Environmental impact of the use of contaminated sediments as partial replacement of the aggregate used in road construction

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A R T I C L E   I N F O

A B S T R A C T

The Indiana Harbor Canal (IHC) is a waterway extensively polluted with heavy metals and petroleum. Since there are limited disposal options for the petroleum-contaminated sediments (PCSs) of the canal, the environmental impact of IHC dewatered sediment when used as partial replacement of the aggregate used in hot mix asphalt (HMA) for road construction was investigated. In order to assess the long term migration of the target contaminants into the environment, the TCLP, SPLP, and a Constant pH leaching test were applied to a HMA mixture containing 10% of dewatered PCS, a conventional HMA, and the dewatered PCS. None of the heavy metals significantly leached from any of the tested materials in any of the conducted tests. Despite the presence of PAHs in the PCS, these were not found in any of the leachate samples. Finally, among the measured VOCs, only acetone and 2-butanone were found to leach from the asphalt mixtures and the sediment in the Constant pH experiment. It was concluded that it may be environmentally safe to replace the aggregates of the HMA used in road construction in the studied proportions with dewatered PCS based upon leaching levels as compared to TCLP regulated levels. This could be a viable, beneficial use option for the PCS, and therefore, for the canal remediation.

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1. Introduction

The Indiana Harbor Canal (IHC) is a waterway that was constructed in the early 1900s to connect the Grand Calumet River with Lake Michigan. The heavy industry that was located in the area, steel and petroleum refining among them, has brought contamination to the canal and the sediments [1]. The petroleum-contaminated sediment (PCS) from the IHC ($\sim$3.9–7.7 $\times$ 10^6 m^3) has been identified as among the most toxic and highly contaminated sediments evaluated in the Great Lakes [1–3].

Contamination of heavy metals (Hg, Cd, Cr, Pb, and others), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and polychlorinated biphenyls (PCBs) has been detected in the IHC sediment throughout the years [1,3–7]. PAHs are highly hydrophobic and tend to adsorb onto the organic matter present in sediment particles, thus becoming persistent pollutants in aquatic environments [8–10]. Several VOCs and PAHs have been identified as having carcinogenic and mutagenic effects, and were included in the list of priority pollutants by the U.S. Environmental Protection Agency (EPA) [8,11]. In consequence, the EPA has designated

the Great Calumet River Area, including the IHC, as an area of concern [3,12]. The dredging and disposal of the IHC has been frequently proposed as a remediation approach, but not accomplished, mainly due to the absence of an acceptable disposal site for the PCS [12,13]. The beneficial use of PCS, and other contaminated soils, could reduce their disposal in landfills. Hence, various states have devised guidelines for the use of contaminated soils in applications such as cement and/or asphalt [14–17].

Hot mix asphalt (HMA) is the most common form of pavement used in road construction in the U.S. Since HMA contains petroleum compounds, it seemed logical to add additional petroleum compounds, albeit from PCS, without affecting its physical or chemical properties.

Three beneficial actions occur when a contaminated soil is used as a HMA constituent: incineration, dilution, and solidification [14]. The proportion of contaminated soil that can be used to replace the aggregate depends on the soil characteristics, particle size, porosity, etc. It also affects the proportion of asphalt binder needed in the mixture [15,16].

TCLP, SPLP, and other leaching tests have been used to evaluate the environmental consequences of aggregate substitution in HMAs by several researchers [17,18]. Xue et al. [19] used the Marshall Mix Design and the superior performance asphalt pavement method to prepare mixtures containing municipal solid waste

Table 1
Contaminants of concern.

Type	Method	Compound
PAHs	EPA Method 8270	1-Methylnaphthalene, 2-methylnaphthylene, acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoroanthene, benzo(g,h,i)perylene, benzo(k)fluoroanthene, carbazole, chrysene, dibenzo(a,h)anthracene, dibenzofuran, fluroanthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene
VOCs	EPA Method 8260	Benzene, toulene, ethylbenzene, m,p-xylene, o-xylene, acetone, 2-butanone, trichlorothene
Metals	EPA Method 6010	Arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, zinc

incineration ash as a partial aggregate substitute in a stone matrix asphalt. The authors concluded that the resulting mixtures met the quality standards for stone matrix asphalt. The asphalt adhesiveness and chemical stability were considered as key factors in preventing metal leaching. The asphalt metal stabilization was found to be more effective than cement-based stabilization.

The aim of this study was to assess the environmental impact and potential contaminant migration associated with the use of the IHC sediment that is used in HMA (used as surface pavement in roads in Midwestern states). The objectives were accomplished using a Constant pH leaching test, the toxicity characterization leaching procedure (TCLP), and the synthetic precipitation leaching protocol (SPLP).

2. Materials and methods

2.1. Contaminants of concern

The selected contaminants of concern are reported in Table 1. The Constant pH experiment was conducted with the Control Mix (Section 3.3.2) targeted benzene, toluene, ethyl benzene, and xylenes (BTEX) as the only VOCs of interest. When acetone and 2-butanone were found as constituents of the HMAs, the other VOCs were included.

2.2. IHC sediment

The sediment was collected from the IHC (IN) and was mechanically mixed with a Solve 9222 Organic Cationic Flocculant (Watersolve LLC, Grand Rapids, MI), and then transferred onto a geotube pillow (TenCate Geosynthetics of Commerce, Pendergrass, GA) as described by Gaffney [20] and left to dewater for 10 days. The dewatered sediment was removed from the pillow and stored at room temperature for further use.

2.3. Asphalt binder, mineral dust, aggregate, and Class F Fly Ash (CFFA)

Superpave class PG-64-22 was obtained from a manufacturer in Cincinnati, OH. The mineral dust (size <0.0074 mm) and the dolomitic limestone aggregate (size <9.5 mm) were both procured in Phillipsburg (OH). The CFFA was collected from the Powder River Basin region (WY).

2.4. Hot mix asphalt: Control Mix (0% PCS) and Best mixture (10% PCS)

Two HMAs were prepared following the Marshall Mix Design procedure (ASTM D1559-76). The Control Mix contained 2% of mineral dust, 8% of asphalt binder, and 90% of limestone aggregate, but no sediment. The Best mixture contained 10% of IHC Sed, 2% CFFA, 8% asphalt binder, and 80% limestone aggregate (by weight). The Best mixtures' sediment replacement (10%) was selected to be greater than the proportion that would probably be used in roads in order to ensure that leaching would not be underestimated in this study. The mineral dust, present in the Control Mix, was replaced by CFFA in the Best mixtures in order to obtain a better cementation of the mix, as reported by Çelik [21].

