RECONAISSANCE STUDY OF SEALCOAT APPLICATION IN TORONTO, CANADA AND AN ESTIMATE OF RELATED PAH EMISSIONS

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Introduction

Several years ago the United States Geological Survey (USGS) identified coal tar sealcoat (CTS) as a significant source of PAH in urban runoff and urban surface waters[1]. The reports concluded that CTS is likely used in urban residential driveways and small commercial and residential parking lots[2]. The low cost and availability of CTS through major retail outlets has made this product an easy choice for consumers.

The use of coal tar sealcoats (CTS) results in elevated concentrations and loadings of PAH to urban surface waters as the CTS is abraded from pavement surfaces[1 3]. This result was confirmed in several studies[4 5 6] and is also intuitively obvious since product manufacturers recommend recoating pavements every 2-5 years. PAHs are also released from CTS-coated pavement via volatilization[7].

CTS has been discovered to be a significant source (i.e., ~50%) of PAH to urban surface waters by tracing sources of PAH. Van Metre and Mahler and co-workers[8 1] noted the rise in PAH concentrations in urban surface waters around the US correlated with the rise in vehicle miles travelled. Later studies identified that CTS was contributing to PAH loadings in cities east of the continental divide, in addition to vehicle emissions[9]. The significance of the continental divide arose from the availability of coal tar residues in the east from coking sources, versus asphalt residues in the west from oil production.

Recent work by Diamond and co-workers has yielded loading estimates of roughly 2200 kg y^{-1} of total PAH to nearshore Lake Ontario from the Toronto area, most of which originates from urban tributaries[10]. The importance of impervious surface materials has previously been ignored, whilst over the past 10 years research has begun to acknowledge the impact of various surface materials and use of the products on the wider environment. Sealcoats are also known to be a potential source to the indoor environment due to tread in occurring from the outdoors[11].

This study reports the concentrations of PAHs identified in surface materials collected from the Toronto, CA region. These data are compared via the different source apportionment in each sample, and used to examine the importance of CTS use across an urban region in comparison to the impact from more widely used asphalt materials. Variations were recorded across the city with the majority of samples falling under four main categories including CTS, asphalt sealcoats (AS), asphalt, and other material. A fugacity model is also used to assess the main transportation mode for the PAHs from the sealcoat into other environmental matrices[12].

Materials and Method

Sampling Strategy - Surface scrapings (n=92*)* were taken from parking lots and driveway locations within the Greater Toronto Area (GTA), Canada between February – March 2011. These consisted of commercial parking lots (n=47) and private residential driveways (n=45). Samples were taken by sectioning a 0.25 m^2 surface area, scraped using a stainless steel paint scraper[1], and the particulate material brushed and collected in a dichloromethane (DCM)cleaned glass vial. The samples were collected from dry surfaces, visually free of debris, snow, salt and oil/fuel stains.

Analytical Procedures - Samples were weighed and extracted in DCM (15 mL) via shaking for 10 seconds, followed by ultra-sonication for 20 minutes; the eluent was removed to a DCM cleaned bottle (15 mL). This process was repeated until the eluent remained clear (a sign of the removal of all present binder)[13]. The samples were then stored at -18°C until ready for the conditioning column, and the remaining residual sample contents (the part which was not soluble) were allowed to air dry and were re-weighed (residual fraction).

Samples taken from the raw commercial emulsion were analysed for the PAH content in both wet emulsion and dried emulsion. Wet emulsion (ca. 1.5 g) was dissolved in acetone (140 mL) and sonicated, an aliquot (1 mL) was removed and made up with DCM (10 mL) (9:1 DCM:acetone). The dried emulsion (ca. 0.2 g) was extracted according to the scraping method, DCM extracted (same procedure as the samples), with pre and post weight measurements acquired. Both commercial mixtures contained approximately 50 % solid materials.
The extract was then applied to preconditioned columns containing alumina (8 g), anhydrous silica gel (4 g), and sodium sulphate (1 g). The extract (1 mL) was used and eluted with DCM (30 mL) into round bottom flasks. Samples were then solvent exchanged into hexane via rotary evaporation, further reduced under a stream of nitrogen and exchanged into nonane. The final volume was 200 µL (including the addition of the recovery determination standard (RDS) – *p*-terphenyl).

Results and Discussion

The presence of PAHs and quinoline were detectable in 100 % of the samples analysed and results are available in the appendix and summarized results in *Table 1*. Samples containing coal tar based sealants were identified and differentiated by a number of methods. Initially the samples were identified by their high content of PAHs, and then by the presence of PAH ratios and summed concentrations (indeno[1,2,3-cd]pyrene: benzo[ghi]perylene, benzo[a]pyrene: chrysene, Σ(benz[a]anthracene + chrysene) vs. Σ(fluoranthene + phenanthrene), see *Figure 1* following this the PAH sample signatures were compared with known source fingerprints using PCA and the EPA CMB model 8.2[14]. This has allowed 21 samples from the entire data set to be identified as coal tar sealants. The remaining samples contained PAH concentrations, but at lower sum concentrations, and PAH concentrations were not always present for all compounds. The remaining samples indicated the presence of PAHs in asphalt sealcoats and asphalt coverings, as well as the presence of urban dust contamination in some of the samples. The samples were separated into four subcategories (*Figure 2*) for better representation of the source and type of material in the sample.

