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Leaching behavior of metals from asphalt mixtures modified with crumb rubber from scrap tires

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Abstract

There are concerns about the potential toxicity of bitumen and recycled materials such as reclaimed asphalt pavements from end-of-life roads and crumb rubber from scrap tires used in asphalt mixtures because they contain metals that may be released into the groundwater. This study investigated the potential metal leaching of laboratory-prepared asphalt mixtures modified with polymer coated rubber (PCR) with wet and dry technology, devulcanized rubber (DVR), compared to an unmodified control mixture and a blend modified with a synthetic polymer (SBS). The objectives were to i) quantify concentrations of metals released, ii) calculate the flux rate, the cumulative mass release, and the assessment ratio for each metal, iii) verify if the metals exceeded the EPA drinking water limit, and, finally, iv) assess the source of metals release. Zinc had the highest concentration among all metals and was present in eluates from all mixtures. The cumulative zinc concentration from DVR mixture was 41% and 34% higher than the control and SBS mixtures, respectively. For PCR wet, the cumulative zinc concentration was 9% higher than the control blend and 1% lower than the SBS mix. The assessment ratio indicated that all metal concentrations would not exceed the drinking water limit, except for zinc, for which further evaluations were required. The main source of zinc may derive from aggregates. This work showed that crumb rubber might not be the only source of metal leaching, and its use in asphalt pavements does not cause a metal leaching higher than other materials.

Keywords: Crumb rubber; Scrap tires; Metals leaching; Road pavements

1. Introduction

In the United States (US), crumb rubber (CR) from scrap tires has been used as a modifier of asphalt mixtures since the 1960s to improve the mechanical performance of flexible pavements. The number of states using CR in road pavements has been increasing steadily in the past years (Ghabchi et al., 2021; Kocak and Kutay, 2016; Mohajerani et al., 2020; Nanjegowda and Biligiri, 2020). Recently, CR with enhanced properties has been developed to address the drawbacks of regular CR such as the absorption of the bitumen and premature cracking. For instance, polymer coated rubber (PCR) is an emerging chemically enhanced material developed by mixing CR particles with an emulsion of synthetic polymer (Styrene-butadiene-styrene, SBS, or styrene-butadiene-rubber, SBR) (Kurgan and Dongre, 2015). The presence of the polymer emulsion prevents bitumen absorption by the rubber, improving the bonds between CR and bitumen during their mixture production process (Hasnat et al., 2021). PCR can be used to modify bitumen (wet technology) or partially substitute aggregates (dry technology). Devulcanized rubber (DVR) is a type of rubber from scrap tires generally used to modify the bitumen because the rubber particles can be dissolved almost completely at high temperatures with no suspended particles (Garcia et al., 2015).

The use of bitumen and recycled materials, such as CR from scrap tires and reclaimed asphalt pavements (RAP) from end-of-life roads in asphalt mixtures, raises toxicity concerns (Epps, 1994; Muñoz et al., 2022). CR is produced from a variety of scrap tires and may contain a wide range of metals (e.g., Cu, Co, Fe, and Zn) and chemicals used as stabilizers and additives (Zanetti et al., 2015)(Li et al., 2023). RAP contains aged bitumen and chemicals released on the road surface during the use phase such as lubricating oils, gasoline, metals from brake pads, and vehicle exhaust

(Brantley and Townsend, 1999). Bitumen contains metals (e.g., aluminum, chromium, iron, nickel, etc.) and polycyclic aromatic hydrocarbons (PAHs), that are pollutants classified as carcinogenic, mutagenic, and teratogenic (Al Jitan et al., 2020; Brantley and Townsend, 1999; Shedivy and Meier, 2012). Therefore, the potential toxicity of the asphalt mixtures for flexible pavements using new or recycled materials, such as PCR, has never been tested and needs to be assessed and considered in the decision-making process. There is a risk that stormwater runoff may transfer contaminants like metals, PAHs, and volatile organic compounds (VOCs) contained in the materials used in road pavements to the groundwater. Leaching is a process driven by mass transport principles that define contaminants' movement from a solid phase to contacting water (U.S. Environmental Protection Agency (EPA), 2017). The contacting water may result from rainwater infiltration through overlying soils or direct material contact with groundwater or surface water. Contaminants that leach into the water can further contaminate the adjacent soils or disperse into groundwater or surface water bodies. The Leaching Environmental Assessment Framework (LEAF) is an integrated approach developed by the Environmental Protection Agency (EPA) that includes four laboratory methods for characterizing the leaching behavior of solid materials (U.S. Environmental Protection Agency (EPA), 2017). The four methods, that can be applied individually or in combination, assess (i) liquid-solid partitioning as a function of extract pH using a parallel batch extraction procedure (method 1313), (ii) liquid-solid partitioning as a function of liquid-solid ratio for constituents in solid materials using an up-flow percolation column procedure (method 1314), (iii) mass transfer rates of constituents in monolithic or compacted granular materials using a semi-dynamic tank leaching procedure (method 1315), and (iv) liquid-solid partitioning as a function of liquid-solid ratio using a parallel batch extraction procedure (method 1316). LEAF test methods have been validated for inorganic constituents only.

The existing literature assessed the leaching behavior of the materials used in asphalt mixtures singularly. The concentration of PAHs, VOCs, and metals (e.g., chromium, copper, nickel, zinc) in different RAP samples was determined below the drinking water limits using either the US standard methods (e.g., Toxicity Characteristic Leaching Procedure, TCLP, and Synthetic Precipitation Leaching Procedure, SPLP) or the standard French procedure (AFNOR XP ENV 12920 Standard) (Brantley and Townsend, 1999; Legret et al., 2005). However, manganese and arsenic were significantly higher than the minimum concentration level allowed in drinking water by performing TCLP on RAP samples collected in five locations in the United States (Ohio, Wisconsin, California, New Jersey, and Colorado) (Shedivy and Meier, 2012). A recent study on RAP samples collected from several US locations observed that PAHs (naphthalene, dibenzo (a,h)anthracene, benzo(a)anthracene, benzo(a)pyrene), and metals (arsenic, lead, antimony, manganese) exceeded the US EPA regional screening levels limit for tap water (Spreadbury et al., 2021). Discrepant results from literature proved how the same type of material may differ based on the composition and provenience and the importance of testing the materials locally. The bitumen, assessed through a static test for 64 days and a dynamic test for 24 hours for the existence of PAHs and metals such as nickel, iron, and chromium, did not release any dangerous substances in a concentration higher than the standard drinking water limits and metals were below the detection limits (Giavarini, 2012).