2.5. Particle size reduction

The four HMA cylindrical specimens (Best 1, Best 2, Best 3, and the Control Mix) were crushed by chisel and hammer, and ground using a mill (Model 4E, QCG Systems, Phoenixville, PA) for the leaching experiments.

2.6. Solids characterization

The solid samples were characterized using several parameters according to the objectives and contaminants of concern. Moisture content was determined by the gravimetric method. The pH was determined by taking 5 g of the solid and equilibrating it with 96.5 ml of deionized water for 15 min; the pH was measured using a Thermo Orion 370 pH Meter (Thermo Scientific, Waltham, MA). The particle size distribution (PSD) was determined using sieve analysis (ASTM D6913-04). X-ray diffraction (XRD) was performed using a Diffractometer model X'Pert-MPD PW3040/00 with a Copper X-ray source ($K\alpha_1$ 1.54060 Å) (PANalytical, Westborough, MA) and data analyzed using X'Pert Highscore Plus software based on the mineral intensity factors using the 100% approach. XRD data were collected between 3 and 60° θ. All solid samples were acid digested (EPA Method 3051), filtered (0.45 μm), and analyzed for metals (EPA Method 6010B) using an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES, IRIS Intrepid, Thermo Scientific, MA). Mercury was analyzed using a Direct Mercury Analyzer, DMA-80 (Milestone Inc., Shelton, CT). PAHs were extracted according to EPA Method 3550 using an Organomation N-EVAP concentrator (Organomation Associates Inc., Berlin, MA) and analyzed on an Agilent 6890GC/5973MS (Santa Ana, CA) by EPA Method 8270. The VOCs were extracted following EPA Method 5035 with further GC/MS analysis performed on an Agilent 6890GC/5973MS (EPA Method 8260). Inorganic carbon (IC) and total carbon (TC) were measured using a TOC-V CHP Analyzer (Shimadzu Scientific Instruments, Columbia, MD) equipped with a solid sample module SSM-5000A. Total organic carbon (TOC) was calculated by difference. All analytical work was performed using triplicates, except for pH, PSD, and XRD.

2.7. TCLP and SPLP leaching tests

The TCLP (EPA Method 1311) and the SPLP (EPA Method 1312) tests were performed by a commercial laboratory.

2.8. Constant pH leaching test

This experiment followed the procedure detailed elsewhere [22] with slight modifications. The tested solid (100 g) was placed in a 2.4 L borosilicate glass reactor with 2 L of the SPLP extraction fluid (pH 4.2). The total duration of the experiment was 168 h, with sampling events at 0, 4, 8, 24, 48, 96, and 168 h. The pH controller

(LMI Milton Roy, MA) was set to maintain a pH of 4.2 ± 0.2 using 1 N HNO$_3$ and 0.1 N NaOH as needed. pH and oxidation reduction potential (ORP) were continuously monitored using Cole-Parmer electrodes and a Prober-PH8 interface connected to a computer. The solid residues and the aqueous samples of each experiment were analyzed following similar methods as described for the solid samples, with the exception of EPA Method 3015 which was used for aqueous phase acid digestions.

2.9. Organic fraction extraction (OFE)

An OFE was performed according to Al-Abed et al. [23]. The material (1 g) was equilibrated with 0.7 M NaOCl (20 ml) and the pH adjusted to 8.5 with 1 N HCl in a 40 ml glass vial. The vials were placed in a water bath (90 °C, 6 h) where they were shaken occasionally. They were then cooled and centrifuged. The aqueous samples were acid digested and analyzed for metals. The solid samples were rinsed, dried, and acid digested for metal analysis.

2.10. PAHs photochemical oxidation

A batch test was conducted with 40 ml of the SPLP extraction fluid in 40 ml vials, placed along with 100 μl of EPA 8270 Matrix Spike solution (Restek, Bellefonte, PA), to obtain a concentration of 500 μg/L of each contained PAH. Three vials were agitated (24 rpm, 168 h) using a rotary tumbler model RKVSD (ATR Inc., Laurel, MD). Three more vials with the same contents were wrapped, shielding the PAHs from the ambient light, capped, and tumbled. The PAHs were extracted following EPA Method 3510 and analyzed using an Agilent 6890GC/5975MS (EPA Method 8270).

3. Results and discussion

3.1. Solids characterization

3.1.1. IHC Sed

Moisture, pH, and PSD of the studied solids and the CFFA are shown in Table 2. Since the IHC Sed size was suitable for the leaching tests, it was not crushed. The XRD analysis revealed a semiquantitative composition of 73% quartz (SiO$_2$), 15% gypsum (CaSO$_4$), and 12% dolomite (CaMg(CO$_3$)$_2$) (data not shown). The TC and the IC content of the IHC Sed were measured as 14.88% and 1.01%, respectively; therefore TOC was 13.87%. Barium, chromium, manganese, lead, and zinc were the heavy metals found in high (>200 mg/kg) concentrations in the IHC Sed (Table 3). Several PAHs (concentrations >1200 μg/kg), acetone (370 μg/kg), 2-butanone (87 μg/kg), and toluene (6 μg/kg) were also detected in the IHC Sed (Table 4).

3.1.2. Control Mix (0% IHC Sed)

The Control Mix was a typical mixture that is used as a surface pavement for light traffic roads in the North Central states. Control Mix XRD diffractograms showed the presence of 80% dolomite, 18% ankerite (Ca(Fe,Mg,Mn)(CO$_3$)$_2$), and 2% quartz. The concentrations of mercury, aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, manganese, lead, and zinc were greater in the IHC Sed than in the Control Mix (Table 3).

Two of the PAHs and several VOCs were found in detectable concentrations in the asphalt binder (Table 4). Acetone and 2-butanone, probably coming from the asphalt, were the only organic contaminants found in the Control Mix. A portion of VOCs and PAHs could have been volatilized during preparation. For example, the concentration of acetone in the asphalt binder was 1500 μg/kg, the proportion of asphalt binder in the Control Mix was 8%, giving a potential contribution of 120 μg/kg to the Control Mix. Nevertheless, the measured concentration of acetone in the Control Mix

was 30 μg/kg, suggesting significant volatilization during the specimens' preparation.

