



Dechlorination of PCBs, CAHs, herbicides and pesticides neat and in soils at 25 °C using Na/NH₃

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Abstract

Na/NH₃ reductions have been used to dehalogenate polychlorinated biphenyls (PCBs), chlorinated aliphatic hydrocarbons (CAHs) and pesticides at diffusion controlled rates at room temperature in model compound studies in both dry NH₃ and when water was added. The rate ratio of dechlorination (aliphatic and aromatic compounds) versus reaction of the solvated electron with water is very large, allowing wet soils or sludges to be remediated without an unreasonable consumption of sodium. Several soils, purposely contaminated with 1,1,1-trichloroethane, 1-chlorooctane and tetrachloroethylene, were remediated by slurrying the soils in NH₃ followed by addition of sodium. The consumption of sodium per mole of chlorine removed was examined as a function of both the hazardous substrate's concentration in the soil and the amount of water present. The Na consumption per Cl removed increases as the amount of water increases and as the substrate concentration in soil decreases. However, remediation was still readily accomplished from 5000 to 3000 ppm to sub ppm levels of RCl in the presence of substantial amounts of water. PCB- and dioxin-contaminated oils were remediated with Na/NH₃ as were PCB-contaminated soils and sludges from contaminated sites. Ca/NH₃ treatments also successfully remediated PCB-contaminated clay, sandy and organic soils but laboratory studies demonstrated that Ca was less efficient than Na when substantial amounts of water were present. The advantages of solvated electron reductions using Na/NH₃ include: (1) very rapid dehalogenation rates at ambient temperature, (2) soils (even clay soils) break down into particles and slurry nicely in NH₃, (3) liquid ammonia handling technology is well known and (4) removal from soils, recovery and recycle of ammonia is easy due to its low boiling point. Finally, dechlorination is extremely fast even for the 'corner' chlorines in the substrate MirexTM (structure in Eq. (5)). © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polychlorinated biphenyls (PCBs) and other chlorinated aromatic compounds are distributed in soils and sludges at over 400 sites in the USA. Chlorinated aliphatic hydrocarbons (CAHs) occur as serious contaminants at 358 major hazardous waste sites in the USA and they migrate vertically through soils to form DNAPLs on aquifer bottoms. To give just one example, DOE's Hanford site has massive soil and groundwater contamination with carbon tetrachloride. A subsurface plume extends for over 70 sq. miles. A national need exists for both ex and in situ methods to destroy these pollutants in soils and sludges rapidly at ambient temperature. Successful methods to remediate contaminated materials, parts and bulk stored samples are also required.

Alkali metal-based reductive dehalogenation is well known. Knorre et al. [1] studied the addition of sodium to halogenated organic compounds without solvent but this heterogeneous surface reaction is slow and moisture sensitive. Li, Na, K or Ca in liquid NH_3 generates solvated electrons which dehalogenate dissolved organic compounds at exceptionally fast rates [2,3]. Weinberg and Abel [4,5] and Pittman and Tabaei [6] first showed that PCB-contaminated wet soils can be rapidly remediated with Na/NH_3 or Ca/NH_3 . This discovery eliminated the major problem of the slow rates observed by Knorre et al. [1]. Furthermore, the successful use of Na/NH_3 demonstrated that these dechlorinations occur far faster than the loss of sodium stoichiometry to water. The half-life ($t_{1/2}$) of solvated electrons in purified NH_3 is ca. 300 h but in pure water the solvated electron has a $t_{1/2}$ of only ca. 100 μs [8]. Dechlorination of PCB-contaminated wet soils becomes possible due to the relatively long solvated electron lifetime in 20% $\text{H}_2\text{O}/80\% \text{NH}_3$ ($t_{1/2}$ ca. 100 s.) discovered by Crooks and Bard [7] and Schindewolf [9], coupled with the very fast rate of dechlorination by Na/NH_3 .