Regarding the CR, the only metal present at a percentage higher than 1% by CR mass with respect to the other metals is zinc (Duin, 2020; Rhodes et al., 2012; Zanetti et al., 2015). The high zinc content in CR is due to the use of zinc oxide as an activator for sulfur vulcanization in tire manufacturing (Li et al., 2023). In investigating the environmental-sanitary risk of turf sports fields

made with CR, the zinc content was higher than 1% by mass in turf fields without scrap tires (1.22-1.53% versus 0.58%, respectively) (Ruffino et al., 2013). CR from passenger car tires can have a higher zinc concentration than CR from truck tires. Smaller CR particles may contain more zinc than bigger CR particles (Duin, 2020). The leaching can be associated with lower pH and longer leaching times, and it may increase with smaller CR and longer exposure time (Rhodes et al., 2012). CR particles from cars, trucks, and CR produced using a cryogenic procedure were tested through a leaching test (e.g., SPLP) to assess the release of 23 metals (e.g., zinc, chromium, copper, lead, mercury). Zinc was the only metal that leached from CR for every sample tested, with an average concentration close to the groundwater standard (Lim and Walker, 2009). In sport field turfs, zinc leached in concentration up to 6 times higher when CR was used compared to the reference (2,729 µg/L and 452 µg/L, respectively), and zinc leached out more than other metals (Ruffino et al., 2013). In California, more than 40 waterways have a zinc concentration higher than the Clean Water Act standard limit. The zinc exceedance was attributed to stormwater runoff due to the large number of rubberized asphalt pavements by the California Department of Transportation (CalTrans) (California Department of Transportation -Caltrans-, 2008; California Stormwater Quality Association (CASQA), 2014).

The potential leaching of the materials used in asphalt mixtures (e.g., CR, RAP, bitumen) has been assessed individually in the literature, as well as the potential leaching of the asphalt mixtures. The leaching behavior of asphalt mixture modified with emerging technologies such as PCR and DVR have not been evaluated yet. This work aimed to investigate the potential leaching of metals from asphalt mixtures modified with PCR (dry and wet technology) and DVR, compared to two reference mixes: 1) an unmodified mixture and 2) a blend modified with the synthetic polymer,

SBS. Moreover, this work aimed to assess if the potential leaching of metals might be caused by CR only or other materials used in asphalt mixtures. Using the LEAF method 1315, this work assessed if metals in the asphalt mixtures for surface layers of road pavements could be released into the groundwater due to the rainwater after construction. The objectives were to i) quantify concentrations of metals released, ii) calculate the flux rate, the cumulative mass release, and the assessment ratio for each metal, iii) verify if the metal concentration would be higher than the drinking water limit, and, finally, iv) assess from where metals could be released. There is a significant interest in understanding stormwater runoff and leaching materials from pavements in the scientific community, and this study evaluated for the first time the leaching behavior of asphalt mixtures modified with PCR and DVR compared to synthetic polymer modification and unmodified control mixture. Moreover, in this research, the EPA method 1315 was applied to asphalt mixtures for the first time in the literature. The method was selected because it is applicable when water flows primarily around the material and then percolates through it, which is the case with asphalt pavements. It is important to assess the leaching of asphalt mixtures to ensure materials potentially harmful to the environment are not in use, especially when using recycled materials. Moreover, identifying the possible cause of metal leaching helps address potential problems before placing the asphalt mixtures on site. This study provides new insights on metal migration from asphalt pavements to water and the potential cause of metal leaching.

2. Materials and methods

The first step for this project was performing the mix design and the compaction of each asphalt mixture sample in the Michigan State University asphalt laboratory. The specimens were used to conduct the leaching testing using the LEAF method 1315 to study the metal release over time. At

the end of the 63 days leaching test, the concentration of each metal was determined using chemical analysis on the eluates collected from the leaching test. Based on the method 1315 standard, starting from the metal concentration, the flux rate of mass release, the cumulative mass release, and the assessment ratio were calculated. The assessment ratio correlates the cumulative mass release to the field conditions to compare the test results to the threshold of the drinking water limit concentrations in μg/L. The metal concentration for each individual material used in the preparation of the asphalt mixtures was also assessed using microwave digestion and inductively coupled plasma optical emission spectrometry (ICP-OES). **Fig. 1** is an overview of the methodology used in this study. Each phase is explained in detail in sections 2.1 to 2.5.

Fig. 1. Methodology used in this study.

2.1 Asphalt mixtures and specimens' preparation

Five asphalt mixtures were designed and prepared at the Michigan State University asphalt laboratory based on the Superpave specifications (Asphalt Institute, 2014): control (unmodified), SBS, PCR dry, PCR wet, and DVR. The percentage of each material used in the asphalt mixtures was calculated from the mix design and is reported in Error! Reference source not found.. The SBS mixture was modified with 3.5 % of SBS and 0.4% of a sulfur catalyst solution as cross-linker by the weight of the total bitumen. The PCR dry mix was modified with 0.5% of PCR by weight of the asphalt mixture, using the dry technology (in partial substitution of the natural aggregates). The bitumen in the PCR wet mixture was modified with 7% of PCR, 0.5% of SBS, 3% of the additive Sasobit for reducing viscosity, and 0.4% of cross-linker. The DVR mixture was modified

with 7% of DVR and 2% of SBS by weight of the total bitumen. All mixtures were designed to be used for the top layer of a pavement structure with an expected traffic level of 30 million equivalent single axle loads (ESALs). The five mixes had the same aggregate gradation with a nominal maximum size of 12.5 mm, and a target air void of 3%±0.5%.

Table 1

After preparing the loose mixes, 15 cylindrical specimens were compacted, three specimens for each mix, using a gyratory compactor. The cylinders had a diameter of 150 mm and a height of 60 mm. The air voids were 7% ±0.5% to replicate the field conditions and were checked by following the standard procedure for compacted specimens (AASHTO, 2018). Each specimen was labeled in order to be identified using a non-toxic oil-based water-resistant paint marker that did not affect the results of the investigation.

2.2 Leaching testing procedure

After the preparation of the asphalt mixture specimens, test Method 1315 was used to determine the mass transfer rates of constituents in monolithic or compacted granular materials using a semi-dynamic tank leaching procedure. The prepared asphalt mixture specimens were attached with plastic supports and nylon threads to ensure 98% of the specimen's surface was exposed to water and could be easily removed from the bucket **(Fig. 2)**. To meet the standard geometric requirements, two-gallon buckets were used. Lids were also used to cover the buckets to avoid contamination during the test. The nylon threads were used to easily remove the specimens from the buckets to replace the water.

Fig. 2. Plastic support is attached to the asphalt mix specimens, and specimens are placed in deionized water.

As recommended by method 1315, deionized water (DI) was used as a leaching solution. Each sample was immersed in 5.8 liters of DI (9 mL/cm^2). After being submerged for 2 hours, the specimens were removed from the water, weighted, then immersed immediately in fresh DI water in another set of 15 buckets (5 asphalt mixtures for 3 replicates). Within 15 minutes, the pH and conductivity of the elaute were measured as per the methods 9040 and 9050, respectively (U.S. Environmental Protection Agency (EPA), 2004, 1996). Then, we collected a 100 ml sample of eluate from each bucket and filtered it using 0.45 μm disc filter polypropylene membranes to prepare the solutions for the chemical analysis. These steps were repeated after 2, 25, 48 hours, 7, 14, 28, 42, 49, and 63 days from the start of the test.

2.3 Chemical analyses and parameters calculation

For chemical analysis, we measured 9.8 mL of 0.45 μm filtrated eluate from all buckets and added 2% nitric acid. In total, we analyzed 135 eluate solutions (five asphalt mixtures per three replicates per nine intervals of time) to quantify the metals concentration. At the Department of Earth and Environmental Sciences at Michigan State University, the Thermo iCAP-Q ICP-MS (Inductively coupled plasma mass spectrometry) was used to determine the presence and concentration of the following metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti),

vanadium (V), and zinc (Zn). The concentrations of metals in blank solutions (deionized water and 2% of nitric acid) were also tested to assess the purity of the reagent and equipment.