3.1.3. Best mixtures (10% IHC Sed)

Low moisture, alkaline pH, and PSD comparable to the Control Mix were measured in the Best mixtures (Table 2). The obtained XRD composition of the Best 1 mixture was 51% dolomite, 45% quartz, and 4% ankerite. The metal concentrations of mercury, calcium, chromium and other metals appear to be similar among the Best mixtures; but copper, lead, and zinc concentrations showed significant differences in spite of having the same constituents (Table 3). When compared to the Control Mix, the Best mixtures revealed higher concentrations of mercury, aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, manganese, lead, and zinc. These were the same metals found in higher concentrations in the IHC Sed. The concentrations of mercury and cobalt in the Best mixtures could have been moderately influenced by the CFFA, while barium could have been significantly influenced by CFFA. However, it can be concluded that the presence of sediment is the main cause of the increased metal concentrations found in the Best mixtures.

The organic contaminants found in the IHC Sed and in the asphalt binder also suffered losses during preparation, similar to those described for the Control Mix. In spite of that, acetone and 2-butanone were also found in the Best mixtures. PAHs were found in lower concentrations than those that could have been contributed by the IHC Sed and the asphalt binder to the Best mixtures (Table 4). For instance, pyrene was present in the IHC Sed at a concentration of 43,000 μg/kg, and not detected in the asphalt binder. It was found in the Best 1 and Best 2 mixtures at concentrations of 3100 and 2300 μg/kg, respectively, and less than the expected value of 4300 μg/kg. Overall, the beneficial dilution of contaminants proposed by Meegoda [14] seemed to be supported, although the main benefit would be metal stabilization and encapsulation in the HMA, which were tested using the leaching experiments.

3.2. TCLP and SPLP

The TCLP and SPLP tests were applied to the IHC Sed, Control Mix, and Best 1. The TCLP results of the IHC Sed (Fig. 1) showed only two regulated metals leaching: barium (0.35 mg/L) and lead (0.47 mg/L). Both were lower than the TCLP regulated (40 CFR §261.24) maximum contaminant levels (MCL; shown in Table 5). Additionally, none of the organic regulated contaminants were present in the TCLP leachate, indicating no restrictions for the IHC Sed beneficial use.

The Control Mix showed that barium (0.065 mg/L) and lead (0.05 mg/L) leached during the TCLP. The TCLP performed on the Best 1 mixture reported only barium leaching at a level of 0.50 mg/L. This is a slightly higher leaching concentration of barium than the TCLP reported for the IHC Sed (0.35 mg/L), in spite of the higher barium content in the IHC Sed. This could be a consequence of the heterogeneity of the IHC Sed, but does not compromise the obtained conclusions.

The SPLP test run with the IHC Sed showed only barium leaching at a concentration of 0.29 mg/L. The Control Mix SPLP did not report any contaminant leaching above the method reporting limit (MRL), while Best 1 showed that barium leached at a concentration of 0.16 mg/L. Meanwhile, the SPLP extraction fluid released slightly more barium from the IHC Sed than from Best 1, which could be due to the lower concentration of barium found in Best 1.

Both the TCLP and SPLP results suggested that metals, PAHs, and VOCs present in the IHC Sed and in Best 1 were not significantly released into the environment either under a co-disposal scenario with municipal solid waste (TCLP) or under rainfall influence (SPLP).

Table 2
Moisture, pH, and particle size distribution of the studied solids.

Solid	Moisture	pH	Particle size distribution (mm)				
			>4.75	2–4.75	0.425–2	0.075–0.425	<0.075
IHC Sed	4.34%	6.33	1.26%	19.65%	24.67%	54.15%	0.27%
Control Mix	0.24%	9.66	0.02%	17.12%	69.14%	13.25%	0.47%
Best mixtures	0.08%	9.70	0.34%	29.85%	60.83%	8.49%	0.50%
CFFA	0.08%	11.36	0.00%	0.00%	1.03%	9.04%	89.93%

Table 3
Metal composition of the studied solids (mg/kg).

Metal	IHC Sed	Asphalt binder	Class F Fly Ash	Control Mix	Best 1	Best 2	Best 3
Hg	0.52	–	0.46	0.004	0.070	0.053	0.075
Al	4900	130	72000	350	2300	1100	1100
As	18	<2.0	20	<1.8	3.4	4.4	<1.8
Ba	260	46	4900	47	170	53	61
Ca	41000	420	160000	200000	180000	180000	170000
Cd	4.2	<0.10	2.1	<0.24	0.61	0.41	<0.10
Cr	210	<1.2	57	3.0	21	17	19
Co	3.1	12	24	<0.40	1.8	0.86	<0.40
Cu	75	10	160	30	75	16	45
Fe	18000	110	32000	2000	4300	3600	3800
Mg	11000	43	30000	110000	110000	100000	97000
Mn	850	<0.80	77	120	205	170	180
Pb	860	11	24	7.5	80	56	69
Zn	820	1500	150	49	110	78	99

3.3. Constant pH leaching experiments

This experiment evaluated the long term migration of contaminants under acidic rain conditions. Results from these experiments are presented and discussed in the subsections below.

3.3.1. IHC Sed leaching

The leaching experiments on IHC Sed samples had an average pH of 4.3 and ORP of 266 mV. All metals reported as IHC Sed constituents in Table 3, except arsenic, were found to leach in detectable concentrations varying with time during the Constant

Table 4
PAHs and VOCs concentration in the IHC Sed, Best mixtures, Control Mix, and asphalt binder (µg/kg).

Contaminant	IHC Sed	Asphalt binder	Control Mix	Best 1	Best 2	Best 3
PAHs						
1-Methylnapthalene	3300	490	<570	<570	<570	<570
2-Methylnapthalene	1200	690	<570	<570	<570	<570
Acenaphthene	2200	<1000	<1000	<1000	<1000	<1000
Acenaphthylene	<1900	<1900	<1900	<1900	<1900	<1900
Anthracene	3300	<1100	<1100	<1100	<1100	<1100
Benzo(a)anthracene	20000	<2200	<2200	<2200	<2200	<2200
Benzo(a)pyrene	21000	<960	<960	<960	1600	1100
Benzo(b)fluoranthene	4500	<1400	<1400	<1400	<1400	<1400
Benzo(g,h,i)perylene	5400	<3700	<3700	<3700	<3700	<3700
Benzo(k)fluoranthene	9600	<2400	<2400	<2400	<2400	<2400
Carbazole	<420	<420	<420	<420	<420	<420
Chrysene	29000	<2200	<2200	<2200	<2200	<2200
Dibenzo(a,h)anthracene	3300	<3100	<3100	<3100	<3100	<3100
Dibenzofuran	<1500	<1500	<1500	<1500	<1500	<1500
Fluoranthene	13000	<1600	<1600	<1600	<1600	<1600
Fluorene	2000	<1100	<1100	<1100	<1100	<1100
Indeno(1,2,3-cd)pyrene	<3200	<3200	<3200	<3200	<3200	<3200
Naphthalene	<1300	<1300	<1300	<1300	<1300	<1300
Phenanthrene	6100	<840	<840	<840	<840	<840
Pyrene	43000	<1900	<1900	3100	2300	<1900
VOCs						
Acetone	370	1500	30	18	38	69
2-Butanone	87	170	14	<5	14	22
4-Methyl-2-pentanone	<11	860	<11	<11	<11	<11
1,2,4-Trimethylbenzene	<6	78	<6	<6	<6	<6
Benzene	<5	160	<5	<5	<5	<5
Methyl tert-butyl ether	<50	<50	<50	<50	<50	<50
Ethyl benzene	<5	22	<5	<5	<5	<5
Toluene	6	100	<5	<5	<5	<5
Trichloroethene	<5	<5	<5	<5	<5	<5
Xylenes, Total	<5	340	<5	<5	<5	<5

