A feasibility study on Pd/Mg application in historically contaminated sediments and PCB spiked substrates

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ABSTRACT

A vast majority of literature on bimetals deals with aqueous contaminants, very little being on organics strongly adsorbed on sediments and hence very challenging to remediate. Having previously reported materials, mechanistic and parametric aspects of PCB dechlorination with Pd/Mg bimetals, here we evaluate their ability to dechlorinate (i) PCBs spiked in clean clays and sediments and (ii) historically contaminated aged sediments (Waukegan Harbor, WHS). It was determined that while water, as a medium, dechlorinated low surface area clays it was ineffective with high surface area clays and sediments. Dechlorination was governed by desorption of PCBs, hence addition of 10–25% ethanol improved dechlorination performance. Triton X-100, a surfactant, effectively desorbed PCBs from WHS but their dechlorination was not observed. Investigating possible causes, we found that while (i) Pd/Mg completely dechlorinated multi-component commercial PCB mixtures (i.e. complex PCB distribution in WHS did not limit Pd/Mg effectiveness) and (ii) active components in extraction media did not inhibit dechlorination, sulfide in WHS was poisoning Pd, compromising its activity.

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1. Introduction

Polychlorinated biphenyls (PCBs) abound in numerous rivers, coastal waters and hazardous waste sites all over the country. Their inert and hydrophobic nature and high affinity for sediments makes them hard to treat [1,2]. PCBs partition preferentially to organic components of the environment leading to their prevalence in fine-grained, organically rich sediments. In their sorbed state, they are tightly bound to the organic fraction of the sediments but may become more available over extended time [3], posing a lingering threat of exposure. There is a dearth of technologies to effectively remediate strongly sorbed contaminants such as PCBs occurring in sediments that act as reservoirs for their long-term gradual release [4,5].

In general, treatment of sediments is problematic owing to their limited accessibility and high water content, difficulties in technology selection due to a multitude of ongoing natural and anthropogenic processes affecting contaminant fate and transport, threat of disruption of benthic ecosystems, and limited tools for evaluation of site recovery [6]. Currently for PCB contaminated sediments, dredging followed by treatment and land filling are predominantly used. However, the decontamination chain of dredging,

treatment, and disposal is expensive and often leaves behind residual contaminants in the dredged areas or taints a previously pristine region. *Ex situ* solvent extraction or chemical treatment processes are too expensive and often only marginally beneficial to justify use. On the other hand, *in situ* reclamation technologies including capping, bioremediation and monitored natural recovery are very promising for PCB contaminated sediment sites owing to their sustainable and largely non-disruptive nature. Capping is an attractive alternative due to its relatively inexpensive, easy and less invasive nature [7]. It is especially suitable for sites with low to moderate natural hydrodynamics and navigational traffic, and fine-grained cohesive sediments with net deposition [8].

Among the technologies proposed for PCB remediation, palladium/iron (Pd/Fe) bimetallic systems have been widely researched for more than a decade. However, most of the research has been in aqueous systems with very little work done on PCBs that are strongly adsorbed on sediments. We could find only one study in the literature by He et al. that describes the application of Pd/Fe particles to dechlorinated pentachlorobiphenyl spiked surface soil [9]. No literature was found on bimetallic treatment of 'aged' sediments contaminated with a complex mixture of PCBs which can be very hard to treat.

In our research, we have developed palladium/magnesium (Pd/Mg) bimetallic systems for dechlorination of PCBs [10], reported the preferential site of attack and ensuing dechlorination pathways of PCBs with Pd/Mg [11] and studied Pd/Mg performance in the presence of, among others, common anions and organic

solvents – parameters relevant in natural systems [12]. Having thus explored the materials, mechanistic and parametric aspects of Pd/Mg, in this study we investigate the feasibility of applying these systems for dechlorination of (i) PCBs spiked in clean clays and sediments and (ii) naturally contaminated and aged sediments. During the course of this study, we also explored dechlorination in sediment extracts and Aroclor spiked liquid matrices to determine factors that slow down or inhibit remediation of PCBs in sediments.

2. Experimental

2.1. Synthesis of Pd/Mg

A simple wet-chemistry route was used to reductively deposit Pd^0 onto Mg by intimately mixing it with palladium acetate, a palladium nano-particle precursor in ethanol. Addition of polyvinylpyrrolidone (PVP), a capping agent enabled formation of nano-scaled Pd islands on Mg thereby providing enhanced catalytic activity at drastically reduced catalyst requirements. The procedure is described in detail elsewhere [11]. The Pd content of the particles was 0.02% (w/w, Pd/Mg) as determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The surface morphology of Mg particles (44 μm or smaller) as captured by transmission electron micrographs (TEM) showed the deposition of numerous Pd islands in the nano- and sub-micron range on the Mg surface. Detailed characterization is discussed elsewhere [11].

