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Preliminary Analysis of the Impact of Cold Mix Asphalt Concretes on Air and Water Quality

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Cold-mixed asphalt concretes are common roadway pavement repair materials. Their use is often dictated by the unavailability of a hot-mix asphalt manufacturing plant in the vicinity of a project. Cold-Mixed asphalt concretes consist of aggregates and asphalt binder treated to allow mixing without heating such as in a hot mix asphalt concrete plant. This is made possible through either solvents, such as gasoline, or a combination of water and emulsifying agents, such as saponized tannins or amins. The resulting products are broadly referred to as cut-backs and emulsions, respectively. These are used in a variety of paving maintenance applications, ranging from pot-hole filling and patching to thin surface treatments. Cut-backs are used primarily for pot hole filling and patching, while emulsions are used primarily for surface treatments. Cut-backs harden through the evaporation of the solvent into the air. Emulsions harden through the evaporation of water and the emulsifying agent. The size of the market for cut-backs and emulsions is considerable. A 2001 Usage Survey conducted by the Asphalt Institute revealed 369,500 tons and 1,886,700 tons of binder, (i.e., excluding the aggregates), respectively. Hence, there is a sizeable market for cold-mixed asphalt concretes and their use can have significant environmental implications.

Understanding the mass loading of asphalt constituents into the environment and associated health risks continues to be a major challenge for occupational and environmental health scientists (Melius, 2003). Atmospheric emissions from hot mix asphalt concretes plants have been extensively characterized (EPA 454/R-00-019, EPA 454/R-00-029 and EPA/454/R-00/030). Little is known, however, about the associated health implications of these emissions, particularly from a chronic health standpoint. These atmospheric emissions may include various organic compounds, including polycyclic aromatic hydrocarbons (PAHs) which represent a large class of suspected carcinogens (Ma et al., 2003). In contrast to atmospheric emissions, relatively little is known with regard to the constituents in non-point source runoff originating from hot mix asphalt surfaces. Constituents of interest that pose potential toxic effects to benthic biota include selected trace elements, PAHs, and organochlorine compounds (Azizian et al., 2003; Van Metre et al., 2000; MacDonald et al., 2000).

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To date, there is little independent study of emissions and associated toxicity of cold-mixed asphalt products. One approach in assessing potential emissions and associated toxicity would be to focus on the individual constituents in each product. However, the increasing practice of incorporating recycled and waste products into these cold-mixed asphalt products has expanded the chemical composition and overall complexity of its constituents. Some cold-mixed asphalt products incorporate large percentages of recycled materials, including recycled hot mix asphalt and waste products such as rubber tires or roofing shingles (Azizian et al 2003). In the study reported herein, we present the first independent analyses of potential environmental impacts of cold-mixed asphalt concrete products. Six of the most commonly used and commercially available cold-mixed asphalt concretes were tested for heavy metal leachates, solid waste toxicity, reactivity, ignitability, corrosivity, and air emissions Study of the engineering properties of these cold-mixed asphalt concretes is reported elsewhere (Papagiannakis et al, 2004).

MATERIALS AND METHODS

Potentially, there are hundreds of analytical techniques that can be used to assess the environmental impact of cold-mixed asphalt concrete. In an attempt to narrow these analytical techniques to a manageable number, we sought input from key personnel in regulatory agencies and organizations within the state of California (CA) under the premise that if CA accepted the analyses, other states would follow suit. The regulatory community in CA does not certify products, so the suggestions provided reflect the individuals' knowledge of potential environmental issues of cold-mixed asphalt concrete products. Personal communication with the California Department of Toxic Substances Control (Mr. *David Miller*) and with the California South Coast Air Quality Management District (Mr. *Scott Wilson*) led to the selection of a number of analytical techniques employed in CA for Hazardous Material classification. In addition, they directed us to a list of State certified labs within CA that could perform these types of tests. From this list, we selected *Zalco Laboratories Inc.* of Bakersfield, CA (*Zalco*), to perform the tests related to the hazardous material classification, (i.e., heavy metal leachates, solid waste toxicity, reactivity, ignitability, and corrosivity).

