



ASSESSMENT OF WATER POLLUTANTS FROM ASPHALT PAVEMENT
CONTAINING RECYCLED RUBBER IN RHODE ISLAND

FINAL RESEARCH REPORT

Prepared for

The Rhode Island Department of Transportation

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16. Abstract Use of recycled rubber in asphalt pavement has been considered as a viable alternative on the basis it provides a means for disposal of scrap tires and a savings in quantity of construction materials. In this study hot mix asphalt (HMA) specimens with and without crumb rubber modifier (CRM) were analyzed for different environmental conditions. The CRM was added to HMA through both the wet and dry process. The CRM was procured from three different sources to prepare specimens. Cylindrical specimens were tested in the Particle Entrainment System (PES) at two different temperatures and three different pH levels. Runoff was also tested from slab and chip seal specimens subjected to light, wear and simulated rainfall. Water samples were collected in three phases: (1) water quality extraction of individual CRM samples, (2) water quality evaluation for cylindrical HMA specimens at varying environmental conditions (pH and temperature); and (3) water quality evaluation for slab HMA and chip seal specimens under simulated rainfall. Collected water samples were tested for trace metals and organics. A total of six metals were analyzed in the laboratory, i.e., Cr, Pb, Ni, Cu, Cd, and Zn. In general the majority of metals showed higher concentrations at the extreme environmental conditions, i.e., maximum asphalt pavement temperature and lowest pH, i.e., 2.0. The benzothiazoles had the highest concentrations for the organic compounds studied. The highest benzothiazole concentrations occurred in the dry process at the highest temperature and at the highest pH, i.e., 12.0 conditions. Finally, based on the limited scope of this effort and comparison with water quality criteria, it appears that there is no evidence in this study that there will be a detrimental effect on the environment or to human health.					
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Preface

This is the final report for the research project, "Assessment of Water Pollutants from Asphalt Pavements Containing Recycled Rubber in Rhode Island." The main focus of this study was to evaluate the water quality issues surrounding the use of recycled tires in the construction of asphalt pavement. In general, this project involved a laboratory study which compared pavements with and without Crumb Rubber Modifier (CRM). Specifically, this study included:

- Identification of contaminants from individual CRM samples collected from three different sources for three months;
- Water quality evaluation of both the wet and dry process CRM HMA samples for extended exposure to varying environmental conditions (temperature and pH);
- Water quality evaluation of wet, dry and chip seal CRM HMA specimens for simulated light, wear and rainfall conditions; and
- Comparative analysis of this study's results with EPA's water quality criteria

This study was conducted by the Department of Civil and Environmental Engineering and Graduate School of Oceanography at the University of Rhode Island (URI) under contract No. RIDOT-RTD-95-1/ME-534. Funds were provided through RIDOT and the Federal Highway Administration (FHWA).

This report reflects the combined efforts of the team including Drs. Raymond M. Wright, K. Wayne Lee and James G. Quinn and graduate students Pradeep Vashisth and Christopher Reddy. The authors are also thankful to all the CRM producers and other agencies who supplied necessary materials, especially Asphalt Rubber System, Rouse Rubber and Baker Rubber.

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Table of Contents

Technical Report Documentation Page	iii
Disclaimer	iv
Preface	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
1.0 Introduction	1-1
2.0 Background	2-1
3.0 Experimental Approach and Objectives	3-1
3.1 Objectives	3-2
4.0 Phase I - Contaminant Identification from Individual CRM Samples	4-1
4.1 Procurement of CRM Samples	4-1
4.2 Trace Metals - Phase I	4-4
4.2.1 Atomic Absorption Systems	4-4
4.2.2 Emissions Spectrograph SpectraSpan IV	4-6
4.2.3 Methods	4-7
4.2.4 Trace Metal Analyses Results - Phase I	4-11
4.3 Organics - Phase I	4-18
4.3.1 Methods	4-18
4.3.2 CRM Sample Processing	4-19
4.3.3 Organic Analyses Results - Phase I	4-22
5.0 Phase II - Water Quality Evaluation of CRM Asphalt Samples for Varying Environmental Conditions	5-1
5.1 Modification of the Particle Entrainment System (PES)	5-1
5.2 Selection of CRM for the Cylindrical Specimens	5-1

5.3 Specimens Preparation	5-3
5.4 Experiment Design	5-3
5.5 Trace Metal Analyses Results - Phase II	5-6
5.6 Organic Analyses Results - Phase II	5-10
6.0 Phase III - Water Quality Evaluation of the CRM Asphalt Samples for Simulated Rainfall Conditions	6-1
6.1 Preparation of CRM Asphalt Samples	6-1
6.2 Experimental Design to Simulate Environmental Conditions	6-1
6.2.1 Light Simulation	6-1
6.2.2 Wear Simulation	6-3
6.2.3 Rain Simulation	6-3
6.3 Trace Metal Analyses Results - Phase III	6-5
6.4 Organic Analyses Results - Phase III	6-7
7.0 Discussion	7-1
7.1 Trace Metals	7-1
7.2 Organics	7-5
8.0 Conclusions and Recommendations	8-1
8.1 Conclusions	8-1
8.2 Recommendations	8-3
References	R-1
Appendix A Detailed Results of the Emission Spectrograph Analyses	A-1
Appendix B Metal Concentration by Type and Source - Phase I	B-1
Appendix C Average Metal Concentration by Type and Source - Phase I	C-1
Appendix D Detailed Procedures for the Fabrication of Cylindrical Specimens - Phase II	D-1
Appendix E Effect of Temperature on Water Quality by Type and Source - Phase II	E-1

Appendix F Detailed Procedures for the Fabrication of Slab
Specimens - Phase III

F-1

Appendix G Detailed Procedures for the Fabrication of Chip Seal Slab
Specimens - Phase III

G-1



List of Tables

Table 2.1	Comparison Table for Asphalt and Tires in Leachate Tests	2-3
Table 2.2	Analytical Results of Toxicity Tests for the Lake Mead, Nevada	2-4
Table 4.1	Summary of CRM Samples	4-3
Table 4.2	Simplified Specimens Designation Table for the CRM Samples	4-5
Table 4.3	Results of Emission Spectrograph Analysis	4-12
Table 4.4	Result of the Trace Metal Analysis for the CRM Samples ($\mu\text{g/g}$ dry wt of CRM)	4-14
Table 4.5	Rubber Organic Compound Detected in the Aqueous Leachate of CRM	4-23
Table 4.6	Organic Results from the Repetitive Leaching Experiment for R. 1/4M.DP.9	4-25
Table 4.7	PAH Data from Aqueous Leachate of Crumb Rubber Material (ppb or ng/g dry weight of CRM)	4-27
Table 4.8	List of Polycyclic Aromatic Hydrocarbons Abbreviations	4-29
Table 5.1	Description of the Material Used in Cylindrical Specimens	5-4
Table 5.2	Concentrations of Metals for First and Second Sets and Average of Phase II at 20°C	5-7
Table 5.3	Concentrations of Metals for First and Second Sets and Average of Phase II at 45°C	5-8
Table 5.4	Organic Compounds in Phase II	5-11
Table 5.5	PAHs in Phase II in ng/L	5-13
Table 6.1	Metal Concentrations for the Slab Specimens at a pH of 7.0	6-8
Table 6.2	Metal Concentrations for the Slab Specimens at a pH of 4.3	6-9
Table 6.3	Benzothiazoles and Diphenylamine in Phase III	6-13
Table 6.4	PAH's Concentration in Phase III	6-14
Table 7.1	US EPA's Fresh Water Aquatic Criteria for Total Metals	7-2
Table 7.2	12 Years of Hardness Data for the Pawtuxet River, RI	7-3
Table 7.3	Comparison of Phase II and III Metal Concentrations with EPA's Standards	7-4

List of Figures

Figure 4.1	Phase I - Contaminant Identification from Individual CRM Samples	4-2
Figure 4.2	Chromium Concentration by Type and Source	4-15
Figure 4.3	Average Chromium Vs Type and Source of CRM	4-16
Figure 4.4	Metal Concentration Comparison for CRM Particle Size	4-17
Figure 5.1	Modified Particle Entrainment Simulator	5-2
Figure 5.2	Phase II - Water Quality Evaluation of the CRM Asphalt Samples for Extended Exposure under Varying Environmental Conditions	5-5
Figure 6.1	Phase III - Water Quality Evaluation of CRM Asphalt Samples for Simulated Rainfall	6-2
Figure 6.2	Schematic of Light Simulator	6-4
Figure 6.3	Schematic of Rain Simulator	6-6
Figure 6.4	Slab Specimens vs Metal Concentration at pH 7.0	6-10
Figure 6.5	Slab Specimens vs Metal Concentration at pH 4.3	6-10
Figure 6.6	Chip Seal Slab Specimens vs Metal Concentration at pH 7.0	6-11
Figure 6.7	Chip Seal Slab Specimens vs Metal Concentration at pH 4.3	6-11

1.0 Introduction

The disposal of scrap tires in the United States is a problem of great magnitude relative to the environment and economy. According to one source, 285 million tires are discarded each year and out of that 188 million tires are either stockpiled, placed into landfills or dumped illegally (Hughes 1993). The use of shredded tires in highway construction may offer technical, economical and environmental benefits.

Highway construction consumes a large quantity of materials such as aggregates, asphalt and portland cement. In locations, such as an urban area, aggregate sources are slowly being depleted. Some sources are becoming unavailable because of mining restrictions, environmental regulations and appreciating land values. In addition, resource depletion, environmental degradation and energy consumption are factors that have become critical in recent years. Recycled materials such as scrap tires, waste glass, slag and ashes, building rubble, sewage sludge and incinerator residue have a significant potential to replace conventional materials for various construction applications. Shredded tires in highway construction have various silent benefits such as reduced weight of fill, good drainage media, reduced backfill pressures, longer life, non-destructible in nature, cheap construction material and the environmentally sound reuse of large quantities of recycled waste tires (Ahmed 1992).

Recognizing the problem of disposing of scrap tires in the United States and the potential advantages of using waste materials in construction, government agencies have passed regulations for using waste tires in construction practice. Specifically, the highway industry has recognized the potential for scrap tires to be used as a Crumb Rubber Modifier (CRM) for asphalt paving (Scrap Tire 1990) in highway applications (Epps 1994). The most

important regulation to solve the problem of scrap tire is Section 1038 of Intermodal Surface Transportation Efficiency Act (ISTEA) of 1991. This section mandated each state to use recycled rubber in construction of asphalt pavements, beginning in the year 1996 (Intermodal 1991). Section 1038 had set the minimum quantity of recycled rubber to be used for highway applications, as a percentage of the total tons of asphalt applied: 15 percent in 1996 and 20 percent in 1997 and each year thereafter. However, it may be noted that this mandate was lifted recently.

Although use of recycled rubber has many advantages, there are potential problems. These problems include leachate of metals and organics, fire risk and increased compressibility due to the tire chips (Ahmed 1992). The main focus of this study was to identify potential contaminants associated with CRM asphalt mixtures, specifically trace metals organics. This study was conducted in three phases to evaluate the environmental aspects of the CRM in asphalt pavements.

2.0 Background

Information documenting long term environmental impacts of using recycled tires in construction of highways is very limited. Two interesting studies include: (1) a laboratory study on leachate collected from a shredded tire embankment at the University of Wisconsin-Madison (Edil et al. 1990 and Bosscher et al. 1992); and (2) a laboratory study on leachate from tire and asphalt material in Minnesota (MPCA 1990).

Research done by Bosscher et al. (1992) concluded that the leachate quality showed no likelihood of adverse effects on groundwater quality from shredded automobile tires. According to this study, the shredded tires did not release base-neutral regulated organics. Edil et al. (1990) reported that tests performed on the shredded tire leachate samples show very low concentration of all the substances and that the concentrations were declining in continued leaching. It is suspected that many released substances may be from the surface coating instead of the shredded tires with the exception of barium, iron, manganese and zinc. These metals were found in increasing concentrations with continued leaching. Iron and manganese were reported at or above their applicable drinking water standards, whereas zinc and barium were reported well below their standards.

Minnesota Pollution Control Agency (MPCA) conducted a laboratory study with Twin City Testing Corporation (TCT) to evaluate the compounds that may be released by exposure of scrap tires to different environmental conditions. Composite of old tires, new tires and asphalt samples were prepared and subjected to laboratory leachate procedure at four different pH levels including 3.5, 5.0, 7.0 and 8.0. TCT also conducted field sampling to monitor the effect of scrap tires in different soil conditions. The water and soil samples were collected in areas underneath

the waste tire subgrade and at background locations to monitor a comparison among different soil conditions. Samples were analyzed for 14 metals and for total petroleum hydrocarbons. Based on testing and analysis, TCT reached the following conclusion (MPCA 1990):

1. Under acidic conditions, metals were leached in the highest concentration and the more significant results were for barium, cadmium, lead, chromium, selenium and zinc;

2. Under basic conditions, polynuclear aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons from tire materials were leached at the highest concentration;

3. Under some conditions, asphalt material may leach higher concentrations of contaminants than tire materials (Table 2.1);

4. Recommended Allowable Limits (RALs) may be exceeded for drinking water standards under "worst-case" conditions for certain parameters;

5. Parameters of concern for co-disposal and Extraction Procedure (EP) toxicity limits and Toxicity Characteristic Leaching Procedure (TCLP) criteria are generally not exceeded;

6. No significant difference could be identified between waste tire areas and control areas (without waste tires) for soil samples and for the biological survey during the field studies; and

7. It was recommended that by using the waste tire materials in the unsaturated zone of roadway subgrade, the potential environmental impact from the use of waste tires in highway construction may be minimized. Additional field studies were also recommended in this report.

According to Nelson et al. (1994), the leachate was severely toxic to *C.dubia* (24 hrs LC₅₀ 20.3%) but not to fathead minnows. Analytical results from toxicity tests (Table 2.2) indicated that zinc was the primary toxicant and copper, cadmium, and lead were above background in 100% of the samples. These results are based on toxicity tests conducted by

Table 2.1 Comparison Table for Asphalt and Tires in Leachate Tests
(MPCA 1990)

Asphalt > Tires	Tires > Asphalt
Aluminum Barium Calcium Magnesium Sulphur Selenium (@ 3.5 pH only) Tin Total Petroleum Hydrocarbons Non Carcinogenic PAHs	Arsenic (detected @ pH 5.0) Cadmium (detected @ pH 3.5 and 5.0) Chromium (detected @ pH 3.5) Lead (detected @ pH 3.5) Zinc Carcinogenic PAHs

Table 2.2 Analytical Result of Toxicity Tests for the Lake Mead, Nevada (Nelson et al. 1994)

Parameter	Lake Mead dilution water	Deionized water blank	Tire leachate duplicate 1	Tire leachate duplicate 2
Zn ($\mu\text{g/L}$)	8.7	<4.0	751	755
Cd ($\mu\text{g/L}$)	0.2	<0.1	0.6	0.6
Cu ($\mu\text{g/L}$)	<5.0	<5.0	6.7	5.7
Pb ($\mu\text{g/L}$)	<1.0	<1.0	6.7	6.7
Ni ($\mu\text{g/L}$)	<10.0	<10.0	<10.0	<10.0

soaking 29 tire plugs (10.25 cm diameter) in 16 liters of water from Lake Mead, Nevada, for a period of 31 days. Samples were treated with sodium thiosulfate or ethylene diamine tetra acetate (EDTA) to assess metals toxicity. Methods generally followed were those presented by USEPA (1991). However, the report further states that toxicity caused by zinc concentrations leached from the tires used in artificial reefs would not cause acute or even chronic toxicity. According to Mueller and Liston (1991), tire reefs generally contain 900 tires per kilometer of canal. For the weight of 8 kg/tire and for the canal cross-sectional area of 33.5 m², approximately 33,500,000 liters of water would be contained in that 1 kilometer canal section. Based on Nelson et al. (1994) analysis, 755 μg of zinc could be leached from 0.18 liter tire plug material, and using this value zinc would leach 0.896 $\mu\text{g/l}$ into the 1 kilometer section of canal under no flow condition.

Nozaka et al. (1973) reported that no harmful substances were found in the leachate samples collected from tire material soaked in fresh water. However, studies suggest that copper may be highly toxic at the relatively high pH (Howarth and Sprague 1978, Miller and Mackay 1980 and Meador 1991).

The department of Civil Engineering at Oregon State University is currently working on a project that would find the environmental impact of construction and repair materials on surface and ground waters. This project is sponsored by the National Cooperative Highway Research Program (NCHRP). Under their research scope, they identified the various materials that can be used in the construction and repair of the highway network, which included shredded tires. However, the report on environmental impact is not available at this date. Their preliminary survey report indicates that presently 38 states in the U.S. are using scrap tires in the highway network (NCHRP 25-9 1995).

Mercaptobenzothiazoles and benzothiazole sulfenamides are commonly used as vulcanization accelerators in manufacturing rubber products. These compounds, in the presence of elemental sulfur, degrade when heated into radicals which accelerate the cross linking of sulfur in rubber, a process known as vulcanization. This process, however, allows for some of the accelerator or accelerator residue (like benzothiazole) to remain in the final product (Santodonato et al. 1976). Benzothiazoles have often been found in areas associated with rubber or tires. For example, they have been detected in tire manufacturer wastewater (Jungclaus et al. 1976), water and biota downstream from a Uniroyal Chemicals plant in Elmira, Ontario (Brownlee et al. 1981; Brownlee et al. 1992; Metcalfe et al. 1988), in the leachate of medical rubber products (Salmona et al. 1984), in worn tire particles (Rogge et al. 1993) and in a river downstream from a tire fire (Peterson et al. 1986). Furthermore, benzothiazoles have been found in groundwater (Barker et al. 1988), finished water (Jenkins et al. 1974), marine sediments (Spies et al. 1987), road dust (Rogge et al. 1993), atmospheric suspended matter (Kim et al. 1990), river water (Dietrich et al. 1988), and sorbed to limestone buildings (Fobe et al. 1995). In addition, we have observed benzothiazoles in highway stormwater runoff, highway settling pond water and sediments, and urban particulate matter (Reddy and Quinn, 1995).

A previous study on the leaching characteristics of waste tires have identified some PAHs and other nitrogen or sulfur heterocyclic organic compounds such as dibenzothiophene or acridine (MPCA 1990). The present investigation, however, is the first ever to quantify the leaching of benzothiazoles from CRM. In a related study investigating the impact that artificial tire reefs have on water quality, Nelson et al. (1994) leached tire pieces in deionized water and detected 1-2 mg/L of BT in their sample leachate as well as in their deionized water controls.

Studies by some Canadian researchers have shown that the leachate from both new and used tires was toxic to rainbow trout, but the used tires were generally more toxic. The source of toxicity was not determined, but might be due to environmentally altered chemicals. Also, the leachate from tires used in floating tire breakwater for ten years were not toxic (Day et al. 1993).



3.0 Experimental Approach and Objectives

The overall purpose of this study was to identify potential contaminants associated with asphalt pavement containing Crumb Rubber Modifier (CRM). This study was divided into three phases: Phase I - Contaminant identification from CRM samples; Phase II - Water quality evaluation of CRM asphalt samples for extended exposure under varying environmental conditions; and Phase III - Water quality evaluation of CRM asphalt samples for simulated rainfall conditions. Since each phase had a distinct purpose, each phase required a different experimental approach. The design of each experiment is discussed in detail in chapters 4, 5 and 6.

Water samples were collected in all three phases and were analyzed for a selected group of metals and organics. Specimens were prepared in Phases II and III with and without CRM to find the effect of the CRM on water quality. CRM can be added to Hot Mix Asphalt (HMA) through either a wet or dry process. The wet process is defined as any method that adds CRM to the liquid asphalt cement prior to incorporating the binder with asphalt (Heitzman 1992). When CRM is blended with hot asphalt cement, the rubber particles absorb components of the asphalt and swell to several times their volume, which results in the stiffening of the asphalt cement. The process of absorption and swelling of CRM is referred to as the 'reaction' between asphalt and CRM. The result is an asphalt rubber (AR) binder (Lee et al. 1995).

The dry process is defined as any method of adding CRM directly into the HMA mix process, typically pre-blending the CRM with the heated aggregate prior to charging the mix with asphalt (Heitzman 1992). CRM in the dry process is primarily used as a rubber

aggregate that is incorporated into the gap graded aggregate prior to mixing with asphalt cement, producing Rubber Modified Hot Mix Asphalt (RUMAC).

To prepare the chip seal specimens, control slabs were prepared and were treated with an emulsified asphalt (control specimens) or the AR binder. A mass of 9.5 mm (3/8 inch) mineral aggregates was then applied on the top of the wet surface and was then embedded into the binder using a vibratory compactor.

3.1 Objectives

The objective of Phase I was the identification of contaminants from individual CRM samples. CRM samples representing both the dry and wet processes were to be procured from two different sources over three different months. Each sample was to be analyzed in the laboratory for selected metals and organics. A detailed description of this phase is given in Chapter 4.

