

## QUANTIFYING NON-POINT SOURCES OF VOLATILE ORGANIC COMPOUNDS IN STORMWATER FROM A PARKING LOT

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**Abstract:** A mass balance approach was used to determine the most important non-point source of volatile organic compounds (VOCs) in stormwater from an asphalt parking lot without obvious point sources (e.g. gasoline stations). The parking lot surface and atmosphere are important non-point sources of VOCs, with each being important for different VOCs. The atmosphere is an important source of soluble, oxygenated VOCs (e.g. acetone) and the parking lot surface is an important source for the more hydrophobic VOCs (e.g. benzene). VOCs on the parking lot surface appear to be concentrated in oil and grease, vehicle soot, and other components that comprise the complex mixture of organic material in urban particles. Except in the case of spills, asphalt does not appear to be an important source of VOCs. The uptake isotherm of gaseous methyl tert-butyl ether (MTBE) on urban particles indicates a site-specific interaction between MTBE and a particulate component similar to soot. This also indicates a mechanism for dry deposition of VOCs from the atmosphere. This study demonstrated that a mass balance approach is a useful means of understanding non-point-source pollution, even for volatile compounds, which are difficult to sample.

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**Key Words:** non-point source, urban stormwater, volatile organic compounds, impervious area, atmosphere

## INTRODUCTION

Protecting the quality of sources of drinking water is an important goal of regulatory agencies and water utilities throughout the United States (U.S. Environmental Protection Agency, 1997a). In order for agencies to protect source waters, contaminants and their sources need to be identified. In a national survey, 38% of community water systems identified volatile organic compounds (VOCs) as potential contaminants in their source water (U.S. Environmental Protection Agency, 1997b). Releases from underground storage tanks were cited as the main source of VOCs. However, non-point sources could cause chronic, low-level degradation of source-water quality over a much larger area than point sources. VOCs were commonly detected at low (0.1 to 1 µg/L) concentrations across the United States in urban stormwater (Delzer et al., 1996), streams and rivers (Reiser and O'Brien, 1998; Lundgren and Lopes, 1999), ground water (Squillace et al., 1996 and 1999; Stackleberg et al., 1998), and finished drinking water (Westrick et al., 1984). The frequent detections at low concentrations suggest VOCs could be from non-point sources such as the atmosphere (Plummer et al., 1993; Squillace et al., 1996; Pankow et al., 1997). However, Baehr et al. (1999) concluded that, of the VOCs frequently detected at low concentrations in shallow ground water in southern New Jersey, the atmosphere is a possible source only for the gasoline oxygenate methyl tert-butyl ether (MTBE).

Lopes and Bender (1998) concluded that urban land surfaces are the primary non-point source of VOCs in urban stormwater. An obvious non-point source of VOCs is residue from spills trapped in the pore space of concrete and asphalt. Stormwater flushes these residues into receiving streams and recharges ground water by infiltrating through losing streams, flood control structures (e.g. dry wells, retention basins), and other pathways. Less obvious non-point sources of VOCs are non-aqueous phases (i.e. asphalt, oil and grease) and particles that accumulate on impervious areas. VOCs from the atmosphere, auto exhaust, leaking gas tanks, and other sources may partition and concentrate in asphalt, oil and grease, vehicle soot, vegetation, and other organic particles. Partitioning into oil and grease could be a particularly effective mechanism of concentrating and transporting VOCs and other hydrophobic contaminants. Each year, almost 500,000 tons of oil and grease in urban stormwater and combined sewers are discharged into streams, lakes and reservoirs, and coastal waters of the United States (Hoffman and Quinn, 1987).

This paper describes a study that used a mass balance approach to determine the most important non-point sources of VOCs in stormwater from a parking lot.

## METHODS

### Study area

An asphalt parking lot was chosen specifically to assess the less obvious non-point sources of VOCs. The parking lot is adjacent to a county government building in Brooklyn Center, Minnesota, a suburb in the Twin Cities metropolitan area. The parking lot has a contributing drainage area of 10,030 m<sup>2</sup>, many spots where oil and grease dripped from car engines, and no point sources of VOCs such as gasoline stations. Although the age of the asphalt is unknown, it did not appear to have been paved in several years. Rounded sand- and gravel-sized particles were visible at the surface, indicating erosion of some of the original asphalt. Stormwater originates from the parking lot, flows through a culvert, and discharges into a detention basin.

### Mass balance approach

A mass balance is the quantification of the inflow, outflow, and change in mass stored within a defined area. When all components are accounted for and accurately quantified, the outflow equals the inflow plus change in storage. Comparing the magnitude of inflow components is a practical means of prioritizing management practices designed to protect water quality. For stormwater discharged from the parking lot, the mass balance of VOCs is:

$$VOC_{stormwater} = VOC_{precip} + VOC_{particle} + VOC_{ia} \quad (1)$$

Where:

$VOC_{stormwater}$  is the mass of VOCs discharged in stormwater

$VOC_{precip}$  is the mass of VOCs in precipitation

$VOC_{particle}$  is the mass of VOCs sorbed to particles stored on the parking lot