Given that air emissions from paving operations are not currently regulated, and toxicology studies to date have had difficulty generating asphalt fume at temperatures similar to that experienced at work sites (Melius 2003), we formed a consensus for best fit measurement of air emissions. We assessed Total Organic Carbon (TOC) as a surrogate measure of the potential range of organic compounds originating from cold- mixed asphalt concrete products, (i.e., this was in agreement with advice from CA South Coast Air Quality Management District). Analyses were performed in such a way that the TOC reflects the concentration of organic carbon in the gas phase that volatilized from a defined mass of cold mix asphalt concrete products in a sealed container over a 1-hour period. Hence, anything that will burn in a flame (e.g., the flame of a FID detector) is grouped into the category of TOC (methanes, alkenes, aromatics, and most oxygenated organics above two to three carbons excluding low molecular weight oxygenates).

Samples of each cold-mixed asphalt concrete product were obtained from the Washington Center for Asphalt Technology (WCAT). With the exception of Product C and F, samples of each of these products were obtained from sealed bags delivered to Washington State University (WSU) from the inventory of the Department Utilities and Transportation of the City of Seattle WA. Samples of Product C were obtained from Poe Asphalt, a paving company located near the WSU Pullman campus. Samples of the CRS-2 emulsion were obtained from U.S. Oil of Tacoma WA and were mixed in the WSU laboratory with aggregate obtained from Poe Asphalt. For all bagged products, proper splitting and handling procedures were used to obtain the samples. The samples used in the analyses of heavy metal leachates, solid waste toxicity, reactivity, ignitability, and corrosivity, were shipped over night to *Zalco Laboratories Inc.* under chain of custody. The cold-mixed asphalt products tested were assigned a code letter listed in Table 1.

Table 1. Product names, descriptions, and corresponding code letter designation.

Code	Product
A	*USColdPatch*®[a], a bagged proprietary product
B	*QPR*®[a], a bagged proprietary product
C	MC-250, a bulk generic cutback cold mix, (i.e., MC stands for Medium Curing and 250 is the minimum Kinematic Viscosity for the residual binder in cSt at 60° C).
D	*EZ Street*®[a], a bagged proprietary product
E	*Quickrete*®[a], a bagged proprietary product
F	An emulsion-based cold mix made in the lab using CRS-2 and aggregates, (i.e., CRS stands for Rapid Setting and 2 designates a minimum Saybolt-Fyrol Viscosity of 100 cSt at 50 °C).

[a] These trademark products have websites for additional product information and are listed in the references.

All Hazardous-Materials-related analytical techniques were performed, in duplicate, by *Zalco Laboratories, Inc.* These included heavy metal leachates, solid waste toxicity, reactivity, ignitability, and corrosivity. The method for analysis of air emissions was modified from U.S. EPA method TO-14 using gas chromatography with a flame ionization detector (GC/FID). Air emission analyses were performed at WSU. A brief description of each analytical technique is provided below with reference to specific details.

The Waste Extraction Test Method (USEPA, 1986; Method SW 6010B) characterizes leachates with reference to a list of heavy metals described in the *California Code of Regulations* (CCR) and is a test modified from the Toxic Characteristic Leaching Procedure. The regulated elements are typically described as "CAM Metals" in reference to guidelines developed in the California Assessment Manual. The metals of interest include Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Mercury (Hg), Molybdenum (Mo), Nickel (Ni), Selenium (Se), Silver (Ag), Thallium (Tl), Vanadium (V), and Zinc (Zn). Prior to analysis, samples were milled to homogenize. A random aliquot of 2 grams of each product was analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy.

The Acute Aquatic Toxicity Test Method (California Department of Fish and Game, 1988) employs fathead minnows (*Pimephales promelas*) as sentinels for aquatic health based on the leaching potential of the constituents of a test sample. A sample that has an acute aquatic 96-hr limit concentration lower than 500 mg/l when measured in soft water (total hardness 40 to 48 mg/l of calcium carbonate) is considered hazardous.