Table 5
Metals leaching from the studied materials during the Constant pH experiment and the TCLP regulated level (mg/L). NA stands for non applicable. The average concentration of the Best mixtures was calculated using a half method reporting limit (MRL/2) in the cases of <MRL in mixture.

Time (h)	Hg	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Pb	Zn
IHC Sed														
0.17	<0.002	<0.24	<0.090	<0.038	29	<0.006	<0.025	<0.055	<0.018	<0.26	5.4	<0.036	<0.042	0.17
4	<0.002	<0.24	<0.090	0.075	200	0.015	<0.025	<0.055	0.047	0.33	8.0	1.2	0.22	4.0
8	<0.002	0.27	<0.090	0.11	280	0.024	<0.025	0.028	0.060	0.49	13	2.0	0.30	6.2
24	0.008	<0.24	<0.090	0.16	360	0.030	0.013	0.034	0.065	1.1	22	3.1	0.35	9.0
48	0.003	0.44	<0.090	0.23	440	0.036	0.016	0.047	0.064	1.9	35	4.2	0.43	11
96	0.013	1.3	<0.090	0.28	500	0.038	0.017	0.045	0.049	3.8	55	5.0	0.52	12
168	0.003	2.2	<0.090	0.37	570	0.040	0.022	0.053	0.045	7.0	78	6.0	0.57	12
Control Mix														
0.17	<0.002	<0.24	<0.090	<0.038	8.1	<0.006	<0.025	<0.055	<0.018	<0.26	4.3	<0.036	<0.042	0.039
4	<0.002	<0.24	<0.090	<0.038	100	<0.006	<0.025	<0.055	0.032	0.35	48	<0.036	<0.042	0.043
8	<0.002	<0.24	<0.090	0.042	200	<0.006	<0.025	<0.055	0.059	1.0	97	0.064	<0.042	0.052
24	<0.002	<0.24	<0.090	0.063	600	<0.006	<0.025	<0.055	0.13	3.0	300	0.28	<0.042	0.051
48	<0.002	<0.24	<0.090	0.088	1000	<0.006	<0.025	<0.055	0.16	3.4	510	0.51	<0.042	0.055
96	<0.002	1.1	<0.090	0.12	1600	<0.006	<0.025	<0.055	0.19	3.6	810	0.92	<0.042	0.21
168	<0.002	3.3	<0.090	0.15	2300	<0.006	<0.025	<0.055	0.23	4.2	1200	1.4	<0.042	0.17
Best 1														
0.17	<0.002	<0.24	<0.090	<0.038	1.6	<0.006	<0.025	<0.055	<0.018	<0.26	0.46	<0.036	<0.042	0.026
4	<0.002	<0.24	<0.090	<0.038	19	<0.006	<0.025	<0.055	0.036	<0.26	10	0.013	<0.042	<0.013
8	<0.002	<0.24	<0.090	0.093	100	<0.006	<0.025	<0.055	0.029	1.0	52	0.059	<0.042	0.041
24	<0.002	<0.24	<0.090	0.23	330	<0.006	<0.025	<0.055	0.12	4.9	170	0.23	<0.042	0.16
48	<0.002	0.43	<0.090	0.43	660	<0.006	<0.025	<0.055	0.19	7.1	350	0.46	<0.042	0.32
96	<0.002	2.3	<0.090	0.88	1200	<0.006	<0.025	<0.055	0.24	11.0	560	0.95	0.094	0.70
168	<0.002	3.8	<0.090	1.26	1700	<0.006	<0.025	<0.055	0.19	10.1	850	1.5	0.072	0.74
Best 2														
0.17	<0.002	<0.24	<0.090	<0.038	0.8	<0.006	<0.025	<0.055	<0.018	<0.26	0.3	<0.036	<0.042	<0.013
4	<0.002	<0.24	<0.090	<0.038	22	<0.006	<0.025	<0.055	<0.018	<0.26	12	<0.036	<0.042	0.048
8	<0.002	<0.24	<0.090	<0.038	120	<0.006	<0.025	<0.055	<0.018	<0.26	66	0.050	<0.042	<0.013
24	<0.002	<0.24	<0.090	<0.038	420	<0.006	<0.025	<0.055	<0.018	1.8	240	0.24	<0.042	<0.013
48	<0.002	<0.24	<0.090	0.053	860	<0.006	<0.025	<0.055	0.018	2.7	480	0.54	<0.042	0.12
96	<0.002	1.6	<0.090	0.12	1800	<0.006	<0.025	<0.055	0.024	5.7	930	1.3	0.045	0.35
168	<0.002	4.5	<0.090	0.14	2400	<0.006	<0.025	<0.055	0.078	7.3	1300	1.9	0.040	0.28
Best 3														
0.17	<0.002	<0.24	<0.090	<0.038	1.3	<0.006	<0.025	<0.055	<0.018	<0.26	0.52	<0.036	<0.042	0.014
4	<0.002	<0.24	<0.090	<0.038	24	<0.006	<0.025	<0.055	0.046	<0.26	13	<0.036	<0.042	0.024
8	<0.002	<0.24	<0.090	<0.038	120	<0.006	<0.025	<0.055	0.028	<0.26	67	0.050	<0.042	0.018
24	<0.002	<0.24	<0.090	<0.038	400	<0.006	<0.025	<0.055	0.054	1.2	220	0.24	<0.042	0.053
48	<0.002	<0.24	<0.090	0.050	810	<0.006	<0.025	<0.055	0.066	3.0	460	0.51	<0.042	0.14
96	<0.002	1.2	<0.090	0.10	1600	<0.006	<0.025	<0.055	0.088	5.5	800	1.2	<0.042	0.57
168	<0.002	4.1	<0.090	0.14	2300	<0.006	<0.025	<0.055	0.10	7.3	1200	1.9	0.044	0.41
Best Mix Average														
0.17	<0.002	<0.24	<0.090	<0.038	1.3	<0.006	<0.025	<0.055	<0.018	<0.26	0.41	<0.036	<0.042	0.014
4	<0.002	<0.24	<0.090	<0.038	22	<0.006	<0.025	<0.055	0.041	<0.26	11	<0.036	<0.042	0.020
8	<0.002	<0.24	<0.090	<0.038	110	<0.006	<0.025	<0.055	0.029	1.0	62	0.053	<0.042	0.022
24	<0.002	<0.24	<0.090	<0.038	380	<0.006	<0.025	<0.055	0.086	2.6	210	0.24	<0.042	0.11
48	<0.002	0.43	<0.090	0.178	780	<0.006	<0.025	<0.055	0.090	4.2	430	0.50	<0.042	0.19
96	<0.002	1.68	<0.090	0.366	1500	<0.006	<0.025	<0.055	0.118	7.4	760	1.2	<0.042	0.54
168	<0.002	4.12	<0.090	0.514	2100	<0.006	<0.025	<0.055	0.120	8.2	1100	1.8	0.052	0.48
TCLP regulated level	0.200	NA	5.000	100.00	NA	1.000	NA	5.000	NA	NA	NA	NA	5.000	NA