$VOC_{ia}$  is the mass of VOCs flushed from impervious areas

Chemical and biological degradation rates are too slow to be important for a mass balance of VOCs in stormwater (Mackay et al., 1992), therefore, a term for these processes was not included in equation 1. The change

in mass of VOCs stored on the parking lot is the sum of  $VOC_{particle}$  and  $VOC_{ia}$ . Components of the mass balance that were directly measured were  $VOC_{stormwater}$ ,  $VOC_{precip}$ , and  $VOC_{particle}$ . For this study, it was assumed that all the particles on the parking lot were flushed into the stormwater.  $VOC_{ia}$  was estimated as a residual of the mass balance because it was not possible to quantify the total mass of VOCs in the impervious area, and the fraction of VOCs that is flushed will depend on many factors such as the physical/chemical properties of each VOC, temperature, and the amount of precipitation.  $VOC_{ia}$  consists of VOCs sorbed to fine-grained particles too small to sweep, VOCs in oil and grease, and VOCs that may diffuse from asphalt. Slinn et al. (1978) and Ligocki et al. (1985) concluded that VOCs in air quickly equilibrate with falling raindrops. Thus, concentrations measured in precipitation represent minimum values that might be observed in stormwater. Concentrations in the stormwater greater than minimum values may result from desorption of VOCs from particles and impervious areas and indicate that VOCs are volatilizing from stormwater.

### **Data collection**

Particulate samples were collected from the parking lot on August 14, 1998, following 5 antecedent dry days and 2 days prior to sampling stormwater and precipitation. Particles were swept from flat areas and dry puddles using a pre-cleaned wire brush and metal dustpan and placed in 40-ml vials. Discrete samples were chilled on ice, weighed in the office to determine particulate density ( $g/m^2$ ) of the swept area, and composited by taking equal-weight aliquots from the discrete samples. Discrete particulate samples and two replicates of the composite sample were chilled on ice, shipped overnight to the U.S. Environmental Protection Agency's National Exposure Research Laboratory in Las Vegas, Nevada, and analyzed for VOCs according to Hiatt (1995).

Selected samples also were analyzed for organic carbon, and the composite was analyzed for particle size, surface area, and uptake of gaseous MTBE. These analyses were done at the U.S. Geological Survey's National Water-Quality Laboratory (NWQL) in Denver, Colorado. Particle size was determined by sieving using an ATM Corp. model L3P sonic sifter. Samples were dried in a vacuum under a desiccator for 72 hours prior to analysis. The surface areas of three size fractions of the composite sample were derived from  $N_2$  adsorption data by the BET method (Gregg and Sing, 1982). Nitrogen vapor isotherms were determined at liquid nitrogen temperature using a Gemini 2360 surface area analyzer from Micrometrics. MTBE was used in sorption experiments because it is a common gasoline additive that has received considerable attention recently (Squillace et al., 1996; Pankow et al.,

1997; Baehr et al., 1999) and it was unknown which VOCs would be detected in particles. Isotherms of MTBE uptake by chimney soot, asphalt, and parking lot particles  $<63\mu\text{m}$  were developed using procedures described by Rutherford et al. (1997). Chimney soot was used because of the difficulty in obtaining sufficient samples of vehicle soot. Briefly, about 100 mg of soot, asphalt, or particles was placed in a sorption chamber containing an electrical microbalance. The sample was heated to  $100^{\circ}\text{C}$  for 8 to 10 hours inside the chamber under a vacuum of  $1.33^{-4}$  Pa to remove moisture, then cooled to room temperature. MTBE, purified by vacuum distillation, was then introduced into the chamber. Equilibrium was established at a range of pressures, which were measured using a pressure gauge. The change in sample weight resulting from vapor uptake was recorded. The saturation pressure of MTBE at room temperature (28,264 Pa at  $22.4^{\circ}\text{C}$ ) was determined by monitoring the vapor pressure of saturated MTBE vapor prior to the sorption experiments.

The fraction of VOCs that desorb from particles was estimated from water extractions. Extractions were done by preparing two 33-gram aliquots of the composite sample, placing each aliquot in a 125-ml baked bottle, filling the bottle with analytical-grade water, acidifying to a  $\text{pH} < 2$  with 1:1 HCl, and shaking for 5 minutes. After 35 hours, the extract was slowly decanted into 40-ml vials. The extract and a sample of analytical-grade water were chilled on ice, shipped overnight to the NWQL, and analyzed for VOCs according to Connor et al. (1998). Positive detections of VOCs in water that were less than the method detection limits were reported as estimated concentrations (e-values), which have a mean error of 7.4% (Lopes et al., 2000). Analytical-grade water contained background concentrations of benzene ( $e0.01 \mu\text{g/L}$ ), toluene ( $e0.02 \mu\text{g/L}$ ), acetone ( $4.98 \mu\text{g/L}$ ), and methyl ethyl ketone (MEK;  $e0.58 \mu\text{g/L}$ ). Concentrations of these VOCs in the extract solution were corrected for the background concentrations in the analytical-grade water.

On the morning of August 16, 1998, 2.00 cm of rain fell at the parking lot. Precipitation was measured with a tipping bucket raingage and stormwater discharge was measured with a 7.62-cm Parshal flume. Precipitation and stormwater were sampled at the outlet of the culvert that drains the parking lot. Precipitation samples were collected from a pre-cleaned, galvanized, 25-cm diameter funnel, acidified to a  $\text{pH} < 2$  with 1:1 HCl, chilled on ice, and shipped overnight to the NWQL. An equipment blank had concentrations similar to those of the analytical-grade water, indicating the precipitation sampler did not contaminate samples. Stormwater samples were collected by

manually dipping 40-ml vials in the runoff, acidified to a pH<2 with 1:1 HCl, chilled on ice, and shipped overnight to the NWQL. Duplicate samples of runoff had the same detections and similar concentrations of VOCs, indicating that results of sampling and chemical analysis were reproducible.