After the chemical analysis of the eluates collected from the leaching test, the interval flux rate of mass released *F* over an interval (**Eq. 1**) and the cumulative mass release *R* of the metals for each mixture was calculated (U.S. Environmental Protection Agency (EPA), 2017). The cumulative mass release of the metals was calculated by multiplying the interval mass flux by the interval specific time and summing across all previous leaching intervals (**Eq. 2**). The calculation of these two parameters was carried out to understand the behavior of the mass transport of the metals from the asphalt mixture to the water.

$$F\left(\frac{\mu g}{m^2 s}\right) = E\left(\frac{\mu g}{L}\right) \cdot \frac{V_{leachate\ (L)}}{S_{specimen\ (m^2)}} \cdot \frac{1}{t(s)} \qquad \textbf{Eq. 1}$$

$$R_i\left(\frac{\mu g}{m^2}\right) = \frac{V_{leachate\ (L)}}{S_{specimen\ (m^2)}} \sum_{i=1}^{9} E_i\left(\frac{\mu g}{L}\right) \qquad \textbf{Eq. 2}$$

Where,

F is the interval flux rate of mass released over an interval in μg/m^{2}s;

E is the eluate concentration in μg/L;

$V_{leachate}$ is the volume of leachate in L;

$S_{specimen}$ is the surface area of the asphalt mixture specimen in m^2;

t is the time in s;

R is the cumulative mass release of the metals in μg/m^2.

2.4 Assessment ratio

Eluate concentrations obtained by performing method 1315 do not reflect the expected maximum leaching concentrations. In the field, the actual liquid to surface area ratio is often smaller than the test conditions, and leaching into a limited contacting liquid reduces the concentration gradients; therefore the leaching rate in the field could be less than the measured rate in laboratory testing (U.S. Environmental Protection Agency (EPA), 2017). Therefore, the results of this method should not be compared directly with threshold concentrations, such as the drinking water limits (U.S. Environmental Protection Agency (EPA), 2017). However, it is possible to correlate the mass transport to the field conditions and compare the test results to the threshold of the drinking water concentrations by using the assessment ratio (AR). The AR (**Eq. 3**) correlates the average leaching concentration C_i^{av} (calculated as in **Eq. 4**) to the threshold concentration C_{thres} (drinking water limits in this work) and the dilution attenuation factor (DAF). DAF is the ratio between the original soil leachate concentration and the receptor point concentration. It depends on the interaction of a multitude of site-specific factors, physical and bio-chemical processes, and the nature of the contaminant itself (U.S. Environmental Protection Agency (EPA), 1994). In this study, it was assumed to be equal to one (Garrabrants et al., 2021a). C_i^{av} was calculated as a function of the effective concentration C1 (effective concentration for ≤1 day infiltration events) and C2 (effective concentration for >1 day infiltration events) and the infiltration events N1 and N2. The effective concentrations C1 and C2 are estimated using the cumulative mass release from method 1315 results (**Eq. 5** and **Eq. 6**). The values R1, R2, R3 in **Eq. 5** and **Eq. 6** are the first three values of the cumulative mass release. The three values R1, R2, and R3 represent the mass release from the

over 2-day cumulative leaching, which has been assessed to be a good approximation for release over extended infiltration event >1 day in the field (Garrabrants et al., 2021a).

$$AR = \frac{C_i^{av}}{C_{thres} \cdot DAF} \quad \textbf{Eq. 3}$$

$$C_i^{av} = \left[\frac{N1 \cdot C1 + N2 \cdot C2}{N1 + N2}\right] \quad \textbf{Eq. 4}$$

$$C1 = \frac{(\sum R_2 - R_1) \cdot A_{exp}}{P1 \cdot A_{inf}} \left(\frac{m^3}{1000L}\right) \quad \textbf{Eq. 5}$$

$$C2 = \frac{(\sum R_3 - R_1) \cdot A_{exp}}{P2 \cdot A_{inf}} \left(\frac{m^3}{1000L}\right) \quad \textbf{Eq. 6}$$

$$P = DP - E_{pan} - ET_0 \quad \textbf{Eq. 7}$$

Where,

AR is the assessment ratio;

C_i^{av} is the average leaching concentration in µg/L;

C_{thres} is the threshold concentration µg/L;

DAF is the dilution attenuation factor;

C1 and *C2* are the effective concentration in µg/L;

N1 and *N2* are the number of infiltration events;

R1, *R2*, and *R3* are the cumulative mass release of the metals in $\mu g/m^2$;

A_{exp} is the exposed surface area in m^2;

A_{inf} is the infiltration-impacted area in m^2;

P1 and *P2* are the net infiltration of the rain events in cm;

DP is the daily precipitation;

E_{pan} is the pan evaporation;

$ET_{0\ is}$ the evapotranspiration.

P1 and P2 represent the net infiltration of the rain events less or equal to 1 day and greater than 1-day, respectively. The net infiltration is the infiltration rate of water in the soil environment. It is calculated in **Eq. 7** through the EPA dataset that includes data collected over 30-years (from 1961 to 1990) (U.S. Environmental Protection Agency (EPA), 2021). The dataset for Lansing, Michigan, was used to calculate P1 and P2 as a function of the daily precipitation (DP), the pan evaporation (E_{pan}) depending on climate elements (e.g., temperature, humidity, rainfall), and the evapotranspiration (ET_0) depending on the evaporation from the land surface and transpiration from plants. The results of the Lansing area were compared to those obtained by using data of other areas in Michigan, like Grand Rapids and Muskegon (Table S1).

2.5 Metals quantification

To understand what metals could leach in water from the asphalt mixtures, the metal content of the materials involved in the test was assessed by acid digestion followed by inductively coupled

plasma optical emission spectrometry (ICP-OES) analysis. Microwave digestion is a technique used to decompose the matrix of the materials so that the analytes of interest are entirely released and solubilized (Lamble and Hill, 1998). The microwave digestion of every single material (aggregates, RAP, neat bitumen, PCR, DVR, SBS, and Sasobit) was performed. An adequate amount of each material was placed in vessels with reagents, and the vessels were inserted in a microwave oven (Milestone Mega 1200 mls) for irradiation by microwave energy. The reaction conditions (type and quantity of reagents as well as the timing needed for the digestion), were different for each material. The procedures for the digestion are described in the Supplementary material S4. After the digestion step, 20 mL of DI were added to each digested material. These solutions were then filtered using 542 Whatman filters (2.7 μm pore size) and finally diluted with deionized water to a volume of 50 mL. The samples were analyzed with an ICP-OES (Perkin Elmer, Optima 2000 DV) to identify the metals concentration. The microwave digestion and the consequent quantification of the metals in the materials used in the asphalt mixtures were carried out in collaboration with the Polytechnic of Turin (DIATI - Department of Environment, Land and Infrastructure Engineering), at the Environmental Chemistry laboratory.