pH experiment (Table 5). Calcium (564.80 mg/L) and magnesium (78.11 mg/L) were the metals with the highest leached concentrations. Zinc (11.86 mg/L), iron (6.98 mg/L), and manganese (6.05 mg/L) were found in moderate concentrations in the 168-h leachate. Most importantly, only two regulated metals were found to leach: barium (0.37 mg/L) and lead (0.57 mg/L). These concentrations were only slightly higher than the leaching concentrations reported for the TCLP test on IHC Sed in spite of the difference in leaching time, suggesting that the IHC Sed possessed some metal stability.

A mass balance was used to compare the metal concentrations found in the IHC Sed (taken as 100%) with metal concentrations in the solid residues from the Constant pH experiment added to the 168-h leachate metal concentrations. A majority of the metals showed recoveries of 81–112%, except for mercury, which had a very high concentration in the solid residue as compared to the IHC Sed. Aluminum, chromium, copper, iron, lead, and mercury showed higher concentrations as constituents of the solid residues than in the IHC Sed. Discordant metal concentrations in the solid residues and in the sediment could be explained by the heterogeneity of

the sediment [24], metals associations in the sediment [25], and by analytical procedures. The acid digestion performed using ~0.5 g of the sediment or the solid residue and HNO_3 might not have fully digested the IHC Sed silicates. A significant (~28%) rate of calcium and zinc present in the IHC Sed was found to leach in the Constant pH experiment. Cadmium, cobalt, magnesium, manganese, and mercury were found in the leachate at rates in the range of 10–18%. Barium, lead, and copper leached at lower rates (1–3%). Finally, aluminum, arsenic, chromium, and iron leached at very low rates (<1%).

The TOC analysis of the solid residues gave an average of 14.12% TC, 0.10% IC, and 14.02% TOC. There was not much difference between the TOC in IHC Sed and solid residues (13.87% vs. 14.02%), thus implying that the organic fraction (with its associated metals) was not released during the Constant pH experiments. Contrariwise, the low IC value of the solid residues (0.10%) implied that the IC (presumably carbonates) was released during the experiment.

The solid residues of the Constant pH experiment showed significantly lower PAH concentrations as compared to the IHC Sed (Table 6). The reported PAHs release rate is >93%, except

Table 6
PAHs released during the Constant pH experiment (μg/kg).

PAH	IHC Sed	IHC solid residue (average)	% Released
1-Methylnapthalene	3300	93	97.2%
2-Methylnapthalene	1200	<19	>98.4%
Acenaphthene	2200	80	96.4%
Acenaphthylene	<1900	<62	–
Anthracene	3300	150	95.5%
Benzo(a)anthracene	20000	430	97.8%
Benzo(a)pyrene	21000	400	98.1%
Benzo(b)fluoranthene	4500	320	92.9%
Benzo(g,h,i)perylene	5400	<610	>88.7%
Benzo(k)fluoranthene	9600	<400	>95.8%
Carbazole	<420	<14	–
Chrysene	29000	790	97.3%
Dibenzo(a,h)anthracene	3300	<510	>84.6%
Dibenzofuran	<1500	<49	–
Fluoranthene	13000	360	97.2%
Fluorene	2000	59	97.1%
Indeno(1,2,3-cd)pyrene	<3200	<540	–
Naphthalene	<1300	<42	–
Phenanthrene	6100	230	96.3%
Pyrene	43000	1300	97.0%

Fig. 1. Comparison of the concentrations of barium (left) and lead (right) found in the leachate of the TCLP, SPLP, and Constant pH experiments. The concentrations found below the method reporting limit (MRL) have been replaced by MRL/2 (0.025 mg/L) for comparison purposes.

for benzo(g,h,i)perylene (>88.70%) and dibenzo(a,h)anthracene (>84.55%), implying that a significant portion of the PAHs was released into the aqueous phase. Nevertheless, not a single PAH was detected in the leachate of the experiment, suggesting that PAHs could have been oxidized, volatilized, or simply diluted in the leachate. Butterfield et al. [26] observed that PAHs adsorbed onto particles were more resistant to oxidation than those in solution. The vaporization of PAHs into the reactor's headspace is another possibility. The vapor pressure of the target PAHs has a wide range. For example, Shiu and Mackay [27] reported 9.00 Pa for 2-methylnaphthalene and 1×10^{-7} Pa for benzo(a)pyrene. Therefore, some PAHs that have a high vapor pressure could have evaporated into the reactor headspace. The photochemical oxidation of PAHs in the leachate was assessed using a bench scale experiment as reported in Section 3.5. These results do not affect the potential beneficial use of the IHC, since the asphalt mixture and not the raw sediment would be used for roads.