## RESULTS AND DISCUSSION

### VOCs in particles

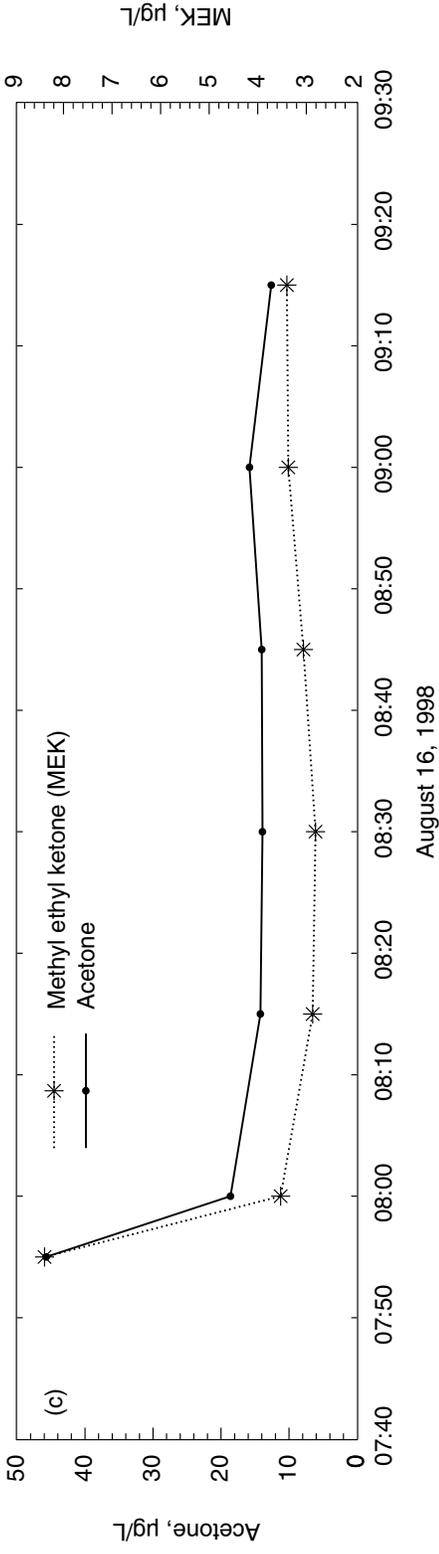
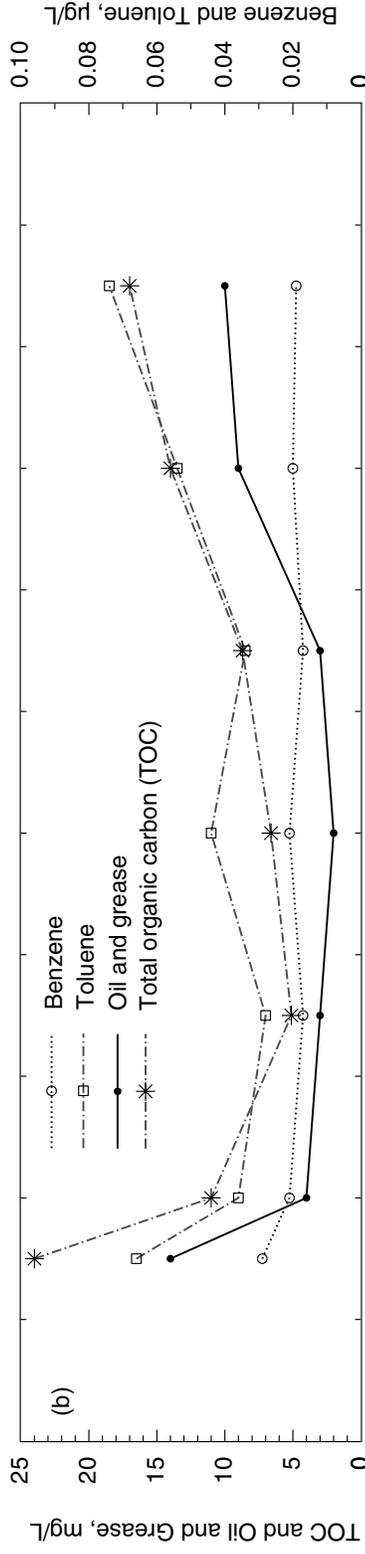
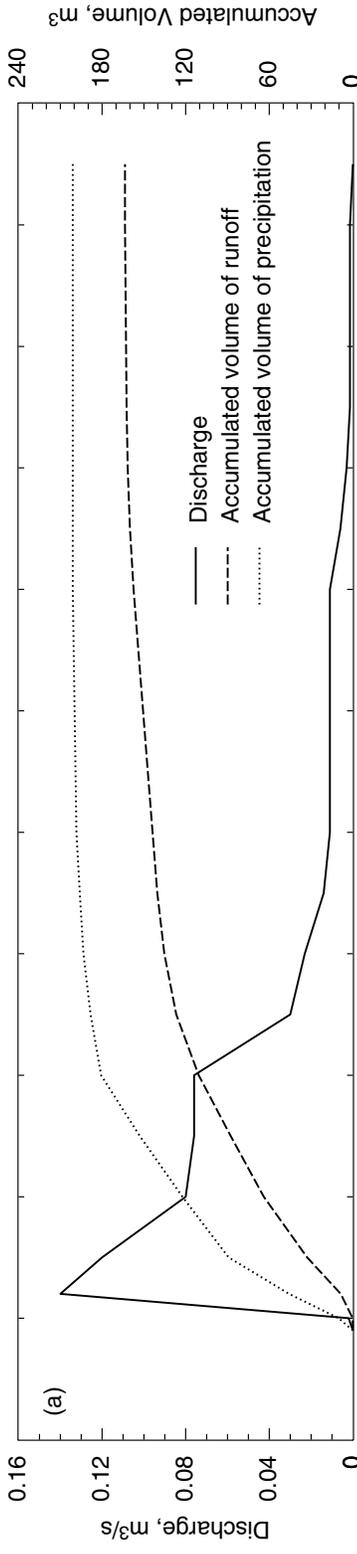
Fifteen VOCs were detected in one or more discrete particulate samples. Most of the detected VOCs are gasoline-related compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX compounds). Eight of the 15 VOCs were detected in more than 50% of the samples and, except for benzene, in one or both of the composite samples (Table 1). The *m* and *p* isomers of xylene could not be separated by the analytical technique. Consequently, the sum of the concentrations of these isomers is given in table 1. The seven VOCs detected in less than 50% of the samples included propylbenzene, 1,3,5- and 1,2,4-trimethylbenzene, n-butylbenzene, 2-methylnaphthalene, methyl butyl ketone (MBK), and 1,4-dichlorobenzene. The highest concentrations occurred near the outlet of the culvert where most cars are parked. Mean concentrations of VOCs, calculated assuming non-detections were zero, have large standard deviations and generally are greater than concentrations measured in composite samples. The difference could be due to greater loss of VOCs from the composite samples because they were exposed more during compositing, not taking representative aliquots from discrete samples due to settling of fine-grained particles, or both. Thus, mean concentrations are assumed to represent best average concentrations of VOCs in particles. Acetone had the highest mean concentration. Acetone is emitted in vehicle exhaust (Kirchstetter et al., 1996; Schauer et al., 1999) and also is an important by-product from the reaction of organic compounds (Ciccioli, 1993). The total mass of particles on the parking lot was estimated by multiplying the mean particulate density ( $7.0 \text{ g/m}^3$ ) by the parking lot area ( $10,030 \text{ m}^2$ ). This product was multiplied by the mean VOC concentrations and a conversion factor to obtain the masses of VOCs in particles ( $VOC_{particle}$ ).