3. Results and discussion

3.2 Leaching test and chemical analysis results

Among all metals analyzed, this research focused on those that may be toxic, such as Pb, and those harmful for the human body under prolonged exposure, such as As, Cd, Cr, Cu, and Zn. **Fig. 3** shows the eluate concentration from the five asphalt mixtures for each interval of time over the 63 days of the leaching test. **Fig. 3**f shows that the zinc concentration in μg/L was higher than the concentration of other metals. Moreover, zinc was present in the eluates of all mixtures, rubberized

297 (PCR dry, PCR wet, and DVR) as well as reference blends (control and SBS), over the duration
298 of the test (63 days). **Table 2** reports the average metal concentrations after 63 days (three
299 replicates for each mixture). The cumulative zinc concentration after 63 days from the PCR dry
300 mixture was 25% and 16% hig her than the control and SBS mixtures, respectively. Similarly, the
301 total cumulative zinc concentration from the DVR mixture was 41% and 34% higher than the
302 control and SBS mixtures, respectively. By comparison, the total cumulative zinc concentration
303 from the PCR wet mixture was 9% more than the control blend and 1% less than the SBS mix.
304 Lower percentage of air voids in the asphalt mixture makes the structure of themixture more
305 compact and thus, more impermeable. Runoff from impermeable asphalt mixtures have been
306 shown to have higher zinc content than permeable mixes (Murphy et al., 2015).The high
307 concentration of zinc leached from the asphalt mixtures analyzed in this study could be explained
308 by the low percentage of air voids in the asphalt mixtures. The asphalt mixtures were designed
309 with air voids of 3% ±0.5% (usually 4%±0.5%) to have better interlocking between the aggregates
310 and improve the mechanical performance. The SBS and DVR mixtures showed a peak
311 concentration for cadmium of 311.02 μg/L and 7.03 μg/L, respectively, after seven days. For the
312 PCR wet mixture, the peak for Cd was 30.55 μg/L after 14 days (**Fig. 3**b).

313 **Table 2**

314 Eluate concentrations were compared with the method detection limit (MDL) and the lower limit
315 of quantitation (LLOQ) to indicate quantitation of measured concentrations. The MDL is the
316 minimum concentration of an analyte for a given analytical technique and sample matrix. The
317 LLOQ is a minimum concentration of an analyte that can be measured within specified limits of
318 precision and accuracy (U.S. Environmental Protection Agency (EPA), 2017). The comparison

with these two limits is due to the leaching test's quality assurance/quality control step, in case a quality assurance project plan is required (U.S. Environmental Protection Agency (EPA), 2017). Eluate concentrations should be greater than the MDLs values but may be higher or lower than the LLOQs. If concentrations are lower than the MDLs, they should be reported at one-half the MDLs values for further calculations or decision-making. The lead concentration after seven days (**Fig. 3**e) was zero due to a lead concentration higher in the blank solution than in the sample that caused a quantification error.

Fig. 3. Eluate concentrations for As, Cd, Cr, Cu, Pb, and Zn compared with lower limit of quantitation (LLOQ) and method detection limit (MDL).

From the eluate concentrations, the interval flux rate of mass released over an interval ($\mu g/m^2$-sec) for each mixture was calculated (**Fig. S4**). The flux rate of mass released described the mass transport, the diffusion of the constituents from the solid material to the water. The specific rate of diffusion is the speed at which a constituent travels through the water, proportional to the magnitude of the concentration gradient (diffusion is faster when the incremental difference in concentrations is greater) (U.S. Environmental Protection Agency (EPA), 2017). The rate of diffusion depends on the distance the constituent has to travel, the effective porosity of the material, and the tortuosity of the porous network. The interval flux typically decays from left to right. When the leaching interval flux decays constantly, it ideally follows the Fickian diffusion' law (Garrabrants et al., 2021b). The ideal diffusion trend is shown as the negative square root of time ($t^{-1/2}$) trend (gray dot-dash line). All metals decay faster than the ideal trend. The diffusion of

copper and zinc in all mixtures was greater than that of other metals as seen by the steeper curve compared to other metals. In the field, the flux may be different from that obtained in laboratory testing because it can be affected by chemical and physical factors that remain constant under laboratory conditions but may vary in the field (e.g., pH, change in liquid-solid ratio due to precipitation, biological activities that alter the oxidation of the state of a constituent, physical degradation due to freeze/thaw cycles or erosion) (U.S. Environmental Protection Agency (EPA), 2017). The other parameter calculated by using the eluate concentrations from the test and the flux rate was the cumulative mass release ($\mu g/m^2$) of the metals from all mixtures (**Fig. 4**). The cumulative release was compared to a trend line proportional to the square root of time ($t^{1/2}$). The cumulative zinc release from all mixtures follows the ideal trend (**Fig. 4**f). The other metals showed less leaching than predicted by the Fickian diffusion trend because the values of the mass release were lower than the ideal trend (**Fig. 4**a-e).

Fig. 4. Cumulative release of mass per exposed surface area of test samples compared with the trend line.

3.3 Assessment ratio

After the calculation of the cumulative mass release, the average leaching concentrations (C_i^{av}), and the effective concentrations (C1, C2), the AR was calculated for chromium, lead, and zinc for each mixture and three areas in Michigan (Lansing, Grand Rapids, and Muskegon) (**Table 3**). Only these three metals were assessed because their eluate concentration was higher than the detection limit in the first three intervals of time (**Fig. 3**). Only the first three intervals of time of the leaching test had to be considered for the calculation of the AR. The coefficients calculated for

363 Lansing, Grand Rapids, and Muskegon, based on the mass release and net filtration for the AR
364 calculation are reported in the Supplementary material S3.

365 **Table 3**

366

367 The AR of each metal was similar in all three areas considered. The AR range for the locations
368 considered was 0.15-0.23 for Cr, 0.11-0.52 for Pb, and 14.33-97.98 for Zn. The AR was higher
369 than one only for zinc. An assessment ratio less than or equal to one ($AR \leq 1$) indicates that the
370 constituent is not likely to leach at concentrations higher than the drinking water threshold limit.
371 By comparison, an assessment ratio higher than 1 ($AR > 1$) does not necessarily mean that
372 constituents will leach at a level greater than the threshold limit in the field, but further evaluation
373 is required. For instance, additional leaching tests using different methods can be performed, or
374 field conditions may be changed to reduce the potential release (U.S. Environmental Protection
375 Agency (EPA), 2017). One solution to prevent zinc leaching is to use calcium carbonate in asphalt
376 mixtures (California Department of Transportation -Caltrans-, 2008; Duin, 2020; Murphy et al.,
377 2015).

378 The AR calculation is affected by uncertainty due to the factors included in the equations (**Eq. 3-**
379 **7**). For instance, DAF is a parameter depending on the interaction of many site-specific factors,
380 physical and bio-chemical processes, and the nature of the contaminant itself (U.S. Environmental
381 Protection Agency (EPA), 1994). DAF was assumed to be equal to one, meaning that the
382 concentration at the receptor point is the same as that in the soil leachate because this study did
383 not refer to any specific site. However, DAF higher than one can reduce the AR. Other factors
384 affecting the AR are the exposed surface area (A_{exp}), and the infiltrated area (A_{inf}) used to calculate

385 the effective concentrations C1 and C2 and then the average leaching concentration C_i^{av}. The
386 exposed and infiltrated area was set to one in this study because this research did not refer to any
387 specific site. However, different values of the area can lower or increase the effective
388 concentrations and, thus, affect the final AR.

