking concentration was 14 mg/L for N-PAHs, including 1-nitropyrene, 9-nitroanthracene, and 2-nitrofluorene. For sediment samples, the spiking concentration was 0.5 mg/g (wet weight) for S-PAHs and triphenylene and 0.7 mg/g (wet weight) for N-PAHs.

Two sets of biodegradation 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.

Sample Extraction

The filtrates were extracted using a solid phase extraction method (Zeng and Khan 1995). The particulates filtered by GF/F filters were extracted using a roller table method (Zeng and Yu 1996). Dibenzothiophene-d_8 was used as a surrogate. Each extract 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 glass column 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 mostly 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 in 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.

Instrumental Analysis

Target analytes were measured using a Hewlett Packard (HP) 5890 II gas chromatograph (GC) with a 5970 mass selective detector. The chromatographic separation was obtained with a 60 m × 0.25 mm I.D. (0.25 μm film thickness) DB-5 column. The oven temperature was initially set at 70° C, immediately ramped to 160° C at 20 °C /min and then to 300° C at 10° C /min where it was held for 21.5 minutes. High purity helium was used as the carrier gas with a flow rate of 2 mL/min at 70° C. The injector and detector were maintained at 250° C. The concentrations of S/N-PAHs were determined using the internal calibration technique. Calibration standard solutions were prepared in 0.4, 1, 2, 5, and 10 mg/mL for thionaphthene, benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene and 4, 5, 6, 7, and 8 mg/mL for 1-nitropyrene, 2-nitrofluorene, and 9-nitroanthracene. Nitrobenzene- d_5, fluorobiphenyl, p-terphenyl- d_{14}, and dibenzo[a,b]anthracene were used as internal standards at 2 μg/mL. In addition, dibenzothiophene- d_8 was included as surrogate standard at 0.4, 1, 2, 5, and 10 ?g/mL in the standard solutions. Molecular ions used for quantitation are listed in Table 1.

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 (dibenzothiaphene) 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_8) was 73.3 ± 25.7%. Measured concentrations of the target analytes were not corrected for the recoveries of the surrogate standard.

RESULTS

Potential Marker Compounds in Stormwater Runoff and Wastewater Effluents

Benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene all were detectable in the Ballona Creek runoff samples, but only benzothiazole was detected in the Santa Ana River sample (Table 2). The runoff samples collected from Ballona Creek on November 13th 1997 contained the highest concentrations of benzothiazole, 2-(methylthio)-benzothiazole, and 2-(4-morphylinyl)benzothiazole. In general, higher levels of target analytes were found in the stormwater runoff samples than in sewage effluent samples. However, benzothiazole and 2-(methylthio)-benzothiazole were also present in the effluents collected during the December 6th-9th 1997 storm from the four major wastewater treatment plants. Interestingly, while the concentrations of 2-(methylthio)benzothiazole were noticeably higher in the effluents than in the Ballona Creek runoff samples, the concentrations of benzothiazole were lower in the effluents than in the runoff samples. In addition, both 2-(4-morpholinyl)benzothiazole and triphenylene were not detected in any effluent samples.

In addition to S-PAHs, our analysis also included some N-PAHs such as 1-nitropyrene, 2-nitrofluorene, and 9-nitroanthracene. None of these compounds were detectable in either runoff or effluent samples (Table 2).

The filtrate and particulate fractions of each water sample were analyzed separately. Relatively higher concentrations of benzothiazole, 2-(methylthio)benzothiazole, and 2-(4-morpholinyl)benzothiazole were found in the filtrate phase than in the particulate phase (Table 3). Triphenylene was detected only in the particulate phase, reflecting the relatively strong hydrophobic nature of this compound. 2-(4-morpholinyl)benzothiazole was detected only in the particulate phase of one runoff sample collected from Ballona Creek on December 5th 1997. The concentration of 2-(4-morpholinyl)benzothiazole in the particulate phase of this sample was 104 ng/L, much higher than its concentrations (0.73 – 29 ng/L) in the storm flow as measured by Kumata *et al.* (1996).

Biodegradation of Potential Marker Compounds

Fours sets of data were generated from the biodegradation experiments: recoveries of the potential marker 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

TABLE 2. Molecular markers in stormwater runoff and wastewater effluents.

