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# Environmental Chemistry of Benzothiazoles Derived from Rubber

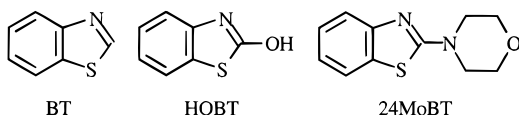
CHRISTOPHER M. REDDY\* AND  
JAMES G. QUINN

Graduate School of Oceanography, University of Rhode Island,  
Narragansett, Rhode Island 02882-1197

Benzothiazole (BT), 2-hydroxybenzothiazole (HOBT), and 2-(4-morpholino)benzothiazole (24MoBT) leach from crumb rubber material (CRM) and asphalt containing 1–3% CRM. To determine whether benzothiazoles would be an environmental problem if roads containing CRM-modified asphalt (CMA) were built in the state of Rhode Island, the source and fate of these compounds were investigated. Benzothiazoles enter the environment from a number of sources such as the leaching of rubber products, fine particles of automobile tires, and antifreeze. Compared to the fluxes of benzothiazoles currently entering rivers from urban runoff, CMA roads may initially deliver substantially more benzothiazoles to the environment; however, with time this source may diminish as the road ages. Because the benzothiazoles are water soluble, it is unlikely that they will sorb to particles, settle to sediments, or be bioaccumulated. In addition, BT can be volatilized, and BT and HOBT can be microbially degraded. Therefore, the environmental chemistry of these compounds suggests that the inputs of benzothiazoles from CMA should not be harmful.

## Introduction

In a previous study (1), we found that benzothiazole (BT), 2-hydroxybenzothiazole (HOBT), and 2-(4-morpholino)benzothiazole (24MoBT) were the major organic compounds that



leach from rubber and asphalt containing 1–3% rubber. These compounds are breakdown products (BT and HOBT) in some of the vulcanization accelerators and antioxidants added to rubber during manufacturing (2, 3) and an impurity (24MoBT) in these materials (4). Crumb rubber material (CRM) is prepared by shredding automobile tires and removing their steel belts; the resulting material can be mixed with hot asphalt to produce CRM-modified asphalt (CMA) (5). The Rhode Island Department of Transportation (RIDOT) funded us to identify organic contaminants that leach from CRM and CMA because they wanted to know if they could safely comply with Section 1038(b) of the Intermodal Surface Transportation Efficiency Act of 1991 (6), which mandated that at least 20% of all federally funded highways must be built with CMA by the year 2000. Although this bill is currently unfunded and stalled in Congress, many states, such as Arizona and California, have miles of roads built with CMA (7).

To determine whether the BT, HOBT, and 24MoBT leached from CMA would be a problem, we investigated the envi-

ronmental chemistry of these compounds. First, we determined the quantifiable sources of these compounds to the environment. Second, we measured the amounts of BT, HOBT, and 24MoBT already in the environment to serve as a baseline against which new inputs from CMA could be compared. Specifically, we analyzed samples of urban runoff, road dust, urban particulate matter, river and pond water, and sediments from rivers, a pond, and an estuary. Third, we used simple calculations and laboratory experiments to predict the major processes that would affect the fate of CMA-leached BT, HOBT, and 24MoBT in the environment. We considered photolysis, microbial degradation, volatilization, uptake in tissue, and sorption. We were particularly concerned about the sedimentary fate of these compounds because there had been conflicting reports in the literature. Spies et al. (4) found traces of BT and 24MoBT in San Francisco Bay, with the concentrations of 24MoBT as high as 500 ppb, and suggested that these compounds could be molecular markers for urban runoff; Brownlee et al. (8) suggested that, because these compounds are very water soluble, they should not be found in sediments.

## Methods

Organic solvents were purchased from Burdick & Jackson and were of pesticide grade. Pure BT, HOBT, and 2-methylbenzothiazole (MeBT) were obtained from Aldrich Chemical Co. 24MoBT was graciously donated to us by Dr. Hideshige Takada of the Tokyo University of Agriculture and Technology.

Extracts were analyzed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a Hewlett-Packard 5971 mass selective detector (GC-MSD) with a splitless injection. Compounds were separated on a 30-M J&W Scientific DB-5ms or DB-XLB fused-silica capillary column (25 mm i.d. and 0.25  $\mu$ m film thickness), and the MSD was operated in the selected ion monitoring (SIM) mode. Data were collected with Hewlett-Packard ChemStation software. Compounds were quantified with calibration curves derived from their responses of their quantification ions relative to the internal standard MeBT. The quantification (boldface) and quality ions for each compound were BT (*m/z* **135**, 108, 69), HOBT (*m/z* **151**, 123, 96), 24MoBT (*m/z* **220**, 163, 135), and MeBT (*m/z* **149**, 108, 69).

Concentrations in aqueous samples are expressed as parts per trillion (ppt), parts per billion (ppb), and parts per million (ppm) for  $\text{ng L}^{-1}$ ,  $\mu\text{g L}^{-1}$ , and  $\text{mg L}^{-1}$ , respectively. For solid samples, the dry weight concentrations are expressed as parts per billion (ppb) and parts per million (ppm) for  $\text{ng g}^{-1}$  and  $\mu\text{g g}^{-1}$ , respectively.

