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Characterization and Potential Environmental Risks of Leachate from Shredded Rubber Mulches

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Abstract

In order to determine whether shredded rubber mulches (RM) posed water quality risks when used in stormwater best management practices (BMPs) such as bioretention basins, batch leaching tests were conducted to identify and quantify constituents in leachates from RM such as metal ions, nutrients, total organic carbon (TOC), and aryl hydrocarbon receptor (AhR) activity (determined by the chemically activated luciferase gene expression (CALUX) bioassay) at varied temperature and initial pH values. The results indicate that aqueous extracts of RM contain high concentrations of zinc (Zn) compared with wood mulches (WM), and its concentration increased at lower pH and higher temperature. Although methanol extracts of RM displayed high AhR activity, none of the aqueous extracts of RM had significant activity. Hence, while unknown constituents that have significant AhR activity are present in RM, they appear to be not measurably extracted by water under environmental conditions relevant for stormwater ($5 < pH < 9$, $10 < T < 40°C$). Our results suggests that organic constituents in water extracts of RM which have AhR activity may not be of significant concern while leaching of Zn from RM appears to be a potentially larger water quality issue for RM.

Keywords

Shredded rubber mulch; Zinc; Ah Receptor activity; wood mulches

1. Introduction

Bioretention basins are potential best management practices (BMPs) for removing metals from stormwater (Davis, 2007). Wood mulches (WM) are typically used in these and other types of stormwater BMPs. Although softwood mulches (SWM) are widely available on the west coast, these mulches are not suitable for use in bioretention basins because their low density means that they will not be effectively retained within the basin. Rubber mulches (RM), which are manufactured from used tires, may be a suitable replacement for SWM in bioretention basins due to their higher density and greater resistance to degradation. However, very little information about the bulk chemical composition of RMs or chemical composition in leachate from RMs is available.

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Zinc (Zn) has been widely identified as an environmental concern associated with tire wear debris (Hildemann et al., 1991; Councell et al., 2004; Wik and Dave, 2005), which is not surprising given that Zn constitutes approximately 1% by weight of tire rubber (Councell et al., 2004). A significant fraction of Zn was found to leach from tire debris during one year weathering period (Smolders and Degryse, 2002). Elevated concentration of Zn can cause reproductive, developmental, behavioral, and toxic responses in various aquatic organisms (Lefcort et al., 1998; Jelmert and van Leeuwen, 2000). Other studies have found Zn to be the major metal in tire crumb leachate, while other metals including selenium, lead and cadmium were found as minor constituents (Sadiq et al., 1989; Brown, 2007).

Although few investigations of the organic content of leachate from shredded tires have been reported and the results are somewhat inconsistent, it is well known that rubber tire debris contains toxic compounds such as highly aromatic oils and other reactive additives (Ahlbom and Duus, 1994; Wik and Dave, 2005). Exposure of rainbow trout (*Oncorhynchus mykiss*) to tires present in their exposure tanks resulted in elevated ethoxyresorufin-*O*-deethylase (EROD) activity and mRNA levels of CYP1A1 (Stephensen et al., 2003). These authors concluded that elevation of these activities resulted from exposure of fish to leachate from tires containing highly aromatic oils. The detection of hydroxylated PAH and aromatic nitrogen compounds in the bile of exposed fish suggested PAHs as one of the biggest concerns of RM leachate. Some volatile and semi-volatile organic compounds (carbon disulfide, methyl ethyl ketone, toluene and phenol) were also identified in scrap tire leachates using the TCLP test, although reported levels were far below regulatory limits (Envirologic Inc., 1990). A recent study demonstrated that ground tires released benzothiazole; butylated hydroxyanisole; *n*-hexadecane; and 4- (*t*-octyl) phenol in both the vapor phase and the leachate (Brown, 2007). The 24 hr EC_{50}s of rubber pieces toward various aquatic test organisms (*D. magna, P. promelas, S. capricornutum*) were determined (Birkholz et al., 2003; Wik and Dave, 2006)), and this toxicity was attributed primarily to nonpolar organic compounds (Wik and Dave, 2006). Hence, the organic content of leachate from RM appears to be a significant concern.

The purpose of this study was to determine whether the use of shredded RM for stormwater BMPs or similar applications poses a risk to water quality and to subsequently identify the responsible chemicals. RM and WM extracts were studied in order to identify and quantify constituents (metal ions, nutrients, and total organic carbon (TOC)) that leach out of the RM under various conditions. The presence of Ah receptor (AhR) agonists in the leachate was determined using AhR-dependent chemically-activated luciferase expression (CALUX) bioassay (Denison et al., 2004; Han et al., 2004; Windal et al., 2005), and the organic solvent extract of the RM were analyzed using gas chromatograph mass spectrometry (GC-MS) with full scan mode to identify organic compounds responsible for AhR activity. CALUX is a recombinant cell bioassay that has been used for detection and quantification of dioxin-like chemicals (DLCs), including halogenated aromatic hydrocarbons (HAHs) and polycyclic aromatic hydrocarbons (PAHs), known high affinity AhR agonists (Safe, 1990; Barbach et al., 1992; Wei et al., 1998), as well as diverse array of other chemicals (Seidel et al., 2000; Amakura et al., 2003; Denison et al., 2004; Bohonowych et al., 2008). Since RMs contain toxic compounds such as highly aromatic (HA) oils (Ahlbom and Duus, 1994; Wik and Dave, 2005), it can be expected that extracts of RMs may exhibit significant AhR activity. Taken together, the results of this study will allow evaluation of the potential risk associated with exposure to RM leachate.