Location* Date of Sampling	BC 11/13/97 (ng/L)	BC 12/5/97 (ng/L)	BC 1/9/98 (ng/L)	SA 12/8/97 (ng/L)	HTP 12/6/97 (ng/L)	CSDOC 12/8/97 (ng/L)	JWPCP 12/6/97 (ng/L)	PLWTP 12/9/97 (ng/L)
Compound								
Thionaphthene	0	0	0	0	0	0	0	0
Benzothiazole	555 ± 12	334 ± 300	230 ± 11	86 ± 9	55 ± 15	87 ± 9	67 ± 5	120 ± 5
2-Mercaptobenzothiazole	0	0	0	0	0	0	0	0
2-(Methylthio)benzothiazole	160 ± 17	93 ± 44	36 ± 1	0	148 ± 30	329 ± 3	142 ± 72	112 ± 53
2-(4-Morpholinyl)benzothiazole	215 ± 21	150 ± 213	79 ± 5	0	0	0	0	0
1-Nitropyrene	0	0	0	0	0	0	0	0
Dibenzothiophene	110 ± 13	0	0	0	0	0	0	0
2-Nitrofluorene	0	0	0	0	0	0	0	0
9-Nitroanthracene	0	0	0	0	0	0	0	0
Triphenylene	151 ± 7	240 ± 26	76 ± 107	0	0	0	0	0
Total	1191 ± 32	818 ± 530	421 ± 112	86 ± 9	203 ± 46	416 ± 11	209 ± 77	232 ± 58

* 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.

TABLE 3. Distribution of molecular markers in stormwater runoff collected from Ballona Creek

Sampling Date	11/13/97 Filtrate (ng/L)	11/13/97 Particulate (ng/L)	12/5/97 Filtrate (ng/L)	12/5/97 Particulate (ng/L)	1/9/98 Filtrate (ng/L)	1/9/98 Particulate (ng/L)
Compound						
Thionaphthene	0	0	0	0	0	0
Benzothiazole	396 ± 19	159 ± 31	203 ± 188	132 ± 112	189 ± 31	41 ± 20
2-Mercaptobenzothiazole	0	0	0	0	0	0
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
1-Nitropyrene	0	0	0	0	0	0
Dibenzothiophene	48 ± 22	62 ± 9	0	0	0	0
2-Nitrofluorene	0	0	0	0	0	0
9-Nitroanthracene	0	0	0	0	0	0
Triphenylene	0	151 ± 7	0	240 ± 26	0	76 ± 107
Total	777 ± 71	413 ± 39	372 ± 339	446 ± 191	304 ± 25	117 ± 87

afterwards were different between the seawater and sediment samples (Figures 3-6).

The recoveries of most target analytes showed different patterns between the unexposed and sunlight-exposed seawater samples. Most target analytes (except for 2-mercaptobenzothiazole and 9-nitroanthracene) in the unexposed seawater samples remained abundant (20 to 60% of the original spiking amounts) even after 6 months (Figure 3). In the sunlight-exposed seawater samples, most target analytes were substantially depleted shortly after the exposure was initiated (Figure 4). Only small amounts of benzothiazole and triphenylene (10 and 1.8% of the original amounts, respectively) in sunlight-exposed water samples were detected after 6 months.

Target analytes were in low abundance 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 unexposed and sunlight-exposed samples contained approximately the same concentrations of all of the target analytes (Figures 5 and 6). Several compounds including benzothiazole, dibenzothiophene, and triphenylene remained abundant in both the unexposed and sunlight-exposed sediment samples (about 30%), compared to being almost non-detectable in the sunlight-exposed seawater samples (Figure 4).

FIGURE 3. Time-dependent recoveries of potential marker compounds from spiked filtered seawater samples maintained in the dark at 16-17°C.