**Analysis of CRM (Recycled Automobile Tires).** To determine the total amount of BT, HOBT, and 24MoBT in CRM, a sample ( $\sim 150 \mu\text{m}$  diameter) was spiked with MeBT, refluxed in methanol for 2 h, cooled, and then filtered through a precombusted Whatman GF/C glass-fiber filter (particle retention of 1.2  $\mu\text{m}$ ). [This sample of CRM, brand name GF80A, was obtained from Rouse Rubber, St. Louis, MO, and was 1 of 12 different samples of CRM investigated previously (1)]. The filtrate was diluted with preextracted deionized water and extracted three times with methylene chloride. The extracts were combined, rotary-evaporated to  $\sim 1 \text{ mL}$ , and solvent-exchanged into hexane. The hexane extract was chromatographed, using nitrogen pressure, on a 0.5-cm (i.d.)  $\times$  15-cm column containing activated silica gel (Grace grade 922, 200–325 mesh size), and two fractions ( $F_1$  and  $F_2$ ) were collected. The first fraction ( $F_1$ ) was obtained by elution with 15 mL of a 50/50 mixture of hexane/methylene chloride. The second fraction ( $F_2$ ), which contained the benzothiazoles, was eluted with 15 mL of an 80/20 mixture of methylene

\* Corresponding author: Telephone: (401) 874-6612; Fax: (401) 874-6811; e-mail: redchris@gso.uri.edu.

chloride/acetonitrile, rotary-evaporated to a small volume, spiked with an external standard (*o*-terphenyl), and analyzed by GC-MSD.

**Leaching of CRM.** The leaching of benzothiazoles from CRM was investigated by shaking a ~4-gram sample with 100 mL of deionized water in a sealed centrifuge tube at 25 °C for 24 h. (In earlier experiments, we had found that equilibrium was reached in 20 h). The pH of the mixture was ~5. The mixture was then filtered through a precombusted glass-fiber filter. The CRM was returned to the centrifuge tube, another 100 mL of deionized water was added, and the mixture was leached for another 24 h. The last step was repeated three more times. Each of the five filtrates was spiked with MeBT and extracted three times with 30 mL of methylene chloride. The methylene chloride extracts were combined, rotary-evaporated, and analyzed by GC-MSD.

**Antifreeze.** Samples of used antifreeze were collected from the radiators of five cars. One sample of unused antifreeze was taken from its plastic container. Each sample (0.1–2 mL) was diluted with 15–30 mL of a 90/10 mixture of deionized water/methanol. To protonate and increase the extraction efficiency of HOBT [ $pK_a \sim 8$  (9)], the pH was adjusted to ~4 by adding a few drops of 4 N hydrochloric acid. (For the rest of this paper only protonated HOBT will be considered. Also, all other extractions for all samples were done at slightly acidic pH values, 4–6, which was an optimum pH range for extracting both BT and HOBT). Each unfiltered solution was spiked with MeBT and extracted three times with methylene chloride. The extracts were combined and analyzed by GC-MSD.

**Urban Runoff.** Eleven samples (~4 L) of urban runoff draining into the Pawtuxet, Woonasquatucket, and Moshassuck Rivers were collected during storms in February, May, and September of 1995 and filtered through a precombusted glass-fiber filter. A complete description of the sampling has been published (10). All samples were from roads built with only asphalt. Except for the February samples, in which five sequential samples were collected, all other samples were collected during the first 20 min of each storm. The filters (particulate phases) were frozen until analyzed (see below). The filtrate (dissolved phase) was spiked with MeBT and extracted three times with methylene chloride. The extracts were combined, fractionated with silica gel chromatography, and analyzed by GC-MSD.

After being thawed, the filters were cut into 10–20 pieces with solvent-rinsed scissors, spiked with MeBT, refluxed in methanol for 2 h, cooled, and then filtered through a precombusted glass-fiber filter. The filtrate was then diluted with deionized water and extracted three times with methylene chloride. The extracts were combined, fractionated with silica gel chromatography, and analyzed by GC-MSD.

For the February storm, the filters were analyzed for the 23 National Oceanic and Atmospheric Administration (NOAA) Status and Trends polycyclic aromatic hydrocarbons (PAHs) (11) but not benzothiazoles. Briefly, the filters were spiked with perdeuterated PAH internal standards, refluxed in acetonitrile, and filtered. The filtrate was diluted with an equal portion of deionized water and extracted three times with hexane. The hexane extracts were combined and fractionated with silica gel chromatography, and the F1 fraction was analyzed by GC-MSD.

**Water from Highway Settling-Pond and the Pawtuxet River.** Water (~4 L) from a highway-settling pond (intersection of RI Routes 102 and 4) and from the Pawtuxet River (under RI Route 114 bridge) was collected and filtered through a precombusted glass-fiber filter. The dissolved phases were preserved with methylene chloride and then analyzed according to the same method used for urban runoff. The particulate phases were not analyzed.

**Sediments, Road Dust, and Urban Particulate Matter.** In August 1995, 12 surface sediments (top 2–3 cm) were

collected—two from the highway settling-pond, 1 from the Pawtuxet River, and 9 from mid to lower Narragansett Bay. The bay sediments were collected by diver. Road and highway dust was collected by scooping it into a glass jar; the contents of the jar were sieved, and the <63  $\mu\text{m}$  fraction (silt/clay) was saved for analysis. Two samples of urban particulate matter, Standard Reference Materials (SRMs) 1648 and 1649, were obtained from the National Institute of Standards and Technology (NIST). Information on the collection and preparation is available with each SRM's certificate of analysis (12,13). Each sediment, dust, and SRM was analyzed in the same manner as the urban runoff particulates.