The rate of dechlorination must be exceptionally fast in order for solvated electron reductions to be useful for the remediation of PCB- or CAH-contaminated soils or sludges. Consider a soil, containing 20 wt.% water, that is contaminated by 10 ppm of a PCB. The mole ratio of $\text{H}_2\text{O}/\text{PCB}$ present is $\sim 2.5 \times 10^5$. Thus, the reaction rate of the solvated electron with the PCB needs to be on the order of 2.5×10^5 greater than that with water for dechlorination to compete successfully. At 0.5 ppm of PCB, the $\text{H}_2\text{O}/\text{PCB}$ ratio is about 5×10^6 ! Furthermore, while the half life of a solvated electron in 80% $\text{NH}_3/20\% \text{H}_2\text{O}$ is ca. 100 s [7,9], this is true only when these solvents are highly purified. It is well known that solvated electrons are consumed more rapidly in liquid ammonia in the presence of transition metal ions and dissolved oxygen [10,11]. Both Fe^{3+} and O_2 catalyze the reaction of solvated electrons with NH_3 to generate amide ion and hydrogen (Eq. (1)). Therefore, the solvated electron must react extremely fast with chlorinated pollutants for removal of such pollutants from wet soils and sludges. Holm [12] demonstrated that the half life of methyl iodide reduction in Na/NH_3 is less than 200 μs using secondary isotope effects. This reaction is complete in the mixing period of $\sim 10^{-3}$ s. Therefore, generation of solvated electrons by dissolving Na in soil—liquid NH_3 slurries can still result in efficient dechlorination in the presence of dissolved metal ions and oxygen.



The patents of Commodor Solution Technologies (formerly Sandpiper Corp.) [4,5,13,14] and publications of Pittman and co-workers [6,15–17] demonstrate that both PCB-, CAH- and metal-contaminated soils (as received clay, loam and sandy type soils), containing up to 25% water were successfully decontaminated within 30 s at 25 °C. PCB and CAH destruction efficiencies >99.9% were achieved. A major goal now of our work is to develop solvated electron chemistry (e.g. Na/NH₃) as a single, portable technology that is applicable to both on-site ex situ and on-site in situ destruction of PCBs, CAHs, pesticides, herbicides, chemical warfare agents, polynuclear aromatic hydrocarbons (PAHs) and ammunition/explosive residues. Thus, this single technology could have broad application. To achieve this goal, the breadth of solvated electron dehalogenations, aromatic reductions and both nitro and nitrate group reductions must be established. In this manuscript, the efficiency of Na utilization per chlorine removed has been established for some model compounds, both neat and as soil contaminants. Furthermore, some highly contaminated soils, sludges and oils are remediated as example applications of the method.

The question might arise: can soil be used after Na/NH₃ treatment? The answer is yes. Direct ammonia injection into soils is a standard agricultural fertilization method. After soils are slurried in ammonia, the residual NH₃ is readily removed by stripping (bp of NH₃ is –33 °C). Acidic sites in soils result in NH₄⁺ retention. The amount of NH₄⁺ retention depends upon the number and strength of acid functions in the soil sample treated and the stripping temperature which can regenerate NH₃ and the original acid site. Soil pH adjustment after treatment may also be employed to achieve specific desired results.

2. Results

2.1. Model compounds

Sample aromatic, phenolic, aliphatic and olefinic chlorinated molecules were dissolved in NH₃ in thick walled glassware. Then varying amounts of solid Na were added at room temperature until no detectable chloroorganic remained. These same experiments were also performed when varying amounts of water had been added to the NH₃. The specific experimental techniques have been described elsewhere [17]. Table 1 summarizes the amount of Na required to completely dechlorinate specific model substrates. Eqs. (2)–(5) illustrate the reactions observed. Notable features which can be seen from the data in Table 1 include: (1) Na consumption increases with increasing amounts of water present, (2) modest Na consumption was required per chlorine removed, even in the presence of a 50 mole excess of water, (3) no –NH₂ group incorporation occurred during reduction of chloroaromatic substrates when water was present (amination occurred only in the absence of water as seen in Eq. (2)), (4) the equivalents of Na consumed (per chlorine removed) decreased with an increase in the number of chlorines present per substrate molecule. This latter point was observed for each class of substrate (e.g. aromatic, phenolic, aliphatic, etc.). Thus, in the absence of water, the number of equivalents of Na required (per chlorine removed) to remove all chlorine from chlorobenzene, 1,2-dichlorobenzene, 1,2,3-trichlorobenzene and 1,2,3,4-tetrachlorobenzene was 1.5, 1.4, 1.33 and 1.25, respectively. In the presence of a 50 mole excess of water, 2.5, 2.5, 2.33 and 2.15 eq. of Na, respectively, were required per