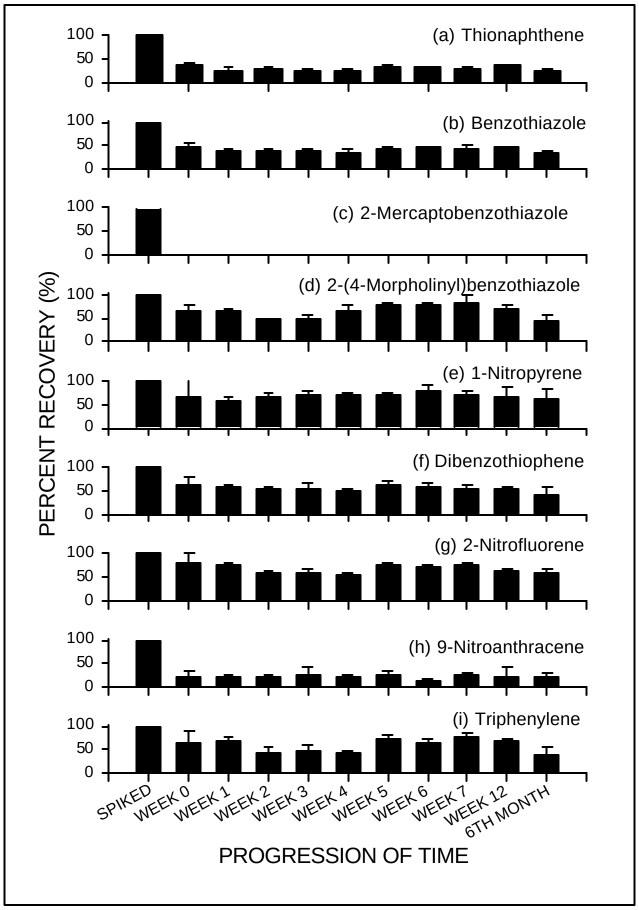
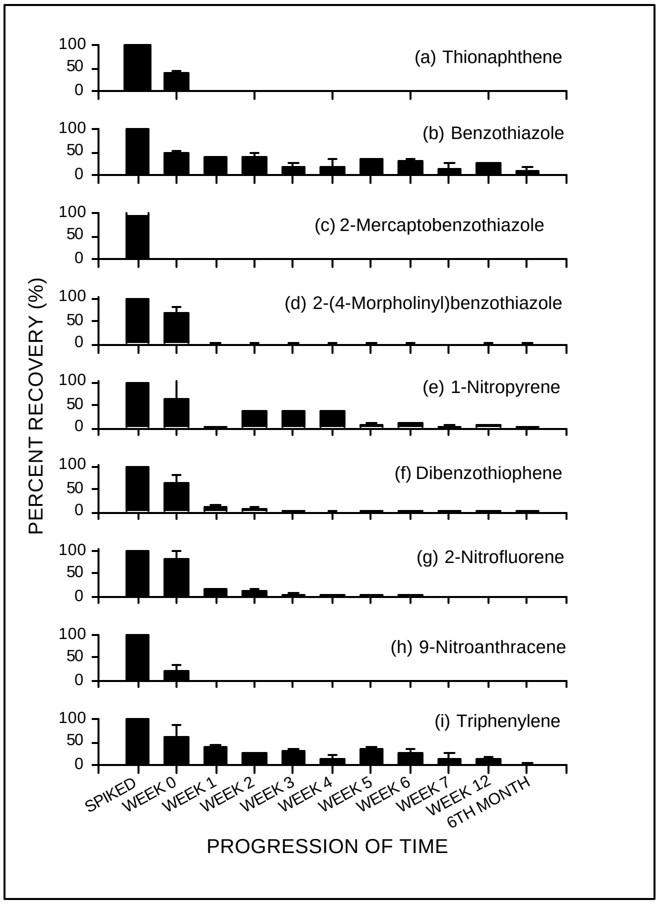


FIGURE 4. Time-dependent recoveries of potential marker compounds from spiked filtered seawater samples exposed to direct sunlight and maintained at 16-17° C.



DISCUSSION

Abundance and Source Specificity of Potential Stormwater Runoff Marker Compounds

The abundances of benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, and triphenylene, found in urban runoff samples collected from Ballona Creek during three different storm events, generally decreased as the storm season progressed (Table 2). 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 2). These results were consistent with the characteristics of storm events responsible for removing road dust from street surfaces into storm drains.

The potential marker compounds found in the stormwater runoff samples were likely derived from vehicle emissions (tire tread debris, exhaust, motor oil, brake linings, etc.). Like many other pollutants, these compounds may attach to road dust and stay on the road surface. During a storm event, road dust may be washed into the stormwater channels, rivers, streams, or stormwater treatment facilities. In a coastal city such as Los Angeles, the majority of road dust entering the stormwater channels would eventually be transported to the ocean. The amounts of road dust entering the coastal environment, however, depend upon several factors, including the storm duration, precipitation, etc. During a persistent storm with sporadic, low precipitations, road dust 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 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 marker compounds in stormwater runoff thus may vary with time when the samples are collected. In addition, the number of “dry” days between storms when no precipitation has occurred over 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.