**Biodegradation Experiments.** Water from the highway settling-pond was collected in the early and late fall. The water, at room temperature, was spiked with solutions of BT and HOBT to concentrations of 15–25 ppm, shaken daily, and analyzed every 3–4 days. For most experiments, the experiments were run in duplicate along with azide-poisoned controls.

**Quality Control.** For aqueous samples of urban runoff, pond water, and river water, the recoveries of the internal standard, MeBT, were usually better than 40%. Samples were corrected for blanks; the levels of BT, HOBT, and 24MoBT in the samples had to be at least twice the blank value to be included in the dataset, but they were usually much larger. The recoveries of blanks spiked with BT and HOBT ranged from 70% to 120%. The precisions for duplicate analyses of spiked blanks, expressed by relative standard deviation (RSD), were about 10 and 15% for BT and HOBT, respectively.

The recoveries of MeBT in the antifreeze samples were always better than 65%. Amounts of BT, HOBT, and 24MoBT in the samples were usually ten times larger than the blanks. Two samples were analyzed twice, and the precision was better than 5% for all cases.

For solid material (CRM, sediments, urban dust, and filters), the recoveries of the internal standard were usually better than 40%. Samples were corrected for blanks. Levels of BT, HOBT, and 24MoBT in the samples had to be at least twice the blank value. The RSDs for duplicate samples were <20%. The recoveries of blanks spiked with BT and HOBT ranged from 70 to 130%.

The method detection limit (MDL) for each analysis was based on the sample size, matrix, and blank. When an analyte was not detected, the estimated MDL is listed. Generally, the MDLs for BT and HOBT were higher than for 24MoBT because the blanks contained more BT and HOBT than 24MoBT.

## Results and Discussion

### Sources of BT, HOBT, and 24MoBT to the Environment. (1)

**Rubber.** To investigate benzothiazoles in tire particles, we analyzed CRM as a surrogate because we felt that it was better than scraping an automobile tire for particles and because CRM is a relatively homogeneous mixture made from tires of different makes, ages, and histories. The chemical composition of the CRM (Table 1) was similar to published values for tire particles. The concentration of BT was 171 ppm versus 124.3 ppm in tire particles ( $\leq 2 \mu\text{m}$ ) that were generated mechanically from a used automobile tire (14). The concentration of 24MoBT in CRM was 3.8 ppm, and Kumata et al. (15) found a mean concentration of 2.0 ppm in particles generated mechanically from four different tires.

Benzothiazoles also leached from CRM (~150  $\mu\text{m}$ ) into deionized water (Figure 1). When CRM was leached five consecutive times, approximately 50% of the total amount of these compounds in the material were removed or solubilized. If the efficiency of leaching depends on the diameter of the particle, >50% of the benzothiazoles in ordinary tire particles, with diameters <100  $\mu\text{m}$  (16), can probably be leached by water.

Again, if CRM is chemically similar to ordinary tire particles, the fluxes of benzothiazoles from tire particles can be

TABLE 1. Concentrations of BT, HOBT, and 24MoBT in Sources of These Compounds to the Environment

	BT (ppm)	HOBT (ppm)	24MoBT (ppm)	BT/HOBT
rubber				
CRM <sup>a</sup>	171 ± 21	80.9 ± 7.2	3.76 ± 0.78	2.1 ± 0.3
antifreeze (unfiltered)				
used (1995 Volkswagen Jetta)	<0.090	0.117	<0.001	not calcd
used (1987 Ford Mustang)	0.898	0.465	0.028	1.9
used (1984 Toyota pickup)	1.30	0.787	0.022	1.7
used (1989 Toyota Corolla)	5.69	14.7	0.068	0.4
used (1995 Ford Escort)	29.6	20.1	0.081	1.5
av ± SD	7.51 ± 12.5	7.23 ± 9.48	0.040 ± 0.033	1.0 ± 2.1
new (PEAK)	0.131	0.047	<0.001	2.8

<sup>a</sup> Results are from duplicate analysis.

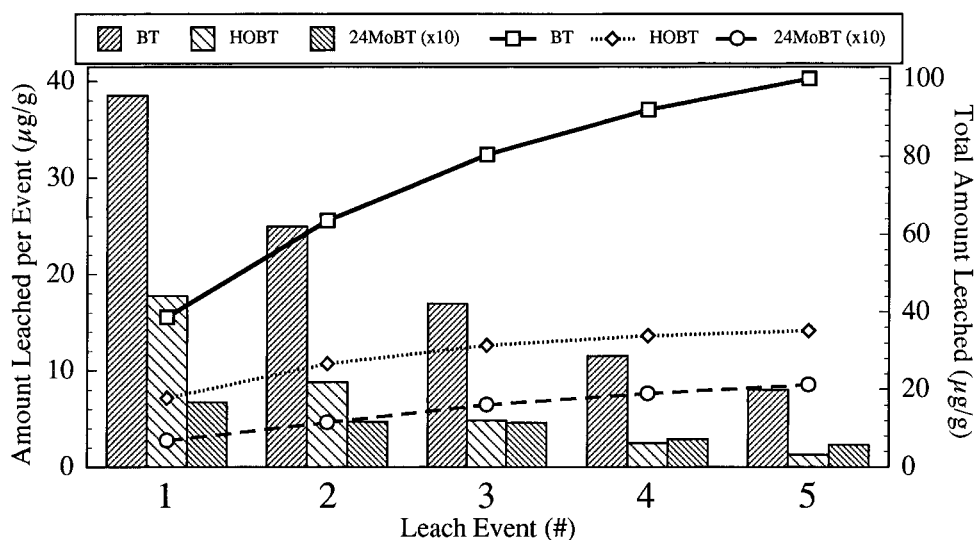


FIGURE 1. Graph showing the amount of dissolved benzothiazoles leached from CRM per event (bar graph, left axis) and total amount leached from CRM (line graph, right axis).

