WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Dechlorination of PCBs, CAHs, Herbicides and Pesticides in Soils, Sludges, DNAPLs and Bulk with Na/NH_2 Ca/NH_3 at Ambient Temperature.

Focus categories: TS, GW, TRT

Keywords: Water Quality, Groundwater Quality, Hazardous Waste, Toxic Substances, Chlorinated Aliphatic Hydrocarbons, Polychlorinated Biphenyls, Dechlorination, Pesticides, Herbicides, Soil Decontamination, Reductions, Sludge, Subsurface Drainage, Water Treatment.

Duration: March 1, 1999 to February 29, 2001

Fiscal Year 1999 Federal funds:

14,000	(14,000)
(Total)	Direct

Non-Federal funds allocated:

34,235	(20,947)	(13,288)
Total	Direct	Indirect

Name(s), university, and city of principal investigator(s):

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Congressional District of university performing the research: District No. 3

Statement of the critical regional water problems:

Polychlorinated biphenyls (**PCBs**) and other chlorinated aromatic compounds are widely distributed in soils, sludges, estuaries, etc. at **over 400 sites in the United States**. This demonstrates a **national need** for a variety of **rapid remediation methods**. Every state is represented in this problem. The EPA's Emergency Response Notification System (ERNS) shows that from 1988 - 1992, alone, almost 3,600 accidents occurred with PCBs (more than for any other category of hazardous substances) and these accidents continue unabated. This highlights the need to develop remediation technology to decontaminate soils and sludges containing PCBs and to invent portable methods to destroy PCBs not yet released into the environment. Chlorinated aliphatic hydrocarbons (**CAHs**) are widely used for degreasing/cleaning engines, auto parts, electronic components, and dry cleaning. They occur as serious contaminants **at 358 major hazardous waste sites in the United States**. Since CAHs migrate vertically through soils to form dense nonaqueous phase liquids **(DNAPLs)** on aquifer bottoms, *ex-situ* methods of CAH

decontamination/destruction are needed for soils, sludges, bulk zones (DNAPLs in the valdose zone) and industrial process wastes.

We propose to investigate a reduction technology to destroy PCBs, CAHs and other chlorinated pesticides and herbicides using solvated electron chemistry (Na/NH_3 or Ca/NH_3) at room temperature. The method will be applicable to *ex-situ* and some *in-situ* treatments. *In situ* remediation of DNAPLs is a very high priority research area at EPA, DOE and DOD in critical need of a variety of solutions.[1-6] To give just one example, DOEs Hanford site has massive soil and groundwater contamination with carbon tetrachloride with a subsurface plume extending for over 70 sq. miles. Many contaminated sites exist in the Gulf Coast region (Texas through Florida) where the largest concentration of chemical manufacturing plants in North America is located together with many DOD sites. Furthermore, wood treatment sites have contaminated sites in the Southeast with pentachloraphenol.

Statement of the results, benefits, and/or information expected to be gained

The proposed research will test the hypothesis that virtually all chlorinated organic molecules (PCBs, CAHs and chlorine-containing herbicides and pesticides) can be rapidly **dechlorinated at ambient temperature in the presence of water**. Furthermore, the proposed work will demonstrate if all of these classes of chlorinated organics can be economically **dechlorinated while present in soil matrices or as sludge contaminants**. At high pollutant dilution (e.g. for example 500 to 10 ppm in soils or sludges) can solvated electron reductions employing Na/NH_3 or Ca/NH_3 destroy 99.9% of the toxic/hazardous organochlorine pollutants in the presence of large amounts of water, humic acids, clays, etc.? This requires the relative rates of organochlorine compound reduction be far faster (´10^4 or ´10^5) than that of water. Furthermore, the reduction rates of organonitro and nitrate compounds will be established in lab solutions and soil decontamination studies to see if Ca/NH_3 chemistry could be used in demilitarization/environmental restoration. If model CAHs (carbon tetrachloride, chloroform, trichloroethylene, tetrachloroethylene and trichloroethane) exhibit rapid dechlorination kinetics and if CAH-contaminated soils are suitably decontaminated in laboratory studies, **the way will be opened for direct Ca/NH_3 injection into DNAPLs as a way to *in-situ* treat such dense underground liquid plumes. This would permit CAH remediation prior to more widespread migration and entry of CAHs into groundwaters.** Since ammonia is already directly injected into soils in agricultural practice, injection of Na/NH_3 or Ca/NH_3 solutions into DNAPLs, or slurrying soils in liquid NH_3, appears reasonable. Ammonia retained by the soils as NH_4^+ ions can serve as a fertilizer component.