During the 1997/1998 wet weather season, the “El Niño” phenomenon was strongly experienced in southern

FIGURE 5. Time-dependent recoveries of potential marker compounds from spiked sediment samples maintained in the dark at 16-17 °C.

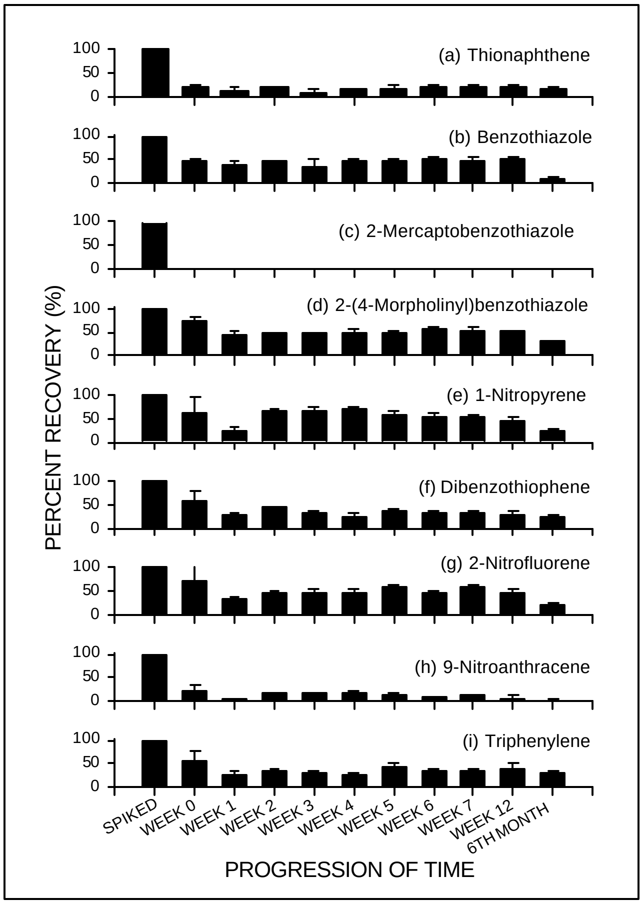
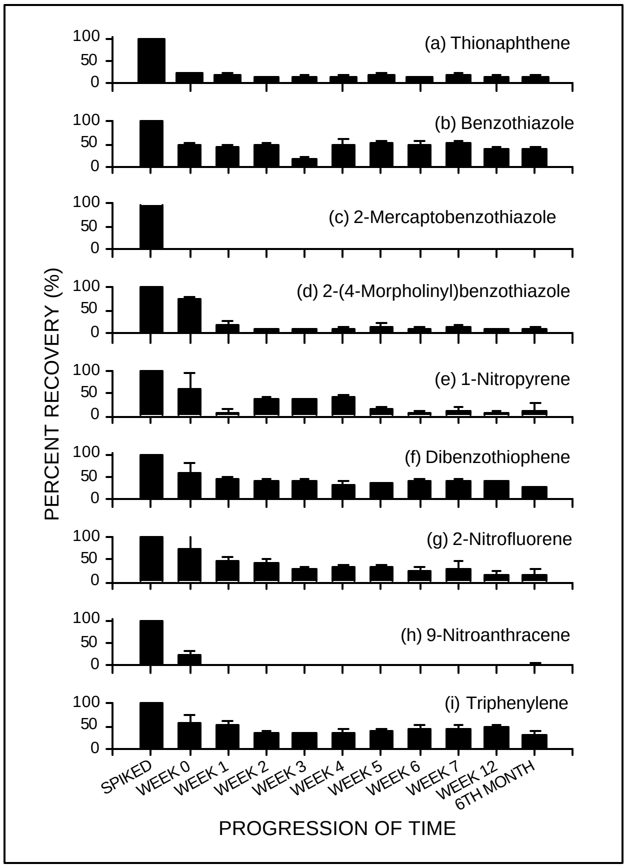


FIGURE 6. Time-dependent recoveries of potential marker compounds from spiked sediment samples exposed to direct sunlight and maintained at 16-17 °C.