estimated. If a typical tire loses ~90 mg of tire/km (16, 17) and each of the 191 million registered vehicles in the United States travels 19 000 km per year (18), then  $1.3 \times 10^9$  kg of rubber are released into the environment each year. This corresponds to an annual flux of  $2.2 \times 10^5$  kg of BT,  $1.1 \times 10^5$  kg of HOBT, and  $4.9 \times 10^3$  kg of 24MoBT in tire particles, at least 50% of which should be leachable by aqueous solutions.

**(2) Antifreeze.** The concentrations and proportions of the benzothiazoles differed in the five samples of used antifreeze (Table 1). In the most concentrated antifreeze (1995 Ford Escort), the concentrations of BT, HOBT, and 24MoBT were 29.6, 20.1, and 0.081 ppm, respectively, while the least concentrated antifreeze (1996 Volkswagen Jetta) had detectable amounts of only HOBT (0.117 ppm). The BT/HOBT ratio ranged from 0.4 to 2.8.

Benzothiazoles enter antifreeze in at least three ways. First, they are added as corrosion inhibitors (3), but unfortunately their concentrations are trade secrets and it is beyond the scope of this paper to analyze every commercial brand of antifreeze. We did analyze one brand of unused antifreeze, Peak, which contained only traces of BT and HOBT. Second, benzothiazoles can be leached from the rubber hoses in the cooling systems of automobiles. Third, they may be in small particles of rubber suspended in the antifreeze, which was not filtered before being analyzed.

To estimate the annual flux of benzothiazoles entering the environment from used antifreeze, we used the amount of antifreeze produced each year [ $750 \times 10^6$  L of antifreeze (19) plus an equal amount of water to dilute it]. We then estimated percentages of antifreeze that are leaked into the environment and discharged illegally (1 and 10%) and the range of concentrations of the benzothiazoles in used

antifreeze (Table 1). This calculation gives ranges of 1.5–4000 kg each of BT and HOBT and 0.02–12 kg of 24MoBT that are released each year. These fluxes range several orders of magnitude, but they are still smaller (0.0004–4%) than the estimated inputs from tire particles.

**(3) Tire Landfills.** Approximately  $2 \times 10^9$  used tires are currently landfilled in the United States (20). We collected water from a creek downstream from one of the largest tire landfills in the country located in Smithfield, RI; the only benzothiazole detected was 24MoBT (40 ppt). Because the history of the tires and hydrodynamics of runoff from tire landfills are unknown, it is impossible to estimate the flux of benzothiazoles from tire landfills at the present time.

**(4) Other Sources of Benzothiazoles.** Benzothiazoles are also used in photography and as fungicides (3). One fungicide, 2-(thiocyanomethylthio)benzothiazole (TCMTB), is gaining in popularity in the wood and leather industries. It also can degrade into BT and HOBT (8). Data were not available to estimate the fluxes of BT and HOBT from TCMTB.

BT, HOBT, and 24MoBT have also been detected in industrial wastewater. One study done in the 1970s on the effluents of two tire plants found 350 and 10 kg yr<sup>-1</sup> of BT was discharged into undisclosed rivers (21). In the 1980s, about 100 kg yr<sup>-1</sup> of BT were entering Canagagigue Creek from the Elmira Water Pollution Control Plant (8, 22). In 1989, 1.6 ppm of 24MoBT was also detected in wastewater (23), but the flux could not be estimated because flow data were not available.

Only the toxicity of BT in aquatic environments has been investigated. Reemtsma et al. (24) found that luminescence was inhibited at water concentrations of 4.3 ppm, which is

TABLE 2. Concentrations<sup>a</sup> of BT, HOBT, and 24MoBT in Environmental Samples

type of sample	description	BT	HOBT	24MoBT	BT/HOBT
urban runoff	Pawtuxet River	378 ± 149 (D) <sup>b</sup>	721 ± 444 (D)	198 ± 68 (D)	0.5 ± 0.4 (D)
	February 1995 (n = 5)				
	Moshassuck River	1210 (D)	6910 (D)	278 (D)	0.2 (D)
	May 1995 (n = 1)	135 (P)	114 (P)	<10 (P)	1.2 (P)
	Pawtuxet River	940 (D)	5450 (D)	274 (D)	0.2 (D)
	May 1995 (n = 1)	46.6 (P)	76.5 (P)	<10 (P)	0.6 (P)
	Woonquatucket River	883 (D)	6270 (D)	249 (D)	0.1 (D)
	May 1995 (n = 1)	152 (P)	60.2 (P)	<10 (P)	2.5 (P)
	Pawtuxet River	819 ± 202 (D)	5640 ± 293 (D)	154 ± 29 (D)	0.1 ± 0.04 (D)
	September 1995 (n = 2)	<50 (P)	<50 (P)	<5 (P)	not calcd
river and settling-pond water	highway settling-pond (n = 7)	<50 (D)	<50–516 (D)	<5–13.5 (D)	not calcd
	Pawtuxet River (n = 2)	<50 (D)	<50 (D)	<5 and 6.10 (D)	not calcd
sediments	Narragansett Bay, RI (n = 9)	<20	<20	<1	not calcd
	Pawtuxet River, RI (n = 1)	<20	31.0	<1	not calcd
	highway settling-pond (n = 2)	<20	<20	1.16 and 1.31	not calcd
urban particulate matter	NIST SRM 1648	393	696	63.2	0.6
	NIST SRM 1649	813	893	107	0.9
road dust	residential (<63 μm)	78.7	24.6	2.45	3.2
	highway (<63 μm)	149	90.2	1.68	1.7