Benefits Expected from Ca/NH_3 Decontamination Processes

Several advantages seem obvious based on the work that has been performed so far in our laboratory[7,8] and at Commodore Solutions Technology[9,10] (small startup company) on PCB remediation both neat and in contaminated soils. The advantages include: (1) Solvated electron soil dehalogenations **operate at room temperature or lower**. (2) Their

rate is very rapid. (3) Ammonia solvent **breaks down soil into very small easy-to-slurry particles** aiding *ex-situ* treatment possibilities. Even difficult-to-manage clay soils are rapidly broken into a fine dispersion in ammonia. (4) Ammonia is **easily removed** from slurried soil due to its low boiling point and ammonia can be **recovered with well know technology**. (5) Liquid ammonia can **readily penetrate, diffuse and flow through many soil types and strata making it more likely that *in-situ* treatments of contaminated subsurface zones will work as a lower cost remediation technique**. This technology may compete then wherever (1) direct ammonia injection is permissible or (2) soil excavation, followed by on site treatment and return of remediated soil to the excavation, can be practiced.

Nature, scope and objectives of the Research

The goal of the proposal research is **to develop a generalized technology to decontaminate soils (*in-situ* and *ex-situ*) and sludges contaminated with PCBs, CAHs, chlorinated pesticides, herbicides and possibly even organic nitro and nitrate compounds** (from munition/propellant wastes). **We have recently demonstrated that neat PCBs[7] and PCB-contaminated soils[8] (as received clay, loam, sandy soils containing up to 30% water) can be decontaminated in liquid ammonia slurries when treated with either Na/NH_3 or Ca/NH_3. PCB-destruction efficiencies >99.9% were achieved in 30 sec. at room temperature.[7,8]** The products were biphenyl and $CaCl_2$. It is now necessary to determine how much water can be present and still get complete PCB destruction at reasonable Ca consumption. Can sludges with high fractions of water be economically treated? Will this chemistry destroy carbon tetrachloride, tetrachloroethylene, trichloroethylene, trichloroethane (major **CAH**-polutants) rapidly and in the presence of water? Demilitarization activities have emphasized existing problems with nitro and nitrate compounds (explosives), nitration factory soil contamination, and propellent residues.[11,12] All of these might be reduced rapidly by Na/NH_3 or Ca/NH_3. Several model nitroaromatics have been very rapidly and quantitively reduced using Na/ethylenediamine in our labs in 1994-95.[13] **The major goal is to develop solvated electron chemistry** (e.g. Na/NH_3, Ca/NH_3) as a **single, multifunctional, portable technology applicable to both on site** *in-situ* **and on site** *ex-situ* **destruction of PCBs, CAHs, and munition/explosive residues.** Even if only half of these classes of pollutants can be rapidly destroyed in solvated electron media, this single technology would have broad application. **The major focus and concern is to demonstrate that this chemistry can lead to a new remediation technology.**

The following figure from our laboratory (next page) shows a typical soil sample being treated in an ammonia slurry with solvated electrons. Calcium was introduced into the ammonia soil system at a starting clock time of approximately 8 min and 34 sec. The reaction activity was monitored by measuring the resistance of a soil/ammonia slurry in a reactor. By 9 min and 8 sec., the reaction was complete and *the soil was reduced from a pretreatment level 280 ppm PCB (aroclor 1260) to less than 1 ppm PCB.* Total treatment time was *roughly 34* seconds! Can this result be generalized to sludges? Will this chemistry operate on CAHs? Such experiments will be done on bulk CAH samples and on CAH-contaminated soils. Competitive rate experiments will also be performed in the

presences of various water concentrations to examine the dechlorination of several model CAHs (CCl_4, $CHCl_3$, CH_3CCl_3, $Cl_2C = CCl_2$) versus the reduction.