The objective of Phase II was the water quality evaluation of both the wet and dry process CRM HMA samples for extended exposure to varying environmental conditions. Specimens were prepared and were tested in the laboratory under varying conditions of pH and temperature. Water samples were collected from each test and analyzed for metals. A select group of samples were also tested for organics. Phase II is discussed in detail in Chapter 5.

The objective of Phase III was the water quality evaluation of wet, dry and chip seal CRM HMA specimens for simulated rainfall. Specimens were prepared and exposed to varying conditions including natural light, traffic (wear) and rain. Water samples were collected for analysis of selected metals and organics. Chapter 6 explains this phase in detail.

4.0 Phase I - Contaminant Identification from Individual CRM Samples

4.1 Procurement of CRM Samples

CRM samples were procured from two sources for the first month, i.e. August. The sources selected were the Asphalt Rubber Systems, RI (Producer A) and Baker Rubber, IN (Producer B). Specifically the samples from Producer A included TR-24 and TBS-20 and the ones from Producer B or Plus Ride were GR-16 and 1/4" mesh (Figure 4.1). Of these two sources Producer A always uses the TR-24 and TBS-20 together and only in the wet CRM process. The samples were to be obtained at one month intervals for three months to monitor any significant differences in the quality at one source over time. Four different CRM samples were procured from two sources for the first month (Table 4.1). For the last two months Producer B could not supply any samples because Plus Rider went out of business. Instead, Rouse Rubber, MS (Producer R) provided GF-80A for both months and supplied 1/4" mesh and number 12 mesh samples for the second and third months, respectively. It should be noted that these materials are the same ones used for the companion engineering study (Lee et al. 1995).

The size of the CRM particles is an important parameter for the wet process. The wet process requires a reaction to take place between the CRM and asphalt. The required temperature for the reaction is dependent on the size of CRM particle. The coarser the particle the higher the temperature required for the reaction. Coarsely graded CRM is usually preferred in the dry process because there is no reaction.

An extraction of contaminants from the CRM samples may be influenced by the exposed surface area of CRM. Since the CRM particle size varies depending on the

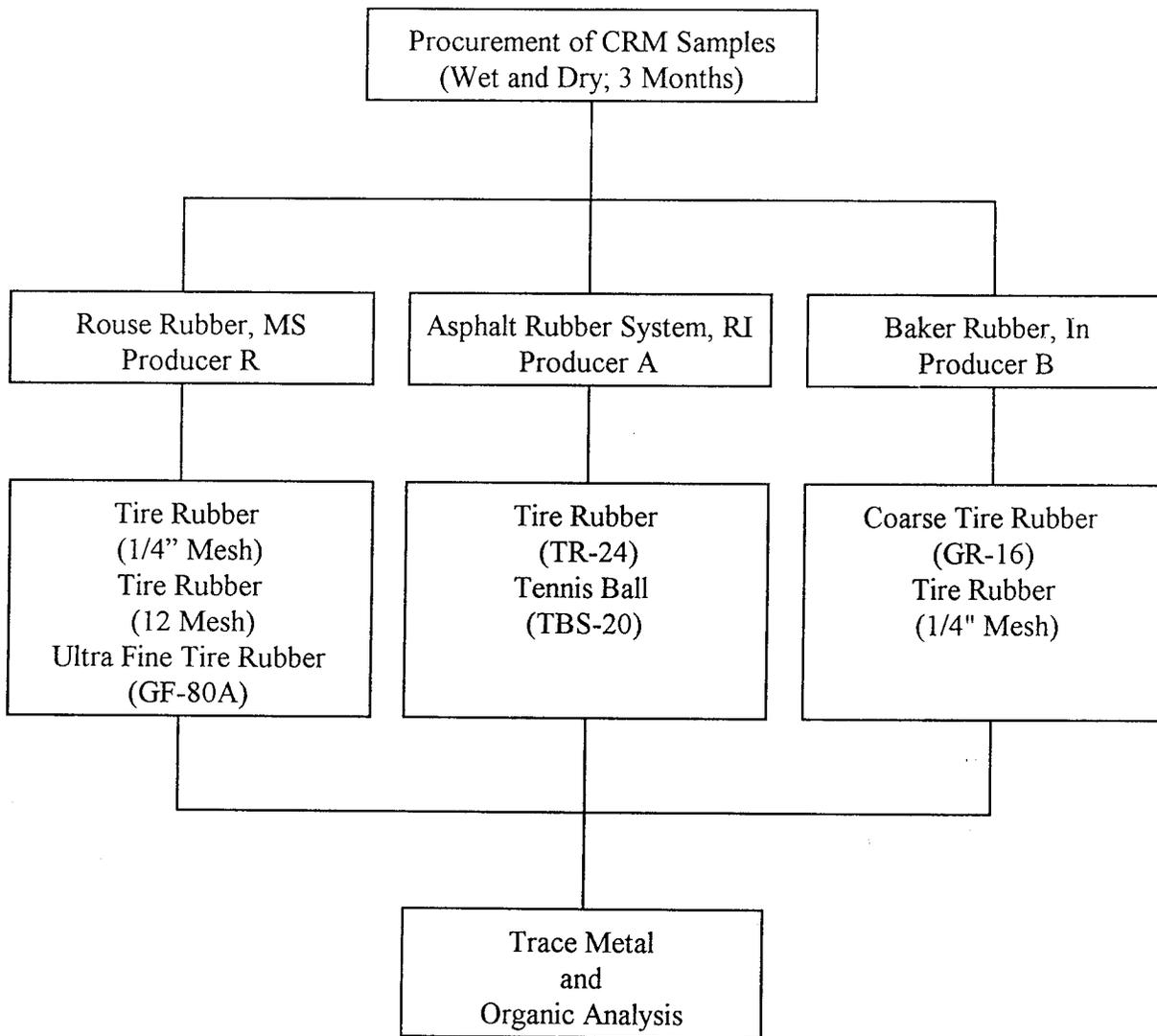


Figure 4.1 Phase I - Contaminant Identification from Individual CRM Samples

Table 4.1 Summary of CRM Samples

Sample Specification	Source of sample	Physical Description	Month	Process	Sample Designation
TR-24	Asphalt Rubber	Fine Crumbed Tire	August	Wet	A.TR.WP.8
TBS-20	Asphalt Rubber	Fine Crumbed Tennis Ball	August	Wet	A.TB.WP.8
GR-16	Baker Rubber	Coarse Crumbed Tire	August	Dry	B.GR.DP.8
1/4" Mesh	Baker Rubber	Coarse Crumbed Tire	August	Dry	B.1/4M.DP.8
TR-24	Asphalt Rubber	Fine Crumbed Tire	September	Wet	A.TR.WP.9
TBS-20	Asphalt Rubber	Fine Crumbed Tennis Ball	September	Wet	A.TB.WF.9
GF-80A	Rouse Rubber	Ultra Fine Crumbed Tire	September	Dry	R.GF.DP.9
1/4" Mesh	Rouse Rubber	Coarse Crumbed Tire	September	Dry	R.1/4M.DP.9
TR-24	Asphalt Rubber	Fine Crumbed Tire	October	Wet	A.TR.WP.10
TBS-20	Asphalt Rubber	Fine Crumbed Tennis Ball	October	Wet	A.TB.WP.10
GF-80A	Rouse Rubber	Ultra Fine Crumbed Tire	October	Dry	R.GF.DP.10
No. 12 Mesh	Rouse Rubber	Coarse Crumbed Tire	October	Dry	R.12M.DP.10

process used, it may be expected that the results between the fine particle grain size (wet process) vs coarse size particle (dry process) may be quite different.

Each CRM sample was assigned an alpha numeric designation based on its source, CRM components, process in which the CRM was to be used, and the month in which the CRM was obtained (Table 4.1). The first two characters represent the source of CRM used (A-Asphalt Rubber System, R-Rouse Rubber, B-Baker Rubber). This is followed by the specification of CRM (TR for TR-24, TBS for TBS-20, 1/4 M for 1/4" mesh, and 12M for 12 mesh) and industrial process application either WP (wet process) or DP (dry process). Finally the time of CRM procurement is coded by the month in which it was received. For the convenience of graphical representation these designation were further simplified (Table 4.2).

4.2 Trace Metals - Phase I

Trace metal analysis for the extracted samples were done with the two techniques. They included the Atomic Absorption Spectrophotometer (AAS) for quantitative determination of six trace metals (cadmium, chromium, copper, lead, nickel and zinc) and the emission spectrograph for the qualitative determination of a broader range of metals.

4.2.1 Atomic Absorption Systems

Two different types of atomic absorption systems were used, i.e. the Perkin-Elmer Model 5100 PC with graphite furnace and the Perkin-Elmer Model 3030B with a flame. The 5100 is a powerful and versatile atomic absorption spectrometer for fully automated element determinations. Except for a few setup procedures, one can control the 5100 PC almost entirely by computer. The 5100 PC provides a user interface. High energy optics, new

Table 4.2 Simplified Specimens Designation Table for the CRM Samples

Actual CRM Sample Designation	Simplified CRM Sample Designation
A.TR.WP.8	TR1
A.TB.WP.8	TB1
B.GR.DP.8	GR1
R.1/4M.DP.8	1/4M1
A.TR.WP.9	TR2
A.TB.WP.9	TB2
R.GF.DP.9	GF1
R.1/4M.DP.9	1/4M2
A.TR.WP.10	TR3
A.TB.WP.10	TB3
R.GF.DP.10	GF2
R.12M.DP.10	12M1

automatic gas controls and a power dual-option burner system are some prominent features. Its main advantages are as follows: (1) efficient automated operation serves the analyst running routine samples as well as the researcher performing method development; (2) accessories allow analysis by flame, Zeeman or conventional graphite furnace, and mercury cold vapor or hybrid generation techniques; (3) instrument operation is integrated using a personal computer; (4) computer entries allow to control wave length, slit width lamp current, gas flows, and autosampler operation; and (5) high energy optics provides optimum precision and detection limits.

The Perkin-Elmer Model 3030B was used to determine zinc. It was used because zinc was expected to be an order of magnitude higher than the other five metals and sensitivity limits would be exceeded for the 5100. Similar to the 5100, the 3030B is also a computer controlled atomic spectrophotometer.

4.2.2 Emissions Spectrograph SpectraSpan IV

An emissions spectrograph was used in Phase I to determine, which trace metals were contained in each CRM sample. The spectrograph used was a SpectraSpan IV Sequential Spectrometer. The unit is a compact stand-alone atomic emission system. Its main advantages are as follows: (1) determination of more than 70 elements without any lamps; (2) a wide dynamic range, 4-6 orders of magnitude; (3) no explosive gases; (4) reduced chemistries; (5) high tolerance for dissolved solids; (6) complex matrix analyses; (7) determination of elements that are difficult on an AAS (e.g., boron, mercury, zirconium, uranium, and the rare earths); and (8) detection limits are on the order of parts per billion (ppb or $\mu\text{g/L}$). With few procedural exceptions, the SpectraSpan IV is completely controlled by a

microcomputer. The information in its unprocessed form is generated through thermal excitation of sample the in hot plasma. By thermal excitation radiation characteristics of the atoms in the sample passes to an optical demultiplexer. The beam of radiation is comprised of various wavelengths and these wavelengths occupy specific position on a two dimensional plane. Photographic output is created by reflective optics beam focused on a photographic plate.

4.2.3 Methods

About 1 gm (0.0022 lb) of each CRM sample was weighed and place into 30-ml tubes. All the samples were acidified to a pH of 2 by using nitric acid. The pH of 2 for the extraction solution was considered based on similar research experience and literature (Munns et al. 1991). To accomplish metal extraction from the CRM sample, an ultrasonic bath was used (Munns et al. 1991). Each CRM sample was subjected to two baths of 16 hours each. Although the yield of extracted metals may not be 100%, the yield should be consistent between samples. Extracted samples were collected in 60 ml trace metal bottles and were kept in the refrigerator until metal analysis on the Emissions Spectrograph SpectraSpan IV and AAS. These 60 ml Nalgene, HDPE bottles and accessories used in the analysis of trace metals were pre-soaked for three 48 hour periods in a 3% nitric acid solution and then rinsed with deionized (DI) water. The polycarbonate filters were soaked in 3% nitric acid for 10 days and tested for contamination by filtering DI water.

The precision of the AAS procedures for trace metals analysis is measured as the relative standard deviation (RSD) of triplicate analyses carried out on a minimum of 2 samples per set of samples to be selected at random. RSDs in this study for all the samples were 10%

or better.

Calibration was usually performed by using a standard calibration curve, which was a series of standards (at least three) and a reagent blank that results in a linear relationship between the analyzed signal and concentration. Standards were prepared using reagent grade chemicals. For automated analyses, calibration curves are run at least twice for each sample tray loaded. Continuing calibration standards were run at least once between each calibration curve.

The method of standard additions was run concurrently for one sample per sample tray on the AAS. This was a check for possible matrix interferences. This was also a measure of the recovery of standards.

In the event that the slope of the standard calibration curve and method of addition curve were not similar, matrix effects were considered to affect the analyses. In such cases, the methodology was adjusted to take care of such interferences. Examples of such adjustments are: a) using a method of addition calibration curve for samples with similar matrices; b) dilution of sample to lower matrix effects; and c) addition of matrix modifiers for metals.

Thus, having established the calibration method the samples were run along with the spiked samples. All constituent concentrations were corrected by using reagent and procedural blanks.

Typically, each AAS run included both samples and standards. Calibration curves were developed using 3 standards. The calibration curves were run before samples 1 and 15. The middle calibration standard or a "continuing calibration standard" was rerun after samples

7, 21, and 28 to ensure that the analyses continues to conform to the calibration curve. In the event that any problems were detected during analyses, the samples after the last successful calibration standard were rerun.

Reagent blanks were prepared at the URI Civil and Environmental Engineering laboratory for total metals by adding the same volume of acid used for extracting the metals to the same volume of sample DI water. The reagent blanks were run along with the initial calibration and then after every 7 samples during the analyses run.

Spiked standards were prepared and measured in addition to the method of additions in two samples for total metals for each set of extracted samples. The 2 samples were selected at random and were spiked with a known metal concentration. Percent recovery of spiked standards was greater than 90%.

For QA control in the laboratory the following general rules applied:

- 1- Method of standard addition was conducted on the constituents indicated on 5-10% of the samples.
- 2- Initial calibration with 3 to 5 standards was run for all analytical methods.
- 3- Continuing calibration standards were conducted at least every 10 samples.
- 4- Reagent blanks were always conducted with the calibration standards.

The samples in this study were analyzed using established procedures for similar studies. Most of these procedures have been reported in many articles which have been published in refereed scientific journals such as *Science*, *Nature*, *Environmental Science and Technology*, *Geochimica et Cosmochimica Acta*, *Organic Geochemistry*, *Chemical Geology*, *Marine Chemistry*, *Marine Biology*, *Marine Environmental Research*, *Toxicologica* and

Environmental Chemistry, and *The Journal of the Water Pollution Control Federation*.

The completeness of the analysis was measured as the percentage of total samples collected that were completely analyzed. Since all samples were analyzed, it was anticipated the 100 percent completeness would be achieved. The detection limits per metal were: Cd - 0.05 $\mu\text{g/L}$; Cr - 0.2 $\mu\text{g/L}$; Cu - 0.2 $\mu\text{g/L}$; Pb - 0.2 $\mu\text{g/L}$; Ni - 0.2 $\mu\text{g/L}$; and Zn - 0.8 $\mu\text{g/L}$.

The analytical procedure outlined below follows the procedure used by the EPA Narragansett Environmental Research Laboratory (NERL). Recent communications with EPA personnel has confirmed that these methods are still in use and are acceptable (Boothman, personal communication 1995). The major difference between this procedure and that indicated in *Standard Methods* is the avoidance of the digestion step. According to NERL, glassware used in the digestion process can add a significant amount of inconsistency to the analyses, which is unacceptable.

For the analyses of total metals an experimentally determined volume of HNO_3 (Baker-Ultrex II) were added to the 60 ml bottles containing total trace. The acid volume was sufficient to leach the trace metals from the particulate phase (one week) and keep the trace metals from adsorbing to surfaces or complexing. Cadmium, chromium, copper, lead and nickel were analyzed in duplicate samples directly using the 5100 AAS equipped with HGA Graphite Furnace. The 5100 is also equipped with a Zeeman/500 system designed to provide the graphite furnace with background correction. Such systems enhance the measurement sensitivity by reducing any interferences in the sample background. Zinc was analyzed on 3030B flame atomic absorption spectrophotometer.

Based on past experience in the analysis of metals in surface water samples, this

recommended method has proven successful in terms of consistency of results and minimal contamination problems as opposed to digestion. Quantification was based upon calibration curves of standard solutions of metals made up in the approximate acid proportions to the samples. The calibration curves were plotted and all concentrations were calculated by Perkin-Elmer analytical software.

4.2.4 Trace Metal Analyses Results - Phase I

After extraction, water samples were analyzed on both the emission spectrograph and AAS. All the samples were run twice on SpectraSpan IV to get photographic output for the further analysis. The first run was done with type 55 Polaroid Film, while the second run was completed using the recommended type 57 PN Polaroid Film. Type 55 Polaroid film is negative type film that gives the result in the form of negatives only. It is a high resolution film and allows for appreciable enlargement of the negative without loss of information, but it is a much slower film than the type 57 and exposure times or slit size must be increased. Whereas, type 57 PN is very fast type of film and gives both positives and negatives of the photographs.

From the photographs and the key overlay supplied by the manufacturer, targets were interpreted. To confirm the presence of any element at least two targets of an element must be matched. The circles on the overlay correspond to the position of a spectral line on the photograph. The results of the spectrograph analysis are included in Appendix A. The results of the analysis using the type 57 PN film are summarized in Table 4.3. Fewer metals were targeted using the type 55 film. All the metals observed using the type 55 film were also indicated with the 57 PN film. Few metals were found which had two targets indicated. Only

Table 4.3 Results of Emission Spectrograph Analysis

Sample Code	Element Present
A.TR.WP.8	<i>Si, V, Ti, Na</i> , Mg, Al, Fe, Ca
A.TB.WP.8	<i>Si, V, Ti, Na</i> , Mg, Al, Fe, Ca
B.GR.DP.8	Si, V, Ti, Na, <i>Mg, Al, Fe, Ca</i> , Cr
B.1/4M.DP.8	<i>Si, V, Ti, Na</i> , Mg, Al, Fe, Ca, Cr
A.TR.WP.9	<i>Si, V, Ti, Na</i> , Mg, Al, Fe, Ca
A.TB.WP.9	<i>Si, V, Ti, Na</i> , Mg, Al, <i>Sr</i> , Fe, Ca, Cr
R.GF.DP.9	<i>Si, V, Ti, Na</i> , Mg, Al, Fe, Ca, Cr
R.1/4M.DP.9	Si, V, Ti, Na, <i>Mg, Al, Fe, Ca</i> , Sr, Cr
A.TR.WP.10	Results are not available
A.TB.WP.10	Si, V, Ti, Na, <i>Mg, Al, Fe, Ca</i> , Cr, <i>Ba</i>
R.GF.DP.10	Si, V, Ti, Na, <i>Mg, Al, Fe, Ca, Sr</i> , Cr
R.12M.DP.10	Results are not available

Note: The elements indicated in *italic* were confirmed by emission spectrograph analysis.

chromium of the six metals (Cd, Cu, Cr, Pb, Ni, or Zn), which were to be determined on the AAS, were targeted at any time. However, the presence of chromium could not be confirmed since chromium did not match more than one target at any time.

In the contrast to the findings from the spectrograph, the AAS indicated the presence of all six metals in significant quantities (Table 4.4). The average concentrations were on the order of parts per million per gram of CRM sample (ppm/gm). Zinc was the highest metal in each CRM sample by several orders of magnitude. This is not surprising since zinc oxide is an ingredient in CRM (Baker Rubber 1993).

An example of samples presented by type and source is given in Figure 4.2. A complete set of figures is presented in Appendix B. These figures show the overall mean and 95% confidence level for all CRM samples. Figure 4.3 is an example of the average concentration for the three month period for each CRM type. A complete set of these figures is presented in Appendix C. In some cases, such as for Producer A, the concentration of zinc, cadmium and chromium showed no significant difference over the time period and in other cases data were not conclusive (i.e., GR-16 and 12M CRM).

Figures 4.4 illustrates the metal concentration comparison for rubber particle size. It can be observed from the figures that the variability between producers is too great to reach a definitive relationship between particle size and metal concentration. However, if we considered just Producer R, which supplied the 1/4" M, the number 12 sieve size and the GF-80A samples, the concentrations of three metals (Cr, Cd and Ni) were inversely related to particle size.