<sup>a</sup> Urban runoff and river and settling-pond water concentrations are given in ppt; sediment, urban particulate matter, and road dust concentrations are given in ppb. <sup>b</sup> (D), dissolved fraction; (P) particulate fraction.

lower than in some antifreezes. The toxicity of HOBT and 24MoBT has not been evaluated.

In summary, benzothiazoles enter into the environment from a variety of sources. Only inputs from tires and antifreeze could be estimated, while sources such as tire landfills, fungicides, and wastewater could not be evaluated at the present time due to insufficient data.

**Benzothiazoles in the Environment. (1) In Urban Runoff.** Since all of the runoff samples were collected from roads without any CMA, the benzothiazoles in these samples should be the baseline for which the amount of benzothiazoles from CMA can be compared. Dissolved benzothiazoles (<1.2 μm) were detected in all samples of urban runoff (Table 2), but the concentration of BT was always at least 1 order of magnitude below toxic levels (24).

Mean concentrations of dissolved benzothiazoles were generally greater in the May and September storms than in the February storm. Both the dissolved and particulate phases were analyzed in the May and September storms (Table 2). For the five samples that had detectable quantities in either phase, >85% and 98% of the total BT and HOBT, respectively, were dissolved and no particulate 24MoBT was detected. Thus, dissolved benzothiazoles may be a better choice, rather than particulate benzothiazoles (4), as molecular markers for urban runoff. The dissolved benzothiazoles could have leached from tires on cars, leached from thin films of rubber that are on the pavement (like skidmarks), leached from tire particles on the road, or be from used antifreeze.

If "tire particles" are chemically similar to CRM, then the percentage of tire particles in the particulate phases of urban runoff can be estimated by normalizing the concentrations of benzothiazoles in the particulates to the concentrations of benzothiazoles in CRM. In these samples, tire particles represented 0–3.4% of the particulates, by using BT or HOBT. However, one should be very careful when using this approach because as the rubber ages and the benzothiazoles leach, the percentage of tire particles in samples may be underestimated. In two of the three samples with both detectable particulate BT and HOBT, the estimates of tire particles calculated using HOBT were greater, and in the third sample the estimates were approximately equivalent. Using 24MoBT, Kumata et al. (15) estimated that tire wear material represented 0.05% to 9.5% of urban runoff during one storm in Tokyo, Japan.

The ratio of dissolved BT/HOBT also followed a seasonal trend, with ratios decreasing from 0.5 in February to 0.15 in May and September. This ratio is about 2 when CRM is leached in deionized water (Figure 1). If BT and HOBT are

coming from only automobile tires and the leaching characteristics of tires are the same as of CRM, then some environmental process is either removing BT more rapidly than HOBT or transforming BT into HOBT. Additionally, other sources (e.g., antifreeze) may be preferentially adding more HOBT than BT to the environment.

During the February storm, five sequential samples were collected throughout the storm, and the flow rates for each sample were measured. From the concentration and the flow rate, the fluxes of BT, HOBT, and 24MoBT were calculated (Figure 2). Also shown in this figure is the sum of the fluxes of dissolved and particulate polycyclic aromatic hydrocarbons (PAHs) from another study (11). With the exception of HOBT, the fluxes of each compound maximized at 20 min, which is usually called the "first flush". If a flux of 1 μg s<sup>-1</sup> is used as the average flux of BT, HOBT, and 24MoBT during this storm and the storm lasted 14 000 s (10), then 14 mg emptied into the Pawtuxet River at this location. Normalized to the drainage area of 2.4 × 10<sup>8</sup> cm<sup>2</sup> (10), 54 pg of these compounds was washed per square centimeter of highway. This value is about 500 times less than the amount washed from a slab of CMA that was prepared and weathered in the laboratory (1); however, the results from that study are probably a worst-case scenario. The BT, HOBT, and 24MoBT that leached from the slab came from the first and only simulated rain event, but should decrease with each successive rain event (i.e., see Figure 1). Of course, more research is needed, but it appears that although CMA may initially contribute larger amounts of dissolved benzothiazoles to urban runoff than do tires and antifreeze, the contributions from CMA relative to tires and antifreeze will decrease with each successive rainstorm.

**(2) In Highway Settling-Pond Water and Pawtuxet River Water.** The concentrations of dissolved HOBT and 24MoBT in water from the settling-pond ranged from 59 to 516 ppt and from <5 to 13.5 ppt, respectively (Table 2). BT was never detected, a fact that provides additional evidence that it is more environmentally labile than HOBT. Although the exact volume of water in the settling-pond was not measured, the highest concentration of HOBT (516 ppt) occurred when the water level was low. In the Pawtuxet River, a trace of dissolved 24MoBT (6.10 ppt) was detected, but neither BT nor HOBT was detected (Table 2). BT was detected in the Pawtuxet River (24) but only once, at 2 ppb.