Methods for detoxification of hazardous halogenated organic compounds (pesticides, herbicides, PCBs, CAHs), are needed on four different levels. First, bulk quantities of all of these neat agents or their high concentration mixtures need to be disposed of safely (e.g. industrial process wastes or old storage sites). This is level 1. Secondly, on level 2, soils and sludges contaminated with PCBs, CAHs and nitro/nitrate organics, need to be remediated. On the third level, DNAPL plumes spreading below the surface in the Valdose zone need to be remediated. Finally, dilute aqueous solutions such as ground water which is already contaminated need to be purified. This constitutes the fourth level. The proposed research concentrates on developing **reductive chemical methods** based on solvated electron chemistry to treat halogenated organics on the **first three levels**. Any successful detoxification/remediation advances applied at these three levels will eventually reduce the extent of groundwater contamination via formation of dilute aqueous solutions in the environment (fourth level).

PCB DESTRUCTION IN SOIL USING Ca/NH_3

NH_3/SOIL SLURRY CONDUCTIVITY PROFILE

Soil Moisture 9.4% PCB = 280 ppm

The most common current methods to treat chlorinated organics at levels 1-3 include combustion or pyrolysis (levels 1 and 2) and biodegradation (levels 2 and 3). Combustion of neat or concentrated chlorinated organics requires special treatments to remove the HCl generated. HCl, if not removed, can cause major corrosion problems. Combustion or pyrolysis of soil that is contaminated with chlorinated organics is usually expensive. The combustion of concentrated PCBs and other chlorinated organics is also known to produce small traces of dioxins. This fact has made combustion an emotional problem to the public which has enhanced the difficulty of locating and operating incinerators. For these reasons it would be desirable to develop a method which would dehalogenate organic molecules rapidly and cheaply at low temperatures without either HCl generation or dioxin production. **A key point is that the chlorine displaced in solvated electron reductions will end up as stable inorganic chlorides.**

Planed studies. Laboratory studies will be undertaken first to study the proposed dehalogenation of the **following model CAHs: carbon tetrachloride, chloroform, tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane and 1,1,2-trichloroethane**. Reactions, with and without added water, will be conducted using the Na and Ca/NH_3 systems. Neat samples will be studied so no special statistical methods or analytical detection limits apply. The relative rates of reduction versus that of water will

be estimated from competitive experiments. This will be followed by studies of contaminated soils. **CAH-contaminated soils (with known levels of CAHs) will then be slurried with Ca/NH_3 for varying times to see the levels of decontamination efficiency achieved.** Several types of soils (clay, sandy, organic) will be used. Analysis of remediated soils will follow procedures given in the QA/QC plan in Appendix I. Treatments will be performed at low and high soil moisture contents for sandy, organic and clay soils. Then some sample sludge decontaminations will be carried out. A DNAPL will be simulated in the laboratory within a pipe that is packed with a sample soil saturated with a CAH mixture. Then Ca/NH_3 or Na/NH_3 will be pumped through. The contents will then be analyzed (by glc) at various locations along the flow bed to determine the CAH destruction efficiency.

Similar studies will be made with nitro and nitrate compounds and with soils contaminated with wastes from munitions manufacturing sites. The effect of water content will also be studied. Example soil and sludge decontaminations would be conducted to examine the question of ammonia recycle. Ammonia should be readily recovered and recycled from batch reductions by flashing it off after reductions have been completed (NH_3 boils far lower than any other component of these systems). Ammonia recycle will be possible unless some unforseen build up of detrimental impurities in the recovered ammonia occurs during successive recycles.