389 *3.4 Metals quantification*

390 To understand what metals were contained in the materials used in each asphalt mixture and that
391 are expected to leach out from the samples, the microwave digestion and the analytical quantitation
392 of the metals present in each material of the asphalt mixtures were carried out. The metal content
393 of each component of the asphalt mixture (aggregates from Michigan, RAP, bitumen, SBS,
394 Sasobit, PCR, and DVR) is shown in Supplementary material S4. Almost all metals concentration
395 were higher in the aggregates and RAP (approximately constituted by 95% of aggregates by mass)
396 than in the organic materials, such as bitumen and crumb rubber. Nickel was present more in the
397 bitumen than in the other materials, and copper and zinc content was higher in the PCR and DVR.
398 The high zinc concentration in CR products confirms data published in the literature saying that
399 zinc is present in CR more than 1% by weight (Duin, 2020; Rhodes et al., 2012; Zanetti et al.,
400 2015). In PCR particles, zinc was 1.09% by weight, and in DVR particles, it was 0.83% by weight.
401 This result may also confirm the hypothesis that the zinc content is higher in smaller CR particles
402 than in CR with bigger size since the PCR and DVR particles have around 0.6 and 5 mm of
403 diameter, respectively.

404 The metal content in each sample was calculated based on the metal contents present in each
405 material, the percentage of materials in each mixture, and the weight of each specimen used for

406 the leaching test. **Fig. 5** shows the average metal contents of the three specimens for each mixture.
407 **Fig. 5**a depicts that, except for the zinc, all the other metals' content was constant in each mixture.
408 Zinc content was higher in PCR dry, PCR wet, and DVR mixtures because PCR and DVR give
409 their contribution besides the zinc contained in the aggregates and RAP. **Fig. 5**b-f shows that the
410 major contribution of the metals is due to the aggregates. The type of aggregates used in the asphalt
411 mixtures can affect the metal leaching. Even if the bitumen, impermeable per definition, covers
412 the aggregates' surface, the water's effect may reduce the bitumen's ability to adhere to the
413 aggregates (Omar et al., 2020). Since a high contribution to the total metal content in asphalt
414 mixtures seems to derive from aggregates, the aggregates from other states, such as Maryland,
415 North Carolina, and Wisconsin, were tested to evaluate and compare the difference in metal
416 content to those used in Michigan. The aggregates had different sources. Aggregates from
417 Michigan and Wisconsin are derived from rivers, and aggregates are from North Carolina and
418 Maryland from quarries. In North Carolina and Maryland, the zinc was even higher than in
419 Michigan. **Fig. 6 a** gives an overall idea of the difference in metal content per kg of aggregates
420 between Michigan and North Carolina, Wisconsin, and Maryland. **Fig. 6b** shows the difference in
421 mg of metals included in the asphalt mixtures with respect to the content present in the Michigan
422 samples (zero line). The different metal content in the aggregates may lead to different results from
423 the leaching test. The different metal content depends on the aggregates' type, properties, and
424 origin (e.g., rivers, and quarries).

425 **Fig. 5.** a) Total mg of metals present in each mixture, an average of the three replicates; b-f) an
426 average of metals (mg) per specimen of each mixture, the contribution of all materials.

427

Fig. 6. a) Metals content in mg per kg of Michigan, North Carolina, Wisconsin, and Maryland aggregates; b) difference in mg of metals contained in asphalt mixtures samples.

3.5 Discussion

This paper answered questions about toxicity related to using CR and RAP in asphalt pavements. There is a significant interest in understanding stormwater runoff and leaching materials from pavements, as shown by the recent publication of a review paper summarizing 42 manuscripts on the subject (Kriech and Osborn, 2022). The present study contributes to the literature on the leaching of asphalt mixtures by evaluating for the first time mixtures modified with PCR and DVR compared to synthetic polymer modification and unmodified control mixture. Even if results of this study cannot be directly compared to others because there are no studies using PCR and DVR in asphalt mixtures, this research also found that metals were released at lower concentrations than the regulatory thresholds (Kriech and Osborn, 2022). The review paper revealed an overall trend that asphalt pavement appears to have minimal leachate concerns (Kriech and Osborn, 2022). However, when using CR in asphalt mixtures, the main concern is the high zinc content in the rubber. The results of the present research are similar to previous studies assessing the zinc leaching from CR asphalt mixtures.

In other studies, CR particles leached zinc in concentrations higher than other metals and close to the groundwater standard (Lim and Walker, 2009) (Ruffino et al., 2013) and zinc leached much more rapidly from CR particles than CR contained in asphalt mixtures (Duin, 2020). It was

449 observed that the zinc concentration was higher than other metals in CR asphalt mixtures as well
450 as in the other mixtures. The assessment ratio calculated based on the cumulative mass release
451 indicated that further assessments are needed to confirm whether the zinc concentration might be
452 higher than the groundwater standard. Physical factors could also affect zinc concentration
453 leaching. Leaching results obtained from this research may be higher than those obtained from
454 the field due to changes in water flux and other factors that can be controlled under laboratory
455 conditions (e.g., pH, change in liquid-solid ratio due to precipitation, biological activities that alter
456 the oxidation of the state of a constituent, physical degradation due to freeze/thaw cycles or
457 erosion) (U.S. Environmental Protection Agency (EPA), 2017). Therefore, field testing is needed
458 to validate laboratory studies and determine the leachability of the materials through the pavement
459 service life. Differences in the physical characteristics of the pavements are also likely to
460 contribute to the difference in zinc concentrations, such as pavement porosity, age, and gradation
461 (Duin, 2020).

462 Crumb rubber may not be the only source of zinc leaching. A previous study performed a leaching
463 test on an asphalt mixture with CR and an unmodified mixture through a similar procedure used
464 in this manuscript and also compared storm runoff water from field test sections (Duin, 2020). The
465 total zinc concentrations leached from the rubberized asphalt mixture were higher than those
466 obtained from the control unmodified asphalt. However, the high zinc concentrations from water
467 collected from the field test sections from rubberized and unmodified pavements were unlikely
468 attributable to the crumb rubber. Instead, galvanized metal from guard rails was identified as a
469 potential contributor to zinc concentration (Duin, 2020). The US Tire Manufacturers Association
470 (USTMA) and its members collaborate with researchers and regulators to understand if zinc

impacts the environment caused by tires (U.S. Tire Manufacturers Association, 2024). Zinc is used in tire manufacturing to meet federal safety standards because zinc is the component that allows tires to carry the weight of a vehicle and stop safely (U.S. Tire Manufacturers Association, 2024). Therefore, the zinc makes the tires safe and durable, and it is irreplaceable. No studies specify that zinc from tires causes widespread and adverse effects in waterways (U.S. Tire Manufacturers Association, 2024). The primary source of zinc is from agricultural and natural soils, as well as the corrosion of galvanized metal and metal roofing (U.S. Tire Manufacturers Association, 2024). In the study presented in this paper, it was observed that zinc was the metal with concentrations higher than the other metals and was present in the eluates from all asphalt mixtures. Since the asphalt mixtures comprise approximately 80% of aggregates and only 0.34-0.5% of PCR and DVR by weight of the total mix, the main contribution of zinc seems to be from aggregates, where the zinc is also present. This work showed that crumb rubber might not be the only source of metal leaching, and its use in asphalt pavements does not cause metal leaching higher than other materials.