2.2. Characterization of substrates

Two clays, Kaolin and Montmorillonite K10 (referred to as K10) were procured commercially (Sigma). Wet sediments obtained from Ceaser creek in Ohio and Waukegan Harbor in Illinois were dried and sieved (mesh #20 or <850 μm) and designated Caesar creek sediments (CCS) and Waukegan harbor sediments (WHS), respectively. The clays and sediments were characterized for surface area, total organic carbon and PCB content. The substrate pH was determined by taking measurements in a 10% slurry made by mixing 2 g of substrate with 20 mL of water for 1 day. A Tristar 3000 (Micromeritics) porosimetry analyzer was used to determine their Brunauer, Emmett, and Teller (BET) surface area. Organic carbon content was measured using a total organic carbon analyzer (TOC VCS, Shimadzu) with solid module (SSM-5000A).
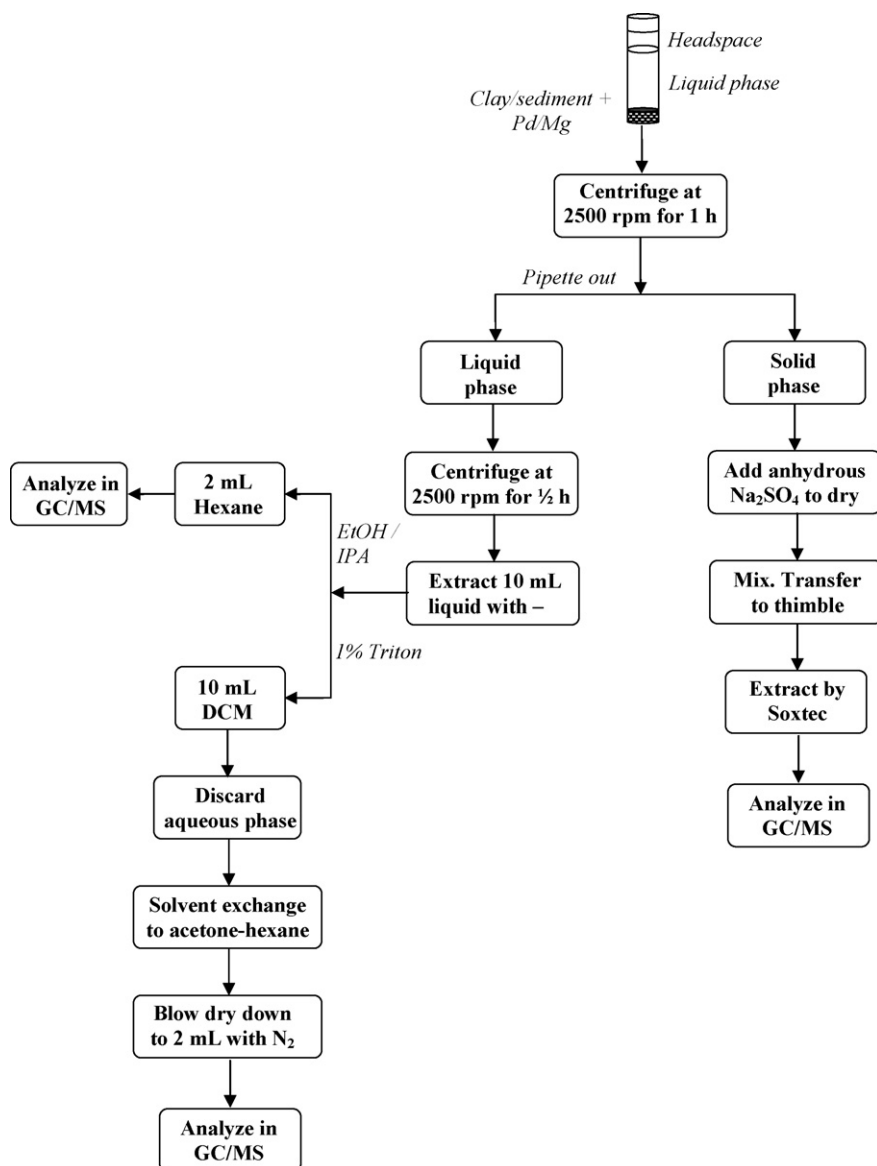

Fig. 1. Flow chart of the procedure followed to separate phases in sediment samples, extract PCBs from the solid and liquid phases, sample preparation and analyses.

Table 1
Characterization of clays and sediments.

Substrate	pH[a]	BET surface area (m^2/g)	Organic carbon (%)	Total PCB (mg/kg)
Kaolin	3.70	18.43	0	0
Montmorillonite K10	3.11	218.12	0.13	0
Caesar Creek Sediment	7.94	2.63	0.99	0
Waukegan Harbor Sediment	7.89	4.68	3.19	45

[a] Measured in liquid portion after shaking 2 g sediment in 20 mL water for 1 day.