GR1 had consistently high concentrations for all five metals. As discussed before, zinc

Table 4.4 Result of the Trace Metal Analysis for the CRM Samples ($\mu\text{g/g}$ dry wt of CRM)

Component of CRM	Sample Code	Chromium ($\mu\text{g/g}$)	Nickel ($\mu\text{g/g}$)	Copper ($\mu\text{g/g}$)	Lead ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)	Zinc ($\mu\text{g/g}$)
A.TR.WP.8	TR1	2.48	3.60	6.84	23.6	1.08	8829
A.TB.WP.8	TB1	3.60	1.02	3.90	14.5	0.78	9533
B.GR.DP.8	GR1	4.56	44.4	21.1	104	1.38	13317
B.1/4M.DP.8	1/4M1	0.96	0.18	3.36	11.9	0.48	1969
A.TR.WP.9	TR2	2.46	1.38	22.5	40.7	1.20	8679
A.TB.WP.9	TB2	3.66	1.14	7.32	15.7	0.78	12218
R.GF.DP.9	GF1	1.44	1.98	14.5	14.8	1.08	7390
R.1/4M.DP.9	1/4M2	1.32	2.22	12.6	5.94	0.12	597
A.TR.WP.10	TR3	0.72	0.54	6.42	12.0	1.08	7234
A.TB.WP.10	TB3	3.42	0.78	9.48	13.0	1.44	9307
R.GF.DP.10	GF2	4.92	25.2	25.8	63.2	1.5	10624
R.12M.DP.10	12M1	1.80	1.7	36.2	48.7	1.32	13448

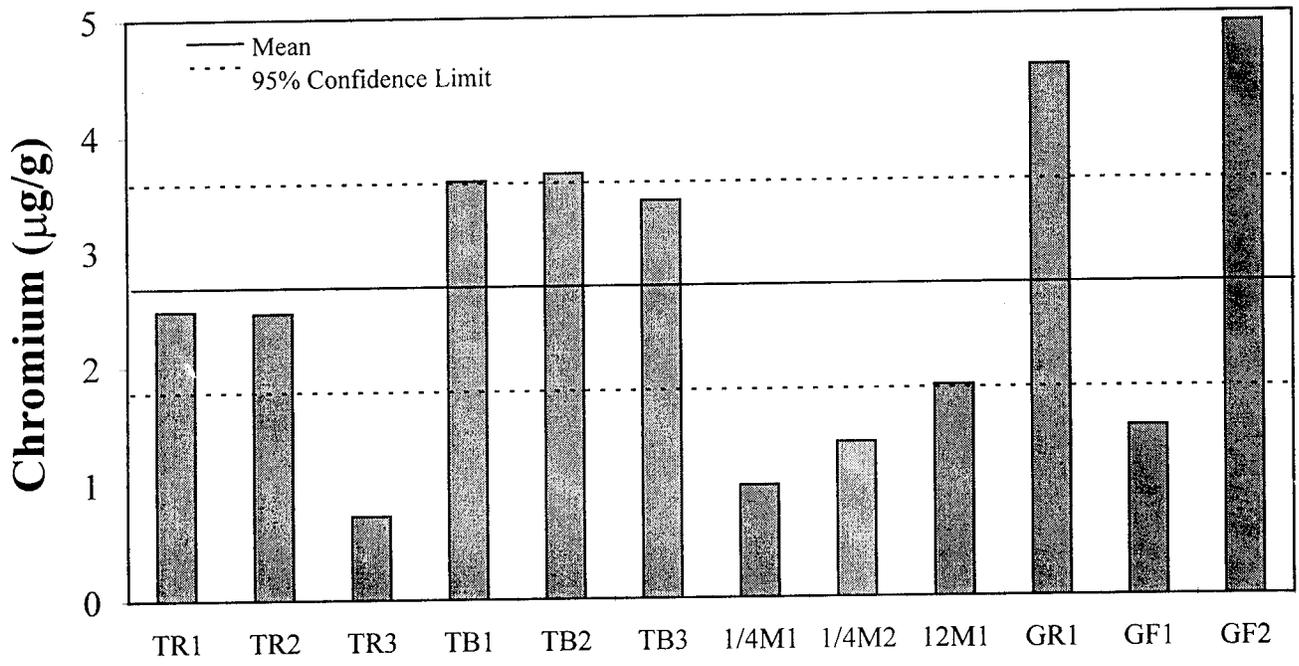


Figure 4.2 Chromium Concentration by Type and Source

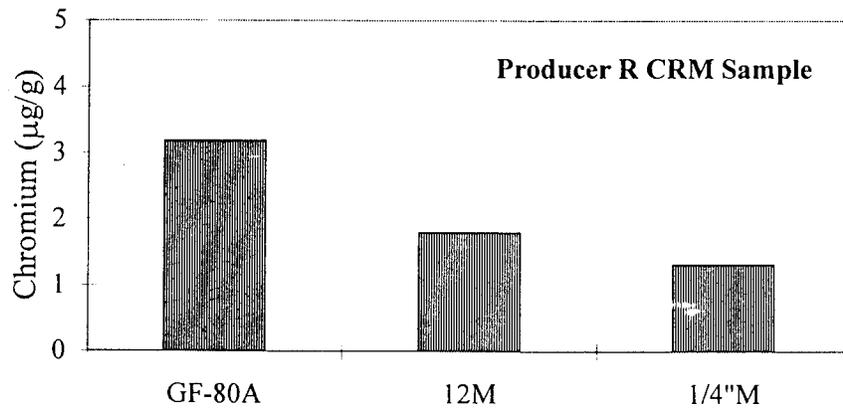
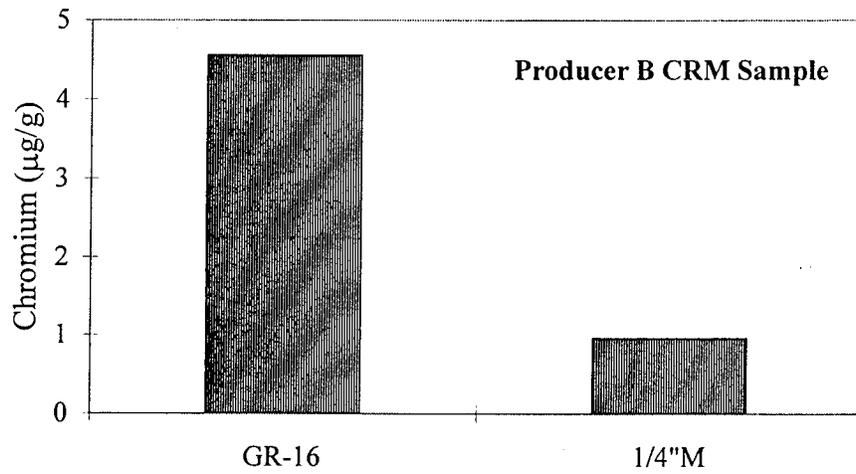
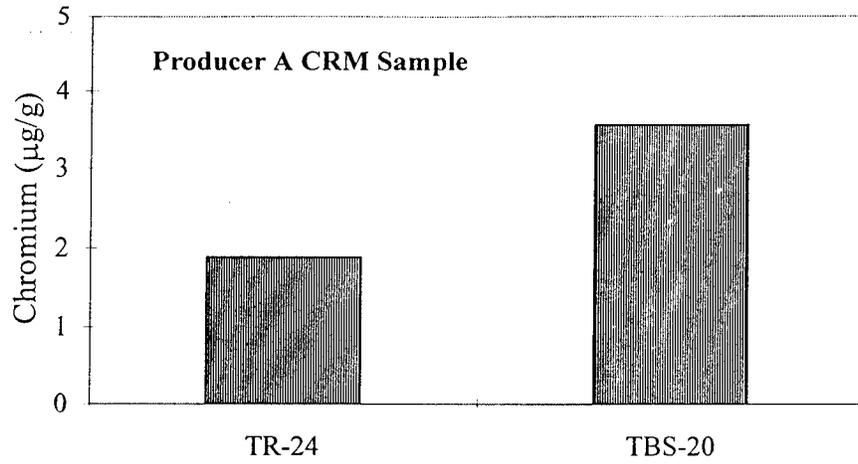


Figure 4.3 Average Chromium Vs Type and Source of CRM

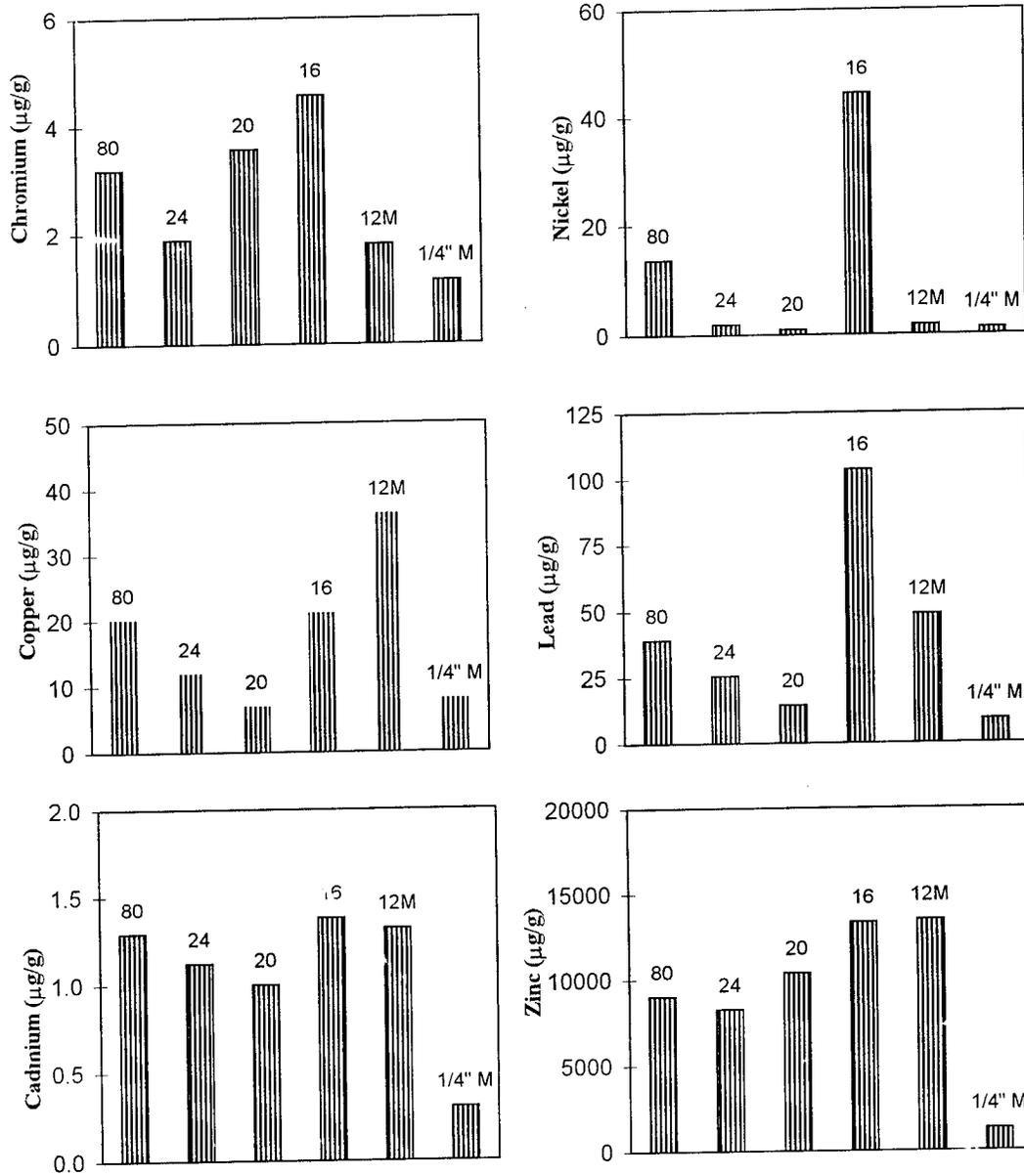


Figure 4.4 Metal Concentration Comparison for CRM Particle Size

had the highest concentration in all the CRM samples, followed by lead. Cadmium was found to be lowest in concentration in most of the samples. Since all six metals were in measurable quantities from the AAS analyses, these results contradicted the emission spectrograph.

4.3 Organics - Phase I

The CRM samples were stored in glass jars or polyethylene bottles and kept at room temperature. The aqueous samples were contained in 4 liter amber glass jugs with Teflon lined caps; they were stored at room temperature and processed within 48 hours of receipt.

4.3.1 Methods

All organic solvents were purchased from Burdick & Jackson and were pesticide grade or better. Benzothiazole (BT), 2-hydroxybenzothiazole (HOBT), 2-methylbenzothiazole (MeBT), 2-methylmercaptobenzothiazole (MTBT), 2-mercaptobenzothiazole (MBT), and diphenylamine (DPA) were obtained from Aldrich Chemical Company. PAH calibration and spiking solutions were prepared from dilutions of National Institute of Standards and Technology (NIST) SRM 2260. Individual deuterated PAHs were purchased from Cambridge Isotope. Milli-Q deionized water was pre-extracted with hexane.

Gas chromatographic analysis was performed on a Hewlett-Packard 5890 gas chromatograph in the splitless injection mode with a Hewlett-Packard 5971 Mass Selective Detector. Separation occurred on a 30 meter J&W Scientific DB-5ms glass capillary column with 0.25 mm id and 0.25 μ m film thickness. Data was collected with Hewlett-Packard ChemStation software. Quantification was based on calibration curves derived from the responses of pure compounds or secondary standards relative to the internal standards. The

recoveries of the internal standards were monitored by external standard.

One of the benzothiazoles, MBT, partially degraded into BT in the gas chromatograph. It was found that when standard solutions of MBT were injected on the GC-MS, about 30% decomposed into BT. In samples that contained MBT, the concentrations of BT and MBT were corrected assuming that 30% of MBT decomposed into BT.

4.3.2 CRM Sample Processing

In order to identify the compounds that could leach from crumb rubber, 1-10 grams samples of CRM were refluxed for two hours in two different solvents, deionized water (BP=100°C) and acetonitrile (BP=82°C). After filtering and adding water to the acetonitrile extract, the leachates were extracted into either methylene chloride or hexane. A portion of the organic extracts were then injected onto the GC-MS in the full scan mode and tentatively identified with the NIST 75,000 compound library in the HP ChemStation software. The acetonitrile extracted a full range of organic compounds, while the deionized water extracted fewer compounds. However, the major compounds detected in the deionized water extracts were BTs and smaller amounts of PAHs. These components were focused on, since deionized water was a more environmentally representative solvent, and also because we felt that the acetonitrile was actually dissolving the CRM while the deionized water was leaching this material. The deionized water used in these experiments was pre-extracted with hexane to remove any trace of organic contaminants. The solubility of hexane in water is about 10 mg/L and as such would be an acceptable surrogate for the dissolved organic matter (natural and/or anthropogenic) found in natural waters. Unfortunately, this refluxing method was not efficient because it was found that some compounds were being steam-distilled. Instead the CRMs

were extracted at a temperature of 50°C. This temperature was used to simulate hot road conditions during summer months.

All CRMs were extracted as follows. Small portions (2-5 grams) of sample were added to 50 mL glass centrifuge tubes with Teflon lined caps. The tubes were filled with deionized water leaving about 2 mL of headspace. The caps were tightly sealed and then shaken in a 50°C metabolic shaker bath for two hours. After cooling, the tubes were filtered thru pre-combusted Whatman GF/C glass fiber filters (approximate particle retention size of 1.2 µm). The pH of the aqueous leachate was monitored before and after with pH paper. The contents of the tube were rinsed two more times with deionized water followed by filtration. The combined filtrate and rinses were delivered to a glass separatory funnel and spiked with the following internal standards in acetonitrile: MeBT, naphthalene-d8, biphenyl-d10, acenaphthene-d10, anthracene-d10, and perylene-d12. The aqueous filtrate was extracted three times with methylene chloride. The methylene chloride extracts were combined, reduced in volume under vacuum to about 4 ml, and then split into two fractions, 75% and 25% of the extract. The 75% fraction was spiked with an external standard (n-dodecane) and injected onto the GC-MS in the full scan mode for determination of benzothiazoles and other organic compounds. The 25% fraction was charged to microcolumns (0.5 cm x 10 cm) containing fully activated silica gel (Grace Grade 922) and eluted with 20 ml of methylene chloride. This extract was reduced in volume to 100 µL, spiked with an external standard (0-terphenyl) and injected onto the GC-MS in the selected ion monitoring mode for the determination of PAHs.

The recoveries of the MeBT internal standard ranged from 46% to 101% and the

recovery of deionized water blanks spiked with BT, HOBT, and DPA ranged from 20% to 55% or 31% to 83%, depending on whether the compounds were spiked into the tubes prior to shaking or before extraction in the separatory funnel, respectively. Duplicate analysis for two samples showed good agreement as measured by relative standard deviation (RSD): BT (<3%), HOBT (<14%), and DPA (<5%). The estimated method detection level (MDL) for individual benzothiazoles and DPA was 1 µg/g of dry weight CRM. A deionized water blank was void of BT, HOBT, MBT, and DPA.

The recovery of the 5 PAH internal standards ranged 40% to 120%. Blank spiked recoveries of 24 individual PAHs ranged from 88% to 137%. The estimated MDL for individual PAHs was 20 ng/g of dry weight CRM.

A crumbed tire and tennis ball material were also extracted in 2N HNO₃ for two hours at 50°C. The pH of the leachate was still acidic prior to extraction with methylene chloride. The samples were analyzed in the same manner as above. No duplicates or spiked blanks were performed, but the recoveries of the MeBT internal standard were good with values from 57% to 101%. PAHs internal standard recoveries (68%-96%) were acceptable for the lower molecular weight PAHs (naphthalene-d₈, biphenyl-d₁₀, and acenaphthene-d₁₀), but poor (1%-7%) for the higher molecular weight PAHs (anthracene-d₁₀ and perylene-d₁₂).

Nine months after the initial extraction, one sample of 1/4" (R.1/4M.DP.9) was leached three consecutive times for two hours at 50°C with fresh deionized water at each interval to determine the extent of leaching of benzothiazoles from CRM. Another sample was extracted for 7 hours concurrently. These extracts were analyzed by GC-MS in the selected ion monitoring mode rather than the full scan. The MDLs for this method were

about 10X times more sensitive than the above method (ca. 100 ppt (ng/g) of dry weight CRM). PAHs were not investigated in this portion of the study.

To determine if the BTs leached were small particles (0.2 μ m-1.2 μ m), the extraction was done for 26 grams of 1/4" (R.1/4M.DP.9) in 300 mL of deionized water. After filtering the leachate through 2 pre-combusted Whatman GF/C glass fiber filters, the filtrate was divided into six equal portions, three of the portions were immediately analyzed for BTs. The other three portions were filtered through 0.2 μ m membrane filters and then analyzed. These samples were also injected on the GC-MS in the selected-ion monitoring mode.

4.3.3 Organic Analyses Results - Phase I

Only three of the samples showed any pH change in the aqueous extracts and they all slightly increased from an initial value of pH 5 to final values of 6 or 7. These samples were TBS-20 received from Producer A.

The major "rubber" organic compounds detected in the aqueous extracts are shown in Table 4.5. The parent compound, benzothiazole (BT) and one of the substituted benzothiazoles, 2-HOBT were detected.

The total amount of the two most abundant benzothiazoles (BT and HOBT) leached from the crumbed tires ranged from 4.9 ppm (μ g/g) to 49.1 ppm (μ g/g). There was generally no difference in the amount leached amongst manufacturers, although the finer crumbed tires (e.g. TR-24 and GR-16) did appear to leach more benzothiazoles (Table 4.5). Another compound, diphenylamine (DPA) was found in the tire products from the from Producer B but at trace quantities (1 to 2 ppm (μ g/g)). We also tentatively identified 1H-isoindeole-1,3(2H)-dione (often referred as phthalimide) in four samples (B.GR.DP.8, B.1/4M.DP.8,

Table 4.5 Rubber Organic Compound Detected in the Aqueous Leachate of CRM

Organic Compound	BT	HOBT	MBT	DPA
Sample Designation	(Concentrations are in ppm ($\mu\text{g/g}$) dry weight of CRM)			
A.TR.WP.8	26.8	13.4	ND	ND
A.TB.WP.8	121	52.1	402	ND
B.GR.DP.8	35.3	12.8	ND	2.1
B.1/4M.DP.8	22.5	22.6	ND	1.4
A.TR.WP.9	49.1	ND	ND	ND
A.TB.WP.9	35.0	26	134	ND
R.GF.DP.9	24.2	10.3	ND	ND
R.1/4M.DP.9	17.8	1.5	ND	ND
A.TR.WP.10	22.6	13.1	ND	ND
A.TB.WP.10	21.5	13.3	142	ND
R.GF.DP.10	3.4	1.5	ND	ND
R.12M.DP.10	10.9	9.1	ND	ND

Note: ND = <1 ppm ($\mu\text{g/g}$ of CRM)

A.TR.WP.8, A.TR.WP.10).

TBS-20, but not the crumbed tires, also leached. This chemical was the most concentrated compound leached from all of the CRM in deionized water, with concentrations ranging from 134 to 403 ppm.