Table 1
Minimum amount of Na required to completely dechlorinate chloroaromatics at 25 °C^a

Substrate	Na/substrate mole ratio and (Na per Cl removed) required for complete dechlorination at different H ₂ O/substrate mole ratios			
	H ₂ O/substrate			
	0/1 ^b	5/1	20/1	50/1
Chlorobenzene	1.5 (1.5) ^c	2.3	2.4	2.5 (2.5) ^c
1,2-Dichlorobenzene	2.8 (1.4) ^c	4.0	4.5	5.0 (2.5) ^c
1,2,3-Trichlorobenzene	4.0 (1.33) ^c	5.5	5.8	7.0 (2.33) ^c
1,2,3,4-Tetrachlorobenzene	5.0 (1.25) ^c	6.5	7.0	8.6 (2.15) ^c
4-Chlorophenol	2.0 (2) ^c	2.9	4.0	4.5 (4.5) ^c
2,4,6-Trichlorophenol	4.6 (1.53) ^c	7.4	8.0	10 (3.33) ^c
1-Chlorooctane	1.7 (1.7) ^c	2.3	2.5 ^d	4.0 ^d (4) ^c
1,1,1-Trichloroethane	3.6 (1.2) ^c	4.2	4.5	5.1 (1.7) ^c
Carbon tetrachloride	4.6 (1.15) ^c	5.1	5.5	6.4 (1.6) ^c
Lindane	6.7 (1.11) ^c	6.7	7.2	7.4 (1.23) ^c
Mirex	13.4 (1.11)	14	14	15 (1.25) ^c

^a Experiments were conducted by Procedure A, defined in [17].

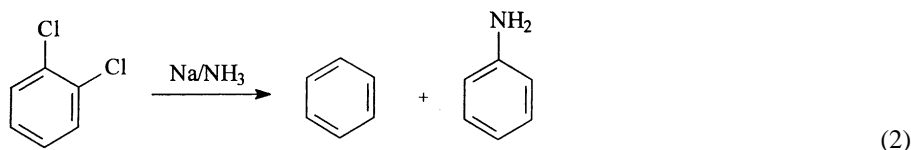
^b No water added.

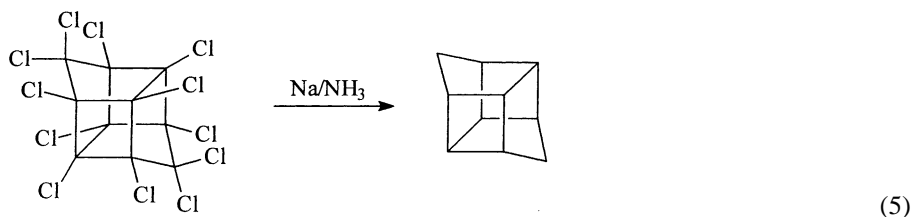
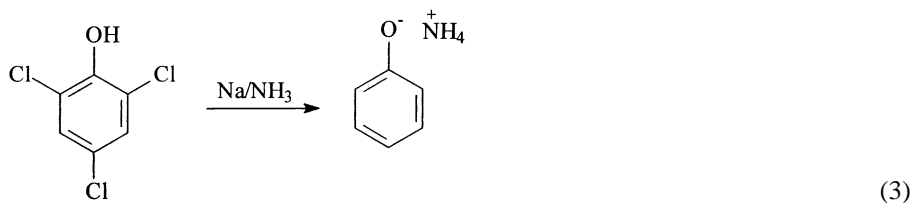
^c Moles of Na consumed per mole of chlorine removed, derived from Na/substrate weighings and divided by the number of chlorines in the substrate. Estimated errors 4%.