2.3. PCB dechlorination with Pd/Mg

In a typical experiment, the contaminated substrate was mixed with the liquid phase and Pd/Mg particles in glass vials with septa caps and contacted intimately by tumbling at 20 rpm. Identical units but without Pd/Mg were used as controls. Details unique to each set have been provided along with the discussion of results. At each sampling event, phase separation, extraction, sample preparation and analyses were done as depicted in Fig. 1. Briefly, phase separation was achieved by centrifuging (Damon/IEC HN-SII centrifuge) reactor vials at 2500 rpm for 1 h. PCBs from the solid phase were extracted into 1:1 acetone:hexane co-solvent using automated Soxhlet (EPA method 3541). Aqueous and ethanol–water liquid phases were extracted with hexane. In case of surfactant solution, the liquid phase was extracted with dichloromethane (DCM) followed by solvent exchange to 1:1 acetone: hexane. The PCB extracts (0.5 mL) were spiked with 10 µL of the internal standard (200 ppm D-8 naphthalene in DCM, Accustandard) and analyzed in a GC/MS. The GC/MS was equipped with a Supelco SPB-5 30 m × 0.32 µm × 0.25 µm column; the calibration curves had R^2 of greater than 0.999 based on eight-point data; the method detection limit was 50 µg/L. All dechlorination experiments were conducted in ambient conditions without any precautions to exclude oxygen.

2.4. Colorimetric method for sulfide

Sulfide analysis was conducted using a portable colorimeter (Model No.: DR/890, HACH® Co.). The Methylene Blue method, for 0–0.70 mg/L S^{2-} (Method 8131) as described in the HACH® manual was followed. The main reactions were: Hydrogen sulfide and acid-soluble metal sulfides react with N, N-dimethyl-p-phenylenediamine oxalate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration.

3. Results and discussion

3.1. Characterization of substrates

Results from characterization of the substrate are shown in Table 1. It can be seen that K10 has a very high surface area, more than an order of magnitude higher than Kaolin, the other clay used here and around 40–80 times higher than the two natural sediments in the study. K10 also showed some organic carbon (OC) content (~0.13%) indicating that it may have a high affinity to PCBs – both due to its high surface area and organic content [2]. The pHs of the two clays were in the acidic range, far removed from the near neutral pHs of the sediments. While the two sediments have comparable surface areas, WHS had an OC of 3.19%, significantly higher than 0.99% of CCS. WHS was the only substrate naturally contaminated with PCBs and showed a PCB content of around 45 mg/kg of sediments. Fig. 2 shows the distribution of PCB congeners in the WHS as extracted by the automated Soxhlet method. Tri- and tetra-congeners constituted the majority of the PCB distribution, the average number of Cls per PCB being 3.31. Overall the PCB mixture in the WHS was 43.8% in total chlorine content.

3.2. Treatment of 2-CB spiked substrates

As a first step in the evaluation of feasibility of using Pd/Mg to treat naturally contaminated and aged sediments such as WHS, clean CCS and clays artificially spiked with 2-chlorobiphenyl (2-CB) were used as target matrices. For this, 1 g each of K10, Kaolin and CCS spiked with 2-CB (~100 mg 2-CB/kg sediment) were mixed with 20 mL of the liquid phase and 0.25 g Pd/Mg in 40 mL glass vials with septa caps and contacted intimately by tumbling at 20 rpm for 14 h. The experiments were run for 14 h as in this range of 2-CB concentrations and Pd/Mg loadings in aqueous systems, complete dechlorination takes place within 4–6 h. Identical units but without Pd/Mg were used as controls. Phase separation, extraction, sample preparation and analyses were done as depicted in Fig. 1. The following three subsections discuss the result of dechlorination studies run by varying the liquid phase composition.