2. Materials and Methods

2.1 Batch leaching tests

Materials used in this study were RM (West Coast Rubber Recycling), SWM (Ace® Cedar Mulch), and HWM (Preen® Mulch Plus® Hardwood). The experiments employed batch

leaching methods with relatively high ratios of mulch mass to water volume ratio (2 g/40 mL = 50 g L^{-1}) and relatively long contact time (3 days). This approach was taken to maximize the detectability of leachate constituents, to allow a wide range of test conditions to be examined and to provide a means of determining which, if any, constituents should be the focus of follow-up studies. The experimental results reported here are likely to represent a "worst case scenario" because any compounds that leach out of the rubber are likely to decline over time as the initial constituent load in the tire particles is leached away (Birkholz et al., 2003) and also because the actual ratio of particle mass to water volume will be lower in most environmental situations. Moreover, the sieved mulches used here had higher specific surface areas than mulches that would be used in the field, potentially allowing more compounds to be leached out. To capture the variable characteristics of stormwater runoff, tests were also conducted at temperatures ranging from 10 to 40°C (10, 25, and 40°C) and initial pH values from 5 to 9 (5, 7, and 9).

After drying at 50°C for 2 days, the mulches were crushed and sieved dry using a 30 mesh U.S. standard sieve (590 μm). Then, 2 g of each mulch was extracted by 40 mL of the synthetic runoff water (SRO, pH 5, 7, or 9), deionized (DI) water, or methanol in 50 mL plastic and glass bottles for 3 days. SROs were prepared to have similar hardness and total dissolved solids concentration as average California stormwater runoff (Kayhanian et al., 2003) using $CaSO_4$ (34 mg L^{-1}) and NaCl (25.5 mg L^{-1}) and were buffered with 25 mM of potassium hydrogen phthalate (pH 5), sodium bicarbonate (pH 7), or ammonium carbonate (pH 9). The batch contact time was selected as 72 hours based on preliminary kinetic studies that suggested that metal leaching from mulch samples was largely complete after this time period. Parallel extractions were performed in plastic and glass bottles to minimize losses of target constituents or input of undesired constituents. The extracts in plastic bottles were used to measure metal ions, nutrients, and pH, and those in glass bottles were used for organic analyses by GC-MS, TOC analyses, and the CALUX bioassay. Samples were diluted as needed to keep constituent concentrations within the quantification range for the relevant analytical instrument following centrifuging and filtering (0.45 μm).

2.2 Digestion tests

The mulches were digested using the HNO_3-H_2O_2 digestion method to quantify metal ion contents. After the pretreatment described in the batch leaching test section, 0.25 g of each mulch sample was digested with 0.5 mL of trace metal grade concentrated nitric acid and 2 mL of 30% hydrogen peroxide for 13 minutes using microwave heating in 15 mL polyethylene centrifuge tubes. The mixtures were diluted up to 15 mL with Milli-Q water before microwave heating. Then, the digests were centrifuged and filtered (0.45 μm) for analyses.

2.3 Analysis of constituents

Metal ion concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500i). All samples were acidified with nitric acid before measurement. Nutrients (NO_3^-, NH_4^+, and PO_4^{3-}) were measured by flow injection analyzer (FIA; Lachat Quick-Chem). TOC was measured using a TOC analyzer (Shimadzu 5050 TOC with ASI-5000). Since pH 7 and 9 buffers in SRO contain high concentration of inorganic carbon, those samples were thoroughly purged by N_2 gas prior to TOC analysis. The CALUX bioassay was conducted for all aqueous extracts, methanol/water mixture extracts, and methanol extracts to determine the presence of AhR ligands in those extracts. All extracts (2 mL) were evaporated and resuspended in 2 mL of dimethyl sulfoxide (DMSO), and 1 μL of the elute was analyzed using the CALUX assay. For CALUX analysis, we used recombinant mouse hepatoma (hepa1c1c7) cell lines (H1L1.1c2 and H1L6.1c2), which are identical except for the AhR-responsive luciferase reporter gene they contain (Han et al., 2004). Although both lines respond to AhR agonists with the induction of luciferase activity, the optimal times for induction differ due to subtle differences in the cellular targeting and stability of the two different luciferase

reporter gene (Promega). Accordingly, maximal induction times in H1L1.1c2 and H1L6.1c2 cells at 4 and 24 hours after treatment, respectively (Han et al., 2004). Experimental procedures for exposing cells and analyzing luciferase activity in these cell lines have been described in detail previously (Han et al., 2004; Bohonowych et al., 2008). To identify AhR agonists in the RM, the methanol extract of RM was dried down and resuspended in 2 mL of hexane and analyzed using an Agilent 6890 gas chromatograph with an Agilent 5973 mass spectrometer (split mode, 5 μL injection at 220 °C, HP19091J-433 capillary column 30 m by 250 μm i.d. and 0.25 μm thickness, initial oven 60 °C ramped at 30 °C min^{-1} to 300 °C, then hold 10 min), and the mass spectrometry was performed in electron ionization mode.