**(3) In Surface Sediments.** Except for the sediment from the Pawtuxet River, where the concentration of HOBT was 31 ppb, all sediment samples had nondetectable amounts (<20 ppb dry weight) of BT and HOBT (Table 2). 24MoBT was

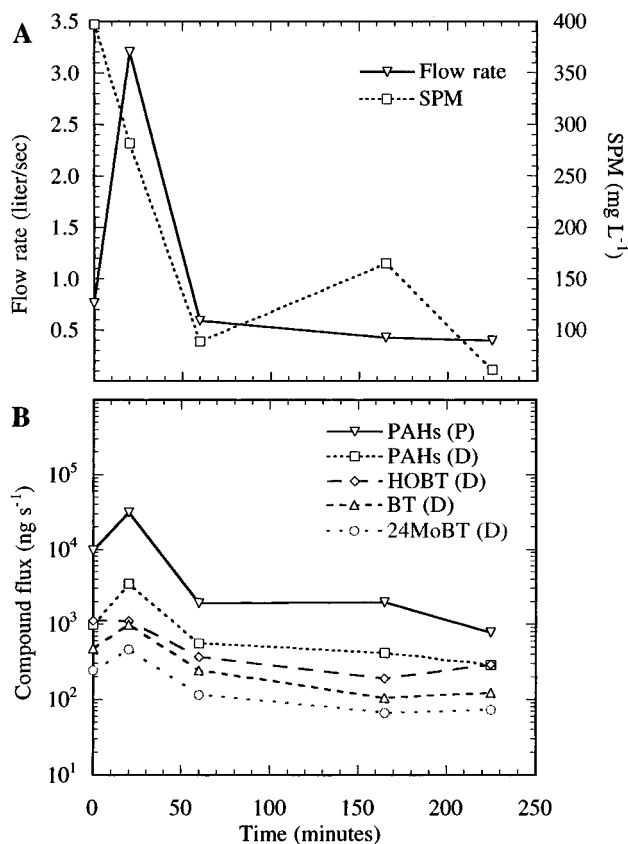


FIGURE 2. (A) Flow rate and suspended particulate matter (SPM) for February urban runoff. (B) Fluxes of PAHs and benzothiazoles draining into the Pawtuxet River in February 1995. (P) is the particulate phase ( $>1.2 \mu\text{m}$ ), and (D) is the dissolved phase ( $<1.2 \mu\text{m}$ ).

detected only in the sediments from the highway settling-pond, with the very low concentrations of 1.16 and 1.31 ppb. These concentrations of 24MoBT are smaller than, but of the same magnitude as, sediments from Sumidagawa and Tamagawa Rivers, Tokyo, Japan (15). If the HOBT and 24MoBT in the sediments that we analyzed were from tire particles, then the sediments from the Pawtuxet River and highway settling-pond are  $\sim 0.04$  and  $\sim 0.03\%$  tire particles, respectively. Since most of the benzothiazoles in urban runoff were dissolved, it is not surprising that these compounds are at such low levels in sediments. Furthermore, these results are consistent with those of Brownlee et al. (8) and Jungclaus et al. (25) but contrary to those of Spies et al. (4), who detected some benzothiazoles (as high as 500 ppb) in sediments of San Francisco Bay. Spies's values may be higher than Kumata's and ours because their samples were collected under the San Francisco–Oakland Bay Bridge, which is 4.5 mi long, double-levelled, and one of the United State's busiest bridges at  $\sim 250\,000$  cars per day (26).

**(4) Urban Particulate Matter.** Both NIST SRMs contained all three benzothiazoles (Table 2). The concentrations of BT, HOBT, and 24MoBT in SRM 1649 were 813, 852, and 107 ppb, respectively. In SRM 1648 the values were smaller, with concentrations of BT, HOBT, and 24MoBT at 393, 696, and 63.2 ppb, respectively. Aerosols from suburban locations in Japan had 24MoBT concentrations of 195 and 103 ppb, respectively (15). The estimated percentage of rubber ranged from 0.2 to 1.7% in SRM 1648 and from 0.5 to 2.8% in SRM 1649. For both SRMs, the estimates of rubber were lowest when using BT and highest when using 24MoBT.

The rubber in these samples also contributes to the total amount of PAHs. For example, we also measured 41.4 ppm of pyrene in the CRM. SRMs 1648 and 1649 contain 7.2 and 6.4 ppm of pyrene, respectively (27). Using the estimates of

rubber content in the SRMs from above, then 1.3–9.6% of the pyrene in SRM 1648 and 3.1–18% of the pyrene in SRM 1649 is from rubber particles.

**(5) Residential and Highway Road Dust.** The silt/clay fraction ( $<63 \mu\text{m}$ ) of the road dust samples also contained all three benzothiazoles; generally more were in the highway sample (Table 2). Consistent with other matrices, our values for 24MoBT in road dust are lower than Kumata's (15). This difference may be because of different analytical methods. Our method was targeted for BT and HOBT, while Kumata's was for 24MoBT.