3.2.1. Water as liquid phase

From the summary of results in Table 2, CCS shows 14% partitioning of PCBs into the liquid phase most likely due to its OC component which binds the 2-CB. For K10, desorption into the liquid phase was higher at 31% but still significantly lower than that from Kaolin which showed 83% liquid partitioning of 2-CB. This difference can be attributed to the high surface area of K10 as compared to Kaolin (218 m^2/g vs.18 m^2/g) which leads to the increased PCB partitioning on the clay in case of K10. Dechlorination for Kaolin was quite high at 90% whereas for CCS, it was only 7%. The results indicate that while pure water was able to desorb 2-CB from a low surface area clay (Kaolin) and bring about its near complete dechlorination, it failed to do so with high surface area clays or for sediments with organic matter. Since dechlorination with Pd/Mg takes place on Pd surface [13], extracting 2-CB into the liquid phase may be the limiting factor in the reaction. To address this aspect, ethanol was added to the liquid phase to make a 10% ethanol–water co-solvent for enhancing desorption [14].
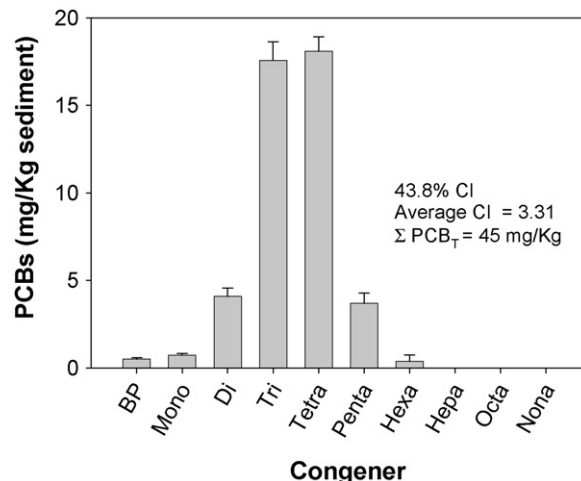

Fig. 2. Distribution of PCB congeners in Waukegan Harbor sediments.

Table 2
Treatment of 2-CB spiked clays and Caesar Creek sediment with water as a medium.

Experimental units	PCB in liquid (ppb)		PCB in solid (ppb)		Total nano-moles	% partitioning		% dechlorination		
	BP	2-CB	BP	2-CB		Liquid	Solid	Liquid	Solid	Total
K10	–[a]	–	–	–	–	–	–	–	–	–
Kaolin	1905	234	749	116	382	71	29	91	89	90
CCS	131	978	273	5224	712	17	83	14	6	7
Controls										
K10	34	2683	37	5935	926	31	69	2	1	1
Kaolin	34	2925	31	586	382	83	17	1	6	2
CCS	32	913	36	5754	718	14	86	4	1	1

Each unit consisted of 1 g of the substrate, 20 mL water and 0.25 g Pd/Mg (controls were without bimetals). All units were tumbled at 20 ± 2 rpm for 14 h.
[a] Lost sample while centrifuging.

Table 3
Treatment of 2-CB spiked clays and Caesar Creek sediment with 10% ethanol-water as a medium.

Experimental units	PCB in liquid (ppb)		PCB in solid (ppb)		Total nano-moles	% partitioning		% dechlorination		
	BP	2-CB	BP	2-CB		Liquid	Solid	Liquid	Solid	Total
K10	440	4074	247	1826	717	68	32	12	14	12
Kaolin	2103	264	756	220	423	71	29	91	81	88
CCS	125	1180	148	4146	602	24	76	11	4	6
Controls										
K10	34	2364	34	3943	680	38	62	2	1	1
Kaolin	34	3032	31	392	373	88	12	1	9	2
CCS	32	1161	35	5158	681	19	81	3	1	1

Each unit consisted of 1 g of the substrate, 20 mL 10% ethanol–water co-solvent and 0.25 g Pd/Mg (controls were without bimetals). All units were tumbled at 20 ± 2 rpm for 14 h.

3.2.2. 10% ethanol–water as liquid phase

Comparing the results of this study as summarized in Table 3 with that in Table 2, it was noted that while addition of ethanol did enhance 2-CB partitioning into the liquid phase (38% vs. 31% for K10; 88% vs. 83% for Kaolin; and 19% vs. 14% for CCS), the increase in desorption was not significant. The extent of dechlorination remained comparable to that seen in water only units suggesting a correlation between the solvent content and degree of dechlorination achievable.

3.2.3. 25% ethanol–water as liquid phase

In an attempt to further improve dechlorination, two measures were adopted: (i) ethanol content was increased to 25% and (ii) 50 mL of the liquid phase was used, up from 20 mL used in the studies so far. These efforts led to significantly enhanced desorption into the liquid phase compared to 10% ethanol units (89% vs. 38% for K10; 97% vs. 88% for Kaolin; and 78% vs. 19% for CCS). This clearly indicates that the nature of the liquid phase, as well as the ratio of the liquid: sediment can be optimized to aid desorption of 2-CB from the sediment. Further, the extent of dechlorination also increased substantially from 12% to 36% in K10 and from 6% to 45% in CCS. Increased dechlorination is the direct result of enhanced

desorption of the PCB into the liquid phase. An interesting observation made from Table 4 was that in case of K10 and CCS, 35% and 49%, respectively, of the 2-CB in the liquid phase was dechlorinated. This goes against the hypothesis that dechlorination is governed by the extent of desorption and suggests that (a) interferences from constituents extracted from the substrates (other than PCBs) may inhibit dechlorination or (b) Pd/Mg loses reactivity before 2-CB is desorbed.