What Can be Accomplished in the First Year? Many advances have already been made in our lab with neat and soil-bound PCBs. In one year similar advances will be made with neat CAHs and CAH-contaminated soils. Work on nitro contaminants has started (Mohammad, MS Thesis, 1997). Competition experiments with the model CAHs versus water where water is present in varying amounts will be completed and compared to CAH structure. Also, the relative efficiencies of Na vs. Ca will be established (with PCBs in soil initial work shows Na is more efficient). Other funding sources to leverage this work and scale-up studies will be sought. In the following years the first year's lab results on PCBs, CAHs and nitro contaminants will be applied to a variety of contaminated soil and sludge samples (EPA standard samples, samples from super fund and other contaminated sites). Also laboratory versions of direct injections into DNAPLS will be performed.

Can this concept work? The presence of significant quantities of so many constituents capable of competing for the solvated electron might lead one to conclude that a huge excess of Ca or Na would be needed relative to the stoichiometry of the hazardous PCBs or CAHs present in the soils or sludges. However, work on PCB-contaminated soils from three superfund sites (see Table 1, next pg.) has shown that this is not the case. **The PCBs were destroyed in high efficiencies even in the presence of a huge stoichiometric excess of water and large amounts of ferric and ferrous ions**. Preliminary calculations from our labs suggest that the PCB dechlorination is probably 10^5 times (or greater) faster than the rate at which solvated electrons react with water and the variety of reducible organic and inorganic groups present in soils.

Why could the use of solvated electron solutions to decontaminate soils, sludges and DNAPLs be feasible in the presence of excess water? The reaction of solvated electrons with water (i.e. $e^-_{(s)} + H_2O$ ® ½H_2 + ^-OH) has a far higher kinetic barrier (activation energy) than electron transfer to chlorinated or nitrated organic molecules. Furthermore, when ammonia is present with water, the half-life of the solvated electron dramatically increases. **In pure water the half-life of the solvated electron is short ($t_{1/2}$ = ~100 ¼sec)[14] yet its transfer to chlorinated organic compounds is far faster than this. For a 20% solution of water in ammonia the half-life of the solvated electron is around 100 sec.![15,16] In pure ammonia $t_{1/2}$ = ~300 hrs.![15]** Thus, all the current evidence suggests that the desired detoxification reductions of chlorinated organic molecules will occur far faster than side reactions with water when ammonia is used as the solvent. The transfer of an electron to RCl occurs in ~ 1 ¼sec versus transfer to H_2O to give ½H_2 (in 20% H_2O/80% NH_3) in ~100 sec. **One can estimate that chloroorganics might reduce ~10^7 to ~10^8 times faster than water even when the medium contains 20% water! Thus, a practical technology does appear possible.** However, soils and sludges contain complex mixtures of other organics, inorganics, metal ions etc. Unfavorable catalysis of reactions with water can still be envisioned. Mass transport may play an unforseen role. Therefore, research needs to be carried out on a variety of systems (as proposed herein).

TABLE 1. TREATMENT OF PCB-CONTAMINATED PIPELINE COMPRESSOR STATION SOILS WITH Ca/NH_3 AT ROOM TEMPERATURE.

Soil Matrix	Pre-treatment PCB Value	Post-treatment PCB Value	Destruction Efficiency
Clay	290 ppm	0.05 ppm	>99.9%
Clay	29 ppm	<0.06 ppm	>99.9%
Sand	6,200 ppm	1.60 ppm	>99.9%
Organic	660 ppm	0.16 ppm	>99.9%
Organic	83 ppm	<0.04 ppm	>99.9%

Economics. As the chlorocarbon is dechlorinated in Na or Ca/NH_3, its concentration gets lower but the concentration of water stays almost constant. Thus, the ratio of the rate of dechlorination to that of water reduction will decrease as the chlorocarbon concentration drops. The process economics will depend on how low the chlorocarbon concentration is required to be. Each situation is different and specific. A

key economic question for soil/sludge clean up is the amount of Na or Ca required to reduce the chlorocarbon concentration to a specified level.