BT, HOBT, and 24MoBT were 5, 14, and 41 times less concentrated in the residential and highway road dusts ( $<63 \mu\text{m}$ ) than the two samples of urban particulate matter, which were a smaller size. Rogge et al. (14) found that the concentration of BT was 4.4 ppm in the  $<2 \mu\text{m}$  fraction of road dust from Pasadena, CA, 30–60 times more concentrated than our samples. These results suggest that the finer particles of dust are enriched in rubber relative to larger particles and are consistent with the findings of Kumata et al. (15). The predicted amount of rubber in the residential road dust was 0.03–0.07%, and the corresponding value for the highway road dust was 0.04–0.1%.


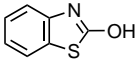
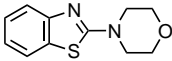
In addition, the BT/HOBT ratio in the CRM, particulate phases of urban runoff, urban particulate matter, and road dusts ranged from 0.6 to 3.2 (Tables 1 and 2). There appears to be no clear trend in these ratios.

In summary, BT, HOBT, and 24MoBT have been detected in urban runoff, settling-pond water, urban particulate matter, road dust, and sediments. When benzothiazoles were found in solid materials, the source was probably small tire particles. In addition, there was a decrease in the calculated amount of tire particles from particulate phases of urban runoff (0–3.4%) to urban particulate matter (0.2–2.8%), to road dust (0.03–0.1%), and to sediments (0.03–0.04%), which may be from the dilution of other materials (15), selective size fractionation (15), leaching of benzothiazoles, or a combination of all of these factors. It appears that during weathering, dissolved BT is removed more rapidly than dissolved HOBT. The most important finding of this study is that benzothiazoles in the environment are either dissolved in water or contained in tire particles, which, in turn, greatly influences the fate of these compounds. Since CMA will leach dissolved benzothiazoles, the fate of these chemicals will be considered next.

**Laboratory and Calculation Results. (1) Chemical and Physical Characteristics.** To predict the fate of the benzothiazoles dissolved in natural waters, many of their chemical and physical properties were compiled (Table 3). While most of the properties were available in the literature, some had to be estimated using methods outlined in Schwarzenbach et al. (28) or with commercially available software. We then applied some simple calculations used by others (28, 32) as well as results from some laboratory experiments with BT and HOBT (pure 24MoBT was not available at that time). We considered photolysis, volatilization, microbial degradation, sorption, uptake in tissue, and chemical transformation.

**(2) Photolysis.** Organic compounds can photolyze directly or indirectly. In direct photolysis, the compound of interest absorbs light and reacts. Since both BT and HOBT absorb sunlight only very weakly at wavelengths  $>290 \text{ nm}$  (30, 31), direct photolysis of these compounds will be a minor fate (28). Although the absorption spectrum for 24MoBT could not be found in the literature, 24MoBT probably will not also photolyze directly because the morpholino moiety does not strongly absorb light at wavelengths  $>290 \text{ nm}$  (33). Indirect photolysis occurs when a chemical species absorbs light and transfers the energy to the compound of interest, which then reacts; however, indirect photolysis is generally difficult to predict (28). For example, Spies et al. (4) exposed an aqueous solution saturated with a commercial vulcanization accelera-

TABLE 3. Chemical and Physical Properties of BT, HOBT, and 24MoBT at 25 °C in Distilled Water

			
	BT	HOBT	24MoBT
CAS Registry No. <sup>a</sup>	95-16-9	934-34-9	4225-26-7
molecular mass	135	151	220
melting point (°C)	2	138	126–127
boiling point (°C)	231	360	NA
solubility in water (mol L <sup>-1</sup> )	$2.2 \times 10^{-2}$ <sup>a</sup>	$4.6 \times 10^{-3}$ <sup>b</sup>	$\sim 1 \times 10^{-3}$ <sup>c</sup>
vapor pressure (atm)	$1.4 \times 10^{-4}$ <sup>d</sup>	$4.2 \times 10^{-9}$ <sup>e</sup>	NA
molecular diffusivity in water (cm <sup>2</sup> s <sup>-1</sup> )	$1.0 \times 10^{-5}$ <sup>f</sup>	$9.7 \times 10^{-6}$ <sup>f</sup>	$8.0 \times 10^{-6}$ <sup>f</sup>
molecular diffusivity in air (cm <sup>2</sup> s <sup>-1</sup> )	0.095 <sup>g</sup>	0.090 <sup>g</sup>	0.074 <sup>g</sup>
octanol/water partition coefficient	98 <sup>h</sup>	58 <sup>i</sup>	420 <sup>j</sup>
organic matter/water partition coefficient [L (kg of om) <sup>-1</sup> ]	60 <sup>k</sup>	40 <sup>k</sup>	180 <sup>k</sup>
Henry's law constant, $K_H$	$2.6 \times 10^{-4}$ <sup>l</sup>	$3.8 \times 10^{-8}$ <sup>l</sup>	$2.3 \times 10^{-11}$ <sup>m</sup>
molar absorptivity @ $\lambda_{\max}$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	1510 @ 296 nm <sup>n</sup>	3020 @ 287 nm <sup>o</sup>	NA <sup>p</sup>