4. Conclusions

This work aimed to investigate the potential metals leaching from asphalt mixtures modified with crumb rubber with enhanced properties, such as polymer coated rubber (PCR) and devulcanized rubber (DVR), compared to two reference blends, one unmodified and another modified with a synthetic polymer SBS. Zinc concentrations were higher than other metals, and it was present in the eluates from all mixtures, rubberized and reference blends. The cumulative zinc concentration from the DVR mixture was 41% and 34% higher than the control and SBS mixtures, respectively. For PCR wet, the cumulative zinc concentration mixture was 9% higher than the control blend and

493 1% lower than the SBS mix. The assessment ratio indicated that no metal concentrations would
494 exceed the drinking water limit. However, the assessment ratio for zinc was higher than one,
495 meaning that further evaluation is required to understand if zinc will leach at a level greater than
496 the drinking water limit. Zinc was present in the aggregates too. Since the asphalt mixtures
497 comprise approximately 80% of aggregates and only 0.34-0.5% of PCR and DVR by weight of
498 the total mix, most of the zinc may come from aggregates. This work is important because it
499 showed that the cause of metal leaching might be attributed not only to crumb rubber but also that
500 its use in asphalt pavements does not cause metal leaching higher than other materials. The scope
501 included only metals, which is the main limitation of this work, and future work on toxicity should
502 consider polycyclic aromatic hydrocarbons and other organic compounds. To date, the EPA 1315
503 leaching testing followed in this research has been validated for inorganic constituents only. This
504 work represents the first application of the 1315 method to asphalt mixtures, which is suitable for
505 this study because it is the only method assessing the mass transport of compacted materials. For
506 the first time in literature, this study compared five asphalt mixtures modified with different agents
507 and technologies, including PCR, an emerging recycled material. Results from this work are useful
508 for synthetic and recycled polymer manufacturers and transportation departments that want to use
509 asphalt mixtures modified with SBS, PCR, or DVR since it shows that their use will not lead to
510 toxic metal leaching.

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515 comminution of the aggregate samples.

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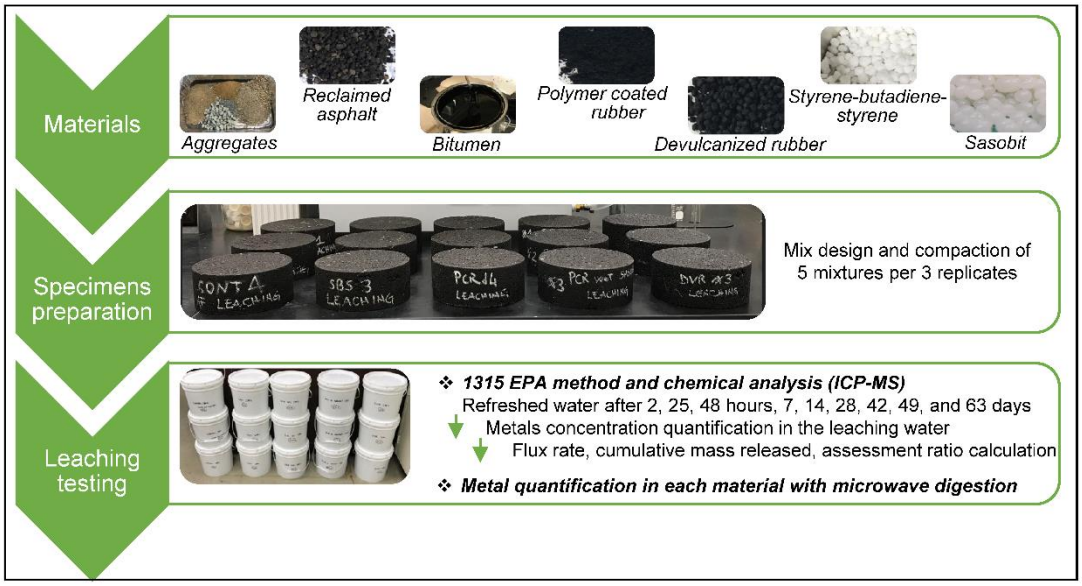
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618

619 **Fig 1.** Methodology used in this study.