3. Results and discussion

3.1 Metal ions and nutrients

Metal ions, nutrients, TOC concentrations, and final pH values in all batch leaching tests are summarized in Table 1 together with total metal ion concentrations in the mulches (unit: μg g^{-1}) determined by the digestion tests and the calculated leaching fraction. Since the digestion tests confirmed that Zn concentrations in the RM were significantly higher than those in SWM or HWM, it is not surprising that high concentrations of Zn (2,000 – 28,000 μg L^{-1}) were detected in RM extracts. The extracted Zn concentrations were generally higher at lower pH as would be expected from the generally higher desorption or dissolution of metals under acidic conditions (Table 1, Figure 1). At pH 5 there was also an obvious trend toward increased Zn concentration with temperature (Figure 1). Zn concentrations in RM were higher than those in SWM and HWM by a factor 40 to 200 (Table 1). The observed concentrations of Zn in leachates are generally consistent with those from previous studies of rubber tire debris (Wik and Dave, 2006;Brown, 2007). Besides, given tire-tread material has a Zn content of approximately 1 wt % (Councell et al., 2004), approximately 50% of Zn in RM appeared to be extracted in the digestion tests (Table 1). The calculated leaching fraction of Zn based on our extraction results, however, was less than approximately 10% in any scenario. The calculated leaching fractions of almost all metal ions for RM were also relatively lower than those for WM. These results imply that metal ions contained inside RM particles are less readily leached out than for WM due to higher resistance to degradation. Chromium (Cr), cupper (Cu), and lead (Pb) concentrations in RM extracts were below detection in almost all cases. Concentrations of Mg, Mn, As, Rb, Sr, and Ba in RM samples were almost always lower than those in WM samples at the corresponding pH and temperature. The concentrations of Fe and Al, which are major crustal components, were higher in the HWM extracts than in the RM extracts but these are not typically of water quality concern. Concentrations for almost all metals from the mulches were highest at the lowest pH (pH 5) and the highest temperature (40°C) studied.

Nutrient concentrations in the leachate samples are also summarized in Table 1. Nitrate (NO_3^-) was detected in RM extracts (30 – 92 μg L^{-1} as N), but was not detectable in SWM and HWM extracts except for a single extraction using water. While ammonium concentrations in RM extracts were similar to or greater than those for the WM samples at pH 5 or 7, no clear concentration trend was observed with varying temperature and pH. High concentrations of PO_4^{3-} (6,700 – 14,000 μg L^{-1} as P) were detected in SWM and HWM extracts and concentrations of tended to decline as pH was increased. Since PO_4^{3-} levels in RM extracts were far lower (< 800 μg L^{-1} as P), PO_4^{3-} leaching from RM would not be a significant concern.

Although the batch leaching tests were unfortunately conducted without replication, the extraction reproducibility was estimated as the relative percentage difference between SRO extraction (pH 7, 25°C) and the DI water extraction using the formula shown in the footnote of Table 1. For almost all metal ions, the EERs were less than 100, and the effects of initial pH, temperature and mulch type were much larger than the EER values.

3.2 TOC and organic compounds

The TOC concentrations in the extracts were highest for WM (Table 1). The SWM and HWM extracts were yellowish and blackish, respectively, so the high TOC concentration probably derived from natural organic matter including humic and fulvic acids. Basic conditions were employed to extract humic materials from soils or sediments so it is not surprising that the TOC concentrations generally increased with increasing extraction pH. The acidic nature of the extracted organic materials in the WM was further confirmed by the relatively large decrease in initial pH observed for extractions starting with the highest pH (Table 1). The pH of the HWM extracts decreased from 9 to below 8 at all temperatures, while the decrease for SWM was somewhat smaller. These changes are directly correlated with TOC levels in the extracts. TOC concentrations in the RM extracts were always much lower (10 – 160 mg L^{-1}) compared to (252 – 853 mg L^{-1}) in the WM extracts.

3.3 AhR activity

Analysis of the extracts for the presence of AhR agonists was carried out using in recombinant mouse hepatoma (heap1c1c7) cell lines (H1L1.1c2 and H1L6.1c2), containing an AhR-responsive luciferase reporter gene. The differential cell targeting and stability of the two slightly different luciferase reporter gene products (resulting from selected mutation in the luciferase gene) these two cell lines facilitate detection and characterization of metabolically labile AhR agonists. The gene induction response in H1L1.1c2 cells is greatly enhanced at 4 hours after AhR agonist treatment and suppressed at 24 hours (Garrison et al., 1996; Han et al., 2004), while the more stable luciferase in H1L6.1c2 cells accumulates over 24 hours and can allow characterization of more metabolically stable AhR agonists (Han et al., 2004). The level of luciferase activity in H1L6.1c2 cells at 4 hours is relatively low (compared to the H1L1.1c2 cells) and as such, it is not particularly useful for detection and characterization of metabolically labile AhR agonists. Accordingly, since the only difference between these cells is that of the stability of the luciferase gene product, these cell lines have been used extensively to detect and differentiate between metabolically labile and stable AhR agonists and extracts containing such chemicals (Garrison et al., 1996; Gebremichael et al., 1996; Seidel et al., 2000; Ziccardi et al., 2000; Seidel et al., 2001; Denison et al., 2004). While significant induction of AhR dependent luciferase activity was observed at 4 hours after treatment in H1L1.1c2 cells by all methanol extracts (with RM > HWM > SWM (Figure 2)), maximal induction was only observed with the RM extract. Thus, while each extract contains AhR agonists, the RM extract contained the greatest concentration of and/or most efficacious AhR agonists. These results combined with the lack of luciferase induction by the water extracts and the very low level of induction (< 10% of TCDD) by the water:methanol (50:50) extracts indicates that the induction results from a nonpolar chemical(s) in the extract. Comparison of the level of induction by each extract at 4 and 24 hours after treatment revealed that all three extracts were significantly less potent at the later time point (Figure 2), consistent with the induction being by metabolically labile chemicals. A time-dependent decrease in the overall level of luciferase induction has been observed previously and results from metabolism of the inducing chemical by the cells into AhR inactive forms (Machala et al., 2001; Nagy et al., 2002; Han et al., 2004; Bohonowych et al., 2008). The reduction in luciferase gene induction at 24 hours also demonstrates that the responsible AhR active chemicals in the extract were not HAHs, as these chemicals are resistant to metabolic degradation and thus are persistent activators of AhR-dependent gene expression (Ziccardi et al., 2000; Denison et al., 2004).