In the Releasable Cyanide and Sulfide Test Method (USEPA, 1986; Methods SW 7.3.3.2 and SW 7.3.4.2), a sample is considered hazardous if the toxic off-gases of cyanide and sulfur are produced at a pH of 2 to 12.5. If the concentrations of HCN exceed 250 mg/kg or H_2S exceed 500 mg/kg, the waste is deemed hazardous. The detection limits of releasable cyanide and sulfide are 1.0 and 10.0 mg/kg, respectively.

In the Ignitability Pensky-Martens Closed Cup Method (USEPA, 1986; Method SW 1010), the sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample. Samples are considered hazardous if the flashpoint is lower than 140°F.

In the Corrosivity Soil and Waste pH Test Method (USEPA, 1986; Method SW 9045C), the sample is mixed with reagent water and the pH of the resulting aqueous solution is measured using an electrometric procedure. Samples are considered hazardous if pH values are less than or equal to 2 or greater than or equal to 12.5.

The test method used to quantify TOC air emissions was adapted with some modifications from USEPA Method 10-14A (USEPA, 2002). TOC emissions were measured in duplicate from six asphalt products, obtained immediately after either opening the sample bag for Products A-E or mixing constituents in the laboratory for Product F, using gas chromatography with a flame ionization detector. A weighed amount of each sample was placed in a sealed glass 1-L jar and stored at room temperature (ca. 24 °C) for 1-hour. A known volume of gas was extracted from the sample jar, concentrated in a six-port sample-trap loop filled with glass beads and maintained at -183 °C, and analyzed on Hewlett-Packard 5890 gas chromatograph equipped with a DB-1 fused silica capillary column purchased from J&W Scientific. After injection of sample the column oven was temperature programmed from –50 C to 180 °C at 4 °C/min. The output signal was captured by a HP Chemstation data system. A standard gas of 608 ppbC 2, 2 dimethybutane was used as the primary standard. Each sample chromatogram's peak area was totaled to determine total organic compounds in parts per million (ppmC).

RESULTS AND DISCUSSION

The results of the concentration of heavy metals leached from the cold-mixed asphalt concrete products are graphically illustrated in Figure 1 and summarized in Table 2. Table 2 also lists the regulatory and detection limits (Total Threshold Limit Concentration (TTLC) and Total Threshold Limit Concentration (TTLC), respectively), expressed in mg/kg, for each of the 17 metals of interest. Extracts from representative samples that have a concentration equal to or greater than the regulatory level are considered a Hazardous Material. Any concentration lower than the TTLC suggests a non-hazardous Material. All six products would be classified as non-hazardous material based on results from WET analyses.