Particles from oily areas had higher organic carbon content (6.80 and 8.75%) than other sites (<2.50%). Most Spearman rank correlations between VOCs and organic carbon in particles were not statistically significant ( $\alpha = 0.05$ ). VOCs that were significantly correlated with organic carbon included naphthalene, 1,3,5-trimethylbenzene,

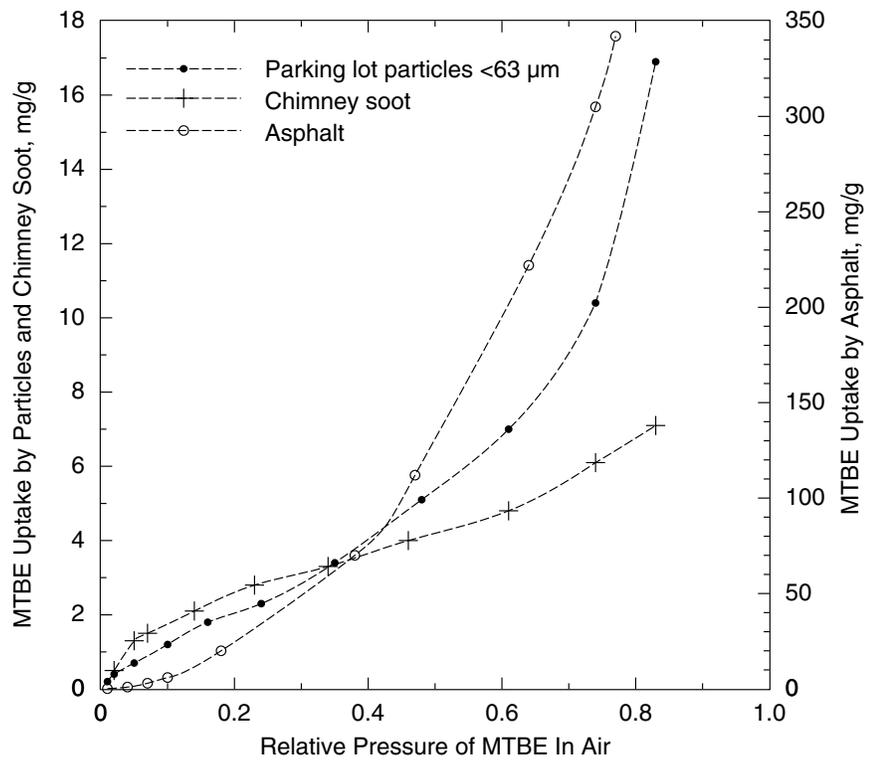
MBK, and methyl isobutyl ketone (MIK) (Fig. 1a,b). In general, sorption is inversely related to water solubility (Mackay et al., 1992). Consequently, it is unusual that the soluble ketones, but not the more hydrophobic BTEX compounds, were correlated with organic carbon. Lack of a correlation between certain VOCs and organic carbon could be due to VOCs concentrating mainly in certain organic fractions (e.g. oil and grease, vehicle soot).

The wire brush did not efficiently sweep fine-grained particles from crevices in the parking lot and may have abraded the asphalt. The composite sample was 75% medium sand (250  $\mu\text{m}$ ) and coarser. The coarse grain size also could be due to non-representative aliquots taken from discrete samples and oil and grease binding small particles into large aggregates. Nitrogen BET surface area was not measurable for particles between 125 and 250  $\mu\text{m}$ . The BET surface area was 0.04  $\text{m}^2/\text{g}$  for particles between 62.5 and 125  $\mu\text{m}$  and 0.12  $\text{m}^2/\text{g}$  for particles less than 62.5  $\mu\text{m}$ . The BET surface areas for these fractions are low, which could be due to oil and grease coatings reducing surface roughness.