^d Experiments were performed using Procedure B, defined in [17].

chlorine removed. In the aliphatic series, which includes 1-chlorooctane, 1,1,1-trichloroethane, carbon tetrachloride and LindaneTM (a 1,2,3,4,5,6-hexachlorocyclohexane isomer mixture), these quantities were 1.7, 1.2, 1.15 and 1.11 in dry NH₃ and 4.0, 1.7, 1.6 and 1.23 in the presence of 50 eq. of water, respectively. Similar studies on other model molecules have appeared elsewhere [16,17].

As observed in Table 1 and elsewhere [16,17], the more highly chlorinated a specific substrate structure becomes, the more efficiently sodium accomplished the dechlorination. Thus, the sodium consumption per chlorine removed drops for both aromatic and aliphatic substrates as the number of chlorines in the substrate goes up. This trend is observed under both anhydrous and wet conditions. This can be rationalized in terms of competing reaction rates. The more highly chlorinated a molecule is, the faster it will add electrons followed by loss of chloride. Slower competing reactions still occur and frequently these competing substrates are present in far higher concentrations. Any increase in dechlorination rate that occurs leaves less time for competing side reactions to take place. Hence, sodium consumption will decrease (efficiency increases) as was experimentally observed.





Of particular interest is the facile dechlorination of the ‘corner’ chlorines of Mirex (Eq. (5)). These chlorines cannot be removed by nucleophilic substitution or elimination mechanisms due to this molecule’s constrained geometry. However, efficient dissociative electron transfer occurs in Na/NH₃ solutions.

The dechlorination of chlorinated aromatic and aliphatic model compounds in Na/NH₃ have been shown to take place by diffusion control [17]. For example, reductions of both 3,4-dichlorotoluene and CCl₄ with substoichiometric amounts of Na produced only completely dechlorinated products (toluene, methane) and the unreacted substrates. No partially dechlorinated products were obtained. Reductions, deficient in Na, have now been carried out with tetrachloroethylene in Na/NH₃. Ethylene was observed along with small amounts of vinyl chloride. Some vinyl chloride escapes into the gas phase on formation and it reequilibrates with the liquid phase during work up. No trichloro or dichloro products were detected (Eq. (6)).



The model PCB mixture, Aroclor 1016TM, which contains 2% mono-, 19% di-, 57% tri- and 22% tetrachlorinated congeners, was completely dechlorinated to biphenyl when aliquotes were dissolved in NH_{3(l)} and chunks of either Ca or Na were added at 22 °C followed by quenching into water in a few minutes. The complex gas chromatogram (gc) of the starting material was replaced by a gc trace showing that biphenyl was the only product peak. Based on these results, PCB-contaminated soils were studied.

2.2. Soil decontamination studies

Soils, purposely contaminated with Aroclor 1016, were slurried for 10–20 min in NH₃ at 21–24 °C within a 1.3 l steel reactor and then a calcium bar was added. The calcium bar dissolved in seconds and the dechlorination occurred immediately. After a few minutes, the

Table 2
Ca/NH₃ treatments of PCB (Aroclor 1016)-contaminated soils^a

Soil type	Pre-treatment PCB level (ppm)	Post-treatment PCB level (ppm)	Destruction efficiency (%)
Clay ^{b,c}	2140	2–3	>99.8
Clay ^{b,c}	486	<1.5	>99.7
Clay ^d	290	0.05	>99.9
Clay ^d	29	<0.06	>99.9
Sandy ^c	6200	1.6	>99.9
Organic ^c	660	0.16	>99.9
Organic ^c	83	<0.04	>99.9
Organic ^c	695	<1.5	>99.8

^a Pre-weighed soil samples (75–100 g) were slurried 10–20 min at ambient temperature in NH₃ in a stirred 1.31 reactor.

^b Montmorillonite clay-rich soil from Starkville, MS.

^c Soils were partially dried and then water added to 20 wt.% H₂O plus the H₂O present after drying following the contamination step.

^d Soil used as received and exact water level was not determined.