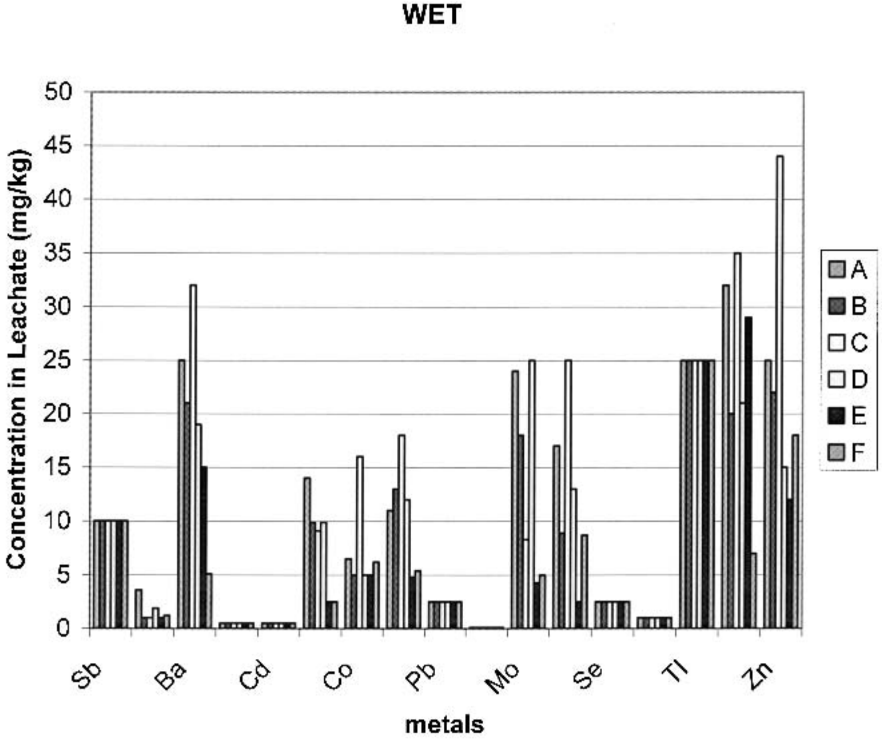

Figure 1. Summary of 17 metal concentrations leached from six cold mix asphalt products.

Table 2. Concentration of 17 metals in extracts from products tested[a]

Metal	TTLC[b] (mg/kg)	DLR[c] (mg/kg)	Cold Mix Asphalt Concrete Products A	B	C	D	E	F
Antimony	500	10	<10	<10	<10	<10	<10	<10
Arsenic	500	1.0	3.6	<1.0	<1.0	1.9	<1.0	1.2
Barium	10,000	5.0	25	21	32	19	15	5.1
Beryllium	75	0.50	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cadmium	100	0.50	<0.5	<0.5	<0.5	<0.5	<0.2	<0.5
Chromium	2,500	2.5	14	9.9	9.1	9.9	<2.5	<2.5
Cobalt	8,000	5.0	6.5	<5.0	16	<5.0	<5.0	6.2
Copper	2,500	2.5	11	13	18	12	4.8	5.4
Lead	1,000	2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Mercury	20	0.10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Molybdenum	3,500	5.0	24	18	8.3	25	43	<5.0
Nickel	2,000	2.5	17	8.9	25	13	<2.5	8.7
Selenium	100	2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Silver	200	1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Thallium	700	25	<25	<25	<25	<25	<25	<25
Vanadium	2,400	5.0	32	20	35	21	29	7.0
Zinc	5,000	2.5	25	22	44	15	12	18

[a] Characterized using WET analytical techniques, (Source: *Zalco Laboratories)*

[b] Total Threshold Limit Concentration, expressed as mg of metal per kg of product.

[c] Detection Limit of Reporting, expressed as mg of metal per kg of product.

Results of the analytical techniques employed to solid waste toxicity, reactivity, ignitability, and corrosivity, are summarized in Table 3. All five products (A-F) had acceptable values in their respective analyses, and hence, would be classified as non-hazardous materials under California regulations. Results of air emission analyses (Table 4) showed that the total carbon output varied significantly between these products. The proprietary bagged cold-mixed Products A, B and E, had significantly lower emissions than the generic MC-250 cutback material. In addition, the high level of TOC from the laboratory prepared Product F was very surprising, given the reputation of emulsions to emit lower TOC's than cutbacks.

Table 3. Results from analyses of acute aquatic toxicity, reactive cyanide and sulfide, ignitability, and corrosivity.

Analyses	Units	Cold Mix Asphalt Concrete Products A	B	C	D	E	F
Acute Aquatic Toxicity	mg/L	>500	>500	>500	>500	>500	>500
Reactive Cyanide	mg/kg	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Reactive Sulfide	mg/kg	57	35	57	<10	19	35
Ignitability	°F	>200	>200	>200	>200	>200	>200
Corrosivity/pH	units	9.0	7.9	8.2	7.5	8.0	7.9

Table 4. Atmospheric emission of TOC.

Product	Atmospheric emission of TOC (ppmC/g)
A	11.9
B	19.6
C	747.0
D	319.0
E	7.5
F	294.0

This study provides the first analyses of the potential environmental impact of several cold- mixed asphalt products in reference to the State of California Pollution Control Standards. Future investigations should be expanded and developed under real-time simulated conditions, focusing in part on: (1) temperature gradient conditions representing climatic seasons, (2) material compaction simulating vehicle weight, and (3) extended time point analysis of atmospheric emissions.

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