The uptake isotherm of MTBE on particles <63  $\mu\text{m}$  (Fig. 2) indicates two sorption mechanisms with the dominant mechanism depending on the relative pressure of MTBE in the air. The varying dominance could be due to MTBE sorbing into different fractions of the complex mixture of organic particles. At low pressures of MTBE, the uptake curve for particles is similar to the isotherm for chimney soot, which indicates a site-specific interaction between MTBE and a particulate component similar to soot. The non-linearity of the isotherms (and corresponding high distribution coefficients) observed at low vapor pressure for MTBE on chimney soot and parking lot particles suggests that soot particles contribute more to the total sorption of MTBE than their fraction of the total mass might suggest. This also suggests a mechanism for dry deposition of MTBE from the atmosphere. Although MTBE was not detected during this study, most VOCs partition into organics to a greater extent than MTBE (Mackay et al., 1992). Thus, dry deposition likely is a mechanism for concentrating other VOCs. At higher pressures, the curve is similar to the isotherm for asphalt, which indicates infinite dissolution of MTBE into asphalt and oil and grease in particles. However, these pressures are much higher than those in urban air, indicating transfer of MTBE from air to asphalt is not an important mechanism. Solubilization of VOCs into asphalt would only be important in the case of fuel spillage. Similarly, solubilization of VOCs into oil and grease could be important if gasoline dissolves into



August 16, 1998



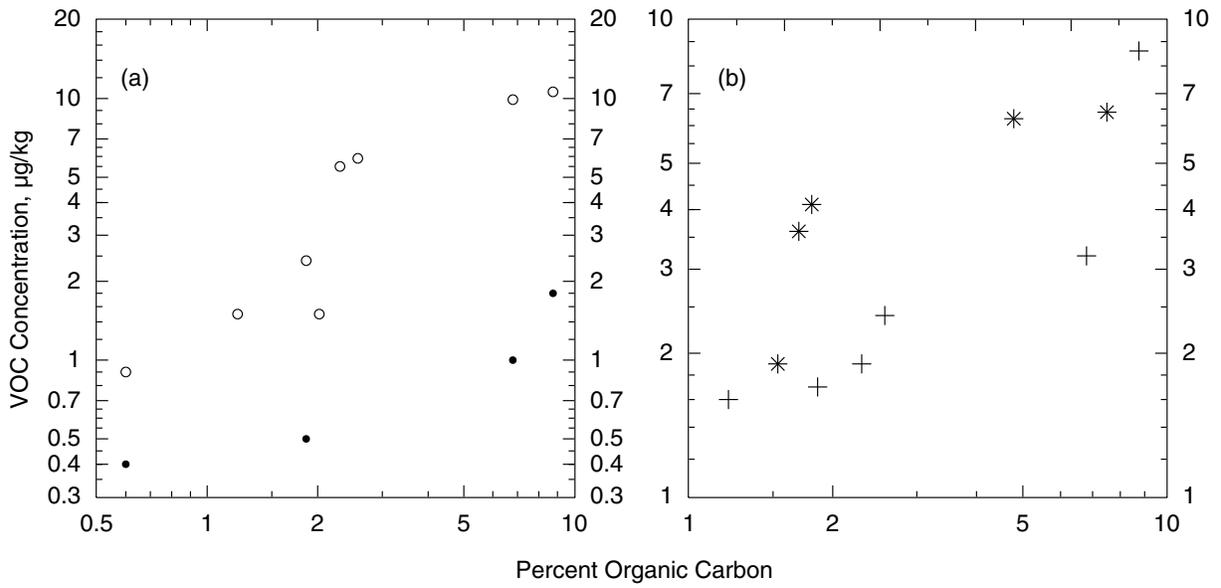
motor oil in a vehicle's engine and the oil drips onto the parking lot surface. In this case, oil and grease spots on the parking lot could be storage reservoirs for VOCs.

Eight VOCs were detected in particulate water extracts (Table 2). Except for *o*-xylene, VOCs were detected in both extracts and have similar concentrations. Except for 1,2,4-trimethylbenzene and MEK, the VOCs detected in the extracts were detected in >50% of particulate samples (tables 1,2). Estimated extract concentrations were compared to measured concentrations to determine the amount of the VOCs desorbed from particles. Estimates were calculated using mean particulate concentrations (Table 1), the volume of the 125-ml bottles, and by assuming a sediment density of 2 g/cm<sup>3</sup> and 100% desorption. When completely full, the bottles actually hold 128 ml. Percent recovery ranges from 0 to 185% and is significantly correlated with water solubility (rank correlation 0.92). Results indicate that VOCs with solubilities less than about 600 mg/L do not completely desorb from particles in acidified water. The more soluble VOCs (i.e. acetone, MIK) may quickly desorb from impervious areas during the first part of a storm, whereas less soluble VOCs (i.e. toluene) may continually desorb throughout the storm. Desorption of the least soluble VOCs (i.e. xylenes, naphthalene) may be too little and/or so slow that they aren't detected in stormwater.

### **VOCs in precipitation**

About two-thirds of the precipitation and runoff on August 16, 1998, occurred within the first 20 minutes of the storm (Fig. 3a). Consequently, only two samples of precipitation were collected that had sufficient water for chemical analysis. Toluene, acetone, MEK, and chloroethane were detected in the first sample (Table 3). Only acetone was detected in the second sample. Fewer detections in the second sample could be due to a first flush of VOCs in the atmosphere. It is unlikely that the fewer detections were due to the low scavenging efficiency of raindrops during high rain intensity (Ferronato et al., 1998) because rainfall intensity had decreased when the second sample was collected. Concentrations in precipitation were greatest for the soluble ketones (acetone and MEK).