To test above possibilities, we extracted the 2-CB spiked substrates with 25% ethanol–water co-solvent and treated the extracts with Pd/Mg to check for interferences from sediment components. From Table 5 which summarizes the result of this study, it can be seen that extracts from all three substrates produced near complete dechlorination within 14 h. This indicates possible erosion of reactivity of Pd/Mg in presence of highly buffered clays and sediments which may act as a source of protons. This is in agreement with other reports that at low pH intensive corrosion resulted in possible loss of Pd, and inhibition of the reaction as the surface became covered by H_2 leading to lower dechlorination efficiency [9]. Hence, in our study we saw higher levels of dechlorination in CCS (49%) which had an intital pH of 7.94 than in K10 (35%) where pH was highly acidic at pH_o 3.11. Further, by adjusting pH of substrate slurries we

Table 4
Treatment of 2-CB spiked clays and Caesar Creek sediment with 25% ethanol-water as a medium.

| Experimental units	PCB in liquid (ppb)		PCB in solid (ppb)		Total nano-moles	% partitioning		% dechlorination		
	BP	2-CB	BP	2-CB		Liquid	Solid	Liquid	Solid	Total
K10	623	1387	222	445	647	88	12	35	38	36
Kaolin	1173	104	201	46	440	93	7	93	84	93
CCS	585	742	201	595	477	81	19	49	29	45
Controls										
K10	33	2163	30	678	662	89	11	2	5	1
Kaolin	32	1762	30	97	493	97	3	2	27	2
CCS	32	1619	30	1150	567	78	22	2	3	1

Each unit consisted of 1 g of the substrate, 50 mL 25% ethanol–water co-solvent and 0.25 g Pd/Mg (controls were without bimetals). All units were tumbled at 20 ± 2 rpm for 14 h.

Table 5
Clays and Caesar Creek sediment spiked with 2-CB was extracted with 25% ethanol–water co-solvent and treated with Pd/Mg.

Experimental units	Stock (ppb)		After 18 h (ppb)		Dechlorination (%)	Mass balance (%)
	BP	2-CB	BP	2-CB		
K10	33	2326	1319	152	91	74
Kaolin	32	1700	1339	35	98	96
CCS	32	1772	1171	35	98	81

Each unit consisted of 15 mL of the substrate in 20 mL septa capped vials and 0.25 g Pd/Mg. All units were tumbled at 20 ± 2 rpm for 14 h.
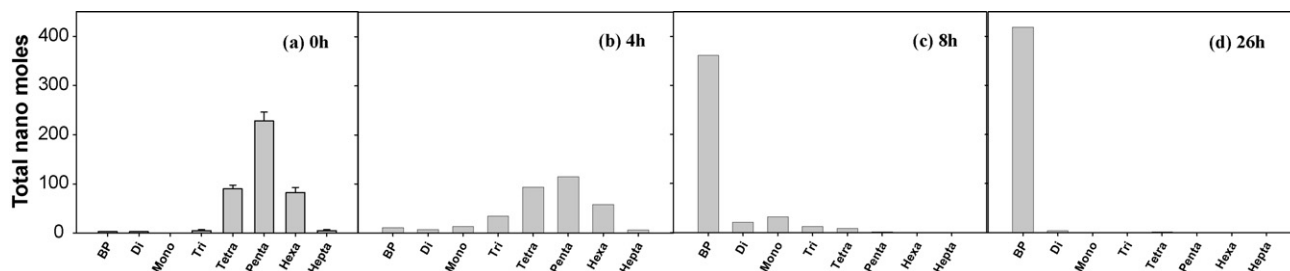
Fig. 3. Dechlorination of 3 ppm solution of Aroclor 1254 at a Pd/Mg loading of 6 g bimetals/l PCB solution in a 40% ethanol–water matrix. A distinct shift in the chlorination pattern can be seen going from 0 through 4, 8, and 26 h as the PCBs changed from a mostly higher chlorinated mixture to lower congeners, before getting completely dechlorinated to biphenyl at the end of 26 h.
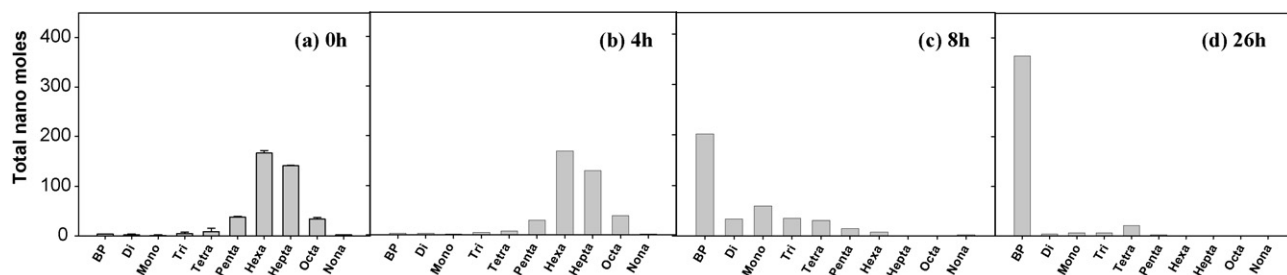
Fig. 4. Dechlorination of 3 ppm solution of Aroclor 1260 at a Pd/Mg loading of 6 g bimetals/l PCB solution in a 40% ethanol–water matrix. A distinct shift in the chlorination pattern can be seen going from 0 through 4, 8, and 26 h as the PCBs changed from a mostly higher chlorinated mixture to lower congeners, before getting completely dechlorinated to biphenyl at the end of 26 h.