<sup>a</sup> Reference 8. <sup>b</sup> Determined in the laboratory as part of this study. <sup>c</sup> Estimated from the plot of  $K_{ow}$  versus water solubility of HOBT, 2-(methylthio)benzothiazole, 2-mercaptobenzothiazole, and 2-(thiocyanomethylthio)benzothiazole (from data listed in this table and in ref 8). <sup>d</sup> Estimated using equation 4–18 in ref 28. <sup>e</sup> Estimated using eqs 4–18 and 4–21 in ref 28. <sup>f</sup> Estimated with eq 9–30 in ref 28. <sup>g</sup> Estimated with eq 9–25 in ref 28. <sup>h</sup> Reference 8. <sup>i</sup> Reference 29. <sup>j</sup> The average of seven estimates obtained from the following software: ACD/LogP, Advanced Chemistry Development Inc., Toronto, ON; ClogP, Biobyte Corp., Claremont, CA; KOWWIN, Syracuse Research Corporation, Syracuse, NY; PrologP 5.1, CompuDrug Chemistry Ltd., Budapest, Hungary; Softshell Properties, Softshell, Inc., Grand Junction, CO. <sup>k</sup> Estimated using eq 11–24 in ref 28. <sup>l</sup> Estimated by dividing vapor pressure by water solubility and then dividing by RT. <sup>m</sup> Estimated by using Softshell Properties, Softshell, Inc., Grand Junction, CO. <sup>n</sup> Reference 30. <sup>o</sup> Reference 31. <sup>p</sup> NA, not available. <sup>q</sup> Supplied by the authors.

tor to direct sunlight for 4 months but observed no direct or indirect degradation of 24MoBT.

**(3) Volatilization.** Using methods outlined by Schwarzenbach et al. (28), the half-lives of BT, HOBT, and 24MoBT are 15 days, 235 years, and > 1000 years in 1 m of stagnant water at 25 °C with the wind blowing at 10 m above the surface at 1 m s<sup>-1</sup>. However, volatilization may be the important factor controlling the BT/HOBT in the environment. When the half-lives are recalculated at a water depth and speed of water more realistic of urban runoff (0.1 cm and 1 m s<sup>-1</sup>, respectively), the half-lives become 30 min and 86 days, respectively.

**(4) Microbial Degradation.** While others (24, 34) have shown that BT and HOBT can be degraded microbially, their experiments used much higher concentrations (parts per thousand) than those occurring in the environment and with activated sewage waste as the inoculum. To simulate more realistic environmental conditions, we spiked BT and HOBT into water collected from the highway settling-pond. In our first experiment, we spiked the water with BT and HOBT at 15 ppb, and 8 days later, we found that 60% of the BT had transformed into HOBT. At first, we thought that these results would explain some of the differences in the BT/HOBT ratio in our field samples in which bacteria were transforming BT into HOBT, a “dead-end” product. Unfortunately, we could not replicate this experiment, and in later work both BT and HOBT always degraded within 30 days. Yet, we did see traces of HOBT being formed in the samples that were spiked only with BT. These differences may also be due to the time of year when the water for these experiments was collected. In our initial experiment, the sample was collected in September. In later experiments, in which both BT and HOBT were completely degraded, the water was collected in November and December. Hence, these different results may be due to different populations of bacteria that reside in the pond or other seasonal factors (e.g. road salts). Nevertheless, both BT and HOBT at reasonable concentrations can be microbially degraded in water in a relatively short time.

Pure 24MoBT was not available for this part of the study; however, this compound is probably more resistant than BT and HOBT because it is more complex in structure and more hydrophobic (see Table 3) and because we sometimes

detected it in water samples (Pawtuxet River and downstream from the tire dump), while BT and HOBT were not detected.

**(5) Sorption.** BT, HOBT, and 24MoBT will most likely sorb to particles by partitioning into the organic coatings. If a linear isotherm and equilibrium conditions are assumed, the percentage of BT, HOBT, and 24MoBT sorbed to particles can be calculated with eq 1 (32):

$$\text{percent sorbed} = \frac{K_{om}f_{om}\text{SPM}}{1 + K_{om}f_{om}\text{SPM}} \times 100 \quad (1)$$

where  $f_{om}$  is the mass fraction of organic matter on the particles,  $K_{om}$  is the compound's organic matter to water partitioning coefficient [L (kg of organic matter)<sup>-1</sup>], and SPM is the concentration of suspended particulate matter (kg L<sup>-1</sup>). Regardless of  $f_{om}$ , sorption of these compounds is a relevant fate only when SPM concentrations exceed 1 g L<sup>-1</sup>.

**(6) Uptake in Tissue and Chemical Transformations.** Although there is evidence that BT can be bioaccumulated (35), their  $K_{ow}$  values are too small for tissue uptake to be a major fate (BT = 98, HOBT = 58), and 24MoBT = 420). Because the structures of BT, HOBT, and 24MoBT do not have hydrolyzable or reactive moieties (like ester bonds), abiotic chemical transformations should not occur.

In conclusion, BT, HOBT, and 24MoBT are already entering the environment from the leaching of rubber, fine particles of rubber, and antifreeze. Compared to the fluxes of benzothiazoles entering rivers, CMA roads may initially deliver significantly more benzothiazoles to the environment, but with time this source will rapidly diminish. Because BT, HOBT, 24MoBT are water soluble, it is unlikely that they will sorb to particles and settle to sediments or be bioaccumulated. BT can be volatilized, and BT and HOBT can be microbially degraded. Although the environmental chemistry of these compounds suggests that the inputs of BT, HOBT, and 24MoBT from CMA will not be harmful, additional research is necessary to confirm this tentative conclusion.

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