3.4 GC-MS analysis

Since the methanol extract of RM showed the highest AhR activity, it was transferred into hexane at a concentration factor of one with the original methanol extract and injected into the GC-MS. The GC-MS chromatogram of the eluate is shown in Figure 3, and the National

Institute of Standards and Technology (NIST) mass spectral library was used to provide information about the identity of compounds in the elute (Table 2). Benzenoid aromatic compounds such as benzothiazole, long chain alkyl groups, and their derivatives were detected. Benzothiazole and their derivatives are typical compounds contained in tire (Kumata et al., 2000). Since the extract is a complex mixture and concentrations of those compounds are unknown, it is not possible to conclude that these listed compounds are responsible for the high AhR activity in the methanol extract of RM. It is, however, possible that these compounds were responsible for the high AhR activitity in the methanol extract of RM.

4. CONCLUSIONS

- Aqueous extracts of RM contain high concentration of one metal, Zn compared to extracts of WMs. Leaching of Zn from RM therefore appears to represent the most significant water quality concern associated with specification of these materials for use in BMPs.
- Extracts of RM contained similar concentrations of nitrate and ammonium and lower concentrations of phosphate and TOC than the WM extracts.
- Aqueous extracts of RM or WMs contained little or no AhR activity as measured by the CALUX bioassay.
- Organic solvent extracts of RM, and SWM induced significant levels of AhR-dependent gene expression indicating the presence of AhR active nonpolar chemicals, and the presence of these activators in both materials.
- The transient nature of the CALUX induction response (i.e. lower at 24 hours) indicates that the responsible AhR active chemicals were not HAHs, as these latter chemicals are metabolically stable and induce persistent activation of gene expression.
- Although the CALUX bioassay results are not a substitute for whole organism toxicity testing, they suggest that the organic constituents leached from RM may not be of significant concern under most environmental conditions relevant to stormwater.
- Benzenoid aromatic compounds, long chain alkyl groups, and their derivatives were detected in the methanol extracts transferred into hexane and analyzed by GC-MS, and these compounds may contribute to the high AhR activity present in these materials.
- The suitability of RM in stormwater BMP applications is therefore highly dependent on the susceptibility of the receiving water to negative consequences from additional Zn inputs and must be evaluated on a site specific basis.

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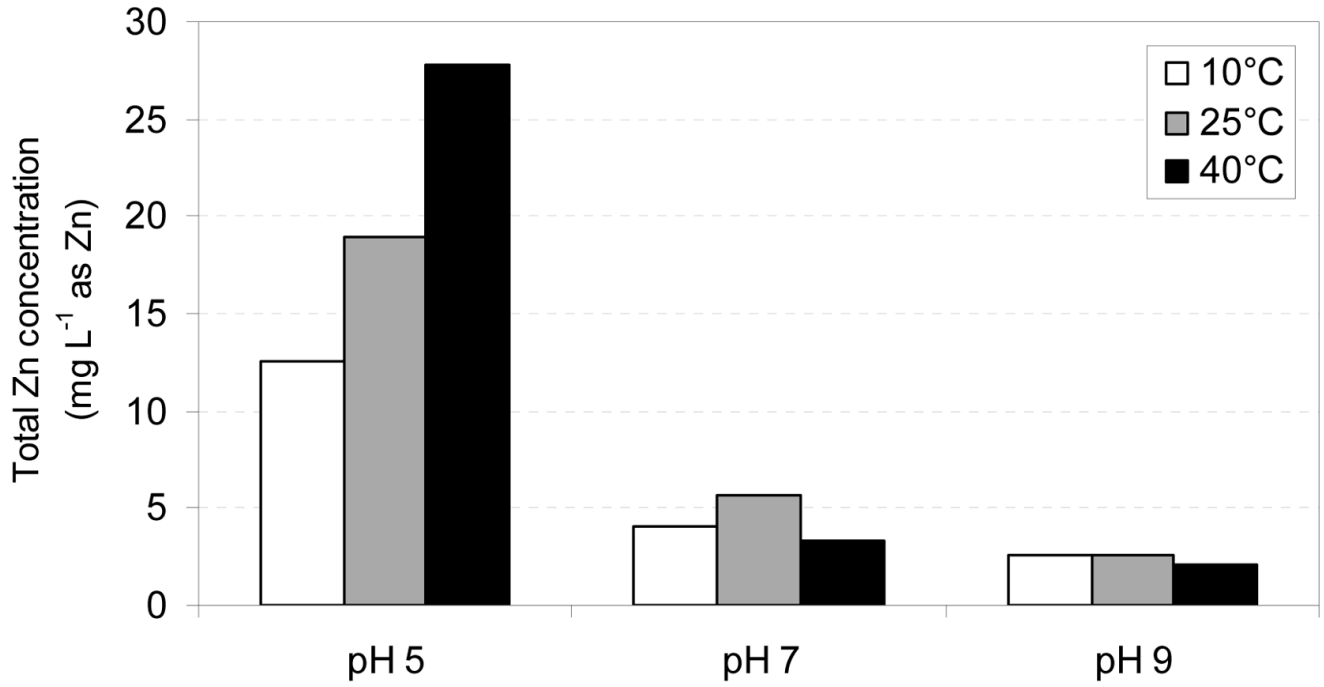

Figure 1.

Total Zn concentration in SRO extracts from RM at varied temperature and initial pH. The batch contact time was selected as 72 hours. All SROs were prepared using $CaSO_4$ (34 mg/L) and NaCl (25.5 mg/L) and were buffered with 25 mM of potassium hydrogen phthalate (pH 5), sodium bicarbonate (pH 7), or ammonium carbonate (pH 9). Total Zn includes both inorganic Zn and organo- Zn. The digestion test result showed that total Zn concentration in RM was 4.89 mg g^{-1} as Zn equivalent to 244.5 mg L^{-1} in the leaching test tubes.