California. As a consequence, a greater number of rainstorms than normal occurred. The first sample, collected from Ballona Creek on November 13, 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 1). Therefore, most target analytes in this sample were detected with the highest abundances among all the runoff samples (Table 2). The third sample (January 9, 1998) that was not collected at the beginning of the storm contained the lowest concentrations of the target analytes (Table 2). 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 December 9, 1997 (Figure 2), was free of most target analytes (Table 2). Kumata *et al.* (1997) reported that the concentration of 2-(4-morpholinyl)benzothiazole in the runoff particles was reduced from 215 ng/g to 150 ng/g and then to 1.2 ng/g 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 3). Since wastewater discharge is a major source of contamination to the Southern California Bight, potential makers 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 December 6, – 9, 1997 storm from four southern California major wastewater treatment plants, were comparable to those in the runoff samples (Table 2). The possible scenario for this may have been the result of effluents from local tire manufacturing plants and other rubber industries entering 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 effluents. Previous studies also found similar compounds in wastewater effluents. Jungclaus *et al.* (1976) reported relatively high concentrations of benzothiazole and 2-(methylthio)benzothiazole in the wastewaters 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 were absent in the effluent samples collected from the nearby Hyperion Treatment Plant or from other treatment facilities (Table 2), it could be due to the breakdown of these compounds during the transport processes.

Persistence of Target Analytes

Another issue that needs to be resolved before a molecular marker can be determined 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 3,000 mg/L and 125 mg/L, 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 3. Most detectable benzothiazoles were more abundant in the filtrates than in the particulates. Meanwhile, triphenylene 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 may have a high 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 readily degraded and largely undetectable in all sunlight-exposed and unexposed samples (Figures3-6). 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 used the most widely in the rubber tire industry among benzothiazoles (Brownlee *et al.* 1981). Other benzothiazoles including benzothiazole and 2-(methylthio)benzothiazole, which were identified as the degradation products of 2-mercaptobenzothiazole (Brownlee *et al.* 1992), were detected in Ballona Creek runoff samples (Tables 2 and 3). Most N-PAHs were degraded completely in less than one month upon exposure to sunlight (Figures 4 and 6), which may explain why these compounds were not detected in both runoff and wastewater samples (Table 2).

The effects of photolysis were evident by the markedly different results obtained from the sunlight-exposed and unexposed samples. Most target analytes photodegraded by more than 50% of the spiked amounts after the first month of direct sunlight exposure (Figures 4 and 6). Target analytes experienced less degradation in unexposed samples, particularly in unexposed seawater samples (Figures 3 and 5). Potential marker 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 4).

The sediment spiking experiments were intended to evaluate the stability of potential marker compounds with low water solubility in suspended particulate matter or sediments. While 2-mercaptobenzothiazole degraded rapidly even without sunlight exposure, other potential marker compounds remained fairly stable in unexposed sediments (Figure 5). Degradation of most compounds was notably enhanced when results from sunlight-exposed and unexposed sediments were compared (Figures 5 and 6). Benzothiazole remained relatively abundant in the sunlight-exposed sediments 6 months after exposure was initiated (Figure 6). This probably resulted from the extra amounts 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 5 and 6), as opposed to their low abundances in sunlight-exposed seawater samples (Figure 4). Triphenylene was also detected in the sediments collected in July 1997 at a station near the mouth of Ballona Creek (Bay *et al.* 1998).

Feasibility of Using the Target Analytes to Trace Runoff Inputs

Several potential marker compounds including benzothiazole, 2-(methylthio)benzothiazole, 2-(4-morpholinyl)benzothiazole, dibenzothiophene, and triphenylene were detected in the stormwater runoff samples collected during the 1997-1998 storm season from Ballona Creek and the Santa Ana River. Among these compounds, 2-(methylthio)benzothiazole, dibenzothiophene, and triphenylene were absent in the effluent samples collected from four major wastewater treatment plants in southern California. Degradation experiments suggested that 2-(methylthio)benzothiazole was degraded rapidly in sunlight-exposed seawater and sediment samples (Figures 4 and 6). Hence, this compound may not be used as marker in the environment. Both dibenzothiophene and triphenylene could be degraded rapidly in sunlight-exposed seawater samples (Figure 4), but remained abundant in sunlight-exposed sediments after six months of exposure (Figure 6). These two compounds remain hopeful as stormwater runoff markers. Since only runoff and wastewater samples were tested in the present study, the source specificity of these compounds needs to be examined with samples from other sources such as riverine and near-shore marine sediments.

LITERATURE CITED

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