Methods, procedures and facilities.

This section briefly describes some of the basic techniques that are being (and will be) applied in solvated electron dechlorination studies: (1) on neat compounds and (2) on contaminated soils and sludges.

Na/NH_3 and Ca/NH_3 Dissolving Metal Dechlorinations

Procedures/Equipment. Typical CAH dechlorinations of pure compounds and soil samples will be carried out at ambient temperatures in liquid ammonia at autogeneous pressure (below 200 psig) in a special ammonia reactor system, which had been previously designed by A. L. Sandpiper corporation. We have constructed a stainless steel version of this reactor which allows the easy introduction of solid calcium or sodium rods into the ammonia/substrate solution at ambient temperature. These rods rapidly dissolve to give a clear blue solvated electron solution. After the reaction is completed ammonia is conveniently evaporated from the products. Ammonia is readily transferred from a storage tank to the reactor vessel via normal metal transfer lines. Copper is avoided in all regulators, values and transfer lines.

A specific substrate or a contaminated soil (or sludge) sample will be weighed, put into the reactor and then the required volume of ammonia added to dissolve the substrate (or slurry the soil). The reaction will be started upon the introduction of Ca or Na metal. Conductance measurements may be used to follow the reaction. At the prescribed time samples of the ammonia solution (or slurry) can be taken for work up and analysis. Alternatively, ammonia may be flashed off and the solid residue worked up. Other reactions (on nitro and nitrate compounds) will be carried out using Na, or Ca dissolved in ammonia.

Analytical Methods and Capabilities. The residual products of the dechlorination reactions will be analyzed by GC, GC-MS, HPLC, IR and NMR. Na or Ca/NH_3 reductions lead to the replacement of halogens by a hydrogen. Therefore, water soluble polyhydroxy compounds (formed for example in $PCB/Ca(OH)_2/H_2O$ reactions) will not be formed. Thus, work up and identification of products should be straightforward. This allows easy extraction of the products from soil. CAHs (CCl_4, trichloroethane, tetrachloroethylene) can produce low boiling hydrocarbons (methane, ethane, ethylene). These will be analyzed by taking aliquotes in pressure-lock syringes and analyzing in special GC columns already on hand.

The reduction of aromatic nitro compounds by solvated electrons could produce a variety of products. Aromatic amines would be favored under conditions of rapid electron transfer and rapid proton transfer. If electron-transfer is rapid but proton transfer is slow, dimeric products or loss of NO_2^- could be favored. These reactions would be temperature

and concentration dependent. Use of Na or Ca/NH_3 and Ca/$H_2NCH_2CH_2NH_2$ systems will be studied. Solids or high boiling liquids may be formed. Thus, GC, GC-MS, or HPLC may be used for separations.

Soil and sludge samples which have been preanalyzed by others (outside laboratories, EPA standard soils, etc.) will be provided to Mississippi State University. These will serve to benchmark our work. Other contaminated soils or sludges will be prepared in our lab. Standard extraction/GC procedures will be used to obtain our own measure of the contamination level. Then the soil (sludge) samples will be reacted with Na or Ca/NH_3 at various stoichiometries. After removing NH_3 the treated soils will be reanalyzed by the same GC and GC-MS techniques to establish the contamination level. The NH_3 can be easily flashed off from the soil. If NH_3 is removed by filtration, the extracted residues will need to be checked after final NH_3 evaporation. Very small quantities of PCBs can be detected in the Mississippi State Chemical Laboratory (MSCL) located in our chemistry building. They have a **trace analysis laboratory equipped with GC instruments having electron capture detectors**. That laboratory performs routine trace analysis of residual hazardous in environmental samples, foods, and animals, etc., **using EPA-approved methods. This laboratory has regulatory enforcement responsibilities and backs up its analysis and methods regularly in legal proceedings.** All soil and sludge analyses will be conducted under GLP.