NH₃ was drained via a bottom drain valve through a mesh and the remaining NH₃ was flashed off under vacuum. Analyses of the PCBs remaining in the soil are given in Table 2 along with the pre-treatment contamination level and the soil type used. Destruction efficiencies were 99.7% or greater.

PCB-contaminated soils and sludge from various locations were treated at ambient temperature with Na/NH_{3(l)} in a manner similar to that used in the Ca/NH₃ remediations discussed above. These samples came from contaminated sites, hence the contaminating PCBs were aged within the soil under environmental conditions. Very high destruction efficiencies were achieved in every case as can be seen in Table 3.

Analyses were carried out by capillary GC (Varian model 3300) using both flame ionization and electron capture detectors. Both Supel-Q PLOT fused silica (30 m, 0.32 mm i.d.) and DB-5 (30 m, 0.32 mm i.d.) columns were used with *n*-octane, dodecane and hexadecane internal standards. GC–MS analyses were performed on a Finnigan 4500 GC–MS. Chloride analyses were carried out as described previously [16,17]. Detailed dehalogenation reaction and work up procedures used in this work have also been described [16,17].

The amounts of Na consumption required to achieve various levels of soil decontamination were studied using 1,1,1-trichloroethane, tetrachloroethylene and 1-chlorooctane. The

Table 3
Na/NH₃ treatments of PCB-contaminated soils and sludges from the environment^a

Soil source	Soil type	Pre-treatment level (ppm)	Post-treatment level (ppm)
Monroe, LA	Sand, silt, clay	29	<1.0
New York, NY	Sand, silt	1540	<2.0
Harrisburg, PA	Sand, clay	810	<1.0
New Bedford Harbor, MA	Sludge	33000	1.3

^a Reactions performed on 75–100 g soil samples in a 1.31 stirred steel reactor containing 500–600 ml of NH₃ and 2.5–3.5 wt.% Na.

Na efficiency was expressed as the equivalents of Na consumed per equivalent of Cl mineralized. Dried soils were purposely contaminated with each of those chlorinated substrates. Then Na/NH₃ treatments were performed on both dry contaminated soil samples and contaminated samples containing various amounts of water. The use of different volumes of NH₃ per gram of soil were also investigated.

1,1,1-Trichloroethane-contaminated B1 clay and B2 organic soils were treated with specific amounts of Na and the amount of chlorine mineralized was determined by post-treatment analysis. Then the amount of Na consumed per chlorine removed was calculated. Using this method, the effect of NH₃ volume used and the effect of added water could be ascertained (Table 4).

Decontaminating dry B1 clay, from an initial CH₃CCl₃ contamination level of 3000 to 7.5–9.6 ppm levels, required a Na consumption of 7.4 eq. Na per equivalent of Cl removed. The Na consumption level was independent of the volume of NH_{3(l)} employed when the weight of soil was held constant. When 7 and 15% H₂O was added to B1 clay soil contaminated at this 3000 ppm CH₃CCl₃ level, Na consumption per equivalent of chlorine removed remained independent of the volume of NH₃ used. However, more Na was required per

Table 4
Remediation of CH₃CCl₃ in B1 (clay) and B2 (organic) soils with Na/NH₃^{a,b,c}

Entry no.	Soil type and water content	NH ₃ volume (ml) per gram soil	CH ₃ CCl ₃ level in soil (ppm)		Na consumed per Cl removed
			Start	Finish	
1	B1 Dry	3	3000	9.6	7.4
2		5	3000	8.0	7.4
3		10	3000	7.5	7.4
4	B1 7% H ₂ O	3	3000	133	15
5		10	3000	131	15
6		3	3000	9.5	22
7	B1 15% H ₂ O	10	3000	2.2	22
8		5	3000	381	22
9		10	3000	361	22
10	B2 Dry	5	3000	1.7	5
11	B2 7% H ₂ O	5	3000	7.2	22
12	B2 15% H ₂ O	5	3000	4.1	22

^a Sodium consumption per chlorine mineralized at different levels of water and using different amounts of NH₃.