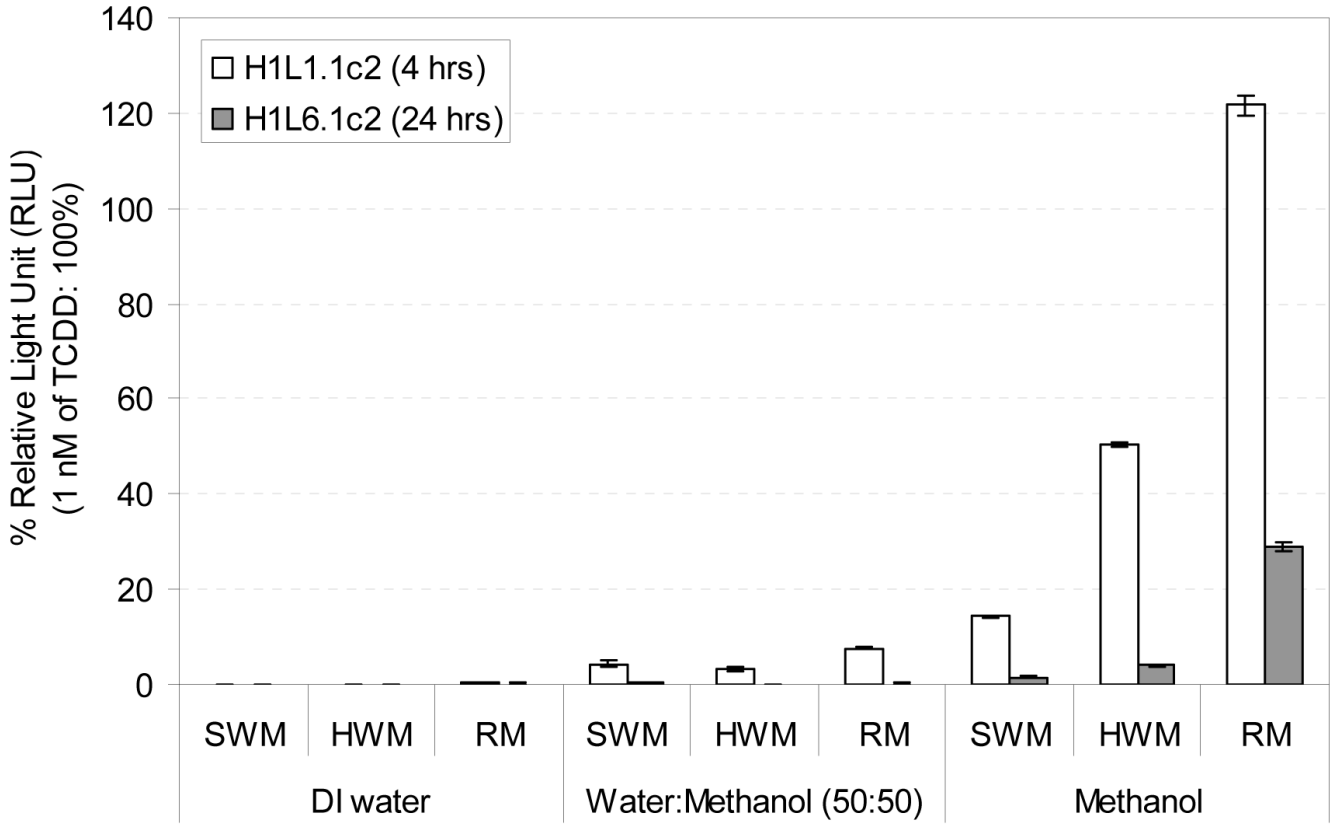

Figure 2.
Induction of AhR-dependent luciferace reporter gene expression in H1L1.1c2 and H1L6.1c2 cells by DI water extracts, water/methanol mixture extracts (50:50), and methanol extracts of mulches (SWM, HWM, and RM). Percent RLU of all method blanks were less than 2% and 1% for H1L1.1c2 and H1L6.1c2, respectively. Percent RLU results are presented as an average ± SD of triplicate incubations.