found that K10 was highly buffered, needing a lot of 1N NaOH to take it to near neutral pH while CCS was poorly buffered becoming highly basic on addition of a few drops of NaOH. Hence, the difference in dechlorination performance in the two substrates can be attributed to difference in their initial pHs and their buffering capacities which strongly influence the corrosion of Mg.

3.3. Treatment of WHS

Based on somewhat encouraging results from our study on clays and CCS spiked with 2-CB, WHS naturally contaminated at around 45 mg PCB/kg sediment were treated with Pd/Mg. Details on the distribution of congeners, average degree of chlorination and % Cl have been provided in Fig. 2 and Section 3.1. Using 1% Triton X-100 (a surfactant, called Triton from here on), 10% ethanol and water as the liquid media, these dechlorination studies were run in batches with sacrificial sampling on 1, 3, 12 and 30 days. Controls run without Pd/Mg showed as much as 50% partitioning in the liquid phase in case of 1% Triton in the 1 and 3d sampling events. The water and 10% ethanol units showed less than 2% desorption to the liquid phase indicating that the surfactant is a much superior additive for enhancing PCB desorption from aged sediments. However, no reduction in the level of chlorination, shift in congener distribution towards lower congeners or biphenyl production in any of the matrices was observed (results not shown). Complete lack of dechlorination could be desorption limited especially for highly aged sediments with a high degree of chlorination. How-

ever, we saw substantial PCBs in the liquid phase in case of 1% Triton units without any signs of dechlorination diminishing that possibility. Other potential reasons could be: (i) Pd/Mg may be unable to dechlorinate a complex mixture of PCB congeners, (ii) interferences from active components of the co-solvent, or (iii) Pd poisoning by species leaching into the liquid phase from WHS. These possibilities are discussed in the following subsections.

#### 3.3.1. Treatment of multi-component PCB mixtures

This study was performed to evaluate the potential of Pd/Mg to dechlorinated complex PCB mixtures such as Aroclors 1254 and 1260. Dechlorination of 3 mg/L solution of Aroclor 1254 at a Pd/Mg loading of 6 g bimetals/l PCB solution in a 40% ethanol–water matrix was conducted. A distinct shift in the chlorination pattern can be seen in Fig. 3 going from 0 through 4, 8, and 26 h as the PCBs changed from a mostly higher chlorinated mixture to lower congeners, before getting completely dechlorinated to

Table 6
Characterization of Waukegan Sediment extracts with three different extraction media.

Extraction medium	% Cl	Average Cl per PCB	Extraction η (%)
2-Propanol	47.1	3.77	27.0
Ethanol	46.4	3.69	22.1
1% Triton	46.7	3.71	20.2
WHS	43.8	3.31	–
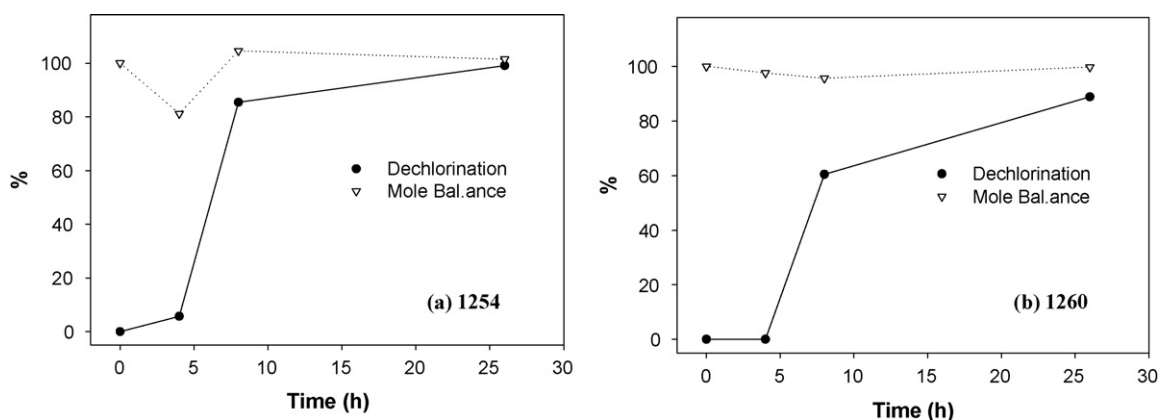
Fig. 5. Dechlorination and mass balance profiles for (a) Aroclor 1254 and (b) Aroclor 1260. Experiments were conducted with 3 ppm Aroclors using 6 g Pd/Mg per liter of PCB solution in 60 mL EPA vials tumbling at 40 rpm. Near complete conversion of the Aroclors to biphenyl was observed at the end of 26 h.