^b Cumulated over the drop in CH₃CCl₃ concentrations shown in each example. The same amount of Na was added to entries 1–3 but that amount was different than that added to entries 4 and 5. Entries 6–9 and 11–12 all used the same amount of Na (but that amount was different than the other runs). All reactions were run until all the sodium was consumed.

^c B1 soil is a clayey, mixed thematic type Tapludults soil obtained at a depth of 80–100 cm. Its main composition is shale with 0.2–0.4% organic matter and pH 4.18. It exhibits a cation exchange capacity of 31.6 mol/kg and a citrate–dithionate extractable Fe content of 8.25 g/kg. NH₄OAc-extractable levels of Ca (11.2 mol/kg), Mg (16.8 mol/kg), K (0.59 mol/kg) and Na (0.93 mol/kg) were present. The clay minerals were 2:1 hydroxyinterlayered vermiculite:smectite with minor amounts of mica, kaolinite and quartz. The B2 soil is an organic soil with 3.4% organic matter, 10.2% clay, 39.1% silt, 50.7% sand exhibiting pH 4.67. It has a cation exchange capacity of 8.79 mol/kg, 6.44 g/kg extractable Fe, a base saturation of 27.9% and NH₄OAc-extractable levels of Ca (2.25 mol/kg), Mg (0.97 mol/kg), K (0.16 mol/kg) and Na (0.02 mol/kg).

Table 5
Remediation of tetrachloroethylene in B1 and B2 soils using Na/NH₃^{a,b}

Soil type/water content	Cl ₂ C=CCl ₂ level in soil (ppm)		Na consumed per Cl removed
	Start	Finish	
B1 Dry	3000	0.9	9
B1 7% H ₂ O	3000	0.8	26
B1 15% H ₂ O	3000	1.0	38
B2 Dry	3000	4.0	9
B2 7% H ₂ O	3000	4.6	21
B2 15% H ₂ O	3000	2.6	27

^a Consumption per chlorine mineralized versus water content of soil.

^b When the volume of NH₃ used was varied, the amount of Na consumed per chlorine removed remained unchanged. B1 and B2 soils were described in 'footnote b' of Table 4.

chlorine removed. When 7% H₂O was present, decontaminations from 3000 to 132 ppm required 15 Na per Cl while decontaminations from 3000 to 9.5–2.2 ppm consumed 22 Na per Cl. With 15% H₂O, it took 22 Na per Cl to achieve remediation from 3000 to ~370 ppm. The Na efficiency decreases as the amount of H₂O in the soil increases. The same trends were observed with CH₃CCl₃-contaminated B2 organic soils. Addition of water decreased the Na efficiency but little difference was seen going from 7–15% H₂O in the soil.

Tetrachloroethylene-contaminated B1 clay and B2 organic soils responded in a similar fashion to Na/NH_{3(l)} treatment (Table 5). The addition of water to contaminated B1 soil increased the amount of Na consumption per chlorine removed from 9 (dry soil) to 26 (7% H₂O) to 38 (15% H₂O) for remediations that reduced the Cl₂C=CCl₂ levels from 3000 to 0.8–1.0 ppm. Similar results occurred with tetrachloroethylene-contaminated B2 organic soils (Table 5) and the water dependence was less going from 7 to 15%.

1-Chlorooctane was used as a model soil contaminant because we had observed that it required more Na consumption per chlorine removed than any of the chlorinated aliphatic or aromatic model compounds other than phenols (Table 1). Dechlorination of 1-chlorooctane is slower than the other model compounds. Therefore, competition for the solvated electron by other reactions might be more serious with 1-chlorooctane and the Na efficiency in 1-chlorooctane dechlorinations was expected to drop sharply at low substrate concentrations. The amount of Na consumed per chlorine removed was determined for contaminated B1 clay soils, both dry and with 5 and 10 wt.% water added (Table 6). The amount of Na required per chlorine removed went up sharply as the 1-chlorooctane concentration was reduced in both dry and wet soil. For example, upon decontaminating 1-chlorooctane in dry B1 clay soil from 5000 to 870 ppm, only 7 eq. of Na were consumed per Cl removed. However, decontaminating from 1000 to 22 ppm of 1-chlorooctane consumed 65 Na per Cl. Furthermore, remediating 1-chlorooctane from 50 to 0.6 ppm consumed 1200 Na per Cl removed. A cumulative experiment demonstrated 30 Na were required per Cl removed when dry B1 soil was remediated over the entire range from 5000 to 0.6 ppm. When the soil contained 10 wt.% water, 80 Na per Cl removed were needed for remediation over this same 5000–0.6 ppm range. Overall, more Na was consumed per chlorine removed as the water level increased.