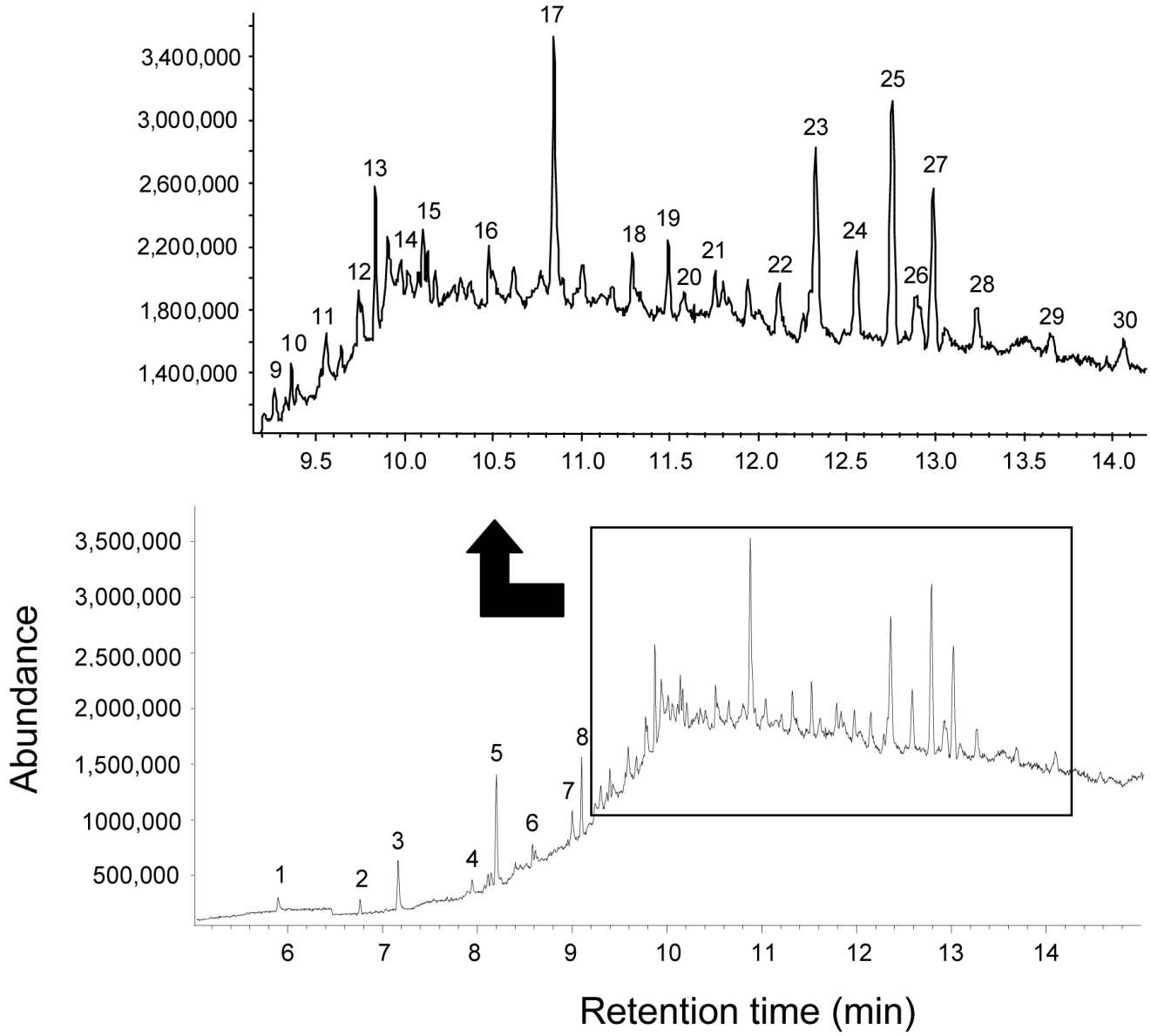

Figure 3.
GC-MS chromatogram of the methanol extract of RM transferred into hexane. The numbers shown in this figure correspond to the numbers in Table 2.

Table 1

Metal ions, nutrients, and TOC concentration in SRO and DI water extracts of mulches(SWM, HWM, and RM) at varied temperature and initial pH.

Mulch		Solution	Temperature	Initial pH	Final pH	Metal ions (μg L^{-1})												Nutrients (μg L^{-1})			TOC (mgC L^{-1})
						Mg	Al	Cr	Mn	Fe	Cu	Zn	As	Rb	Sr	Ba	Pb	PO_4^{3-} as P	NO_3^- as N*	NH_3^+ as N**	
RM	Leaching test	SRO	10°C	5.0	5.1	945 (6.77)	130 (0.6)	0.835 (0.5)	51 (12.2)	541 (0.2)	0 (0.0)	12,483 (5.1)	2.56 (10.4)	2.35 (1.8)	35.1 (17.4)	107 (20.4)	12.10 (2.8)	786	70.8	4,290	11
				7.0	8.0	348 (2.49)	0 (0.0)	0.108 (0.1)	21 (5.1)	30 (0.0)	0 (0.0)	4,117 (1.7)	0 (0.0)	2.87 (2.2)	15.1 (7.5)	45.1 (8.6)	0 (0.0)	16.6	-	243	87
				9.0	8.9	466 (3.34)	166 (0.8)	0.0273 (0.0)	13 (3.0)	0 (0.0)	0 (0.0)	2,544 (1.0)	0.320 (1.3)	3.74 (2.9)	12.8 (6.3)	22.6 (4.3)	1.20 (0.3)	504	49.4	-	86
			25°C	5.0	5.1	1,200 (8.61)	328 (1.5)	3.21 (2.1)	71 (16.9)	827 (0.3)	0 (0.0)	18,930 (7.7)	3.39 (13.8)	6.23 (4.9)	45.9 (22.7)	146 (27.9)	19.3 (4.5)	775	63.2	1,060	30
				7.0	7.9	445 (3.19)	1.00 (0.0)	0.594 (0.4)	28 (6.7)	52 (0.0)	0 (0.0)	5,597 (2.3)	1.48 (6.0)	4.71 (3.7)	21.6 (10.7)	73.9 (14.1)	0.966 (0.2)	36.1	-	74.3	147
				9.0	8.9	512 (3.67)	122 (0.6)	0.564 (0.4)	14 (3.4)	31 (0.0)	0 (0.0)	2,544 (1.0)	0.837 (3.4)	5.27 (4.1)	16.5 (8.2)	29.4 (5.6)	2.56 (0.6)	502	92.4	-	158
			40°C	5.0	5.1	1,180 (8.46)	289 (1.4)	1.96 (1.3)	83 (19.6)	685 (0.2)	4 (2.6)	27,839 (11.4)	2.77 (11.2)	2.52 (2.0)	41.7 (20.6)	149 (28.4)	23 (5.3)	646	63.2	1,730	50
				7.0	8.2	434 (3.12)	0 (0.0)	0.354 (0.2)	24 (5.7)	0 (0.0)	0 (0.0)	3,263 (1.3)	1.43 (5.8)	4.14 (3.2)	19.8 (9.8)	42.1 (8.0)	0 (0.1)	138	-	1,230	105
				9.0	8.8	525 (3.76)	97.7 (0.5)	0.743 (0.5)	10 (2.4)	0 (0.0)	0 (0.0)	2,082 (0.9)	1.78 (7.2)	5.53 (4.3)	15.7 (7.8)	26.4 (5.0)	1.25 (0.3)	478	31.1	-	111
		DI water	25°C	6.3	6.1	395 (2.83)	0 (0.0)	0.948 (0.6)	23 (5.5)	23 (0.0)	0 (0.0)	4,542 (1.9)	1.24 (5.0)	3.93 (3.1)	18.5 (9.1)	17.9 (3.4)	0 (0.0)	166	73.6	760	88
		ER[3]	-	-	-	11.3	60.0	59.5	18.0	56.2	1.00	18.9	16.1	16.6	14.5	75.8	84.2	359	-	923	40
	Digest[4]		-	-	-	2.79×10^2	4.24×10^2	3.09	8.42	5.50×10^3	2.83	4.89×10^3	4.93×10^{-1}	2.56	4.04	1.05×10	8.65	-	-	-	-
SWM	Leaching test	SRO	10°C	5.0	4.9	34,100 (37.6)	2.13 (0.0)	0.987 (0.4)	680 (32.6)	103 (0.0)	0 (0.0)	48.7 (9.2)	0 (1.4)	26.8 (43.3)	335 (25.4)	192.2 (8.9)	0 (0.0)	8,890	< 1	208	263
				7.0	7.9	16,300 (18.0)	0 (0.0)	1.59 (0.7)	98 (4.7)	81 (0.0)	0 (0.0)	7.08 (1.3)	0 (0.0)	32.2 (52.1)	117 (8.8)	65.0 (3.0)	0 (0.0)	8,530	-	142	347
				9.0	8.1	11,800 (13.0)	0 (0.0)	11.7 (5.2)	20 (1.0)	185 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	33.6 (54.4)	81.9 (6.2)	44.6 (2.1)	0 (0.0)	7,270	< 1	-	420