The mass of VOCs in precipitation was estimated by multiplying VOC concentrations by the volume of precipitation and a conversion factor to obtain micrograms of VOCs ( $VOC_{precip}$ ). The first sample was assumed to represent precipitation from 07:50 to 07:54 a.m. and the second sample represents precipitation from 07:55 to 08:05



EXPLANATION

- MIK, rank correlation 0.96
  - 1,3,5-TMB, rank correlation 1.0
- + Naphthalene, rank correlation 1.0
  - \* MBK, rank correlation 1.0

a.m. Based on the extract data showing 100% desorption, acetone during the remainder of the storm was assumed to be from precipitation with a mean concentration equal to the mean concentration in stormwater from 08:15 to 09:15 a.m. (13.8 µg/L).

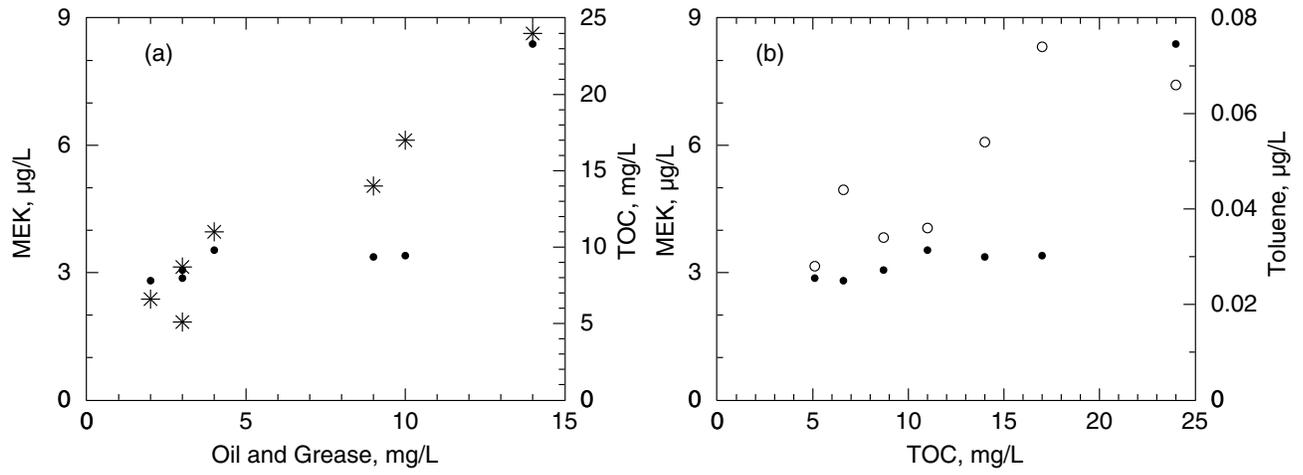
### **VOCs in stormwater**

The first stormwater sample was collected 5 minutes after precipitation began and had eight detected VOCs. Only benzene, toluene, acetone, and MEK were detected in all stormwater samples (table 4). Other VOCs detected in the first sample included MIK, MBK, chloromethane, and styrene. The mass of VOCs was estimated by multiplying concentrations by the volume of stormwater and a conversion factor to obtain micrograms of VOCs ( $VOC_{stormwater}$ ). The volume of precipitation that fell on the parking lot was 200.6 m<sup>3</sup> and the volume of stormwater discharged from the parking lot was 163.7 m<sup>3</sup>. The runoff coefficient of 0.82 is within the range of 0.7 to 0.95 reported for asphalt surfaces (Novotny, 1995).

Concentrations of benzene, toluene, acetone, MEK, oil and grease, and total organic carbon generally were greatest in the first sample (Fig. 3b,c). The greater number of detections and high concentrations in the first sample could be due to the high VOC concentrations in particles near the outlet of the culvert. During the latter half of the period of runoff, concentrations of toluene, MEK, oil and grease, and total organic carbon increased, whereas concentrations of benzene and acetone remained fairly constant. Correlations were statistically significant between oil and grease and MEK and total organic carbon (Fig. 4a), and between total organic carbon and MEK and toluene (Fig. 4b). These correlations indicate that MEK was associated with both organic fractions, whereas toluene was associated with a fraction of organic carbon other than oil and grease. After the first flush, the constant concentration of acetone could be due to the atmosphere being the only source. However, the constant concentration of benzene is difficult to explain because benzene was not detected in precipitation and benzene did not correlate with total organic carbon or oil and grease.

### **Mass balance of VOCs**

Mass balances were calculated for benzene, toluene, acetone, and MEK because they were consistently detected in stormwater (Table 4). All concentrations of benzene and toluene in stormwater were estimated values (Table 4);



EXPLANATION

- \* Total organic carbon (TOC), rank correlation 0.94
- MEK, rank correlation 0.86
- Toluene, rank correlation 0.86
- Methyl ethyl ketone (MEK), rank correlation 0.88

however, Lopes et al. (2000) found the mean error in estimated values is small (7.4%). The mass of VOCs flushed from the impervious area was calculated by subtracting the mass of VOCs in precipitation and particles from the mass in stormwater. Results indicate that the atmosphere and impervious areas are important sources for VOCs with each being important for different VOCs. Acetone was detected in particles and particulate extracts, and a prominent first-flush of acetone was observed in stormwater. However, particles and impervious areas are negligible sources of acetone compared to precipitation scavenging acetone from the atmosphere (Table 5). In contrast, essentially 100% of benzene is from the impervious area, and about 50% of toluene and MEK are from the impervious area and the atmosphere. Coarse particles are a negligible source of all VOCs. However, fined-grained particles are not easily swept with a wire brush and could account for a substantial amount of the VOCs from the impervious area.