For both a crumbed tire (B.1/4M.DP.8) and crumbed tennis ball (A.TB.WP.10) sample, 2N HNO₃ did leach more benzothiazoles, but the distribution of benzothiazoles changed compared to regular leaching with deionized water. Whereas the amount of BT leached for the crumbed tire increased by a factor of 5, the amount of HOBT only doubled. This trend was also observed in the crumbed tennis ball when 35 times more BT was leached as opposed to 6 times more for HOBT. No MBT was detected in the tennis ball leachate.

There also was a pronounced difference in the amount leached from CRMs delivered at different times. For example, considering the three samples of TR-24 received from Producer A (Table 4.5), the second sample A.TR.WP.9 had the highest concentration of BT, but no HOBT. In addition, the two samples of GF80A (R.GF.DP.9 and R.GF.DP.10) had remarkable differences; the sum of the major benzothiazoles (BT and HOBT) was 34.5 ppm and 4.9 ppm, respectively.

Benzothiazoles leaching from CRM is not a one time event as evidenced by the results shown in Table 4.6. The same sample of crumb rubber still leached significant quantities of BT and HOBT even after two previous leaching events. Due to the increase in instrument sensitivity when this experiment was performed, another benzothiazole derivative, 2-(4-morpholinyl) benzothiazole (MLB), was tentatively identified. There was no commercially available reference standard for MLB. It was identified by comparing the URI mass spectra to

Table 4.6 Organic Results from the Repetitive Leaching Experiment for R.1/4M.DP.9

Sample No.	Leaching No.	Organic Compounds					DPA
		BT	HOB	MBT	MLB	DPA	
		(Concentrations are in µg/g dry weight of CRM)					
Sample No. 1	1st leach (2 hours)	13.2	9.6	ND	0.6	ND	
	2nd leach (2 hours)	NA	NA	NA	NA	NA	
	3rd leach (2 hours)	8.8	4.1	ND	0.5	ND	
Sample No. 2	Leached for 7 hours	12.7	12.1	ND	0.5	ND	

Note: NA= not available due to lost sample.
 ND = < 0.1ppm (µg/g of CRM)

that of Spies et al. (1987). In addition, 2-methylmercaptobenzothiazole (MTBT) was detected in each sample but not quantified.

Most of the BTs leached were in the less than $0.2\mu\text{m}$ size fraction. The samples filtered through the $0.2\mu\text{m}$ filter had nearly identical concentrations of BT and about 10% less HOBT compared to the samples only filtered through the glass fiber filters.

Small amounts of PAHs were observed but not quantified in the aqueous extracts because the concentrations were lower than the MDL (Table 4.7); these PAHs were usually the lower molecular weight, more water soluble compounds such as naphthalene and its methyl substituted derivatives. A list of the PAH abbreviations is given in Table 4.8.

Table 4.7 PAH Data from Aqueous Leachate of Crumb Rubber Material (ppb or ng/g dry weight of CRM)

Sample Designation	NAP	2MN	1MN	BIP	DMN	ACL	ACT	TMN	FLU	PHE	ANT	IMP
A.TR.WP.8	ND											
A.TB.WP.8	ND											
B.GR.DP.8	ND											
B.1/4M.DP.8	ND											
A.TR.WP.9	ND											
A.TB.WP.9	ND											
R.GF.DP.9	ND											
R.1/4M.DP.9	ND											
A.TR.WP.10	ND											
A.TB.WP.10	ND											
R.GF.DP.10	ND											
R.12M.DP.10	ND											

Note: ND = non detectable (≤ 20 ppb of CRM); PAH = polynuclear aromatic hydrocarbons

Table 4.7 Continued

Sample Designation	FLA	PYR	BAA	CHR	BBF	BKF	BEP	BAP	PER	INP	DBA	BPE	SUM
A.TR.WP.8	ND												
A.TB.WP.8	ND												
B.GR.DP.8	ND												
B.1/4M.DP.8	ND												
A.TR.WP.9	ND												
A.TB.WP.9	ND												
R.GF.DP.9	ND												
R.1/4M.DP.9	ND												
A.TR.WP.10	ND												
A.TB.WP.10	ND												
R.GF.DP.10	ND												
R.12M.DP.10	ND												

Note: ND = non detectable (≤ 20 ppb of CRM); PAH = polynuclear aromatic hydrocarbons

Table 4.8 List of Polycyclic Aromatic Hydrocarbons Abbreviations

PAH Abbreviations	Compound Name
ACL	acenaphthylene
ACT	acenaphthene
ANT	anthracene
BAA	benzo (a) anthracene
BAP	benzo (a) pyrene
BBF	benzo (b) fluoranthene
BEP	benzo (e) pyrene
BIP	biphenyl
BKF	benzo (k) fluoranthene
BPE	benzo [ghi] perylene
CHR	chrysene
DBA	dibenzo [a,h] anthracene
FLA	fluoranthene
FLU	fluorene
INP	indeno [1,2,3-cd] pyrene
NAP	naphthalene
1MN	1-methylnaphthalene
2MN	2-methylnaphthalene
DMN	2,6-dimethylnaphthalene
TMN	2,3,5-trimethylnaphthalene
PHE	phenanthrene
1MP	1-methylphenanthrene
PER	perylene
PYR	pyrene
SUM	sum of the 24 polycyclic aromatic hydrocarbons



5.0 Phase II - Water Quality Evaluation of CRM Asphalt Samples for Varying Environmental Conditions

5.1 Modification of the Particle Entrainment System (PES)

The URI PES (Figure 5.1) was constructed in 1987 using the specifications from the Narragansett EPA PES. For this unit's application in this project, several modifications were necessary, since trace elements were to be determined. The modifications included replacing all the components in contact with the overlying water and specimen with Teflon to avoid contamination. Teflon was selected since it is an inert material which does not react with other materials.

The URI PES has a drive disc and linking bar driven by a 1/8 horsepower, variable speed motor. The Teflon driving rod connecting the linking bar is kept in alignment through the use of bronze bushings. The bar is set 1.27 cm (0.50 in) off the center of the disc to create a vertical displacement of 2.5 cm (1.0 in) in the water column, i.e., a total of 2.5 cm (1.0 in) agitation in both directions (up and down) was provided and the rate of agitation was kept constant throughout the testing of each sample. The oscillating grid was 11 cm (4.33 in) in diameter and was perforated with 1.2 cm (0.47 in) diameter holes. The holes were 1.5 cm (0.59) center to center, which made the porosity of the grid 42.8%.

5.2 Selection of CRM for the Cylindrical Specimens

The CRM selected for testing in Phase II was based in part on the findings of Phase I, the results of earlier work with this material and material availability (Lee et al. 1995). A mix of 80% TR-24 (A.TR.WP.8) and 20% TBS-20 (A.TB.WP.8) from Producer A was used for the preparation of the wet process specimens. Both samples typically had metal

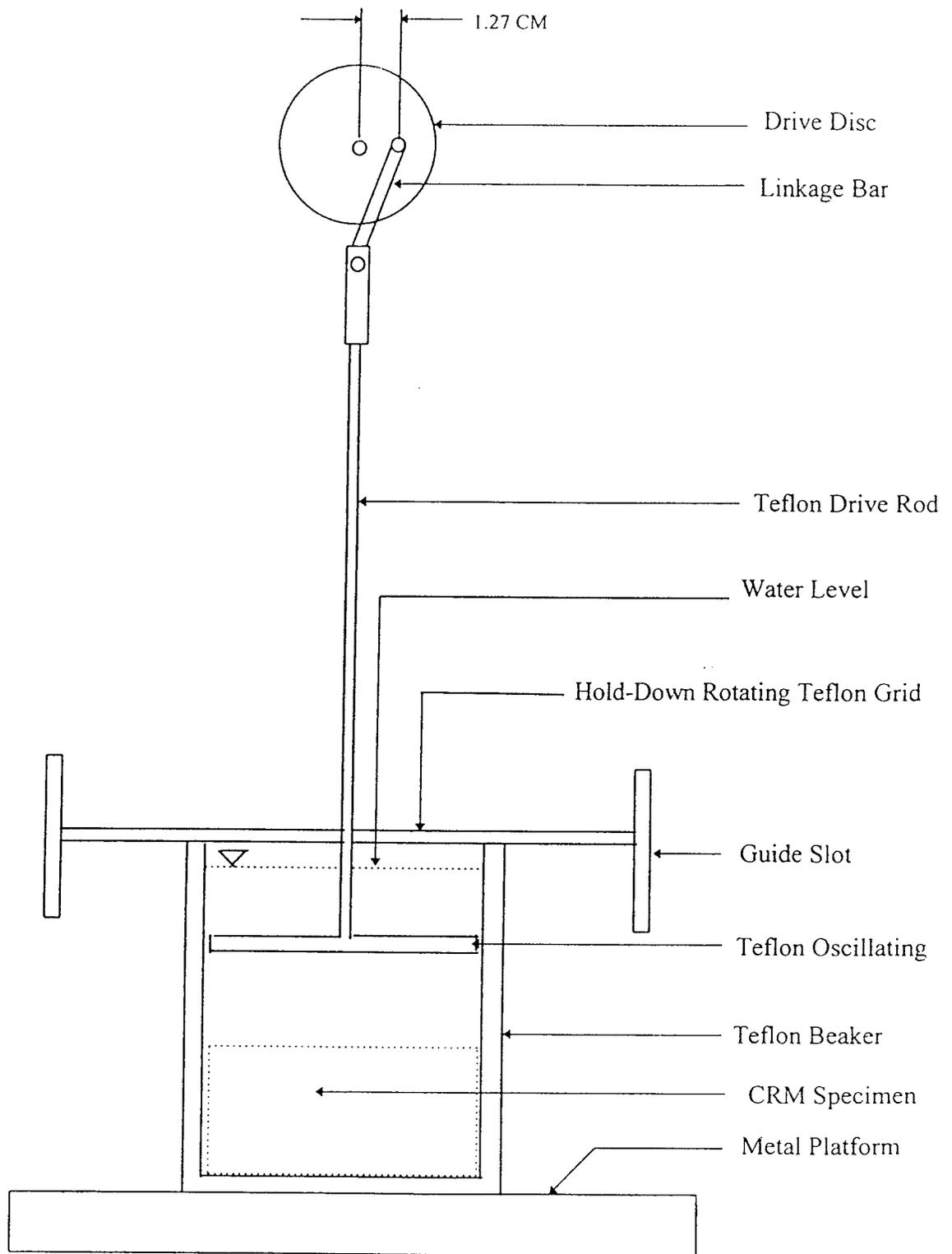


Figure 5.1 Modified Particle Entrainment Simulator

concentrations, which were within the 95% confidence level of the mean of all CRM samples taken (Figure 4.2 and Appendix B). A total of 15% of the CRM (mix of TR-24 and TBS-20) of asphalt rubber binder was mixed in asphalt to prepare the AR binder. Since in the wet process a total of 7.4% AR binder was used, the CRM percentage in the wet process was 1.11% of the total weight of the specimen.

A mix of 80% 1/4" mesh (R.1/4M.DP.9) and ultra fine 20% GF-80A (R.GF.DP.9) from Producer R was used for the dry process specimens to accomplish the required gradation of the CRM. The overriding factor for this combination was the mix design procedure outlined by the manufacturer of Plus Ride (Lee et al. 1995). To prepare the dry process specimens, a 3% CRM of total weight of the specimen was used (Lee et al. 1995).

5.3 Specimens Preparation

The specimens of 100 mm (4.0 in) diameter and 62.5 mm (2.5 in) thickness were prepared in accordance with the Marshall Method of Mix Design (AASHTO T245/ASTM D 1559). Teflon sheets were used to prepare the specimens to avoid any possible contamination. The detailed procedures for fabrication of the cylindrical specimens are included in Appendix D. An experimental design was developed by considering the type of process, aggregate gradation, asphalt binder type, OBC and CRM content as indicated in Table 5.1.

5.4 Experiment Design

As shown in Figure 5.2, a total of 36 cylindrical specimens were tested (12 each: control, wet and dry processes). Two sets of 6 specimens each (2 each: control, wet and

Table 5.1 Description of the Material Used in Cylindrical Specimens

Process	Control Process	Wet Process	Dry Process
Aggregate Gradation	Tilcon-Gammino Dense Grade	Tilcon-Gammino Modified Friction (+Filler Cement)	Tilcon-Gammino Gap Gradation (+Producer R CRM +Hydrated Lime)
Binder	Hudson Asphalt AC-20	Hudson Asphalt AC-10 +Producer A CRM +Extender Oil	Hudson Asphalt AC-20
Optimum Binder Content (OBC)	6.0%	7.4%	7.8%
CRM Content	-	1.11% of total weight	3% of total weight

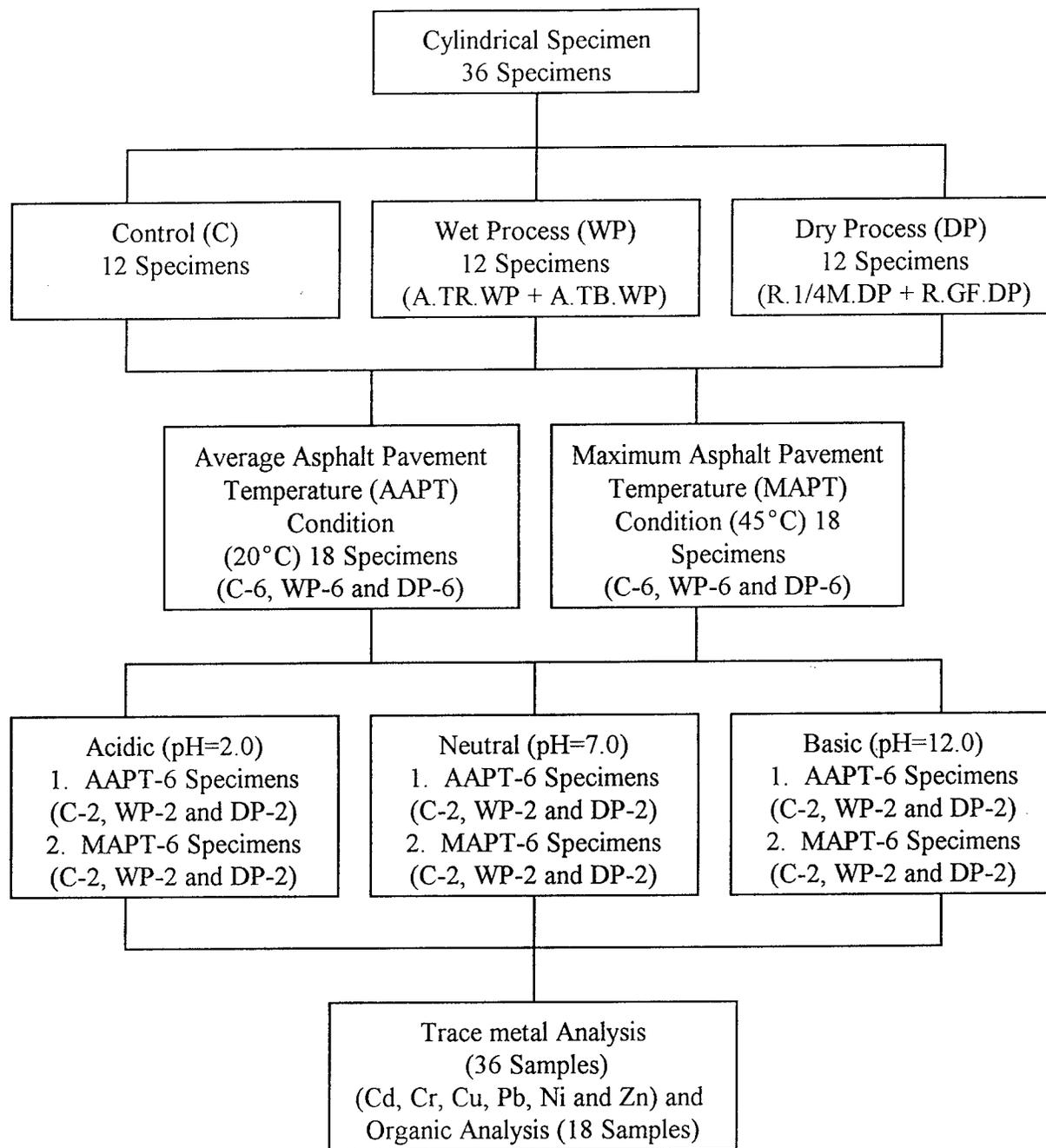


Figure 5.2 Phase II - Water Quality Evaluation of the CRM Asphalt Samples for Extended Exposure under Varying Environmental Conditions

dry process) were analyzed for three different pH levels (2.0, 7.0 and 12.0) and for two temperatures (average and maximum asphalt pavement temperature). Average and maximum asphalt pavement temperatures were taken as 20 °C and 45 °C, respectively. These two temperatures are based on literature values and on earlier URI research results (Lee et al. 1994). The effects of temperature on water quality are reported in Appendix E.

A fixed volume of DI water of the required pH was set over the specimens in the Teflon chamber. The grid in the PES system oscillates vertically in the water and creates agitation that continuously move the water into the void spaces in the surface of the specimen. The nature of agitation and amount of the contaminants are proportional to the grid oscillation. A three-hour agitation period was provided based on preliminary testing to establish the approximate time for chemical equilibrium. Nitric acid (HNO₃) and sodium hydroxide (NaOH) were used to establish a pH level of 2 and 12 in the DI water, respectively.

Temperature was maintained by conducting the experiment in a temperature control chamber. The temperature of the DI water and the specimens was kept at the same temperature, i.e., 20 °C or 45 °C.

5.5 Trace Metal Analyses Results - Phase II

Water samples were collected in 60 mL Nalgene, HDPE bottles for the analysis of the six metals by the AAS. Results of the trace metal analysis are reported in Table 5.2 for the average asphalt pavement temperature (20 °C) and Table 5.3 for the maximum asphalt pavement temperature (45 °C).

The following may be recognized from this data:

Table 5.2a - Concentrations of Metals (µg/L) for First Set of Phase II @ 20 °C

Metals/Process	pH = 2.0			pH = 7.0			pH = 12.0		
	Control	Wet	Dry	Control	Wet	Dry	Control	Wet	Dry
Cadmium	3.43	2.73	4.71	0.53	0.39	0.35	0.15	ND	0.72
Chromium	4.06	2.80	2.64	0.74	0.39	0.45	0.72	0.47	0.75
Copper	5.48	9.14	9.54	0.56	0.37	0.54	1.29	1.67	2.57
Lead	1.26	5.02	10.2	0.48	0.07	0.13	0.17	0.29	12.6
Nickel	8.32	9.40	4.12	1.05	0.83	0.51	2.17	3.32	2.53
Zinc	43.0	84.0	168	7.40	3.60	10.6	15.0	22.2	222

Table 5.2b - Concentrations of Metals (µg/L) for Second Set of Phase II @ 20 °C

Metals/Process	pH = 2.0			pH = 7.0			pH = 12.0		
	Control	Wet	Dry	Control	Wet	Dry	Control	Wet	Dry
Cadmium	4.90	2.05	4.71	0.37	0.05	0.53	0.08	ND	0.09
Chromium	2.94	4.98	2.66	0.16	1.71	0.57	0.41	1.68	0.39
Copper	6.79	6.21	4.41	0.16	0.42	0.41	1.11	1.54	0.67
Lead	1.25	4.20	21.8	0.22	0.03	4.15	0.23	0.10	15.6
Nickel	2.32	5.30	14.4	0.58	0.77	0.90	2.00	2.40	2.85
Zinc	59.0	75.0	110	2.50	1.40	12.3	13.3	17.8	72.0

Table 5.2c - Average Concentrations of Metals (µg/L) for Phase II @ 20 °C

Metals/Process	pH = 2.0			pH = 7.0			pH = 12.0		
	Control	Wet	Dry	Control	Wet	Dry	Control	Wet	Dry
Cadmium	4.17	2.39	4.71	0.45	0.22	0.44	0.12	ND	0.41
Chromium	3.50	3.89	2.65	0.45	1.05	0.51	0.57	0.08	0.57
Copper	6.14	7.68	6.98	0.36	0.40	0.48	1.20	1.61	1.62
Lead	1.26	4.61	16.0	0.35	0.05	2.14	0.20	0.20	14.1
Nickel	5.32	7.35	9.25	0.82	0.80	0.71	2.09	2.86	2.69
Zinc	51.0	79.5	139	4.95	2.50	11.5	14.2	20.0	147

Note: ND = non detectable

Table 5.3a - Concentrations of Metals ($\mu\text{g/L}$) for First Set of Phase II @ 45 °C

Metals/Process	pH = 2.0			pH = 7.0			pH = 12.0		
	Control	Wet	Dry	Control	Wet	Dry	Control	Wet	Dry
	Cadmium	6.05	14.3	4.56	0.10	0.28	0.53	1.19	0.49
Chromium	6.68	5.23	3.36	0.20	0.46	0.48	0.70	0.67	1.04
Copper	8.52	12.7	15.3	0.77	0.61	0.56	1.39	1.92	3.05
Lead	0.47	3.01	18.7	ND	ND	0.38	0.64	3.60	10.7
Nickel	7.44	12.6	28.4	0.77	1.06	1.03	2.17	2.54	1.99
Zinc	50.0	114	1644	6.00	4.20	9.40	294	407	738