Table 6
Remediation of 1-chlorooctane from B1 clay soil^{a,b}

Water in soil (wt.%)	1-Chlorooctane in soil		Sodium consumed per chlorine removed (Na per Cl mole ratio)
	Initial concentration (ppm)	Final concentration (ppm)	
Dry	5000	870	7
	5000	506	13
	1000	22	65
	100	7.4	300
	100	1	650
	50	0.6	1200
	5000	0.6	30
	5%	5000	381
5000		21	30
5000		14	45
200		4	375
100		5	750
100		1	1125
100		0.4	1500
5000		0.4	~60
10%	5000	333	30
	5000	115	30
	5000	54	35
	5000	8.8	45
	200	3.8	1100
	200	0.6	1300
	5000	0.6	~80

^a Determination of the requisite sodium consumed per chlorine mineralized versus the concentration of contaminant in the soil.

^b B1 soil is described in 'footnote b' of Table 4.

A soil sample from Barbers Point Hawaii, contaminated with residues of the pesticides DDT, DDE, was treated with Na/NH₃ using ~3 wt.% Na solutions. A single slurry treatment successfully reduced DDT from 200 to <0.03 ppm and DDE from 70 to <0.03 ppm. DieldrinTM was detected in levels from 30 to 15 ppm in soil samples from Dahlgren, VA. Single Na/NH₃ treatments reduced the DieldrinTM to nondetectable levels.

2.3. Other decontamination studies

A PCBs mixture (Aroclor 1016) was purposely added to a series of oils (octane, mineral oil, motor oil and an oligomeric diphenyl ether-based heat transfer fluid). These were treated using excess Na in NH₃. Single treatments reduced the PCB levels to less than 1 ppm (Table 7). Thus, these fluids could be reused after decontamination.

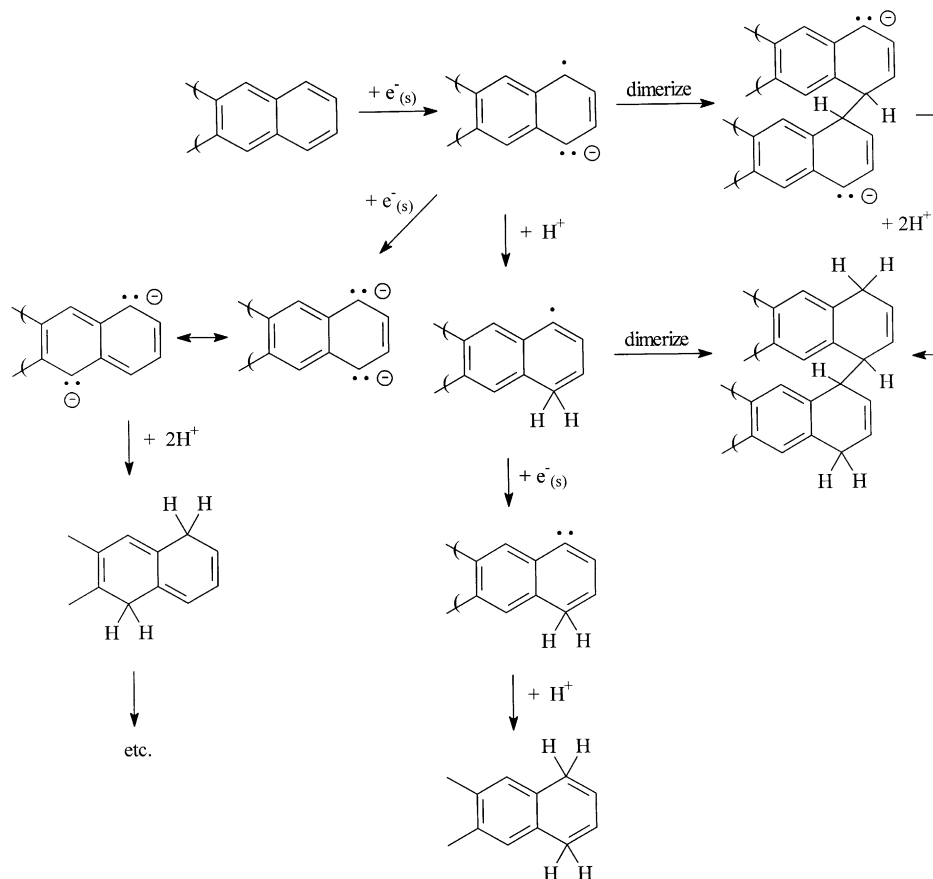
PAHs have been treated by direct injection into NH₃ followed by addition of Na. Commodor Solution Technologies has demonstrated destruction efficiencies ranging from 99.97 to 99.999% in more extensive studies than those reported here [18]. By analyzing the post-treatment residues the following percent destruction efficiencies were achieved for