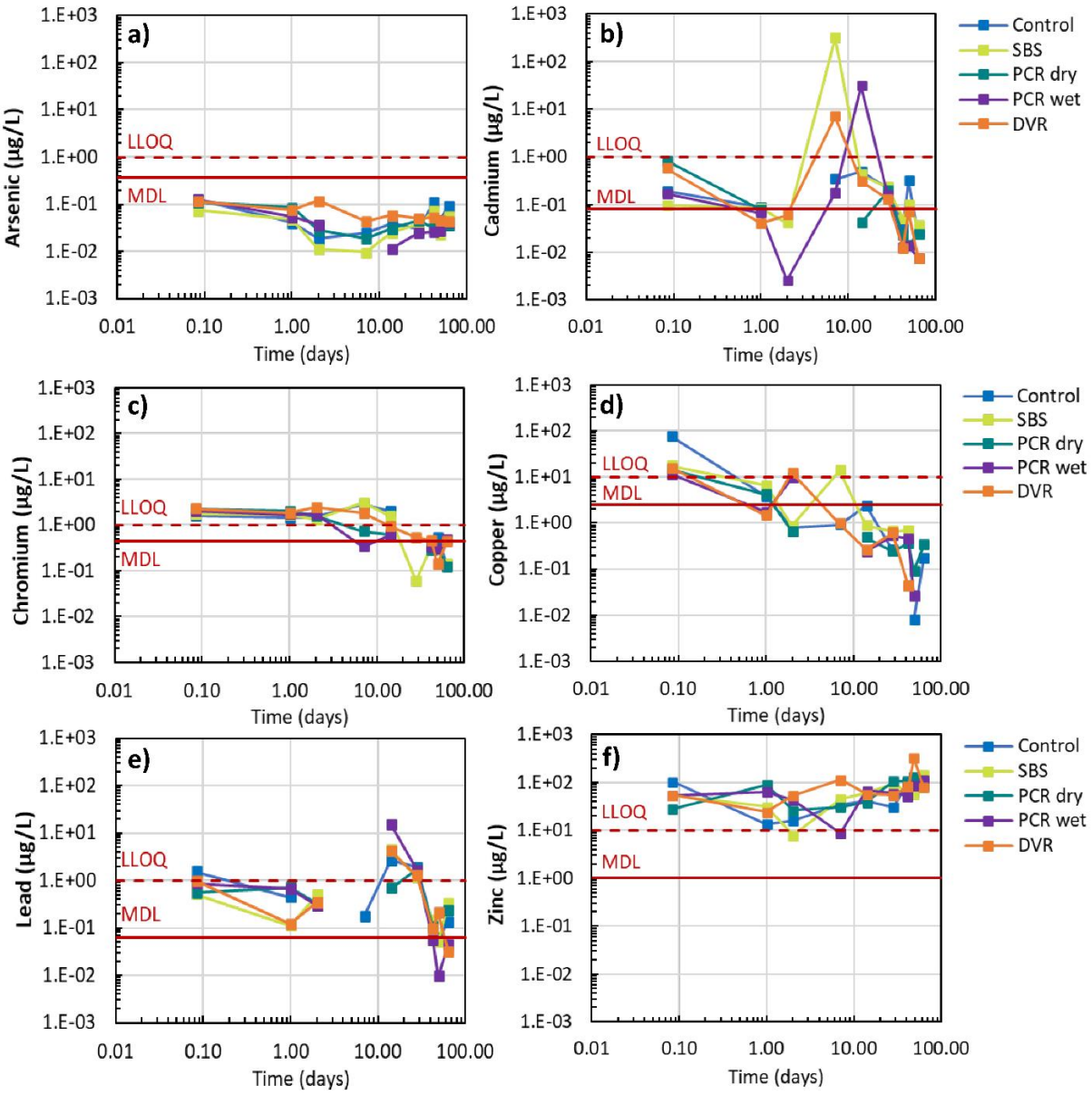


620

621 **Fig 2.** Plastic support is attached to the asphalt mix specimens, and specimens are placed in

622 deionized water.

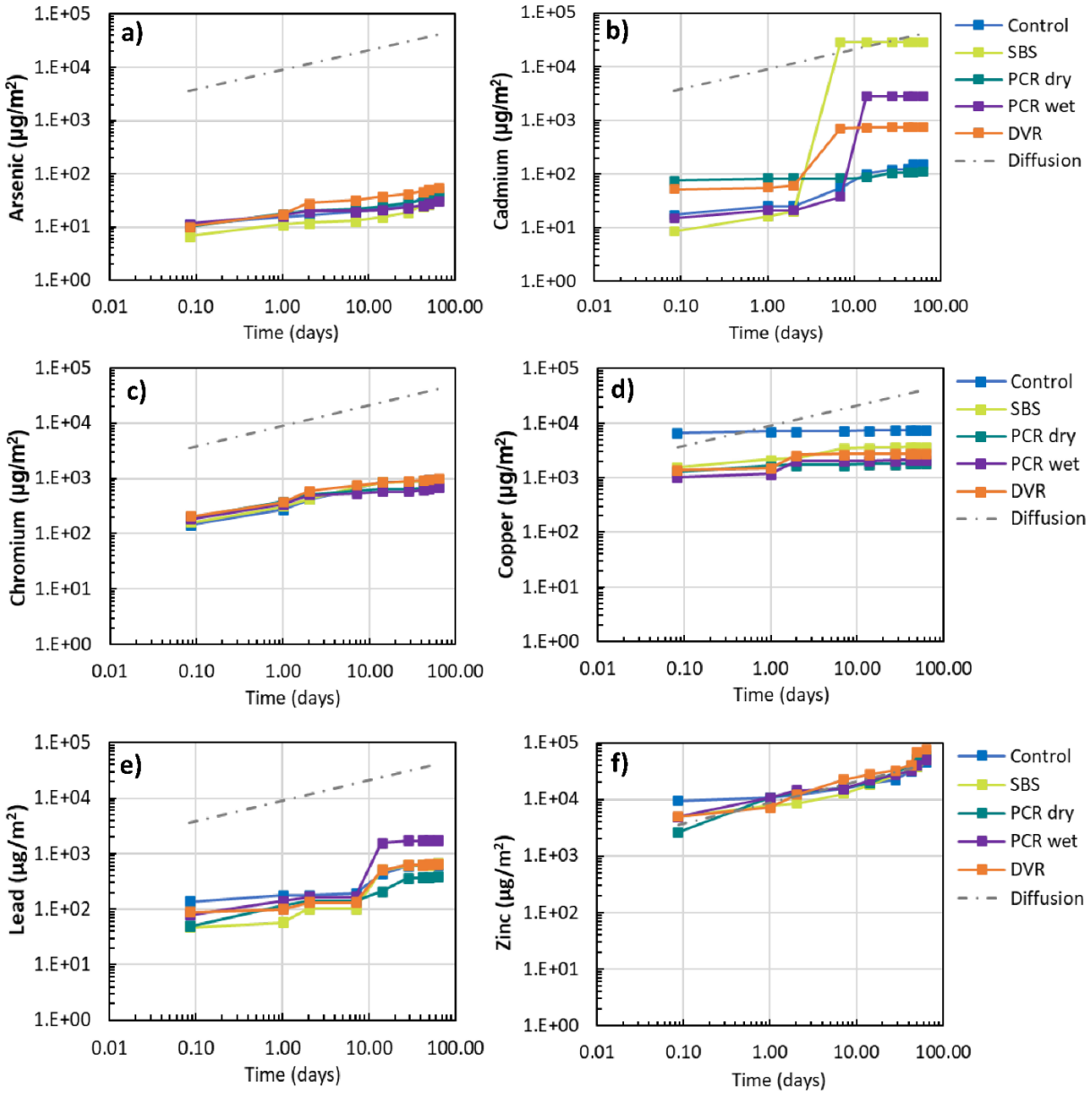
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624

625 **Fig. 3.** Eluate concentrations for As, Cd, Cr, Cu, Pb, and Zn compared with lower limit of

626 quantitation (LLOQ) and method detection limit (MDL).