Table 5.3b - Concentrations of Metals ($\mu\text{g/L}$) for Second Set of Phase II @ 45 °C

Metals/Process	pH = 2.0			pH = 7.0			pH = 12.0		
	Control	Wet	Dry	Control	Wet	Dry	Control	Wet	Dry
	Cadmium	6.10	11.13	5.46	0.11	0.27	0.10	0.05	0.48
Chromium	3.34	5.24	6.98	0.19	2.46	0.46	0.75	0.66	2.24
Copper	10.90	8.80	10.1	0.28	0.36	0.79	1.40	1.61	1.63
Lead	0.37	3.29	10.9	ND	ND	2.92	0.30	0.44	11.0
Nickel	7.4	21.2	19.1	0.49	1.07	1.16	2.63	2.96	2.00
Zinc	126	115	1886	3.00	6.20	10.2	68.0	406	712

Table 5.3c - Average Concentrations of Metals ($\mu\text{g/L}$) for Phase II @ 45 °C

Metals/Process	pH = 2.0			pH = 7.0			pH = 12.0		
	Control	Wet	Dry	Control	Wet	Dry	Control	Wet	Dry
	Cadmium	6.10	12.7	5.01	0.11	0.28	0.32	0.62	0.49
Chromium	5.01	5.24	5.17	0.20	1.46	0.47	0.73	0.67	1.64
Copper	9.73	10.8	12.7	0.53	0.49	0.68	1.40	1.77	2.34
Lead	0.42	3.15	14.8	ND	ND	1.65	0.47	2.02	10.9
Nickel	7.44	16.9	23.8	0.63	1.07	1.10	2.40	2.75	2.00
Zinc	88.0	115	1765	4.50	5.20	9.80	181	407	725

Note: ND = non detectable

- Metal concentrations are higher in samples with a pH of 2.0 compared to 7.0 or 12.0, with only a few exceptions. For the 18 specimens evaluated at 20 °C (6 control, 6 wet and 6 dry), these exceptions included 2 results with higher concentrations at a pH of 12: lead-dry-first set (12.6 vs 10.2 $\mu\text{g/L}$) and zinc-dry-first set (222 vs 168 $\mu\text{g/L}$). For the 18 specimens evaluated at 45 °C (6 control, 6 wet and 6 dry), these exceptions included 6 samples with a higher concentration at a pH of 12: lead-control-first set (0.64 vs 0.47 $\mu\text{g/L}$), lead-wet-first set (3.60 vs 3.01 $\mu\text{g/L}$), zinc-control-first set (294 vs 50 $\mu\text{g/L}$), zinc-wet-first set (407 vs 114 $\mu\text{g/L}$), lead-dry-second set (11 vs 10.9 $\mu\text{g/L}$) and zinc-wet-second set (406 vs 115 $\mu\text{g/L}$).
- In general, the average metal concentrations are the lowest for a pH of 7.0. This has significance since an increase or decrease from the pH level of 7.0 in the system may cause an increase in the mobility of metals from the CRM into the water. The major exception to this was cadmium at 20 °C. The lowest average concentration for cadmium occurred at a pH of 12.
- The highest concentration of any metal was consistently zinc. This was due, most likely, to the presence of zinc oxide in the CRM.
- Metal concentrations are typically higher at the higher temperature for the pH of 2 and 12. The only exception was lead at a pH of 2.
- The variation in metal concentrations between control, dry and wet are not consistently different. Where significant differences do occur, the dry process usually has the highest concentration.

- The higher concentrations in the dry process specimens may be due to the higher proportion of CRM used in the dry vs wet process (3% vs 1.11%). On the other hand, metals may be less mobile in the wet process because of the reaction which takes place between CRM and the liquid asphalt. The liquid asphalt forms a coating which covers the CRM particles and may reduce the rate of the migration of the metals into the water.

5.6 Organic Analyses Results - Phase II

The pH of each PES leachate (ca. 1.4 liters) was adjusted to >8 with NaOH and pH paper; this was done because a recent publication showed good methylene chloride extraction efficiency of BT at a pH of 8.5 (Feihn et al. 1994). The leachate was spiked with internal standards (same as above) and then extracted three times with methylene chloride. The methylene chloride was reduced in volume to 200 μ L, spiked with external standard (o-terphenyl) and injected onto the GC-MS in the selected ion monitoring mode for both benzothiazoles and PAHs.

The recoveries of the internal standard MeBT were usually from 65% to 130% with a mean of 109%. Recovery of the PAH internal standards usually ranged from 30% to 130%. No duplicate samples or spikes were performed. The estimated MDL for benzothiazoles and PAHs were 100 ng/L and 20 ng/L, respectively.

The major compound in all twelve samples was BT with concentrations ranging from 14.1 μ g/L to 162.1 μ g/L (Table 5.4). No significant quantities of analytes were found in the controls or blank. The concentrations of BT were greater for dry process than wet process samples at 45°C, but not at 20°C. Increasing the temperature from 20°C to 45°C leached

Table 5.4 Organic Compounds in Phase II

Sample ID			BT	HOBT	MTBT	MBT	MLB	DPA
Process	Temperature	pH	(Concentrations are in ppb (µg/L))					
Control	20 °C	7.0	0.1	ND	ND	ND	ND	ND
Control	20 °C	2.0	0.1	ND	ND	ND	ND	ND
Control	20 °C	12.0	ND	ND	ND	ND	ND	ND
Control	45 °C	7.0	0.1	ND	ND	ND	ND	ND
Control	45 °C	2.0	0.2	ND	ND	ND	ND	ND
Control	45 °C	12.0	ND	ND	ND	ND	ND	ND
Wet	20 °C	7.0	34.7	ND	0.2	ND	0.6	0.4
Wet	20 °C	2.0	25.3	ND	0.1	ND	0.5	0.4
Wet	20 °C	12.0	37.5	ND	0.2	ND	0.5	0.3
Wet	45 °C	7.0	41.0	ND	1.2	ND	1.3	0.3
Wet	45 °C	2.0	24.6	ND	1.2	ND	1.0	0.2
Wet	45 °C	12.0	18.8	ND	1.0	ND	1.3	0.3
Dry	20 °C	7.0	17.4	ND	0.4	ND	0.4	ND
Dry	20 °C	2.0	14.1	ND	0.5	ND	0.2	ND
Dry	20 °C	12.0	14.3	ND	0.3	ND	0.5	0.1
Dry	45 °C	7.0	83.7	ND	0.2	ND	1.1	0.7
Dry	45 °C	2.0	60.0	ND	0.3	ND	1.8	1.0
Dry	45 °C	12.0	162.1	ND	0.2	ND	4.1	1.0
Blank			0.2	ND	ND	ND	ND	ND

Note : ND = (< 0.1 µg/L)

BT=Benzothiazole

2-HOBT=2-Hydroxybenzothiazole

2-MTBT=2-Methylmercaptobenzothiazole

2-MBT=2-Mercaptobenzothiazole

2-MLB=2-(4-morpholinyl)-benzothiazole

DPA=Diphenylamine

larger amounts of BT for the dry process at all three pH's and for the wet process for a pH of 7.0. The concentration of BT increased as pH changed from 2 to 12 for the dry process leachates, but there was no clear pH dependent BT relationship for wet process leachates. Neither HOBT nor MBT were detected in any of the samples. MTBT and MLB were present in every non-control sample at concentrations that were only 1-5% of BT. Also, DPA was present at trace to low levels in most of the samples.

PAHs were detected in all twelve samples, but at much lower concentrations compared to benzothiazoles; the sum of all 24 PAHs examined was always less than 1 µg/L. (Table 5.5). There was a slight trend of more PAHs in dry process samples. The more water soluble PAHs (naphthalenes and phenanthrenes) were the major PAHs detected. The PAH abbreviations were presented earlier in Table 4.8.

Table 5.5 PAHs in Phase II in ng/L

Process	Temperature	pH	NAP	2MN	1 MN	BIP	DMN	ACL	ACT	TMN	FLU	PHE	ANT	IMP	FLA
Control	20 °C	7.0	25.5	ND	34.7	ND	ND	ND							
Control	20 °C	2.0	35.9	ND	35.9	ND	37.0	ND							
Control	20 °C	12.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	37.3	ND	31.4	ND
Control	45 °C	7.0	37.1	ND	37.9	ND	31.0	ND							
Control	45 °C	2.0	132	110	81.0	25.1	39.4	ND	ND	34.1	33.1	74.2	ND	58.2	ND
Control	45 °C	12.0	Sample highly colored, not analyzed												
Dry	20 °C	7.0	60.4	107	72.0	ND	32.5	ND	ND	ND	ND	42.7	ND	37.6	ND
Dry	20 °C	2.0	201	96.1	72.3	ND	28.5	ND	ND	21.8	ND	40.9	ND	ND	ND
Dry	20 °C	12.0	137	121	74.9	ND	38.4	ND	20.0	37.0	35.8	62.6	ND	63.0	ND
Dry	45 °C	7.0	104	148	73.8	20.4	37.3	ND	22.2	24.6	32.5	86.2	ND	75.7	ND
Dry	45 °C	2.0	145	175	74.5	48.9	ND	23.1	22.3	ND	ND	90.4	ND	29.9	20.2
Dry	45 °C	12.0	133	188	102	29.5	38.8	ND	20.7	34.1	24.7	90.7	ND	27.1	ND
Wet	20 °C	7.0	60.9	79.7	48.3	ND	ND	ND	ND	ND	ND	49.4	ND	ND	ND
Wet	20 °C	2.0	49.8	105	81.4	ND	ND	ND	ND	ND	ND	107	31.2	ND	20.6
Wet	20 °C	12.0	31.9	57.3	50.7	ND	ND	ND	ND	21.5	ND	52.9	23.3	20.0	ND
Wet	45 °C	7.0	93.9	134	82.9	20.0	41.1	ND	ND	23.3	36.0	98.6	ND	90.5	ND
Wet	45 °C	2.0	40.0	49.4	32.2	ND	ND	ND	ND	ND	ND	48.7	ND	ND	ND
Wet	45 °C	12.0	88.3	83.5	56.1	21.5	ND	ND	ND	ND	26.7	95.3	ND	89.5	ND
Blank			ND	52.1	45.2	ND									

Note: ND = < 20 ppt (ng/L)

Table 5.5 Continued

Process	Temperature	pH	PYR	BAA	CHR	BBF	BKF	BEP	BAP	PER	INP	DBA	BPE	SUM
Control	20 °C	7.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	60.2
Control	20 °C	2.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	109
Control	20 °C	12.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	68.7
Control	45 °C	7.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	106
Control	45 °C	2.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	601
Control	45 °C	12.0												
Sample highly colored, not analyzed														
Dry	20 °C	7.0	21.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	374
Dry	20 °C	2.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	461
Dry	20 °C	12.0	36.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	626
Dry	45 °C	7.0	39.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	664
Dry	45 °C	2.0	38.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	667
Dry	45 °C	12.0	21.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	710
Wet	20 °C	7.0	33.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	271
Wet	20 °C	2.0	68.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	464
Wet	20 °C	12.0	44.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	302
Wet	45 °C	7.0	56.6	20.0	20.0	ND	727							
Wet	45 °C	2.0	24.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	195
Wet	45 °C	12.0	63.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	524
Blank			ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	97.3

Note: ND = < 20 ppt (ng/L)

6.0 Phase III - Water Quality Evaluation of the CRM Asphalt Samples for Simulated Rainfall Conditions

6.1 Preparation of CRM Asphalt Samples

To simulate the rainfall conditions on CRM asphalt pavement in the laboratory, the slab specimens of size 300 mm (12 in) x 150 mm (6.0 in) x 62.5 mm (2.5 in) (length x width x thickness) were prepared with the same mix design used for the cylindrical specimens. Compaction of the specimens was done with the Mobile Steel Wheel Compactor (MSWC). The detailed procedures for the fabrication of the slab specimens are included in Appendix F. A total of ten slab specimens were subjected to simulation of light, wear (traffic), and rain in the laboratory including two specimens each for the control, the wet process and the dry process and four chip seal (two each for control and wet process) specimens (Figure 6.1).

To prepare the chip seal specimens the base slabs were prepared and then treated with an emulsified asphalt binder for controls and with the asphalt rubber binder for the wet process specimens. A mass of 0.95 cm (3/8 inch) mineral aggregates was applied on the top of a binder surface and then embedded into the binder using a vibratory compactor. The detailed procedures for the fabrication of the chip seal slab specimens are included in Appendix G.

6.2 Experimental Design to Simulate Environmental Conditions

6.2.1 Light Simulation

The sunlight intensity was monitored in June for the two-week period with a Type-217 light meter (a product of General Electric Lighting Product Services). The sunlight

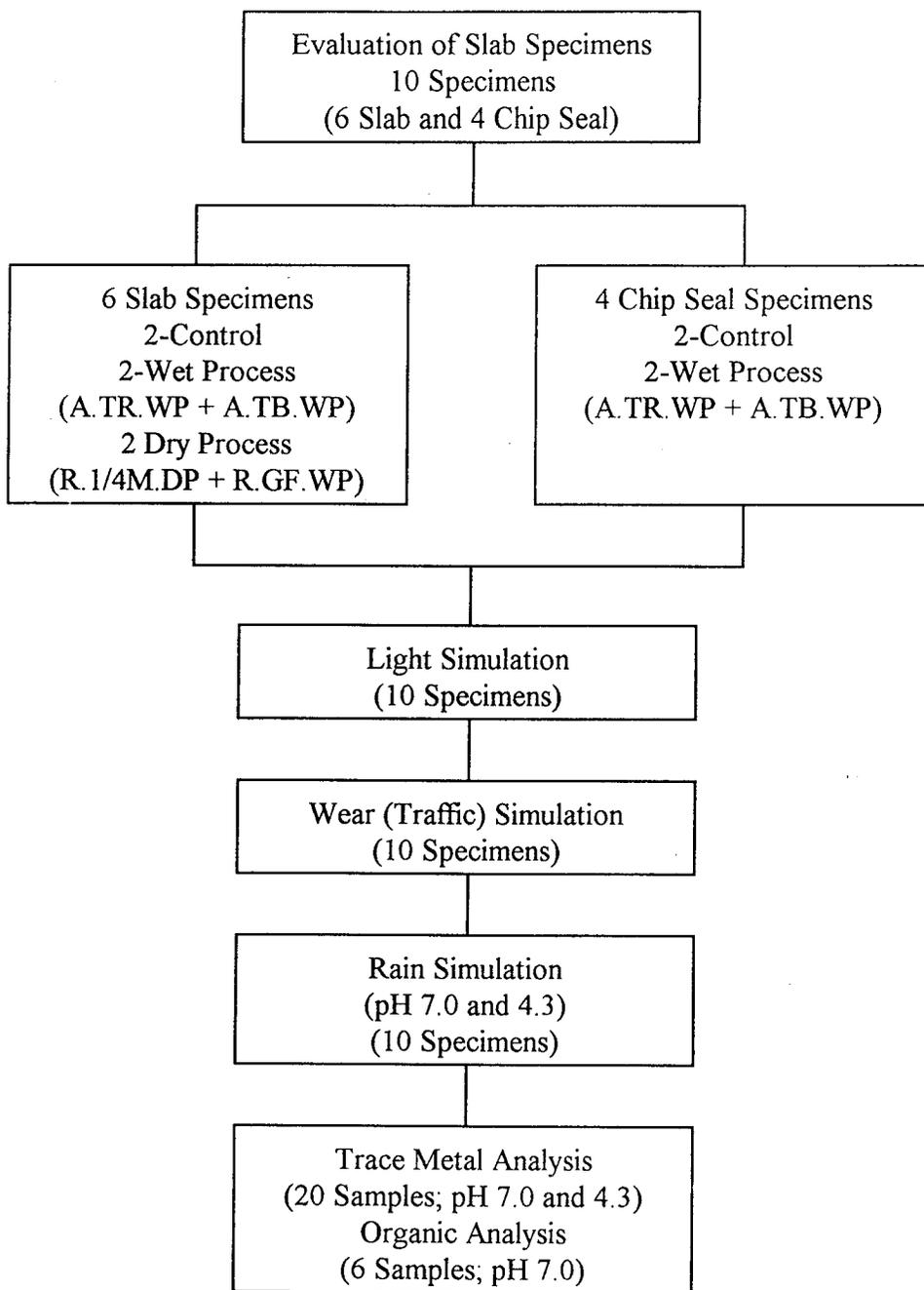


Figure 6.1 Phase III - Water Quality Evaluation of CRM Asphalt Samples for Simulated Rainfall

intensity was in the range of 10,000 foot candles. It was difficult to attain this high light intensity in the laboratory without increasing the temperature of the specimens' surface and the surroundings. Therefore, to avoid the increase in temperature, specimens were subjected to natural sun light.

Slab specimens were placed in a closed box on the roof of a building for 14 days. A HDPE box was used to avoid any contamination from the surroundings. The surface of the box was covered with a transparent plastic to expose the surface of the specimens to the sunlight but to avoid atmospheric deposition. Ventilation holes on the sides of the box were provided to control any temperature increase inside the box (Figure 6.2). After the 14 days sunlight exposure cracks were observed on the surface of all the specimens. It was also noted that the corners of all the wet processes specimens deteriorated during the light simulation.

6.2.2 Wear Simulation

Wear or traffic simulation was accomplished in the URI Transportation Engineering laboratory by using the MSWC. The specimens were subjected to 20 cycles of compaction. Teflon plates were used during the compaction to avoid any metal contact and possible contamination.

6.2.3 Rain Simulation

After the light and wear exposures, specimens were subjected to a high intensity rainfall. The rain simulator was designed to accomplish a rain storm of 125 mm (5.0 in) over 30 minutes. This rain intensity was selected to achieve maximum contamination concentration.

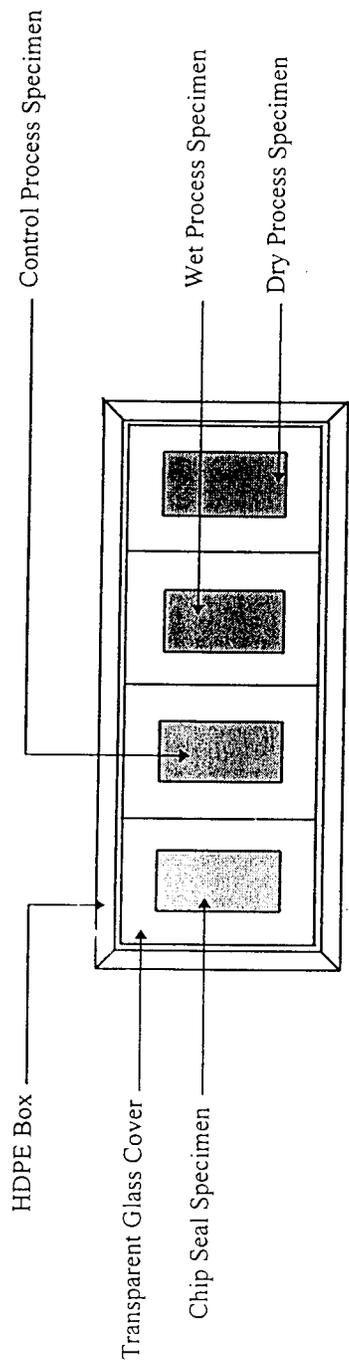


Figure 6.2 Schematic of Light Simulator

To avoid any contamination from the water, DI water was used to simulate the rain. A pH of 7.0 was used for the initial testing of each slab sample. Following this, in order to simulate actual rain, a pH level of 4.30 (Fraher 1991) was tested. A HDPE container was used to hold the water during rain simulation (Figure 6.3). Holes were made at the bottom of the container to allow the water to fall as rain over the slab surface. To simulate the variable intensity of the rain, the head of the water was not kept constant in the container during the rain simulation. Height between the container's bottom and the slab surface was kept constant throughout the simulation to keep the same striking force of the rain water to all the slab surfaces. A calibration chart was prepared for the DI water container to monitor the rain fall depth over the slab surface with respect to time. This calibration chart was mainly use to provide the same time and depth of exposure for all the specimens.

Considering the physical significance of the rain simulation in the laboratory, a water head of 5 feet was provided between the slab surface and the water container. To avoid erosion due to continuous striking of water at any particular spot, a constant movement of the slab specimen was provided. The continuous motion of the slab also helped to expose the full slab surface to the water during the rain simulation.

A tray with a thin Teflon sheet lining was used to keep the slab specimen in place during the rain simulation. A Teflon bucket was used to collect the water runoff to avoid any contamination from the surface of the sample collector.