Concentrations (ng g^{-1}) of:	Mini-mum	5th Percentile	Median	Mean	95th Percentile	Maximum	SD	RSD (%)
Naphthalene	N.D.	0.3	29	130	550	2 400	330	250
Quinoline	0.2	3.5	63	130	410	1 700	210	170
Acenaphthylene	N.D.	0.2	5.5	700	3 600	28 000	3 100	450
Acenaphthene	N.D.	0.5	5.0	2 400	12 000	78 000	11 000	450
Fluoranthene	N.D.	0.7	11	2 400	8 700	101 000	11 000	470
Phenanthrene	0.7	6.0	59	27 000	190 000	630 000	83 000	3100
Anthracene	3.5	8.1	140	30 000	170 000	1 300 000	150 000	490
Fluoranthene	2.8	15.0	160	87 000	440 000	2 300 000	300 000	340
Pyrene	4.7	23.0	650	710 000	1 400 000	35 000 000	4 000 000	570
Benz(a)anthracene	1.3	5.0	240	270 000	720 000	11 000 000	1 400 000	540
Chrysene	2.6	7.0	380	430 000	880 000	20 000 000	2 400 000	560
Benzo[b]fluoro-anthene & benzo[j] fluoroanthene	2.2	10	720	790 000	4 100 000	29 000 000	3 700 000	470
Benzo(k)-fluoranthene	2.7	12	410	410 000	1 200 000	2 000 000	2 000 000	500
Benzo(a)pyrene	2.4	10	350	570 000	760 000	2 800 000	2 800 000	490
Indeno(1,2,3-cd) pyrene	N.D.	5.3	330	83 000	260 000	370 000	370 000	450
Benzo[ghi]-perylene	N.D.	4.2	250	200 000	320 000	1 000 000	1 000 000	510
Dibenzo[a,h] anthracene	N.D.	1.7	47	5 900	4700	29 000	29 000	490

Table 1: Surface Scraping Concentrations (ng g^{-1})

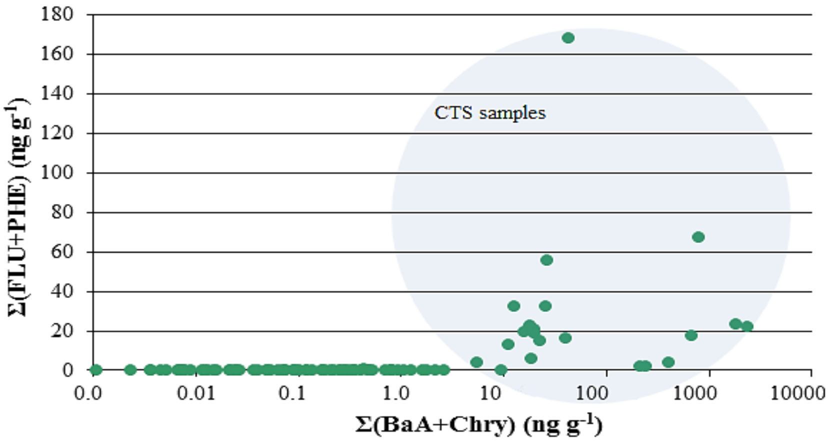

Figure 1: Comparison of the sum concentrations of benz[a]anthracene and chrysene, fluorene and phenanthrene, the shaded area indicating samples containing CTS (ng g^{-1})

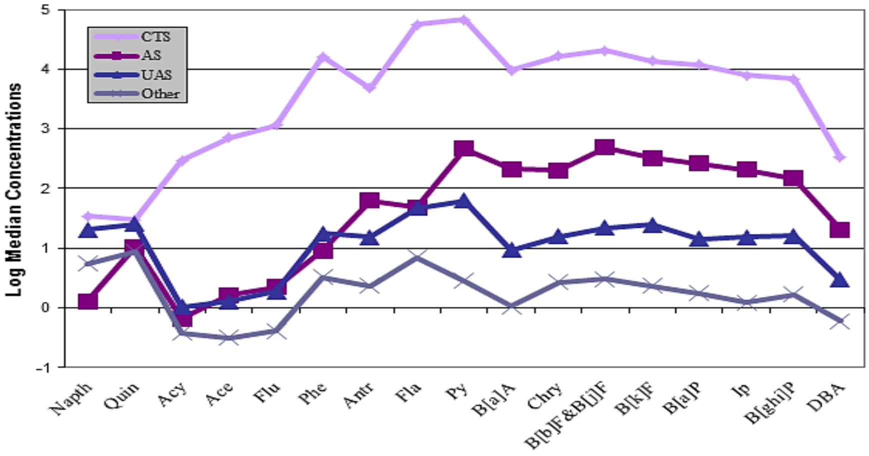

Figure 2: Comparison of subcategory concentrations for individual median PAH concentrations

The ratio of benz[a]anthracene:chrysene was positively correlated with indeno[1,2,3-cd]pyrene:benzo[ghi]perylene with high ratio values being indicative of CTS and, as the ratio values decreased, the profile of materials changed also from CTS>asphalt sealcoats>asphalt>concrete.