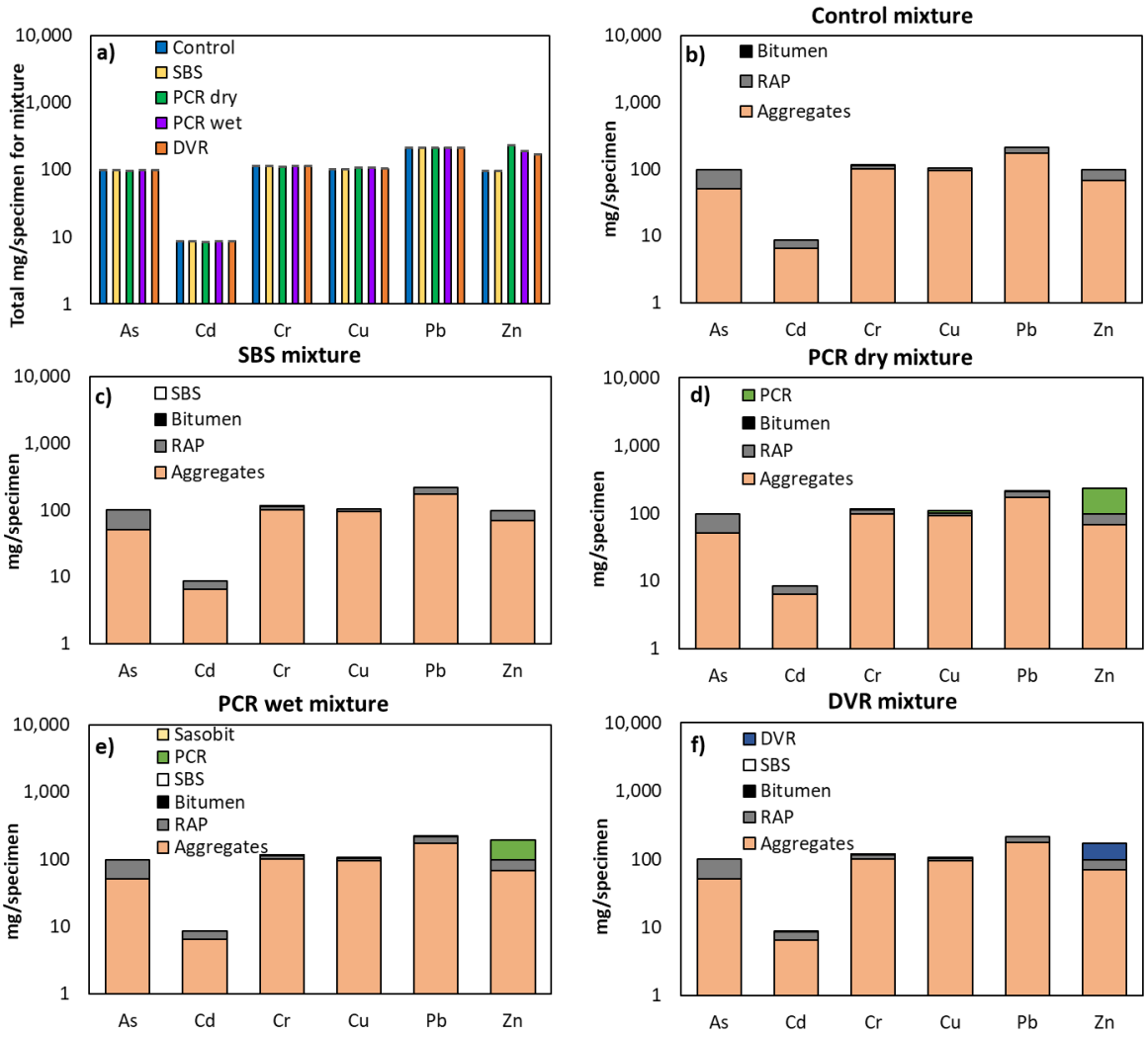


627

628 **Fig. 4.** Cumulative release of mass per exposed surface area of test samples compared with the

629 trend line.

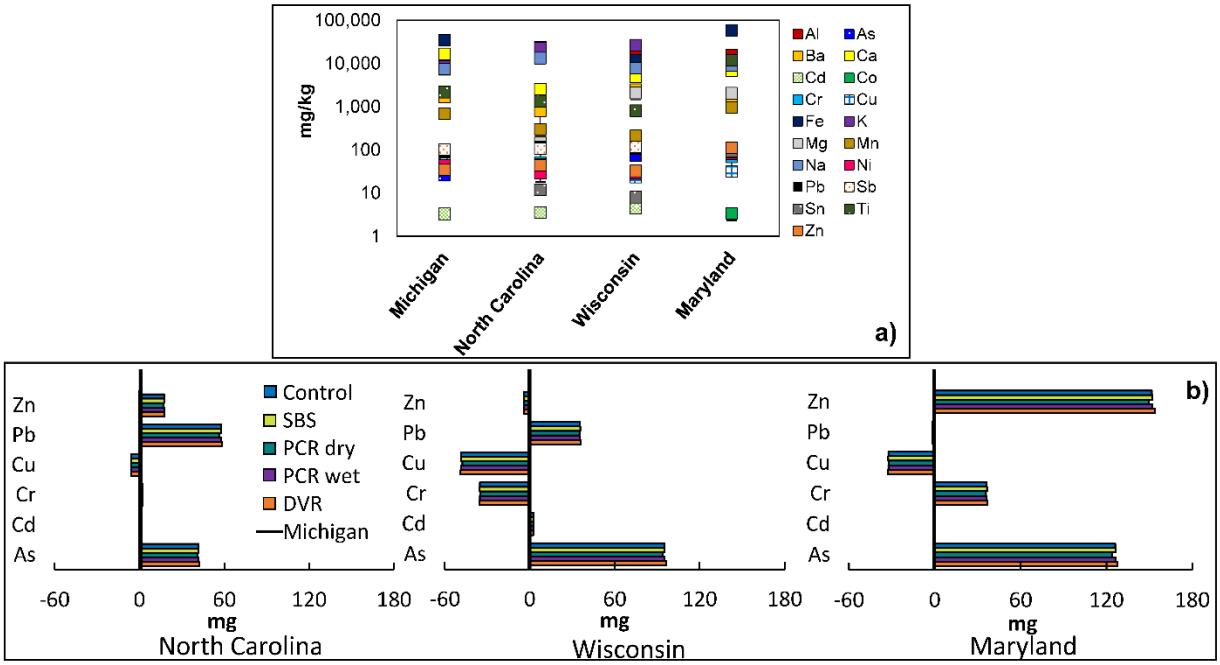
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631

632 **Fig. 5.** a) Total mg of metals present in each mixture, an average of the three replicates; b-f) an
633 average of metals (mg) per specimen of each mixture, the contribution of all materials.

634



635

636 **Fig. 6**. a) Metals content in mg per kg of Michigan, North Carolina, Wisconsin, and Maryland

637 aggregates; b) difference in mg of metals contained in asphalt mixtures samples.

638

Table 1

Mixture's type and material content

	Control	**SBS**	**PCR dry**	**PCR wet**	**DVR**
Mix type	unmodified	wet	dry	wet	wet
Asphalt PG	58-28	70-28	58-28	82-28	70-28
Materials			(%)		
Aggregates	80.34	80.05	79.75	80.04	80.15
RAP	14.96	14.90	14.86	14.91	14.93
Bitumen	4.70	4.86	4.89	4.38	4.46
SBS	-	0.17	-	0.15	0.10
PCR	-	-	0.50	0.35	-
DVR	-	-	-	-	0.34
Sasobit	-	-	-	0.15	-
Cross-linker	-	0.02	-	0.02	0.02

PG: performance grade, range of optimal pavement temperatures for bitumen

643 **Table 2**

644 Cumulative metal concentration after 63 days

	As	**Cd**	**Cr**	**Cu**	**Pb**	**Zn**
				µg/L		
Control	0.53	1.70	10.50	82.75	6.94	501.85
SBS	0.36	312.09	10.20	40.57	7.26	559.21
PCR dry	0.42	1.21	7.90	20.77	4.31	668.55
PCR wet	0.35	31.15	7.49	23.80	18.87	553.15
DVR	0.61	8.24	10.84	31.04	7.17	850.39

645

646 **Table 3**

647 Assessment ratio (AR) in Lansing, Grand Rapids, and Muskegon areas

	Lansing, MI			Grand Rapids, MI			Muskegon, MI		
	Cr	Pb	Zn	Cr	Pb	Zn	Cr	Pb	Zn
Control	0.17	0.31	16.36	0.15	0.26	14.33	0.17	0.30	16.17
SBS	0.19	0.12	33.76	0.17	0.11	29.20	0.19	0.11	33.60
PCR dry	0.23	0.52	97.98	0.20	0.45	84.81	0.23	0.52	97.47
PCR wet	0.20	0.49	72.48	0.18	0.43	63.08	0.20	0.49	71.89
DVR	0.22	0.11	32.10	0.19	0.10	28.43	0.22	0.11	31.52

648

649