6.3 Trace Metal Analyses Results - Phase III

The runoff samples for trace metal analyses were collected in 60 mL Nalgene, high

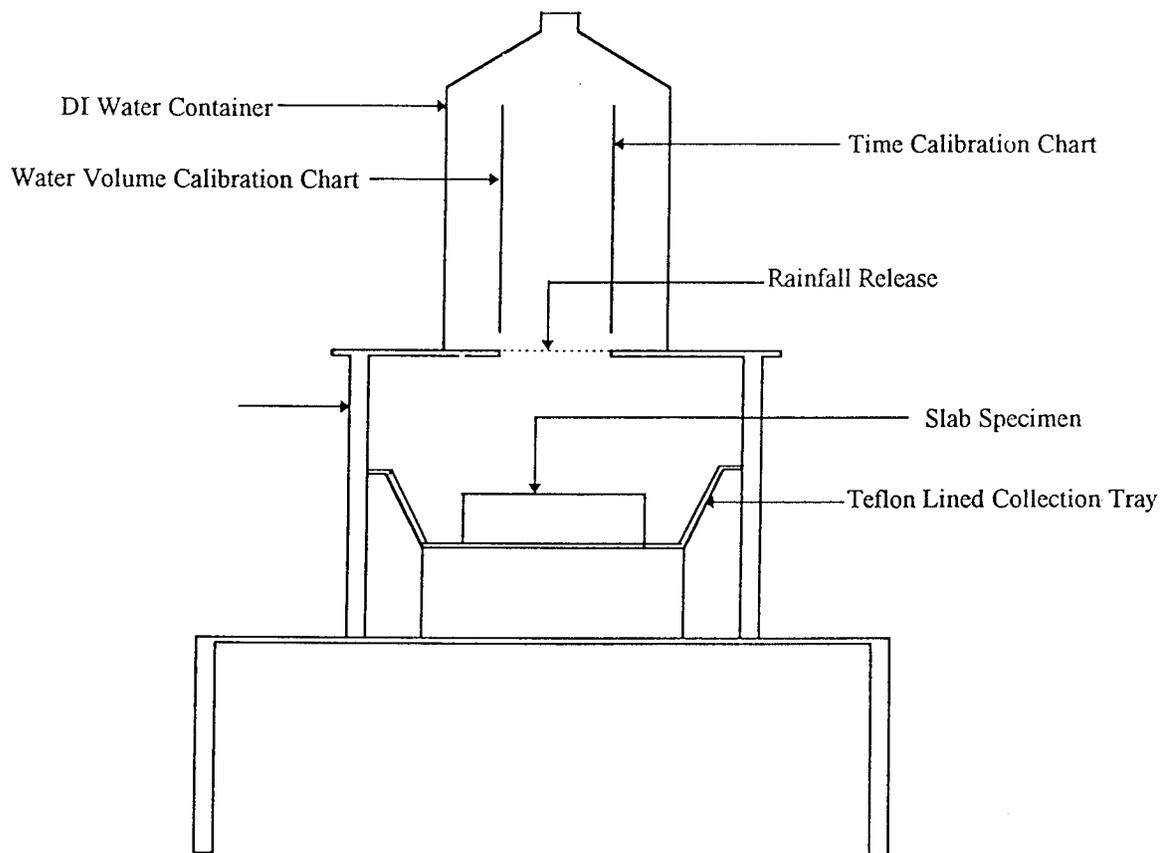


Figure 6.3 Schematic of Rain Simulator

density polyethylene bottles. Analysis procedures were the same as Phases I and II.

Collected water samples were analyzed for the total trace metals on the AAS and results are reported in Tables 6.1 and 6.2 for the pH of 7.0 and 4.3, respectively.

From Tables 6.1 and 6.2 the metal concentrations were very low for both pH levels and for the dry process specimens only two metals were detected. As shown in these tables and Figures 6.4 to 6.7, the metal concentrations for dry process specimens were less than the control and wet process specimens. The reason for this may be the surface finishing of the dry process, which was quite different from the control and wet process specimens. It was observed that the outer surfaces of the dry process specimens were very smooth providing a reduced surface area for water contact, whereas the outer surface of the wet process specimen was very rough. Due to the rough surface the wet process specimens offered more surface area for water contact during rain simulations. In general, there is very little difference in the magnitude of the metal concentration for the wet process, control and chip seal specimens.

6.4 Organic Analyses Results - Phase III

The water samples for organic analyses were taken in 4 liter amber glass jugs with Teflon lined caps; they were stored at room temperature. Immediately upon receipt, the pH of each sample (ca. 3.9 liters) was determined. The samples were spiked with internal standards. Due to time and budgetary constraints, the four chip seal samples were not analyzed. The solutions were extracted three times with methylene chloride. The methylene chloride extracts were combined, reduced to a small volume (200 μ l), and spiked with an external standard, o-terphenyl. The extract was then injected onto the GC-MS in the selected

Table 6.1 - Metal Concentrations for the Slab Specimens at a pH of 7.0

First Set Metals (µg/L)	HMA Slab Specimens			Chip Seal Slab Specimens	
	Control	Wet Process	Dry Process	Control	Wet Process
Cadmium	0.20	0.34	ND	ND	ND
Chromium	0.25	0.50	ND	0.20	0.50
Copper	2.52	1.86	ND	2.20	2.40
Lead	0.19	ND	ND	ND	0.30
Nickel	0.44	ND	ND	ND	ND
Zinc	3.50	8.00	5.23	7.50	9.00

Second Set Metals (µg/L)	HMA Slab Specimens			Chip Seal Slab Specimens	
	Control	Wet Process	Dry Process	Control	Wet Process
Cadmium	0.20	0.33	ND	ND	ND
Chromium	0.26	0.20	ND	0.60	0.24
Copper	2.95	4.61	2.28	2.19	2.39
Lead	0.20	ND	ND	0.36	ND
Nickel	ND	4.30	ND	ND	ND
Zinc	3.50	3.50	3.76	3.50	6.00

Average Metals (µg/L)	HMA Slab Specimens			Chip Seal Slab Specimens	
	Control	Wet Process	Dry Process	Control	Wet Process
Cadmium	0.20	0.34	ND	ND	ND
Chromium	0.26	0.35	ND	0.40	0.37
Copper	2.74	3.24	1.19	2.20	2.40
Lead	0.20	ND	ND	0.23	0.20
Nickel	0.27	2.20	ND	ND	ND
Zinc	3.50	5.8	4.50	5.50	7.50

Note: ND = non detectable

Table 6.2 - Metal Concentrations for the Slab Specimens at a pH of 4.30

First Set	HMA Slab Specimens			Chip Seal Slab Specimens	
Metals (µg/L)	Control	Wet Process	Dry Process	Control	Wet Process
Cadmium	0.84	0.85	0.18	0.13	0.24
Chromium	ND	ND	ND	ND	ND
Copper	1.88	2.25	1.49	0.20	0.71
Lead	2.12	1.56	0.53	0.87	0.65
Nickel	0.42	1.91	0.38	0.92	1.50
Zinc	2.10	4.60	0.67	1.00	3.50

Second Set	HMA Slab Specimens			Chip Seal Slab Specimens	
Metals (µg/L)	Control	Wet Process	Dry Process	Control	Wet Process
Cadmium	0.86	0.85	0.10	0.13	0.16
Chromium	ND	ND	ND	ND	ND
Copper	1.36	2.24	0.20	1.36	0.72
Lead	0.86	1.57	0.53	0.88	0.67
Nickel	0.40	1.04	1.66	0.95	1.24
Zinc	3.50	5.00	0.33	2.00	4.50

Average	HMA Slab Specimens			Chip Seal Slab Specimens	
Metals (µg/L)	Control	Wet Process	Dry Process	Control	Wet Process
Cadmium	0.85	0.85	0.14	0.13	0.20
Chromium	ND	ND	ND	ND	ND
Copper	1.62	2.25	0.85	0.78	0.72
Lead	1.49	1.57	0.53	0.88	0.66
Nickel	0.41	1.48	1.02	0.94	1.37
Zinc	2.80	4.80	0.50	1.50	4.00

Note: ND = non detectable

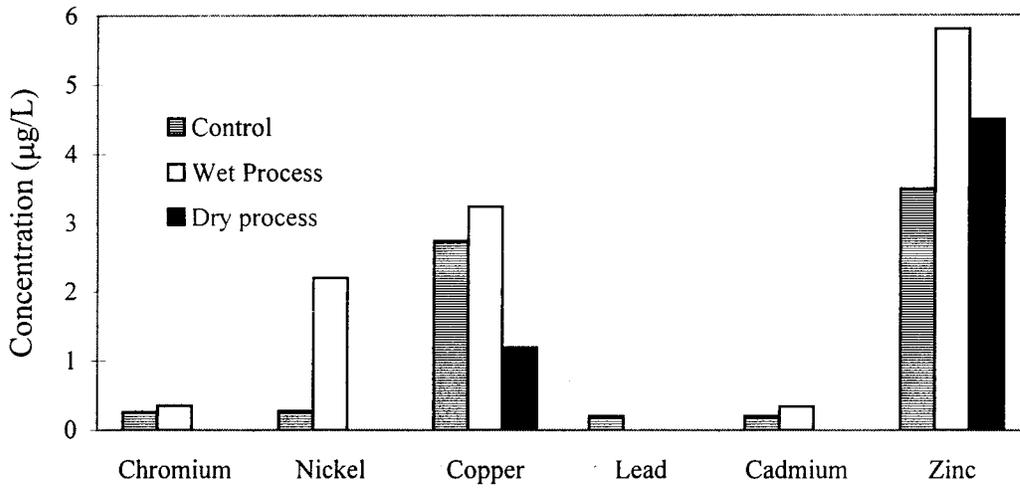


Figure 6.4 Slab Specimens vs Metal Concentration at pH 7.0

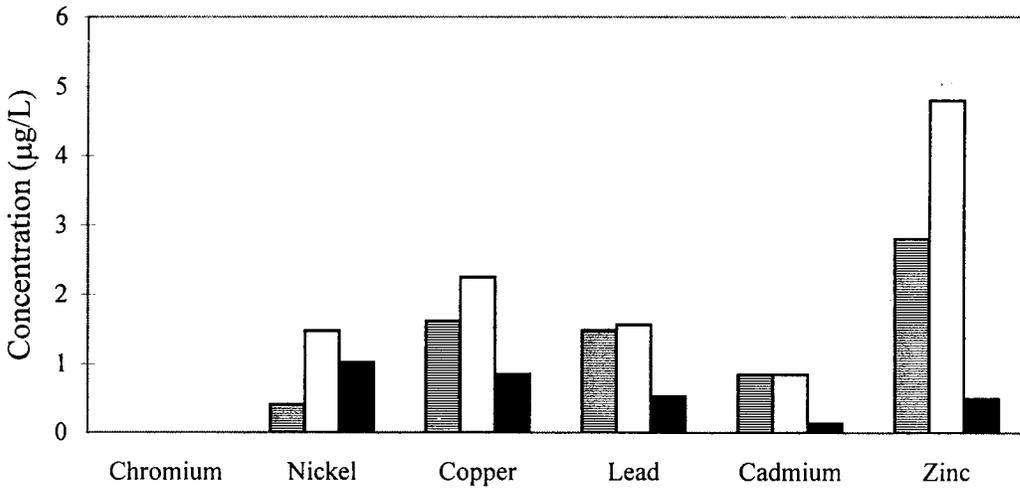


Figure 6.5 Slab Specimens vs Metal Concentration at pH 4.3

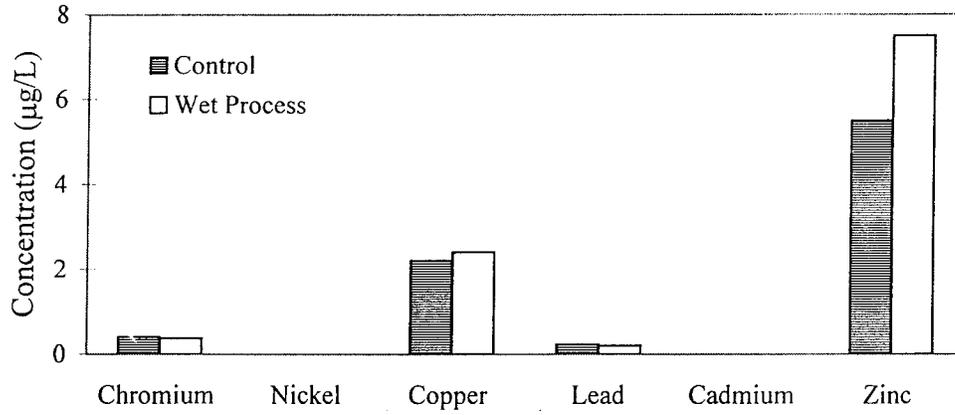


Figure 6.6 Chip Seal Slab Specimen vs Metal Concentration at pH 7.0

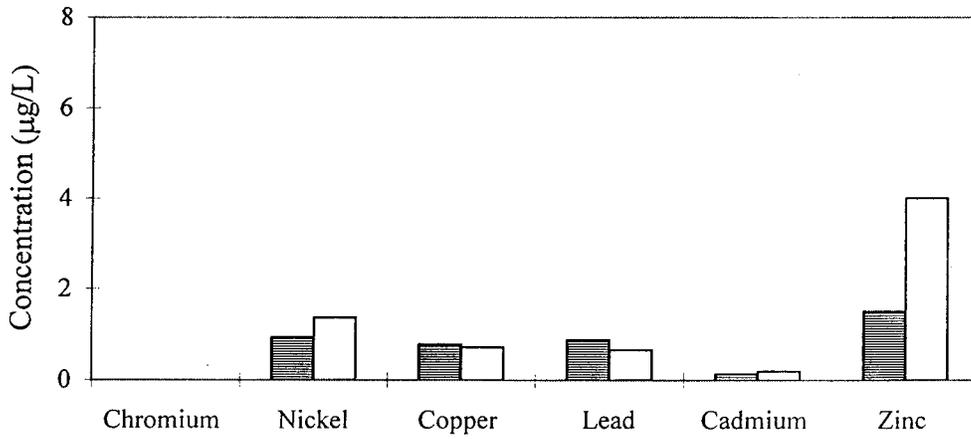


Figure 6.7 Chip Seal Slab Specimen vs Metal Concentration at pH 4.3

ion monitoring mode for the analysis of benzothiazoles. Because the extracts contained large amounts of benzothiazoles relative to PAHs, the extract was cleaned up using silica gel chromatography (same as above) prior to the analysis of PAHs. This fraction was reduced to a small volume (100 μ l) spiked with an external standard (pyrene-d12) and injected onto the GC-MS in the selected ion monitoring mode.

Recoveries of the MeBT internal standard ranged from 38% to 60%. PAH internal standard recoveries generally were 20% to 80%. Spiked blanks for the benzothiazoles and PAHs were very good with recoveries from 70% to 130%. The MDL for both the benzothiazoles and PAHs was 10 ng/L.

The pH of all the samples was 6. In both the wet and dry process samples, the most concentrated compound was BT with values ranging from 798 ng/L to 9990 ng/L (Table 6.3). The average BT concentration in the wet process samples, 8460 \pm 2160 ng/L, was about eight times greater than the dry process samples, 1160 \pm 510 ng/L. The other major compound detected was HOBT, but the difference between the wet and dry processes was much smaller. There was about 25% more of this compound in the average wet process (595 ng/L) than average dry process (470 ng/L). These results are opposite to what was found in the PES aqueous leachates; for the slab samples, the wet processes leached more benzothiazoles while for the PES samples, more benzothiazoles were detected in the dry process samples. MTBT, MLB, and DPA were detected, but they were at much lower concentrations compared to BT or HOBT. The control samples contained some BT and HOBT.

The sum of all PAHs were much less abundant than the benzothiazoles (Table 6.4). Naphthalene, the PAH with the largest aqueous solubility, was the most enriched PAH in both

Table 6.3 Benzothiazoles and Diphenylamine in Phase III

Sample ID	Organic Compounds					
	BT	HOBT	MTBT	MLB	MBT	DPA
	Concentrations are in ppt (ng/L)					
1st control process	120	ND	ND	ND	NA	ND
2nd control process	147	24	ND	ND	NA	ND
1st wet process	6.93E+03	555	65	103	NA	50
2nd wet process	9.99E+03	634	119	128	NA	82
1st dry process	798	471	10	46	NA	13
2nd dry process	1.52E+03	469	17	79	NA	34

Note: NA = not analyzed; ND = < 10 ppt (ng/L)

Table 6.4 PAH's Concentration in Phase III

PAH's	NAP	2 MN	1 MN	BIP	DMN	ACL	ACT	TMN	FLU	PHE	ANT	IMP	FLA	PYR	BAA	CHR	BBF	BKF	BEP	BAP	PER	INP	DBA	BPE	SUM	
Sample ID																										
1st control process	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0
2nd control process	NOT ANALYZED																									
1st wet process	12.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	12.5
2nd wet process	NOT ANALYZED																									
1st dry process	23.4	ND	18.3	ND	41.7																					
2nd dry process	NOT ANALYZED																									

Concentrations are in ppt (ng/L)

Note: ND = < 10 ppt (ng/L)

the wet and dry process with concentrations ranging from 12.5 ng/L to 23.4 ng/L. Although the sum of PAHs in the dry process was greater than the wet process as in the PES study, this is probably not significant since the concentrations of both were relatively low.



7.0 Discussion

7.1 Trace Metals

Acute and chronic toxicity criteria are used as a tool to maintain, preserve and improve the water quality of rivers. It is also used to prevent the system from becoming unsuitable for fishing, swimming and other beneficial uses, thus protecting the public health and the environment. Specifically, these toxicity criteria are used to (1) assess the suitability of environmental conditions for aquatic life (2) establish acceptable receiving concentrations and (3) assess the degree of wastewater treatment needed to meet water pollution control requirements.

The toxicity criteria were calculated using the EPA's fresh water aquatic criteria (Table 7.1). These criteria are based on hardness (USEPA 1991). Hardness values in Rhode Island are typically very low. As an example, data for a 12 year water quality record for the Pawtuxet River are given in Table 7.2 and show that hardness rarely exceeded 50 mg/L as CaCO₃ (Table 7.3). Table 7.3 also shows the EPA's drinking water criteria (USEPA 1994).

The maximum concentrations observed in Phase II and III never exceeded either the aquatic or drinking water criteria for Cr, Ni or Pb. For copper, the maximum concentration did exceed the aquatic criteria for a hardness value of 50 mg/L. However, of the 46 samples determined in Phase II and III only 3 or 6.5% actually exceeded criteria.

For cadmium approximately 13% of the samples analyzed exceeded the metal criteria associated with the lowest hardness value (50 mg/L). The highest observed concentrations even exceeded the acute and chronic criteria at 150 mg/L hardness. For drinking water standards about 4.5% of the samples exceeded criteria. To place these findings into

Table 7.1 US EPA's Fresh Water Aquatic Life Criteria for Total Metals

Metal	Acute ($\mu\text{g/L}$)	Chronic ($\mu\text{g/L}$)
Cadmium	$e^{(1.128[\ln H]-3.828)}$	$e^{(0.7852[\ln H]-3.49)}$
Chromium	$e^{(0.819[\ln H]+3.688)} + 16$	$e^{(0.819[\ln H]+1.561)} + 11$
Copper	$e^{(0.9422[\ln H]-1.464)}$	$e^{(0.8545[\ln H]-1.465)}$
Lead	$e^{(1.1273[\ln H]-1.46)}$	$e^{(1.1273[\ln H]-1.465)}$
Nickel	$e^{(0.846[\ln H]+3.3612)}$	$e^{(0.846[\ln H]+1.1645)}$
Zinc	$e^{(0.978[\ln H]+0.8604)}$	$e^{(0.986[\ln H]+0.7614)}$

Note: Where H is the hardness in mg/L as $\text{CaCO}_3 = 2.497[\text{Ca}] + 4.118 [\text{Mg}]$

Note: Source is the USEPA (1991)

Table 7.2 12 Years of Hardness Data for the Pawtuxet River, RI

Water Year	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1992	1993
Month													
March	16	56	47	27	18	18	NA	28	29	37	39	29	23
June	22	42	65	NA									
September	51	58	76	27	64	24	39	44	58	54	44	39	41
November	36	NA											
December	43	26	35	NA									
Average	34	46	56	27	41	22	40	36	44	47	42	34	32

Source: US Geological Survey Water-Data Reports for Massachusetts and Rhode Island

Note: Annual average hardness (total) as CaCo3 is only for the months, for which hardness data are available in the source.

Note: NA = not available

Table 7.3 Comparison of Phase II and III Metal Concentrations with EPA's Standards

Hardness/Metals	EPA's Fresh Water Aquatic Life Criteria for Total Metals						Maximum Observed Concentration (µg/L)	EPA's Drinking Water Standards Maximum (µg/L)	I-95 Runoff Study Maximum (µg/L)
	Acute (µg/L)			Chronic (µg/L)					
	50 mg/L	100 mg/L	150 mg/L	50 mg/L	100 mg/L	150 mg/L			
Cadmium	2	4	6	1	1	2	12.7	5	7
Chromium	1000	1750	2435	127	218	299	5.24	100	32
Copper	9	18	26	7	12	17	12.7	1300	103
Lead	19	42	66	19	42	66	16	15	93
Nickel	790	1415	2000	88	158	222	23.8	100	42
Zinc	108	214	318	101	200	300	1765	5000	687

Note: Metal concentrations are calculated based on EPA's fresh water aquatic life criteria listed in Table 7.1.