## CONCLUSIONS

This study demonstrated that a mass balance approach is a useful means of understanding non-point-source pollution, even for contaminants such as VOCs, which are difficult to sample. For a selected asphalt parking lot without point sources, the parking lot surface and the atmosphere are important sources but for different VOCs. The atmosphere is an important source of soluble, oxygenated VOCs, and the parking lot surface is an important source for the more hydrophobic VOCs. VOCs on the parking lot surface appear to be concentrated in oil and grease, soot, and other components that comprise the complex mixture of organic material in urban particles. Except in the case of spills, asphalt does not appear to be an important source of VOCs. The uptake isotherm of MTBE on urban particles suggests a site-specific interaction between MTBE and a particulate component similar to soot. This also suggests a mechanism for dry deposition of VOCs from the atmosphere. Additional studies are needed to confirm these results and to determine how temperature, surface type (e.g. concrete), presence of gasoline stations, and other factors affect the results. Studies also are needed to develop a method of directly measuring  $VOC_{ia}$  and to determine whether VOCs are associated with fine-grained particles, vehicle soot, oil and grease, or asphalt, and the mechanisms of concentrating VOCs on land surface (e.g. dry deposition, gasoline dissolved in oil and grease, gasoline leaks from motor vehicles). Although this is but one study, results suggest that VOC concentrations in stormwater from parking lots without obvious point sources and in precipitation may be too low ( $<0.1 \mu\text{g/L}$ ), except for ketones, to explain concentrations measured in urban stormwater (Delzer et al., 1996), streams and rivers (Reiser and O'Brien, 1998; Lundgren and Lopes, 1999), and ground water (Squillace et al., 1996 and 1999; Stackleberg et

al., 1998). VOCs detected during these studies likely were from point sources that had been dispersed or possibly non-point sources with higher concentrations in industrial and commercial land uses. One way of protecting source-water quality is through improved prevention and containment of releases from point sources.

**APPENDIX I. REFERENCES**

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Table 1. VOCs in particles from the parking lot [OC, organic carbon; TMB, trimethylbenzene; MBK, methyl butyl ketone; MIK, methyl isobutyl ketone; NA, not analyzed or does not apply; <, less than the minimum detection limit (Hiatt, 1995); std dev, standard deviation; NC, statistics and mass not computed due to <50% detection]

Site Description	Particle density	OC	Benzene	Toluene	Ethyl benzene	<i>m+p</i> Xylene	<i>o</i> -Xylene	Naphthalene	1,3,5-TMB	Acetone	MBK	MIK
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
Particle density, in g/m <sup>2</sup> , organic carbon, in percent, and VOC concentration, in µg/kg												
Flat area	2.8	1.86	0.5	3.1	1.4	2.9	1.2	1.7	0.5	79.7	1.9	2.4
Flat area	3.0	NA	<0.1	0.7	<0.2	0.4	0.2	<0.3	0.4	80.0	<1.4	0.8
Flat area	2.6	2.02	<0.1	<0.2	<0.2	<0.2	0.2	<0.3	<0.3	7.9	<1.4	1.5
Flat area	5.0	NA	<0.1	<0.2	<0.2	<0.2	<0.2	<0.3	<0.3	<2.7	<1.4	<0.7
Oily flat area	7.8	6.80	0.2	0.8	0.9	1.7	1.0	3.2	1.0	13.7	6.2	9.9
Oily flat area	7.6	8.75	1.0	6.6	2.6	7.6	2.5	8.6	1.8	47.1	6.4	10.6
Oily, dry puddle	6.9	NA	0.5	1.7	0.5	1.5	0.5	7.0	<0.3	59.3	<1.4	1.8
Dry puddle	9.0	NA	<0.1	1.7	0.6	1.2	0.4	0.7	0.4	58.7	<1.4	1.8
Dry puddle	11.8	NA	<0.1	0.8	0.3	0.6	0.2	0.4	<0.3	45.7	<1.4	<0.7
Dry puddle	16.0	NA	<0.1	1.2	0.5	1.0	0.5	0.4	<0.3	136.1	<1.4	<0.7
Dry puddle	15.6	0.60	0.4	1.1	0.5	0.9	0.4	<0.3	0.4	45.8	<1.4	0.9
Dry puddle	3.0	NA	0.6	2.6	1.2	2.7	1.2	2.0	0.5	145.9	<1.4	1.1
Dry puddle	5.7	1.21	0.5	2.6	1.1	3.0	0.7	1.6	<0.3	170.9	<1.4	1.5
Dry puddle	5.8	NA	0.3	0.7	<0.2	0.4	<0.2	<0.3	<0.3	48.3	<1.4	<0.7
Dry puddle	2.7	2.46	0.3	1.5	<0.2	1.0	0.6	<0.3	<0.3	<2.7	<1.4	<0.7
Mean	7.0	3.38	0.3	1.7	0.6	1.7	0.6	1.7	NC	62.6	NC	2.2
Std dev	4.4	3.11	0.3	1.6	0.7	1.9	0.6	2.7	NC	52.7	NC	3.4
Composite #1	NA	2.57	<0.1	0.7	0.3	1.2	<0.2	2.4	<0.3	8.2	4.1	5.9
Composite #2	NA	2.30	<0.1	1.0	0.8	1.1	0.7	1.9	<0.3	18.0	3.6	5.5
Estimated mass of VOCs in particles from the parking lot, in µg												
NA	NA	NA	21	120	42	120	42	120	NC	4,400	NC	150