Table 7
Evaluating interference from active component of the liquid media used for extraction of PCBs from Waukegan Harbor sediments.

Active component	Stock (ppb)		After 24 h (ppb)		Dechlorination (%)	Mass balance (%)
	BP	2-CB	BP	2-CB		
40% 2-propanol	33	4009	756	2829	25	93
40% Ethanol	33	4009	2468	33	99	75
1% Triton	33	4009	2456	137	96	77
Water	33	4009	2576	36	99	79

biphenyl at the end of 26 h. Similar results were observed for Aroclor 1260 (Fig. 4), except in this case dechlorination was not complete (∼90%) with some higher congeners still left after 26 h of treatment, especially tetrachlorinated PCBs. Another important observation is that the dechlorination in both Aroclors continues after 8 h and at least until 26 h as the distribution of PCB congeners shifts towards lower chlorinated PCBs from 8 to 26 h. This has been depicted concisely in Fig. 5 where the dechlorination profiles of Aroclors 1254 and 1260 have been plotted along with the mass balance achieved (80–100% in all cases). Aroclor 1260 shows a slower dechlorination rate as compared to Aroclor 1254 owing to its higher chlorine content (60% vs. 54%, respectively). These results clearly show that Pd/Mg is capable of completely dechlorinating multi-component PCB mixtures and the complexity of distribution of PCB congeners in WHS does not limit their dechlorination by Pd/Mg.

3.3.2. Treatment of WHS extracts

PCBs were extracted using (i) *iso*-propanol (IPA), (ii) ethanol and (iii) 1% Triton. Table 6 shows the extraction efficiencies ranging from 20% for Triton to 27% for IPA, with the extracts in general showing a higher level of chlorination than WHS (3.7 vs. 3.3 Cl/PCB) indicating a slight preference for desorption of higher chlorinated congeners into the organic phase. 10 mL of the extracts in 40% IPA, 40% ethanol and 1% Triton treated with 0.25 g Pd/Mg in 20 mL glass vials showed no reduction in the level of chlorination, shift in congener distribution towards lower congeners or biphenyl production (results not shown). This indicates possible interference from either the active component of co-solvent (such as IPA or Triton) or by species leaching into the liquid phase from WHS (such as sulfide). These possibilities are discussed below.

3.3.3. Possible interference from active components of co-solvent

2-CB spiked in 40% IPA, 40% ethanol, 1% Triton and water matrices was treated with Pd/Mg. For each unit, 25 mL of a 4 mg/L solution of 2-CB was taken in a 40 mL vial with septa cap and treated with 0.25 g of Pd/Mg by tumbling the units at 40 rpm for

24 h. The results summarized in Table 7 show that ethanol and Triton do not affect dechlorination performance of Pd/Mg with respect to the control unit without any additives. IPA showed significant reduction in dechlorination performance but still led to 25% dechlorination. This indicates that while active components in the extraction media may compromise the dechlorination efficiency of Pd/Mg, they do not completely inhibit dechlorination [11]. This leaves the last possibility that has been considered – Pd poisoning by one or more species from WHS extracts.

3.3.4. Pd poisoning by species in WHS extract

Sulfide analysis was conducted using a HACH® portable colorimeter following the Methylene Blue method for S^{2-} (Method 8131). WHS extracts in ethanol tested positive for sulfide and were found to be about 20 mg/L in sulfide concentration. Sulfide is a long established catalyst poison, especially that for Pd, known to inhibit the hydrogenation properties of Pd very rapidly [15–17]. This explains the inability of Pd/Mg to dechlorinated WHS extracts. CCS on the other hand showed no traces of sulfide and hence Pd/Mg was seen to dechlorinated 2-CB in CCS extracts without any problem. To address this issue, sulfate can be removed using an ion exchange resin or in the event of Pd poisoning, it can be regenerated using hydrochloric acid. These solutions, while suitable at the bench scale, have obvious practical limitations.