Mulch	Solution	Temperature	Initial pH	Final pH	Metal ions (μg L^{-1})												Nutrients (μg L^{-1})			TOC (mgC L^{-1})
					Mg	Al	Cr	Mn	Fe	Cu	Zn	As	Rb	Sr	Ba	Pb	PO_4^{3-} as P	NO_3^- as N*	NH_3^+ as N**	
HWM	Leaching test	SRO	5.0	5.0	43,300 (47.7)	122 (0.6)	2.41 (1.1)	789 (37.8)	87 (0.0)	0 (0.0)	100 (18.9)	4.40 (29.3)	33.8 (54.6)	443 (33.6)	255 (11.8)	0.185 (0.2)	9,250	< 1	243	252
		25°C	7.0	7.5	17,400 (19.2)	47.9 (0.2)	1.52 (0.7)	110 (5.3)	37 (0.0)	1 (0.3)	21.2 (4.0)	3.50 (23.3)	31.8 (51.4)	137 (10.4)	72.8 (3.4)	0.100 (0.1)	8,610	-	317	297
			9.0	8.1	12,500 (13.8)	61.4 (0.3)	1.61 (0.7)	29 (1.4)	61 (0.0)	0 (0.0)	20.7 (3.9)	3.91 (26.0)	31.3 (50.5)	100 (7.6)	54.4 (2.5)	0.142 (0.2)	6,730	< 1	-	435
			5.0	4.9	39,100 (43.1)	100 (0.5)	5.02 (2.2)	690 (33.1)	84 (0.0)	45 (24.8)	133 (25.3)	5.22 (34.8)	30.8 (49.8)	408 (30.9)	227 (10.5)	4.37 (5.5)	8,610	< 1	827	267
		40°C	7.0	7.8	8,490 (9.4)	71.8 (0.3)	3.40 (1.5)	12 (0.6)	286 (0.1)	41 (22.8)	13.4 (2.5)	3.40 (22.7)	25.1 (40.5)	59.3 (4.5)	34.1 (1.6)	1.64 (2.1)	6,890	-	750	614
			9.0	8.1	11,500 (12.7)	38.4 (0.2)	2.18 (1.0)	52 (2.5)	145 (0.0)	11 (6.1)	13.2 (2.5)	4.00 (26.7)	28.9 (46.7)	84.5 (6.4)	49.1 (2.3)	0.510 (0.6)	7,880	< 1	-	498
		DI water	25°C	6.3	5.9	12,000 (13.2)	68.4 (0.3)	2.50 (1.1)	137 (6.5)	65 (0.0)	1 (0.3)	25.3 (4.8)	4.94 (32.9)	26.4 (42.7)	85.2 (6.5)	45.3 (2.1)	0 (0.1)	11,100	< 1	262	353
		ER[3]	-	-	-	31.0	42.9	64.4	24.1	73.5	19.2	19.1	41.0	16.9	37.8	37.8	7.72	28.9	-	17.1	19
	Digest[4]		-			1.81 × 10^3	4.42 × 10^2	4.53	4.17 × 10	1.04 × 10^4	3.83	1.05 × 10	1.80 × 10^{-1}	1.24	2.64 × 10	4.33 × 10	1.60				
			5.0	5.1	49,000 (41.4)	1,170 (0.8)	36.1 (2.6)	4,150 (47.4)	877 (0.0)	46 (2.4)	301 (17.8)	257 (32.6)	149 (34.2)	666 (36.1)	265 (9.3)	23.2 (1.6)	11,744	< 1	815	563
		10°C	7.0	7.6	17,700 (15.0)	295 (0.2)	25.1 (1.8)	765 (8.7)	599 (0.0)	32 (1.7)	48.0 (2.8)	213 (27.0)	135 (31.1)	190 (10.3)	54.2 (1.9)	3.41 (0.2)	7,873	-	107	665
			9.0	8.0	11,000 (9.3)	315 (0.2)	28.6 (2.0)	479 (5.5)	976 (0.0)	32 (1.7)	28.1 (1.7)	181 (23.0)	123 (28.2)	131 (7.1)	36.2 (1.3)	4.43 (0.3)	6,873	< 1	-	653
			5.0	5.2	58,400 (49.4)	1,470 (1.0)	47.0 (3.3)	4,415 (50.4)	1,186 (0.0)	58 (3.1)	333 (19.7)	270 (34.3)	150 (34.4)	722 (39.2)	312 (10.9)	29.9 (2.0)	11,657	< 1	1,290	630
		25°C	7.0	7.4	19,000 (16.1)	578 (0.4)	36.5 (2.6)	946 (10.8)	812 (0.0)	50 (2.7)	80.2 (4.7)	237 (30.1)	145 (33.3)	218 (11.8)	73.3 (2.6)	8.87 (0.6)	7,369	-	1,780	638
			9.0	7.8	17,800 (15.1)	734 (0.5)	42.9 (3.0)	875 (10.0)	740 (0.0)	100 (5.4)	84.1 (5.0)	275 (34.9)	144 (33.2)	209 (11.4)	65.0 (2.3)	14.9 (1.0)	7,709	< 1	-	723