Acetone and 2-butanone were detected in the IHC Sed and in the solid residues of the Constant pH reactor (Table 4), while toluene was only detected in the IHC Sed. Acetone and 2-butanone were detected in the leachate, reaching plateau concentrations of ~39 and ~14 μg/L, respectively (Fig. 3a). Since acetone and 2-butanone were detected in the leachate, it is possible to infer the influence of volatilization on PAH removal during the experiment. The comparison of the vapor pressure (25 °C) of acetone (247,000 Pa) [28], 2-butanone (12,080 Pa) [29], and toluene (4470 Pa) [30] with the PAHs vapor pressure indicated that the volatilization of VOCs was higher. Therefore, the role of volatilization over PAHs removal could have been small.

3.3.2. Control Mix (0% IHC Sed) leaching

Asphalt binders have been proven effective in metal stabilization using the Marshall Mix Design, therefore decreasing the contaminants release into the environment. The stabilization was mainly attributed to asphalt adhesiveness [19]. In this study, the particle size reduction could have decreased the asphalt binder shielding effect, since a number of loose particles were visible in the mixtures. Additionally, friction and impact between particles occurring in the reactor could have further reduced adhesiveness. While more surface area was available to liquid–solid interactions, more contaminant mass was susceptible to leach.
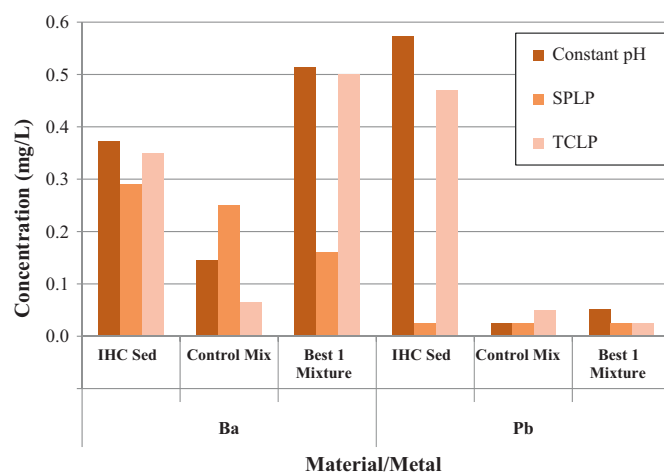
The average pH of the Control Mix experiment was 4.2, while its ORP was 342 mV. Among the target metals, the highest concentrations detected in the 168-h leachate were iron (4.15 mg/L) and manganese (1.40 mg/L) (Table 5). Barium was found in a low concentration (0.15 mg/L) and lead was found below the MRL (Fig. 1).

The mass balance for this experiment showed that the concentrations found in the solid residues plus the concentrations found in the 168-h leachate ranged from 92 to 184% with respect to the concentrations found in the Control Mix. The discussed disaggregation could have been the cause for the metal concentration increase in the solid residues as compared to the Control Mix itself. According to the concentrations found in the 168-h leachate (Fig. 2b), calcium, magnesium, and manganese leached at higher rates (~20%). Copper and mercury leached at rates of ~15% while barium, iron, lead, and zinc leached at lower rates (4–8%). Aluminum was released at a minor rate (0.29%). Arsenic, cadmium, and cobalt were reported at concentrations below the MRL in the Control Mix solids and leachate.

None of the target PAHs was detected in the leachate samples or in the solid residues of the Control Mix (data not shown). This was not surprising, since PAHs were below MRL in the Control Mix. As for the VOCs, only BTEX were measured in the leachate of the Control Mix and were all found to be below the MRL. According to the results, not a single organic regulated contaminant was found to leach from the Control Mix in noticeable concentrations.

3.3.3. Best mixtures (10% IHC Sed) leaching

The Best mixtures Constant pH leaching experiment had an average pH of 4.2 and ORP of 305 mV. Limited amounts of metals were released from each of the Best mixtures during the experiment, as reported in Table 5. Two regulated metals, barium (average 0.51 mg/L) and lead (average 0.05 mg/L), were found in the leachate. The metals leaching out of the mixtures Best 1, Best 2, and Best 3 have been included in Table 5 in order to show the materials heterogeneity, but the discussion is focused on the average leaching concentration of these three (Best Mix Average) mixtures.

In spite of having lower concentrations in the Best mixtures than in the IHC Sed, aluminum, barium, copper, and iron were found to leach at higher concentrations from the Best mixtures than from the IHC Sed. One possible explanation for this behavior is that the binding effect provided by the flocculant during the dehydration process might have been disrupted by the temperature and
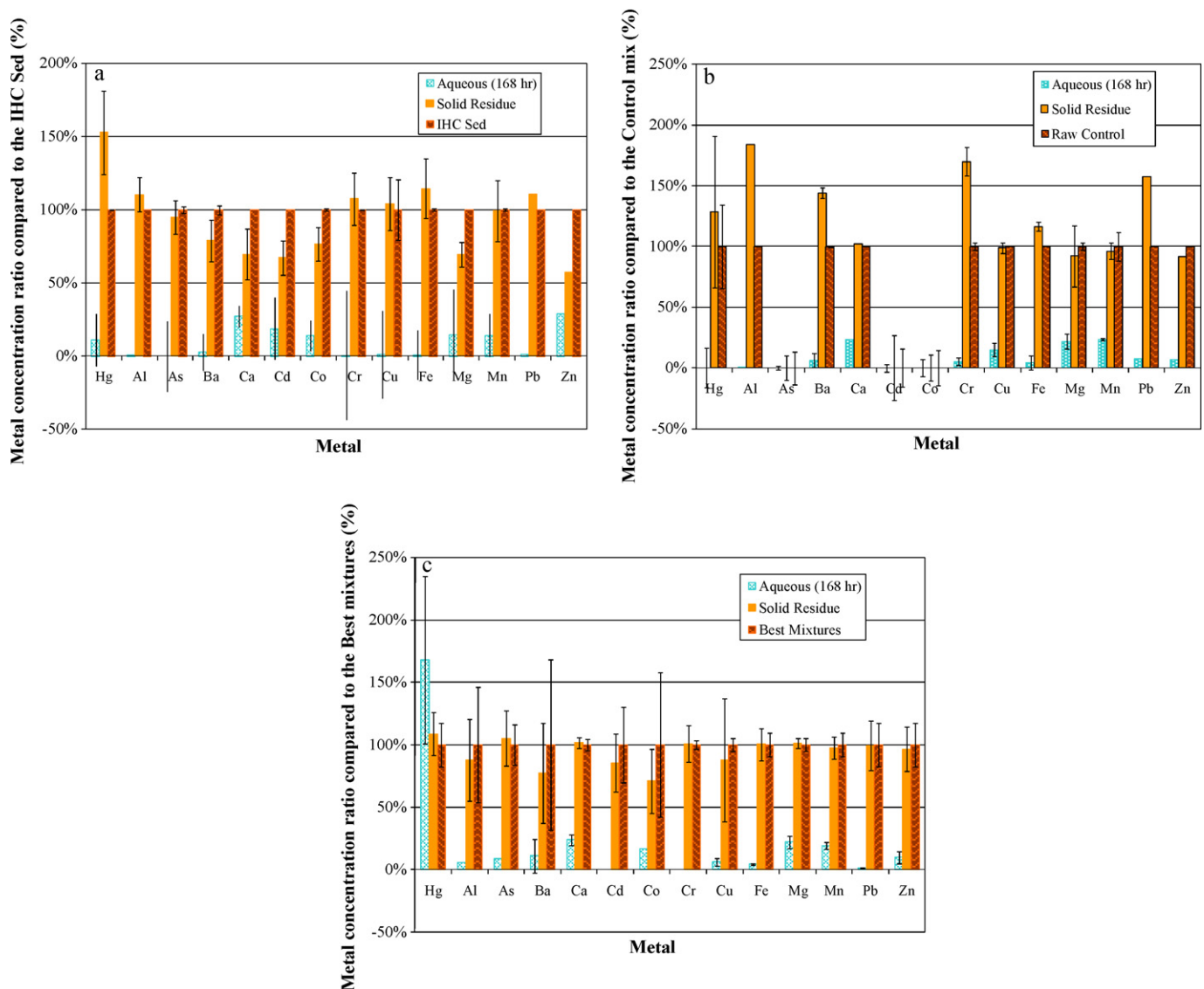
Fig. 2. Metal concentrations' ratio in the material, solid residue, and the 168-h leachate of the Constant pH experiment expressed as percentage of the concentration found in the material for IHC Sed (a), Control mixtures (b), and Best mixtures (c).