Table 7
Remediation of PCB-contaminated oils by Na/NH₃ treatment^a

Oil	Pre-treatment PCB level (ppm)	Post-treatment PCB level (ppm)
Octane	7500	<1.0
Mineral oil	3800	<1.0
Motor oil	12000	<1.0
Diphenylether oligomers	6500	<1.0

^a Aroclor 1016 was added as the contaminant. Reactions were carried out in a stirred reactor at ~30–5 °C for ~1 h.

some sample PAHs: naphthalene (99.99), phenanthrene (99.99), anthracene (99.97), fluoroene (99.99), chrysene (99.99) and pyrene (99.98). The specific reduction products have not yet been identified. Reduction of a PAH occurs by electron transfer to form the radical anion which can dimerize to give the dimer dianion or by transfer of two electrons to a single PAH molecule to form a dianion. These paths are illustrated generally in Scheme 1.



Scheme 1. Possible pathways in PAH reduction.

Either dianion may pick up a proton from an available proton source (NH_4^+ , NH_3 or H_2O). Likewise, the initial radical anion can pick up a proton and the resulting radical can then be further reduced.

3. Conclusions

Treating soils, contaminated with PCBs, CAHs, chlorinated pesticides and chlorinated olefins, with Na/NH_3 is an extremely effective way to destroy these pollutants by diffusion controlled reductive dechlorination which mineralizes the chlorine in the form of sodium chloride. The key question is not: does the chemistry work? Instead, the key question is: how might this technology compete with other methods? What advantages and disadvantages are associated with its application? Several technologies will compete with solvated electron reductions including: landfill, incineration, thermal desorption, plasma arc, sodium dispersion, alkali treatment, bioremediation and washing. Landfilling is least expensive and, it is a viable alternative. None of the technologies (including Na/NH_3) are cost competitive when landfilling can be used. Next lowest in cost, most often, are thermal desorption and washing methods. While reasonably economical, they require the organics to be volatile. Nonvolatile compounds such as PCBs (and even less volatile chlorinated biphenols often produced from PCBs) cannot be remediated to desired standards. Many chlorinated organics do not come out when they are intercalated into clay layers or weathered soils. However, ammonia readily swells clay layers, extracting the toxics for rapid destruction by solvated electrons. Incineration, alkali treatment, sodium dispersion and Na/NH_3 treatments will be approximately similar in cost.

Na/NH_3 treatments have some distinct advantages inherent in the chemistry. Thermal processes produce hazardous by-products such as dioxins but in Na/NH_3 treatments this simply cannot occur. Na/NH_3 can be used as a closed system without an exhaust stack. Bioremediation can often be cost effective and it can be used in situ. However, bioremediation is very sensitive to temperature, moisture content, the geology/morphology of the site and the identity of the toxics to be remediated. Highly chlorinated PCBs, CAHs and pesticides are often highly resistant to in situ bioremediation. They pose no difficulty for Na/NH_3 treatment.

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