Mulch	Solution	Temperature	Initial pH	Final pH	Metal ions (µg L^{-1})												Nutrients (µg L^{-1})			TOC (mgC L^{-1})
					Mg	Al	Cr	Mn	Fe	Cu	Zn	As	Rb	Sr	Ba	Pb	PO_4^{3-} as P	NO_3^- as N*	NH_3^+ as N**	
			5.0	5.3	57,800 (48.9)	1,320 (0.9)	63.8 (4.5)	4,715 (53.8)	2,410 (0.1)	90 (4.8)	364 (21.4)	335 (42.5)	157 (36.0)	774 (42.0)	359 (12.6)	29.1 (2.0)	13,938	< 1	828	680
		40°C	7.0	7.9	17,800 (15.1)	576 (0.4)	40.5 (2.9)	812 (9.3)	843 (0.0)	70 (3.7)	114 (6.7)	275 (34.9)	142 (32.6)	195 (10.6)	66.4 (2.3)	8.96 (0.6)	9,422	-	696	740
			9.0	7.8	14,500 (12.3)	743 (0.5)	48.4 (3.4)	706 (8.1)	1,042 (0.0)	99 (5.3)	62.8 (3.7)	270 (34.3)	142 (32.6)	182 (9.9)	61.7 (2.2)	14.4 (1.0)	10,461	< 1	-	853
	DI water	25°C	6.3	6.0	28,000 (23.7)	909 (0.6)	37.3 (2.6)	1,575 (18.0)	889 (0.0)	45 (2.4)	153 (9.1)	255 (32.4)	88.3 (20.3)	281 (15.2)	78.6 (2.7)	12.8 (0.9)	10,494	11	182	743
	ER[3]	-	-	-	47.4	57.4	2.2	66.5	9.4	10.4	91.3	7.5	39.1	28.7	7.2	44.8	42.4	-	89.8	16.5
Digest[4]		-			2.36×10^3	2.87×10^3	2.83×10	1.75×10^2	4.97×10^4	3.74×10	3.39×10	1.58×10	8.70	3.69×10	5.73×10	2.99×10				

[1] Samples not analyzed for a parameter are indicated by(-)

[2] Because of buffer solution composition or impurities, no results for NO_3^- concentration are presented for any of the pH 7 synthetic runoff extractions and no NH_4^+ concentration data are available for the pH 9 synthetic runoff samples.

[3] Estimated extraction reproducibility EER) was estimated as the relative percent difference between SRO extracts(pH 7, 25°C) and the corresponding DI water extracts using the following equation:

$$EER = \left| \frac{SROextract - DIextract}{SROextract} \right| \times 100$$

[4] unit: µg g^{-1}

[5] Values in parentheses represent the fraction of the total concentration leached out during the batch testing.

Table 2

Organic compounds identified in RM extracts by GC-MS analyses and NIST-library. The numbers correspond to the numbers in Figure 3.

No.	Compound
1	Benzothiazole
2	Pyrazole
3	o-Cyanobenzonic acid
4	Diphenylamine
5	2(3H)-Benzothiazolone
6	Optadecane, Heptadecane
7	Nonadecane
8	Hexadecanoic acid, methyl ester
9	2-Phenylbenzimidazole
10	Tetracosane
11	Benzothiazole, 2-phenyl-
12	Hemeicosane
13	Octadecanoic acid, methyl ester
14	9,10-Anthracenedione, 2-ethyl-
15	Eicosane
16	Tricosane
17	Pyrimidine, 2-(4-pentylphenyl)-5-propyl-
18	Pentacosane
19	Bis(2-ethylhexyl) phthalate
20	Cycloninasiloxane, octadecamethyl-
21	Hexacosane
22	Benzenamine
23	1-Phenanthrenecarboxylic acid, 1,2,3,4,4
24	1,4-Benzenediamine, N,N′-diphenyl-
25	1,1′-Biphenyl, 4, 4′, 5′, 6′-tetramethoxy-
26	Phenol, 2,4-bis(1-methyl-1-phenylethyl)-
27	7-Hydroxybenzo[f]flavone
28	Docosanoic acid
29	Dotriacontane
30	Naphthalene, 2-(bromomethyl)-