Note: Hardness is in mg/L as CaCO₃ = 2.497 [Ca] + 4.118 [Mg]

Note: I-95 Runoff data are based on Bade (1996)

Note: Maximum Observed Concentrations occurred for Phase II and a pH of 2.0

perspective, one must consider that all runoff will be diluted and that this dilution will vary on a case by case basis. Since this comparison is a worst case scenario and does not take into consideration the receiving water dilution, frequency and magnitude of exceedence was considered insignificant.

Results from this study are similar to an earlier study on leaching characteristics of scrap tires (MPCA 1990) and other studies. All the metals were leached in the higher concentration under acidic conditions. As concluded by Nelson et al. (1994) zinc was the primary toxicant. The results from this study also show zinc at the highest concentrations among all tested metals. However, Nelson et al. (1994) further states that toxicity caused by zinc concentrations, leached from the tires used in artificial reefs, would not cause acute or even chronic toxicity. Similar results were concluded by Nozaka et al. (1973) that no harmful substances were found in the leachate from tire materials soaked in fresh water.

7.2 Organics

Detecting benzothiazoles in samples throughout this project was not surprising based on the literature review presented in Chapter 2.

In this study we found similar concentrations of BT as in the Neison et al. (1994) study, although we expressed our results on a microgram per of gram of CRM. Nelson et al. had suggested that the BT was from something other than the tire material; however, it would seem reasonable to suggest that what they observed was, in fact, from the tire material and that their control was contaminated from their sample.

As stated earlier, that the concentrations of MBT and BT in the tennis ball leachate were only an estimate because MBT partially degrades into BT in the GC injector port. One

might ask, is the absence of MBT in the tire leachates due to the MBT being transformed into BT? We can not unequivocally state that no MBT was leached from the tire material; however, we believe that it was probably not leached because of the physical differences in the materials. Tennis balls usually have a protective felt cover and undergo minor environmental weathering during their lifetime compared to automobile tires which are subjected to prolonged cold and hot periods, rainwater, and sunlight. The MBT in rubber tires degrade into BT as the rubber ages due to oxidative processes (Brooks 1963) and it is believed that most or all of the MBT in the crumbed tires had already degraded, while at least some of the MBT in the tennis balls was not degraded. Tennis ball material is only used in the wet process, so MBT may be a factor with wet process crumb rubber modified asphalt.

MBT also degrades in the presence of acid into BT (Weisbull 1962) and in sunlight into a mixture of BT and HOBT (Brownlee et al. 1992). This is consistent with our results when the tennis ball material was leached in acid; there was an absence of MBT and a dramatic increase in BT. Both HOBT and MBT, which were detected in the CRM investigation, were absent in later phases of the study. For the PES investigation, one explanation may be due to the extraction pH. Both HOBT and MBT can ionize into anions in basic solutions; this would greatly reduce the extraction efficiency of these compounds. This is a reasonable explanation for HOBT because in the slab study, when the extraction pH was slightly acidic, HOBT was detected again. Since MBT is thermally, chemically, and photolytically unstable, it is difficult to predict whether any MBT was ever present in the PES and Slab studies

There are no water quality criteria for benzothiazoles. For the individual PAHs in

which there is data available, the maximum contaminant levels for drinking water are from 100 ng/L to 300 ng/L (USEPA 1994); these concentrations were reached for some of the PAHs (i.e. naphthalenes and phenanthrene) in the PES study.

The concentrations of benzothiazoles did not differ significantly between the leaching time of two and seven hours. This suggests that the crumbed material and the solution reached some type of sorption equilibrium; however, the concentration of benzothiazoles did not approach their aqueous solubilities. The sorption characteristics of CRM are beyond the scope of this report, yet these results do pose an important question: Can crumb rubber material in asphalt act as a solid phase sorbent which may accumulate pollutants such as hydrophobic organic contaminants (i.e. PAHs) and metals (i.e. copper)? This is consistent with old tires being more toxic than new tires, as stated previously. A worst case scenario may even have these accumulated contaminants being desorbed when an organic solvent (gasoline or diesel fuel) contacts the crumb rubber material in the asphalt, or washed out as roads expand during summer months and allow rainwater to penetrate into the top layer of the asphalt surface. Another possibility might be the conversion of the water soluble benzothiazoles into hydrophobic compounds due to condensation or polymerization reactions on particle surfaces. These compounds might then be as stable, persistent, and toxic as the PAHs in runoff, but in much higher concentrations.



8.0 Conclusions and Recommendations

This study focused on the issues surrounding the use of recycled rubber in asphalt pavements based on the environmental concerns involving water quality. More specifically, this laboratory study identified potential contaminants associated with recycled rubber in asphalt.

8.1 Conclusions

1. Zinc concentrations were at least an order of magnitude higher than any other metal for all CRM samples.

2. In some cases trace metal results were sufficient to conclude that the CRM samples did not vary significantly over the 3 month time period (Producer A for zinc, cadmium and chromium), while other trace metal data was incomplete and no conclusion could be reached.

3. The concentration of some metals were inversely related to particle size demonstrating the potential between metal availability and surface area.

4. Emission spectrograph results showed that chromium was "targeted" in 7 of 10 samples, but its presence was not confirmed. The AAS results show the presence of chromium in concentrations well above detection.

5. Emission spectrograph results indicated no presence of Ni, Cu, Pb, Cd and Zn whereas, AAS results show the presence of all metals in concentrations well above detection.

6. For most of the cylindrical specimens metals were leached in the highest concentrations at the pH of 2.0 and the lowest at the pH of 7.0.

7. For most of the cylindrical specimens, metals were leached in the highest

concentrations at maximum asphalt pavement temperature (45 °C).

8. The variation in metal concentrations between control, dry and wet cylindrical specimens were not consistently different. Where significant differences do occur, the dry process usually has the highest concentration.

9. Due to different surface finishing and exposed surface area of the slab specimens the lowest metal concentrations occurred with the dry.

10. Metals from slab specimens were leached in very low concentration for both pH levels (4.3 and 7.0).

11. Based on the limited scope of this effort and the comparison of results with trace metal water quality criteria, there is no evidence that there will be a detrimental effect on the environment or to human health.

12. With regards to organics, the major compounds leached from the CRM samples were benzothiazoles including BT, MBT and HOBT; no evidence of large amounts of other possible organic contaminants, e.g., PAHs, were detected.

13. In the PES study, the dry process leached more BT than the wet process at 45 °C, but not at 20 °C. For the both processes, leaching of BT increased with an increase in temperature from 20 °C to 45 °C, except for the wet process at a pH of 2.0 and 12.0. The concentration of BT increased with increasing basic pH for the dry process leachates at 45 °C, but not at 20 °C. There was no clear pH dependent BT relationship for wet process leachates.

14. The wet process leached more benzothiazoles (BT, HOBT, MTBT, and MLB) in the slab runoff samples than the dry process. This trend is consistent with that of the 20 °C PES aqueous leachates.

15. Benzothiazoles are already in the environment from urban runoff. Crumb rubber asphalt would contribute an additional source of these compounds. The magnitude of this input as well as the effects of weathering on the source, fate, and effects of the benzothiazoles are unknown at this time.

8.2 Recommendations

1. It is recommended that Phase III be redesigned and expanded involving a more comprehensive evaluation of the impacts of light, wear (traffic) and rainfall.
2. It is recommended to evaluate existing CRM field sites either in situ or with core samples under controlled laboratory experiments.
3. Finally, it is recommended that field test sections should be constructed using the findings of this and engineering studies for long term experimental monitoring.



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Appendix A

Emission Spectrograph Analyses Results

The data are not included herein. However, the results may be obtained by writing to the authors of this report.