The coal tar samples have much greater concentrations of PAHs than identified in the AS and asphalt samples, which is due to the CTS material containing 1 – 2 orders of magnitude greater concentrations of PAHs in the raw material. The results indicate that the CTS is a source to urban surface waters of the lower molecular weight compounds as well as the higher molecular weight ones, due to the retention of these more volatile compounds in the binding material. The concentrations in the asphalt based samples show much lower concentrations and presence of the lower molecular weight PAHs, due to volatilization.

Previous assessments of PAHs in urban surface waters from the US[1 4] have identified sealcoats to be a major source. However, the analysis has not been focused on the other potential pathways from the sealcoats to the wider environment. Conducting a modelled assessment using the fugacity based multimedia urban model (MUM)[12], the model indicated that the major loss of PAHs from the sealcoats is to the urban surface water via wash-off events, particularly for regions with highly variable climates. Limitations of the model are introduced by the assumptions that have to be made, which produce a significant degree of variability when predicting the PAHs in urban surface waters that are potentially derived from sealcoats, and therefore values could not be accurately determined.

Conclusions

PAH concentrations in sealcoats used across the Toronto area are raised in comparison to uncoated asphalt and concreted areas of driveways and parking lots. From the modelled results there a potentially substantial contributions from the use of sealcoats and PAH surface water concentrations. Thus, this study indicates that the use of sealcoats in urban areas should be considered as an important source of PAH to urban surface waters.

The impervious surfaces used within urban environments are extensive, and must be recognised as a potential source of pollutants to the environment. Research in the UK[15] and US[16] into the use of recycled materials (include building materials, fly ash, fibreglass waste) and their incorporation into concrete may lead to further introduction of new POP sources arising from impervious surfaces.

Assumptions of the parameters in the modelling contribute to a high variability within the results, and thus is not an accurate assessment of the sealant PAH contribution to urban surface waters. However, the model is able to conduct the analysis of the likely pathways of PAHs derived from the sealcoats and indicates that the major pathway is into the urban surface water.

Acknowledgments

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References

1. Mahler, B. J., Van Metre P. C., *et al.,* 2005. Environ. Sci. Technol. 39, 5560-5566.
2. EHS (Environmental Health Strategies) 2010. Final Report Prepared for Products Division, Chemical Sectors, Environmental Stewardship Branch, Environment Canada.
3. Van Metre, P. C., Mahler, B. J., 2010. Sci. of Total Environ. 409, 334-344.
4. Van Metre, P. C. V., Mahler, B. J., et al., 2008. Environ. Sci. Technol. 43, 20-25.
5. Watts, A. W., Ballestero, T. P., et al., 2010. Environ. Sci. Technol. 44, 8849-8854.
6. Ahrens, M. J., Depree, C. V., 2004. Marine Pollution Bulletin, 48, 341-350.
7. Van Metre, P. C. *et al*., 2010 SETAC presentation
8. Van Metre, P. C., and Mahler, B. J., *et al.*, 2000. Environ. Sci. Technol., 39, 4064-4070.
9. Van Metre, P. C., Mahler, B. J., et al., 2009. Environ. Sci. Technol. 43, 20-25.
10. Diamond, M. L., Helm, P., Robson, M., Csiszar S.A., Melymuk, L., 2010. Final Report to Great Lakes Commission.
11. Mahler, B. J., Van Metre, P. C., Wilson, J. T., Musgrove, M., Burbank, T. L., Ennis, T. E., Bashara, T. J., 2010. Environ. Sci. Technol., 44, 894-900.
12. Diamond, M.L., Melymuk, L., Csiszar, S.A., Robson, M., 2010. Environ. Sci. Technol. 44, 2777-2783.
13. Ahrens, M. J., Depree, C. V., 2010. Chemosphere, 81, 1526-1535
14. Li, A., Jang, J.K., Scheff, P.A., 2003. Environ. Sci. Technol. 37, 2958-2965
15. Goosey, M.T., 1999. Plastics for Electronics, 2nd Ed. Ch 4, pp 123-124, Kluwer, Dordrecht, The Netherlands. ISBN 0-412-72560 6
16. Portland Cement Association, 2011. www.cement.org/tech/cct_aggregates_recycled.asp