compaction applied to the specimens during the HMA preparation. Another possible explanation is the heterogeneity of the sediment, as previously mentioned. Barium leached at a level of 1.26 mg/L in the Best 1 experiment, but at a level of 0.14 mg/L in the Best 2 and Best 3 experiments, confirming the variability in the results. Nevertheless, barium leaching was found low when compared to 100 mg/L, which is the TCLP regulated level. A contrasting behavior was observed for lead, zinc, manganese, cadmium, cobalt, and chromium, that is, lower concentrations were detected in the Best mixtures leachate than in the IHC Sed leachate. Hence, these heavy metals seemed to have been successfully diluted and stabilized in these Best mixtures.

A proportion of 10% or less of the metal content of the Best mixtures was released during the experiment, except for calcium, magnesium, and manganese, which were released in percentages of ~20% (Fig. 2c). Cervinkova et al. [31] concluded that the metal stabilization using an asphalt binder was successful due to the encapsulation of the particles provided by the hydrophobic, low permeable, chemically- and biologically- (highly) stable compounds forming the asphalt. In this study, the same qualities of the asphalt seem to be reflected.

Aluminum, arsenic, barium, iron, lead, manganese, mercury, and zinc were found to leach from the Best mixtures on average at concentrations slightly greater than those reported leaching from the Control Mix.

Benzo(a)pyrene, and pyrene were detected in the Best mixtures as constituents, but none of the PAHs was found in the leachate in noticeable concentrations (data not shown). As occurred with the PAHs present in the IHC Sed, these compounds could have been released, and then volatilized, oxidized, or diluted during the experiment.

Among the studied VOCs, only acetone (42 μg/kg average) and 2-butanone (18 μg/kg average) were found in the Best mixtures. These were found also in the leachate in concentrations up to 12 μg/L for acetone, and up to 6 μg/L for 2-butanone (Fig. 3b). Finally, only acetone was found in the solid residues of the Constant pH experiment (17 μg/kg) (data not shown). Considering a VOCs mass balance, there is a portion of these compounds that could have been volatilized during the test.

When comparing the barium and lead concentrations found in the leachate of all the conducted tests, it is possible to conclude that the trend is the following: Constant pH > TCLP > SPLP (Fig. 1).
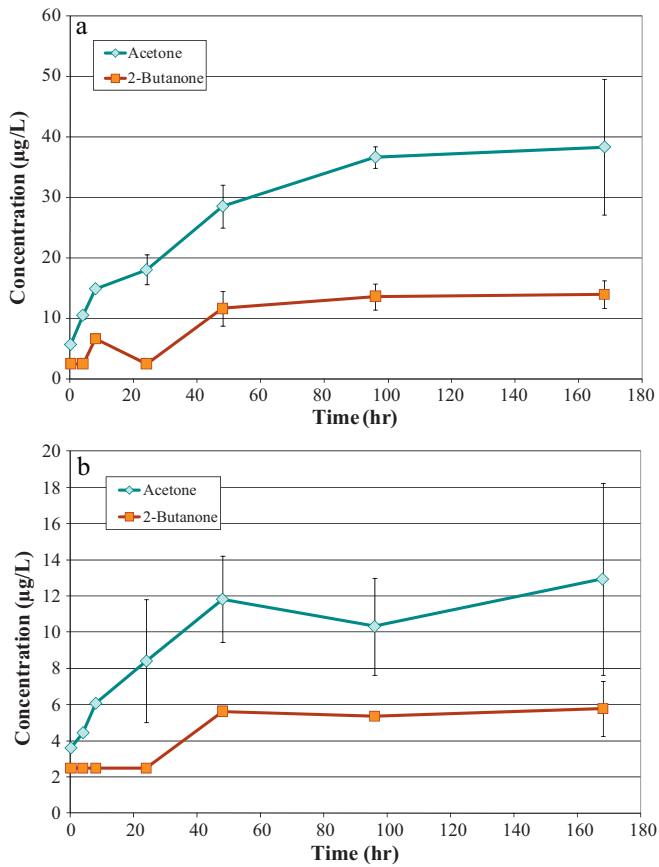
Fig. 4. Metals removed from IHC Sed by the organic extraction procedure.

Fig. 3. VOCs' concentrations leaching from the IHC Sed (a) and Best mixtures (b) during the Constant pH experiment. The concentrations found below the method reporting limit (MRL) have been reported as MRL/2 (2.5 μg/L).

Nevertheless, the Control Mix showed a different profile. Barium leached at higher concentrations from Best 1 than IHC Sed, even though the IHC Sed had a higher concentration of barium as a constituent. This could be explained by the fact that one of the mixtures, Best 1, had an unusually high rate of barium leaching: 1.26 mg/L,

compared to 0.14 mg/L, that leached from the Best 2 and Best 3 mixtures (Table 5). Best 1 had the highest concentration of barium as constituent (170 mg/kg), compared to Best 2 (53 mg/kg) and Best 3 (61 mg/kg) (Table 3), and had the greatest leaching proportion, as well. Overall, it is possible to conclude that the intended metal stabilization was successful in the asphalt mixtures.