4. Conclusions

In sediment matrices, after He et al. [9], this is only the second feasibility evaluation of applying bimetallic particles in sediments. Having previously reported materials, mechanistic and parametric aspects of PCB dechlorination with Pd/Mg bimetals, we evaluated their ability to dechlorinate (i) PCBs spiked in clean clays and sediments and (ii) historically contaminated aged sediments (Waukegan Harbor, WHS). It was determined that while water, as a medium, dechlorinated low surface area clays it was ineffective with high surface area clays and sediments. Dechlorination was governed by desorption of PCBs, hence addition of 10–25% ethanol

improved dechlorination performance. Triton X-100, a surfactant, effectively desorbed PCBs from WHS but their dechlorination was not observed. Investigating possible causes, we found that while (i) Pd/Mg completely dechlorinated multi-component commercial PCB mixtures, complex PCB distribution in WHS not limiting Pd/Mg effectiveness and (ii) active components in extraction media did not inhibit dechlorination, sulfide (20 mg/L) in WHS was poisoning Pd, compromising Pd/Mg reactivity.

Acknowledgements

References

[1] F. Kasštaĭnek, P. Kasštaĭnek, Combined decontamination processes for wastes containing PCBs, J. Hazard. Mater. 117 (2005) 185–205.

[2] H. Choi, S.R. Al-Abed, PCB congener sorption to carbonaceous sediment components: macroscopic comparison and characterization of sorption kinetics and mechanism, J. Hazard. Mater. (2008) doi:10.1016/j.jhazmat.2008.10.100.

[3] M.R. Harkness, J.B. McDermott, D.A. Abramowicz, J.J. Salvo, W.P. Flanagan, M.L. Stephens, F.J. Mondello, R.J. May, J.H. Lobos, K.M. Carroll, M.J. Brennan, A.A. Bracco, K.M. Fish, G.L. Warner, P.R. Wilson, D.K. Dietrich, D.T. Lin, C.B. Morgan, W.L. Gately, In situ stimulation of aerobic PCB biodegradation in Hudson River sediments, Science 259 (1993) 503–507.

[4] K.N. Dimou, T.L. Su, R.I. Hires, R. Miskewitz, Distribution of polychlorinated biphenyls in the Newark Bay Estuary, J. Hazard. Mater. 136 (2006) 103–110.

[5] Y.S. Kim, H. Eun, H.S. Cho, K.S. Kim, E. Watanabe, K. Baba, T. Katase, The characterization of PCDDs, PCDFs and coplanar PCBs during the past 50 years in Gwangyang Bay, South Korea, J. Hazard. Mater. 154 (2008) 756–765.

[6] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, In situ technologies for reclamation of PCB-contaminated sediments: current challenges and research thrust areas, J. Environ. Sci. Eng. 133 (2007) 1075–1078.

[7] J.R. Zimmerman, U. Ghosh, R. Millward, T.S. Bridges, R.G. Luthy, Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: Physicochemical tests, Environ. Sci. Technol. 38 (2004) 5458–5464.

[8] SERDP Research and Development Needs for the In Situ Management of Contaminated Sediments, 2004.

[9] N. He, P. Li, Y. Zhou, W. Ren, S. Fan, V.A. Verkhozina, Catalytic dechlorination of polychlorinated biphenyls in soil by palladium–iron bimetallic catalyst, J. Hazard. Mater. (2008), doi:10.1016/j.jhazmat.2008.07.149.

[10] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, Enhanced corrosion-based Pd/Mg bimetallic systems for dechlorination of PCBs, Environ. Sci. Technol. 41 (2007) 3722–3727.

[11] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, E. Graybill, Reactivity of substituted chlorines and ensuing dechlorination pathways of select PCB congeners with Pd/Mg bimetallics, Environ. Sci. Technol. 43 (2009) 915–921.

[12] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, Impact of organic solvents and common anions on 2-chlorobiphenyl dechlorination kinetics with Pd/Mg, Appl. Catal. B: Environ. (2009), doi:10.1016/j.apcattb.2009.07.029.

[13] I.F. Cheng, Q. Fernando, N. Korte, Electrochemical dechlorination of 4-chlorophenol to phenol, Environ. Sci. Technol. 31 (1997) 1074–1078.

[14] N.E. Korte, O.R. West, L. Liang, B. Gu, J.L. Zutman, Q. Fernando, The effect of solvent concentration on the use of palladized-iron for the step-wise dechlorination of polychlorinated biphenyls in soil extracts, Waste Manage. 22 (2002) 343–349.

[15] M.G. Davie, H. Cheng, G.D. Hopkins, C.A. Lebron, M. Reinhard, Implementing heterogeneous catalytic dechlorination technology for remediating TCE-contaminated groundwater, Environ. Sci. Technol. 42 (2008) 8908–8915.

[16] L.J. Hoyos, M. Primet, H. Praliaud, Sulfur poisoning and regeneration of palladium-based catalysts. Part 2. Influence of adsorbed sulfur on deactivation of carbonaceous deposits, J. Chem. Soc. Chem. 88 (1992) 3367–3373.

[17] A.M. Pridmore, P. Silley, An evaluation of potential hydrogen sulfide adsorbents for the protection of palladium catalyst in anaerobic culture systems, FEMS Microbiol. Lett. 161 (1998) 225–229.