Appendix B

Metal Concentration by Type and Source - Phase I

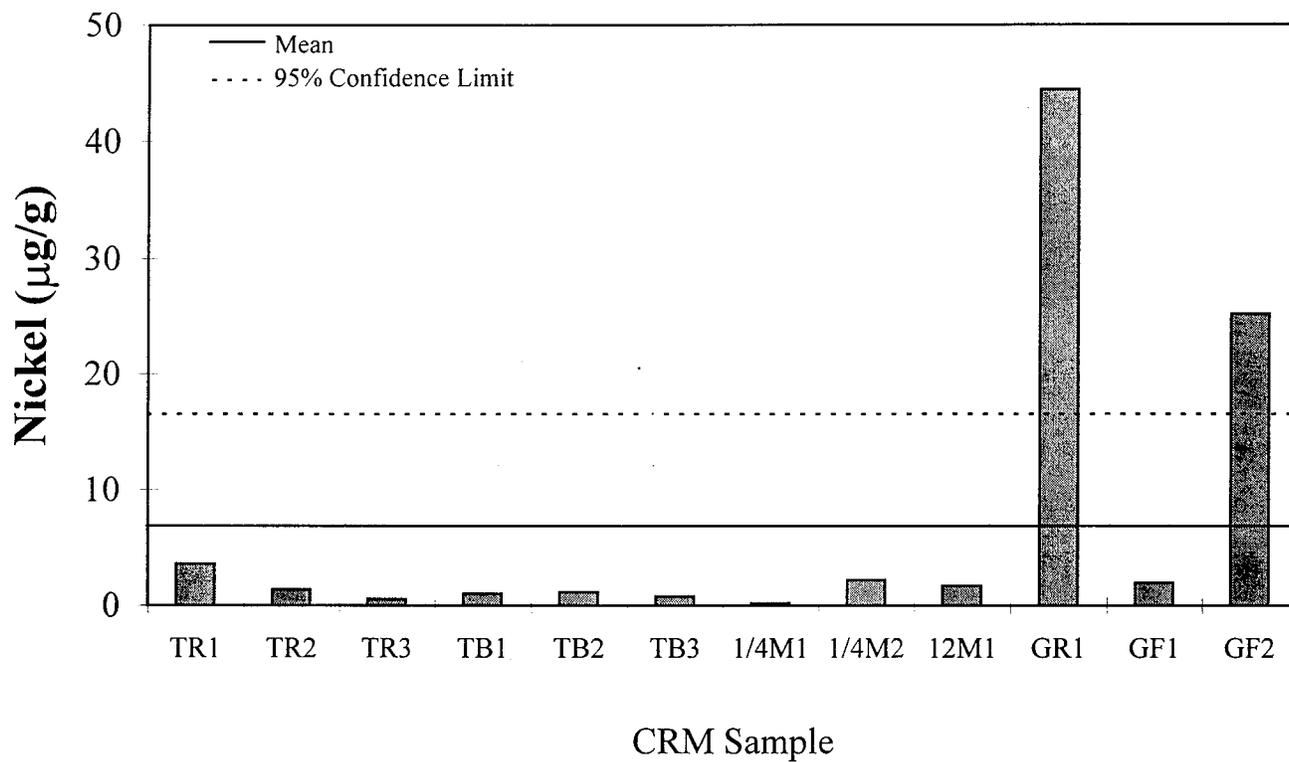


Figure B1 Nickel Concentration by Type and Source

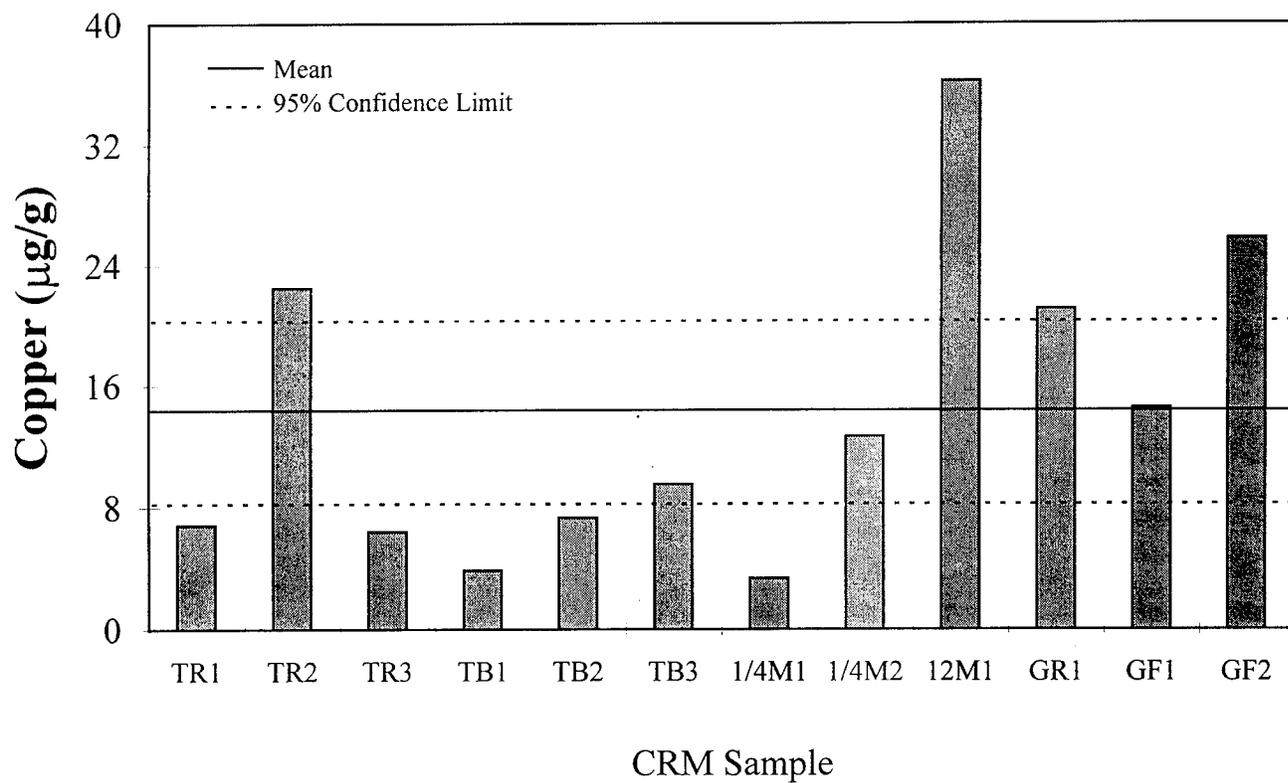


Figure B2 Copper Concentration by Type and Source

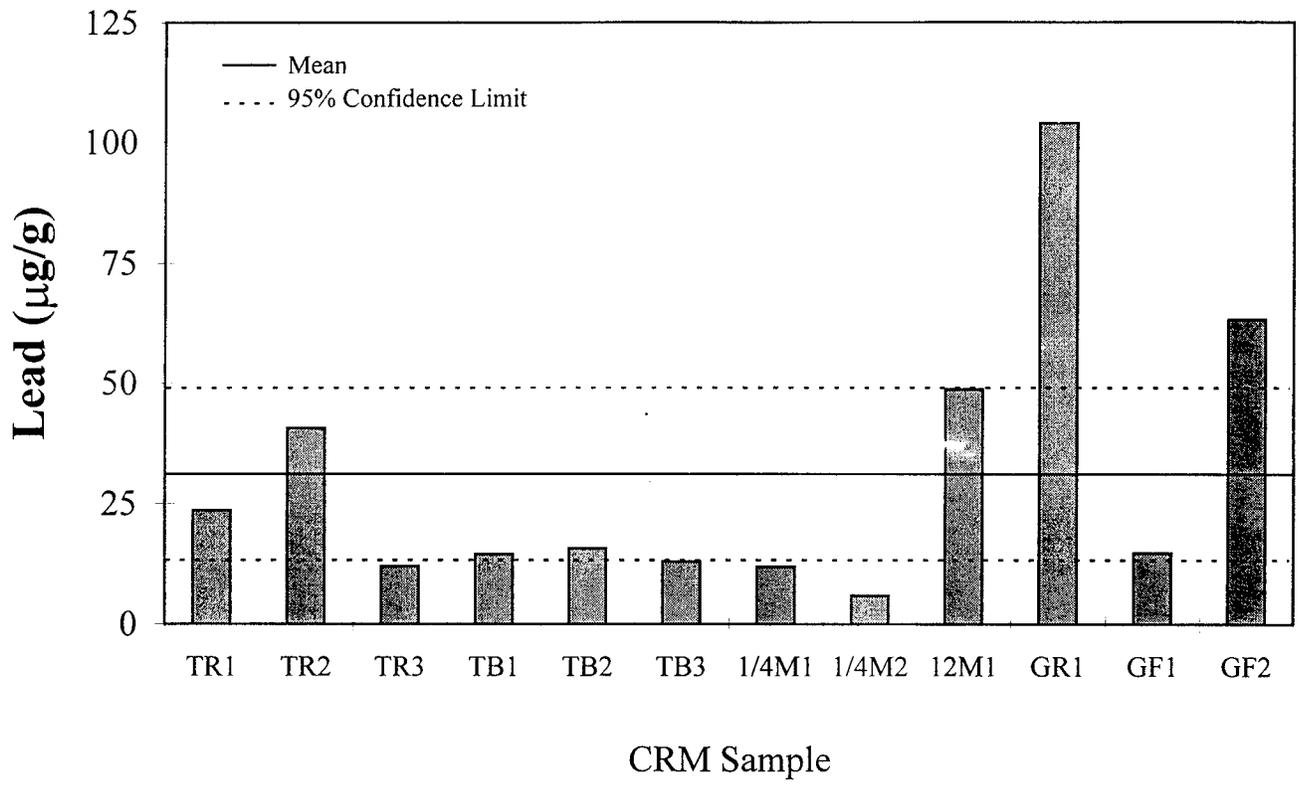


Figure B3 Lead Concentration by Type and Source

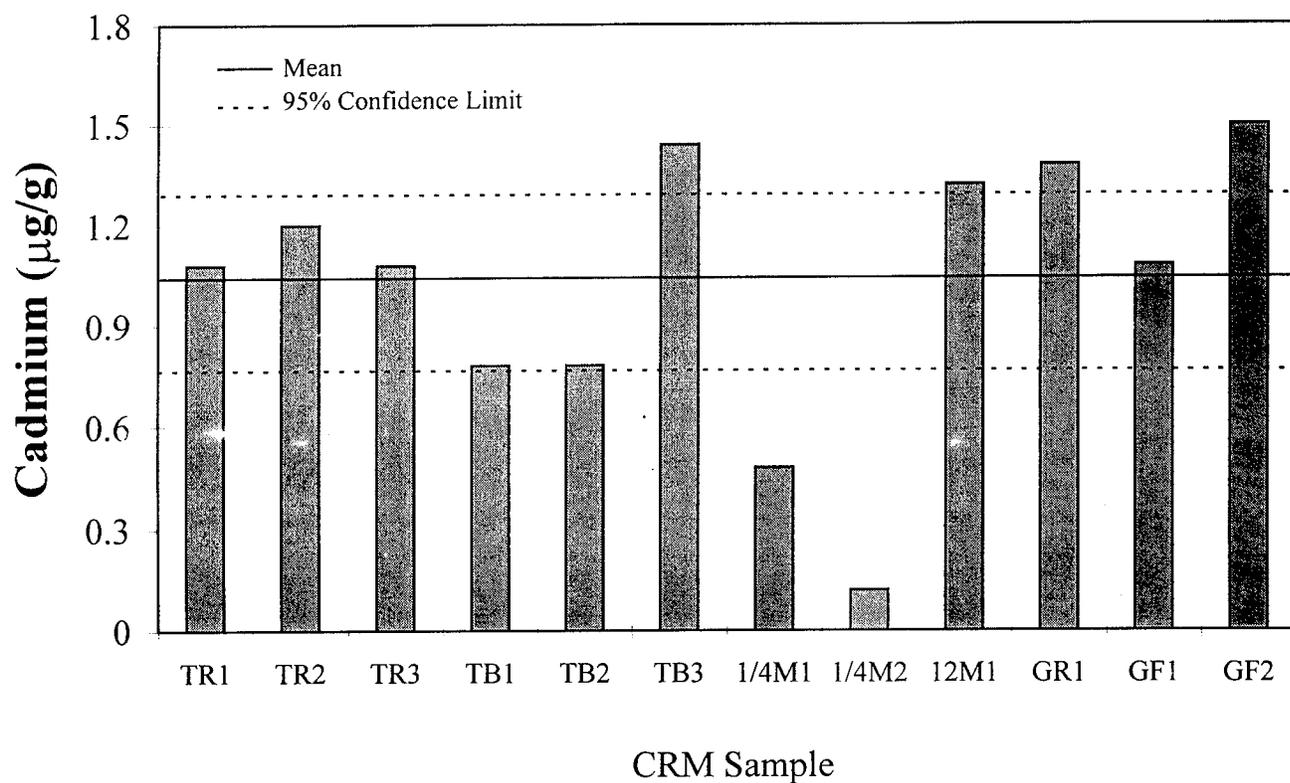


Figure B4 Cadmium Concentration by Type and Source

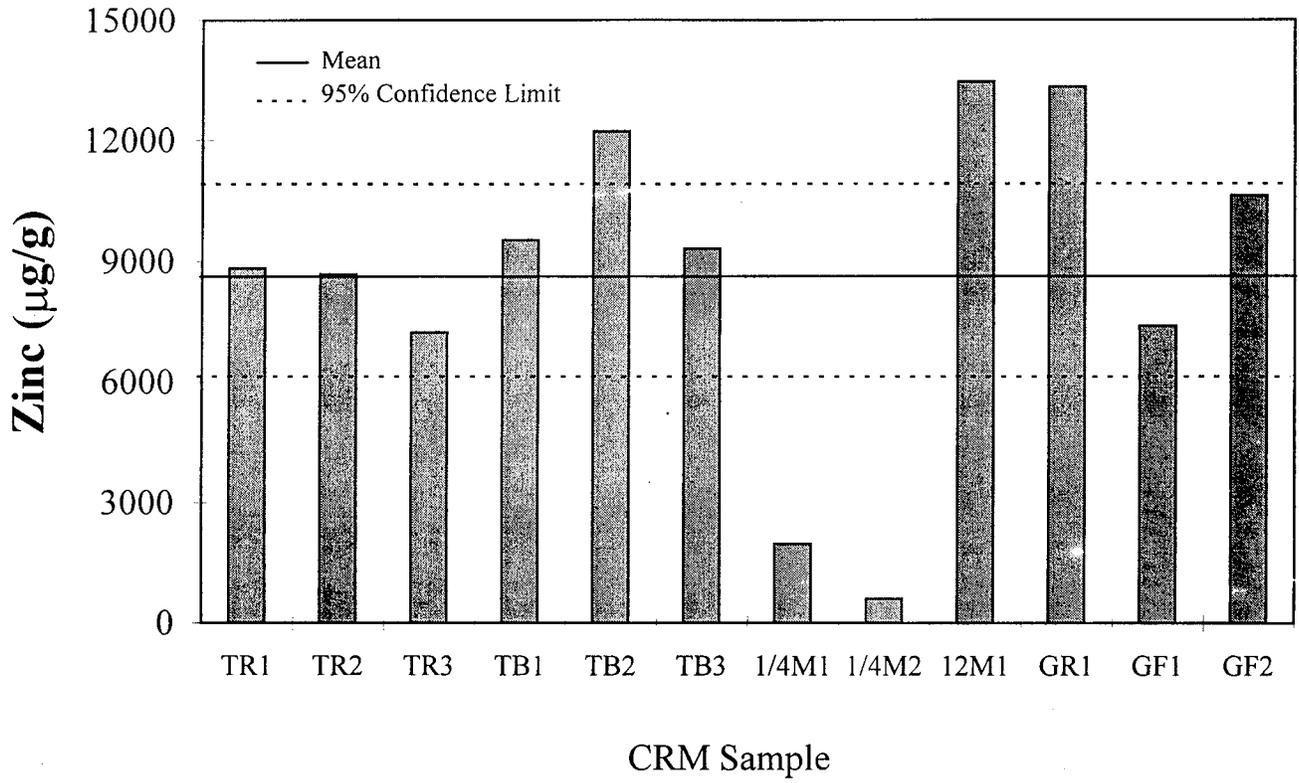


Figure B5 Zinc Concentration by Type and Source

Appendix C

Average Metal Concentration by Type and Source - Phase I

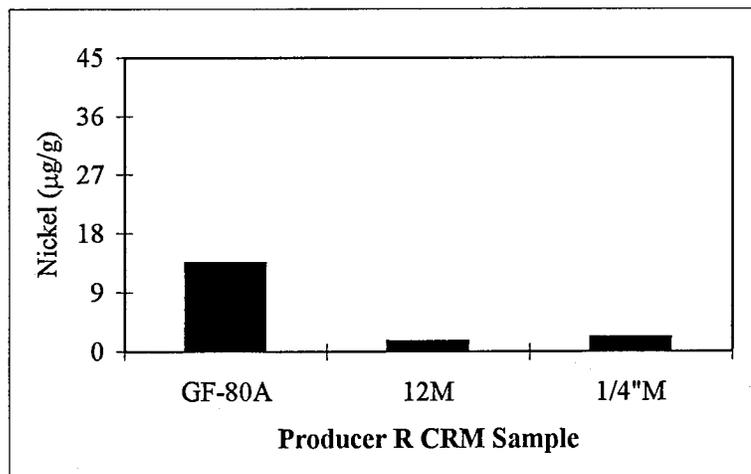
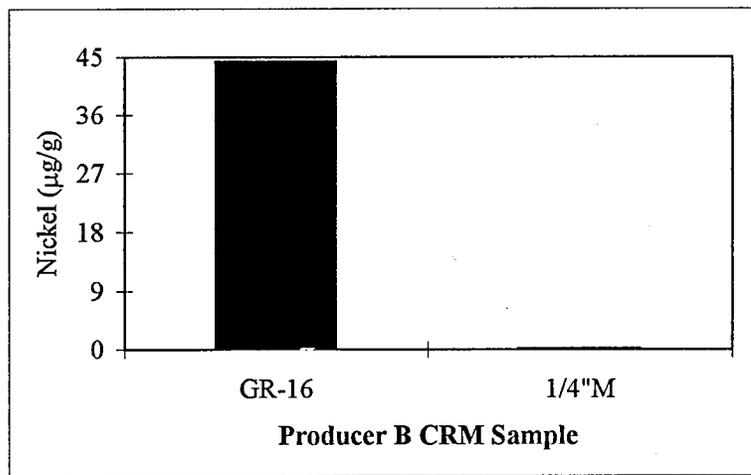
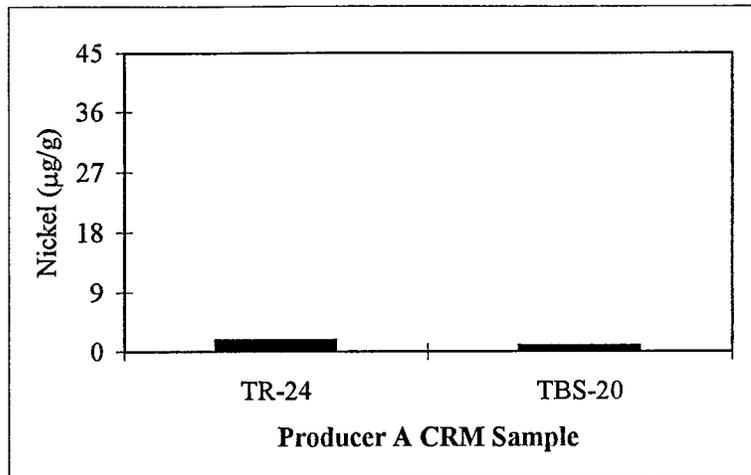


Figure C1 Average Nickel Vs Type and Source of CRM

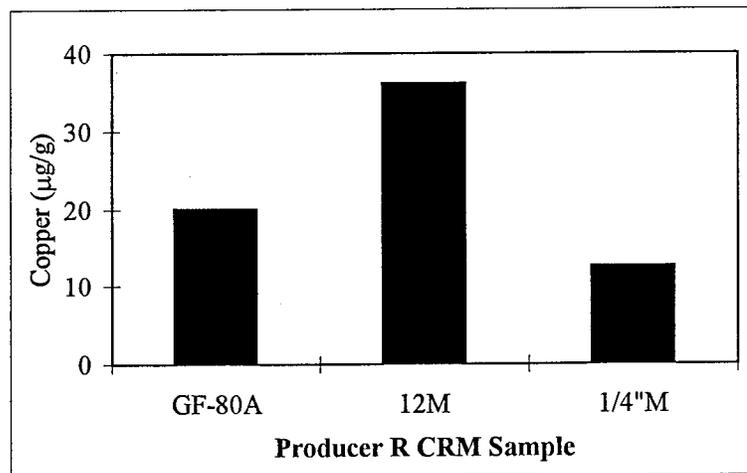
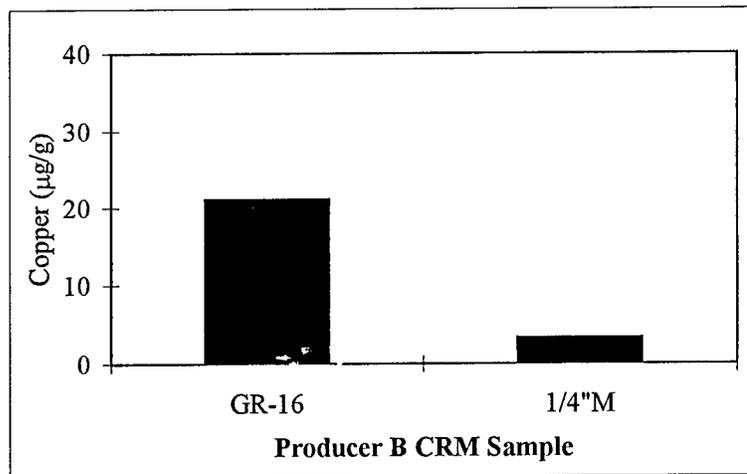
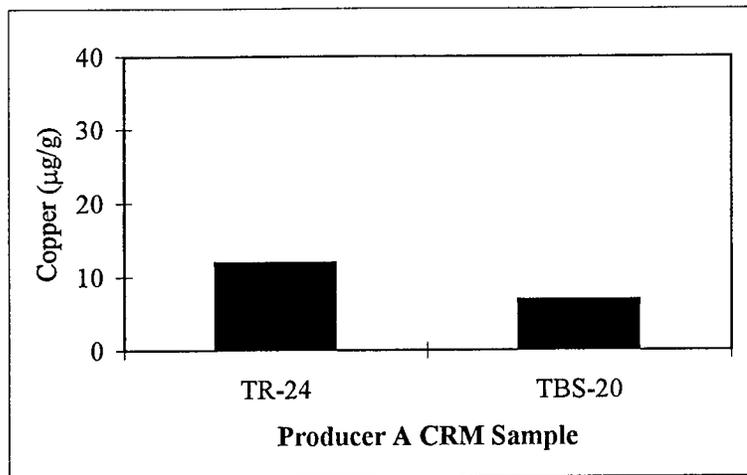


Figure C2 Average Copper Vs Type and Source of CRM

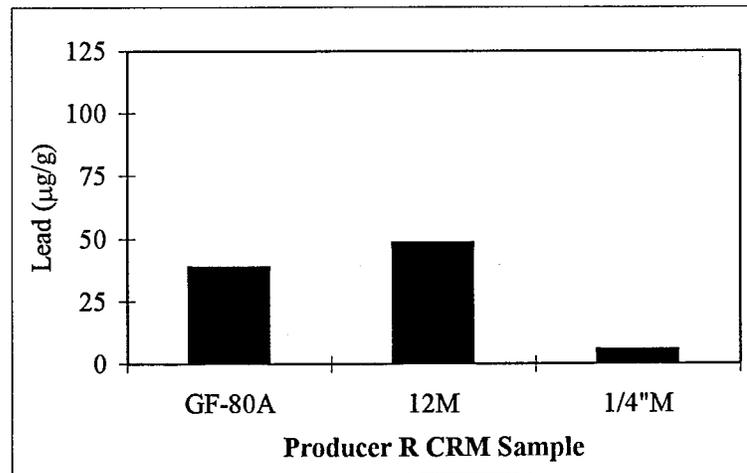
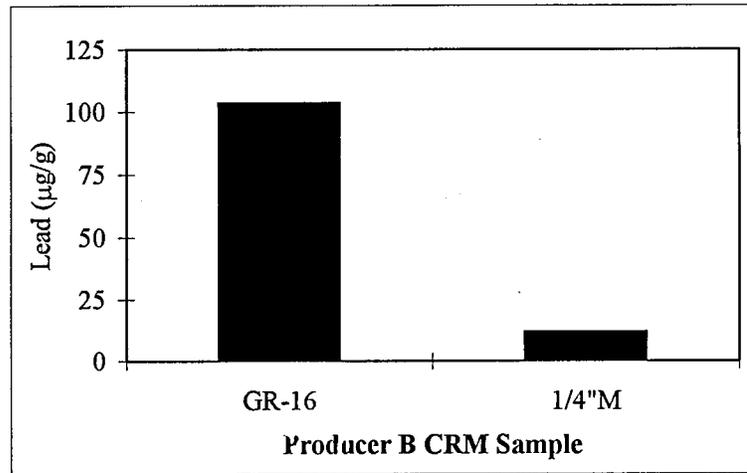
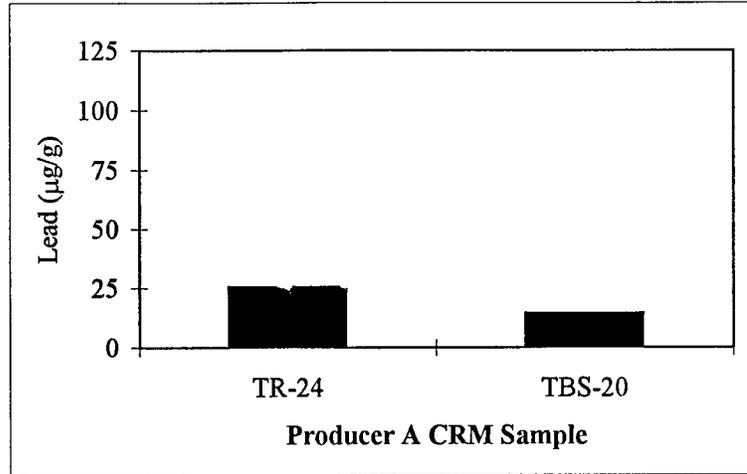


Figure C3 Average Lead Vs Type and Source of CRM

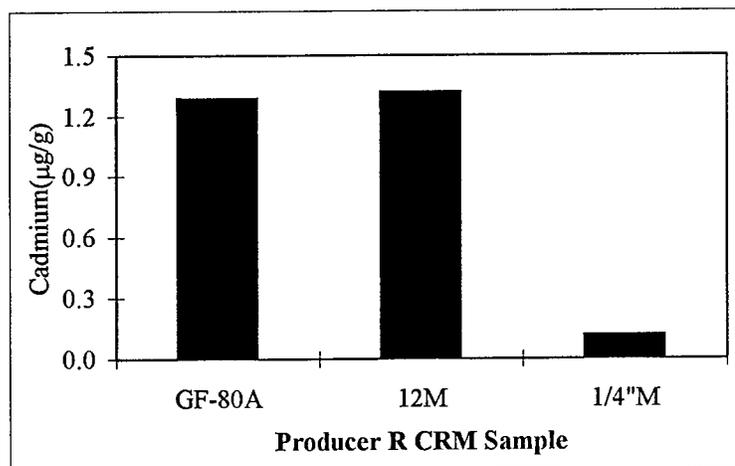
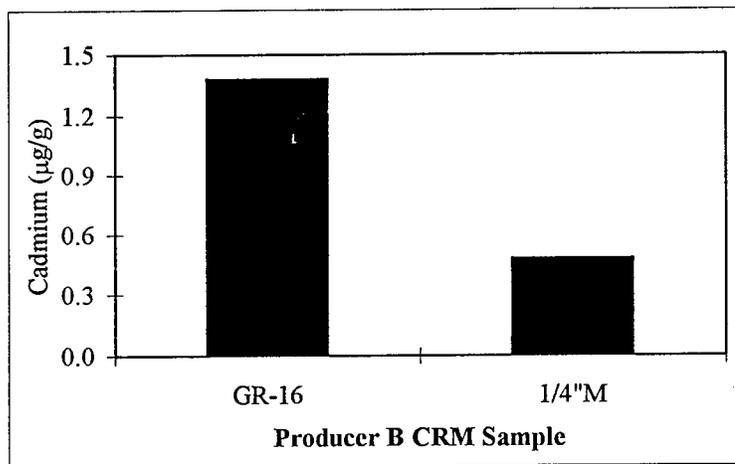
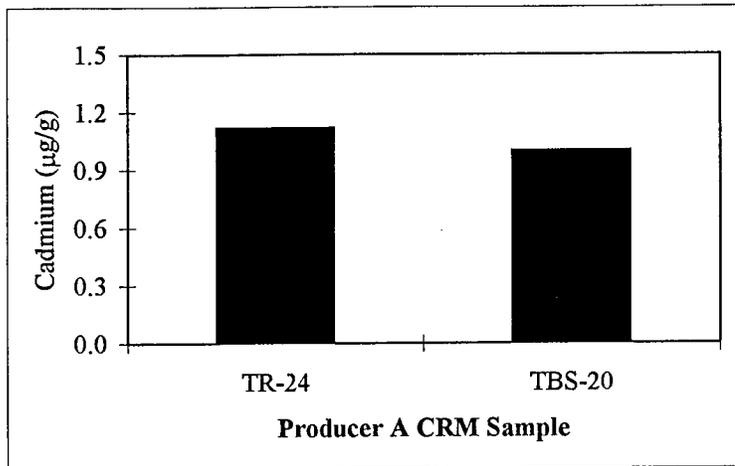


Figure C4 Average Cadmium Vs Type and Source of CRM

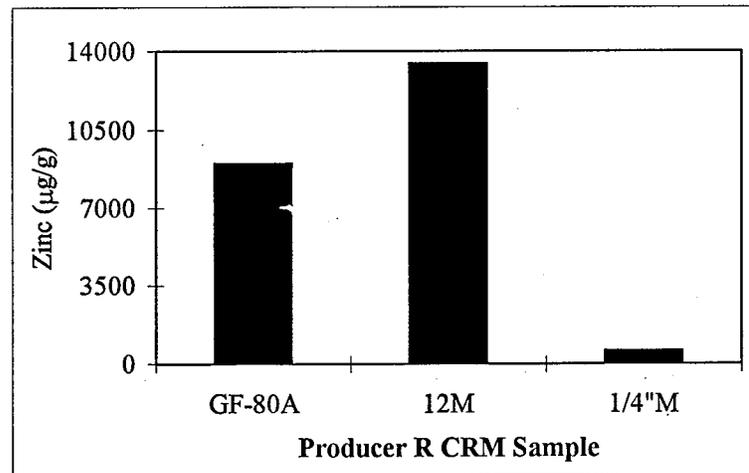
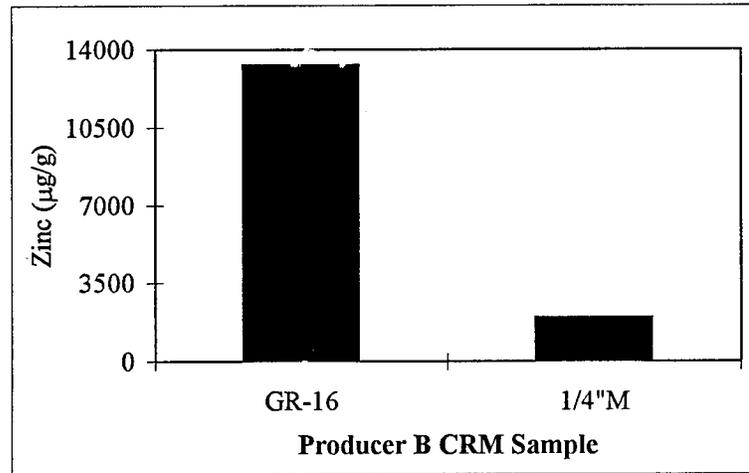
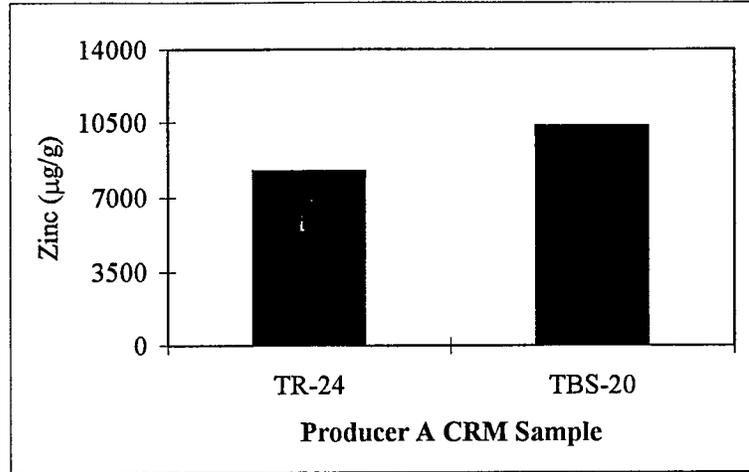


Figure C5 Average Zinc Vs Type and Source of CRM

Appendix D

Detailed Procedures for the Fabrication of Cylindrical Specimens - Phase II

The procedures are not included herein. However, the description may be obtained by writing to the authors of this report.



Appendix E

Effect of Temperature on Water Quality by Type and Source - Phase II

The data are not included herein. However, the results may be obtained by writing to the authors of this report.



Appendix F

Detailed Procedures for the Fabrication of Slab Specimens - Phase III

The procedures are not included herein. However, the description may be obtained by writing to the authors of this report.



Appendix G

Detailed Procedures for the Fabrication of Chip Seal Slab Specimens - Phase III

The procedures are not included herein. However, the description may be obtained by writing to the authors of this report.