3.4. OFE from IHC Sed

The weight loss of the IHC Sed during the procedure was ~25%, which includes the soluble fraction plus the organic fraction (TOC of the IHC Sed was measured as 13.87%). The TOC of the solid residue of the OFE was not measured, since the entire amount of residue was used for the acid digestion. The metals found in the extractant of this procedure showed a release rate of 12–25% for cadmium, chromium, and copper, which were probably associated with the organic fraction. Barium, calcium, and zinc were released at rates from 5 to 7%. Aluminum, arsenic, cobalt, iron, manganese, and lead were released at lower rates (<2%). The results were used to compare the concentration rate, as a percentage, found in the IHC Sed
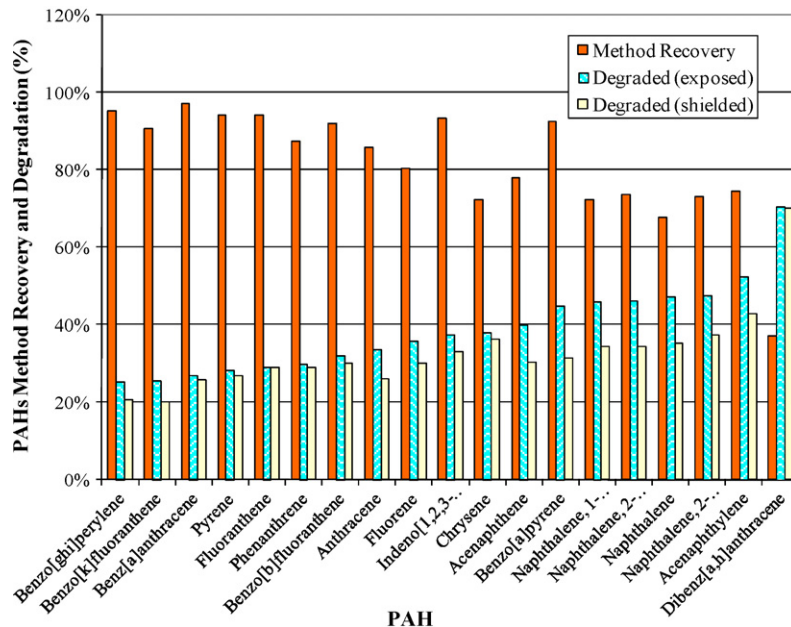

Fig. 5. PAHs degradation measured in the 168-h bench scale test with the SPLP extraction fluid.

(100%), the aqueous phase of the OFE, and the IHC Sed residues of the OFE (Fig. 4). Regarding the metal concentrations found in the solid residues of the OFE, only cadmium, chromium, and copper were extracted at significant rates (22–47%). Additionally, the low metal removal rates obtained during this extraction encourage the application of the polymer addition and the geotextile pillow as dehydration technology for the sediment, prior to the HMA preparation.

3.5. PAHs photochemical oxidation

Kochany and Maguire [9] reviewed the abiotic transformations of PAHs in aquatic environments, finding several reports on the photochemical oxidation of PAHs occurring with half-life times of hours. It was also stated that PAH photoreaction tends to be rapid in clear, well-oxygenated waters, as present in the Constant pH experiment (confirmed by the reported ORP).

The results are reported in Fig. 5. The first column represents the Method Recovery, which is the analytical recovery of the 0-h sample. These recoveries are in the range of 97.17–67.83%, except for dibenz[a,h]anthracene, which was reported as 37.17%. The probable reason for this low recovery is that dibenz[a,h]anthracene eluted with indeno[1,2,3-cd]pyrene in the analytical column. Dibenz[a,h]anthracene showed a degradation of 70.5% on the exposed vials and 70.2% in the shielded vials as being the highest reported degradations, but this could be a consequence of the observed low recovery and is not further discussed. The degradation obtained for the exposed PAHs during this experiment was in the range of 25.2–52.3%. The degradation rate for the shielded vials was reported from 20.6% to 40.2%. Therefore, as a general trend, the vials exposed to the light reported higher degradation than those shielded. These results seem to follow the trend reported by Khodadoust et al. [32], in which higher degradation rates were achieved for the PAHs with lesser ring numbers. It is interesting to note that benzo[a]pyrene, acenaphthene, acenaphthylene, 2-methyl-naphthalene, 2-chloro-naphthalene, 1-methylnaphthalene, and naphthalene were the PAHs that appeared to be more affected by the light, because these were degraded at rates >9.5% more in the exposed vials.

According to the outcome of this experiment, it appeared that oxidation was responsible for at least a portion of the PAHs loss. Nevertheless, it is not possible to state that one of the mechanisms could have prevailed, and all could have occurred simultaneously.

4. Conclusions

- The TCLP and SPLP tests of the IHC Sed showed that the dewatered sediment may be considered as non-hazardous according to current U.S. regulations, and could be eligible for beneficial use purposes with no further treatment. Additionally, the HMAs prepared using the Marshall Mix Design, with and without dewatered sediment, may also be considered as non-hazardous.
- The Constant pH experiments showed that barium and lead were the only regulated metals found in the leachate of all tested solids, always significantly below the corresponding MCL.
- The PAHs found as constituents of the IHC Sed, were found in low concentrations or below MRL in the solid residues of the Constant pH experiment, and should have been released into the extraction fluid. Nevertheless, the PAHs were not detected in the leachate, presumably due to oxidation, volatilization, and dilution occurring during the experiment.
- Only two PAHs were found as constituents of the sediment-containing HMAs in low concentrations, but were not detected in the solid residues of the Constant pH experiment, or in the leachate.

- Acetone and 2-butanone were the only VOCs found in the leachate of the sediment-containing HMA in the Constant pH experiments in concentrations below regulatory levels. Acetone and 2-butanone are common constituents of asphalt and are not considered to be of environmental concern at the detected concentrations.
- The obtained results indicate that dewatered sediment from the IHC used as a partial replacement of the aggregate in HMA for construction of pavement roads could potentially be considered environmentally safe. The optimization of the HMA composition, sediments dewatering, and manufacturing process needs to be assessed according to the available materials, road design and environmental regulations.
- Given the amount of sediment that could be dredged from the IHC, the use of the sediments as aggregate replacement for road construction may be a decisive tool in the remediation of the IHC.

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