Table 2. VOCs in particulate water extracts [TMB, trimethylbenzene; MEK, methyl ethyl ketone; MIK, methyl isobutyl ketone; e, estimated value; <, less than the minimum detection limit (Connor et al., 1998); NC, not computed due to < 50% detection in particles]

Composite sample	Benzene	Toluene	Ethyl benzene	<i>m+p</i> -Xylene	<i>o</i> -Xylene	1,2,4-TMB	Naphthalene	Acetone	MEK	MIK
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Composite #1	e0.11	e0.33	<0.12	e0.15	e0.067	e0.051	<1	e17	e4.9	e1.1
Composite #2	e0.11	e0.31	<0.12	e0.13	<0.256	e0.042	<1	e27	e5.0	e1.2
Average	0.11	0.32	<0.12	0.14	0.034	0.046	<1	22	5.0	1.2
Estimated average	0.09	0.50	0.21	0.47	0.18	NC	0.50	19	NC	0.65
VOC concentration, in µg/L										
Percent recovery	122	64	0	30	19	NC	0	116	NC	185
Water solubility	1,800	550	170	180	180	60	30	miscible	228,000	19,000
Percent recovery and water solubility in mg/L at 25°C										

Table 3. VOCs in precipitation [MEK, methyl ethyl ketone; e, estimated value; <, less than the minimum detection limit (Connor et al., 1998)]

Sampled time interval	Sampled precipitation interval, cm	Toluene	Acetone	MEK	Chloroethane
(1)	(2)	(3)	(4)	(5)	(6)
VOC concentration, in µg/L					
07:50-07:52	0.00-0.46	e0.05	e24	e5.0	e0.10
07:58-08:03	1.02-1.37	<0.216	e22	<6.6	<0.48
Estimated mass of VOCs, in µg					
Time interval	Precipitation, cm	Toluene	Acetone	MEK	Chloroethane
07:50-07:54	0.76	3,800	1,800,000	380,000	7,600
07:55-08:05	0.76	0	1,700,000	0	0
08:06-09:20 <sup>a</sup>	0.48	0	670,000	0	0
Total	2.00	3,800	4,170,000	380,000	7,600

<sup>a</sup>, mass estimated from mean concentration of acetone of 13.8 µg/L in stormwater from 08:15 to 09:15

Table 4. VOCs in stormwater [MEK, methyl ethyl ketone; TOC, total organic carbon; e, estimated value; NA, not analyzed]

VOC concentration, in $\mu\text{g/L}$ , and oil and grease and TOC, in $\text{mg/L}$							
Sample time	Sample type	Benzene	Toluene	Acetone	MEK	Oil and grease	TOC
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
07:55	Runoff	e0.029	e0.066	45.4	8.39	14	24.0
08:00	Runoff	e0.021	e0.036	18.3	3.53	4	11.0
08:15	Runoff	e0.017	e0.028	13.9	2.87	3	5.1
08:30	Runoff	e0.021	e0.044	13.6	2.81	2	6.6
08:45	Runoff	e0.017	e0.034	13.7	3.06	3	8.7
09:00	Runoff	e0.020	e0.054	15.5	3.37	9	14.0
09:12	Replicate	e0.019	e0.068	e16.0	e3.2	NA	NA
09:15	Runoff	e0.019	e0.074	12.3	3.4	10	17.0

Estimated mass of VOCs, in $\mu\text{g}$ , and oil and grease and total organic carbon, in $\text{mg}$							
Time interval	Runoff ( $\text{m}^3$ )	Benzene	Toluene	Acetone	MEK	Oil and grease	TOC
07:40-07:55	32.85	950	2,200	1,500,000	280,000	460,000	790,000
07:55-08:10	77.88	1,600	2,800	1,400,000	270,000	310,000	860,000
08:10-08:25	29.74	500	830	410,000	85,000	89,000	150,000
08:25-08:55	19.54	410	860	260,000	55,000	39,000	130,000
08:55-09:05	2.55	51	1,000	300,000	66,000	180,000	270,000
09:05-09:20	1.13	21	84	14,000	3,800	11,000	19,000
Total	163.69	3,532	7,774	3,884,000	759,800	1,089,000	2,219,000

Table 5. Mass balance of VOCs [mass is in µg; MEK, methyl ethyl ketone]

VOC	Mass in stormwater (2)	Precipitation		Particles		Impervious area	
		Mass (3)	Percent of mass in stormwater (4)	Mass (5)	Percent of mass in stormwater (6)	Mass (7)	Percent of mass in stormwater (8)
Benzene	3,532	0	0	21	<1	3,511	99
Toluene	7,774	3,800	49	120	1	3,854	50
Acetone	3,884,000	4,170,000	107	4,400	<1	0	0
MEK	759,800	380,000	50	0	0	379,800	50

**Figure Caption**

Figure 1. Statistically significant relations between VOCs and organic carbon in particles from the parking lot (MIK, methyl isobutyl ketone; 1,3,5-TMB, 1,3,5-trimethylbenzene; MBK, methyl butyl ketone).

Figure 2. Uptake of gaseous methyl tert-butyl ether (MTBE) by solid phases as a function of the relative pressure of MTBE.

Figure 3. (a) Discharge and accumulated volumes of runoff and precipitation and (b and c) concentrations of selected constituents in stormwater as functions of time.

Figure 4. Statistically significant relations between VOCs, oil and grease, and total organic carbon in stormwater.