Facilities

The PIs has a 2600 ft.^{2} laboratory in Hand Lab and an 650 ft^2 laboratory in Etheridge Lab. These labs are equipped with a variety of hoods. A $6.8MM NSF-funded laboratory renovation (awarded to the PI) is underway. The PI's laboratory will be finished by June 1998 to include 12 hoods. Equipment includes 5 GCs, 3 HPLCs (including a Hewlett Packard Series II 9090 HPLC with full computer control), recorder integrators, data stations, Parr pressure reactors, photochemical reactors, a 40 kiloHz plasma generator (advanced Plasma Systems, model B-12), a Waters Associates GPC instrument equipped with differential refractometer and differential microviscometer (Viscotek, Model H502) detectors. The PIs graduate students are equipped with 8 PCs (200 MHz, pentium chip, 1.2 to 10 Gbyte hard disks), adequate vacuum pumps, temperature controllers, analytical and other balances, autoclaves, gas delivery systems and vacuum lines.

The Department of Chemistry houses the Mississippi Magnetic Resonance Facility with four NMR spectrometers including: a GE QE-300 multi nuclear narrow bore instrument, a two channel Bruker AMX-300 (narrow bore) equipped with a solid level I accessory for CP-MAS experiments at variable temperatures with spinning rates to 7KHz; a two channel GE-Omega 400 wide-bore spectrometer equipped with the S-35 proton microimaging accessory; a four channel Bruker AMX-600 spectrometer equipped to perform triple resonance experiments, 3D experiments, gradient enhanced experiments, pulse shaping etc. The 300 MHz and 400 MHz instruments are equipped with liquid state direct detection X-nucleus and inverse detection probes with variable temperature capabilities. A Silicon Graphics Crimson workstation (400 MB of RAM, 8GB disk space, stereo view and top of the line VGX graphics) and two Silicon Graphics Indigo

workstations (400MB of RAM, 8GB disk space, stereo view and top of the line VGX graphics) and two Silicon Graphics Indigo workstations (20MB of RAM and 500MB of disk space) are available for molecular modeling with various BIOSYM software packages (discover, NMRichect, Insight Bilder etc.). A microwave spectrometer (HP-8460), an IR spectrometer (Nicolet 7199 with far IR and GC capability), 20DX FT-IR and Miadac FT-IR spectrometers, a Spex Laser Raman spectrometer, Dynamic light scattering (Ar^+ laser) and static light scattering (He and Ne lasers) spectrometers are available with multiple angle light scattering detectors.

Mass spectroscopy is available via a Finnigan 4500 automated GC-EI/CI MS, a Kratos MS80REA GC-MS system, a Hewlett-Packard 5990A GC/MS system with an HP5992 data system, a Hewlett-Packard 5930A GC/MS, a Dupont 21-490F with EI and CI. A variety of flourescence spectrometers, GC and HPLC instruments are available. Of special interest to this research are the trace analysis capabilities of both the Mississippi state Chemical Lab (in our building) and the Forest Products Research Laboratory. Both of these labs are equipped to perform (and experienced) EPA trace analysis of soils or other environmental samples for organochlorine compound.

Releated Research

The chemical destruction of bulk halogenated organic waste materials, such as pesticides and PCBs, has been carried out by incineration[17-19] (particularly in cement kilns), plasma incineration[20] and wet oxidation[21] to name a few approaches. General Electric pioneered the use of polyethyleneglycol/KOH to dechlorinate PCBs[22-24] in bulk and in soils and sludges and this work was extended at the EPA Cincinnati Labs to rapid dehalogenation of a variety of halogenated organics using tetraethyleneglycol/KOH and related systems.[25,26] Pittman and co-workers at Mississippi State Univ. have subsequently reported the very facile destruction of Mirex[27] and various chlorinated aromatics[28] (including PCBs[29]) using TEG/KOH promoted with $NaBH_4$ or $NaBH_{4-x}(OR)_x$. These borohydride systems have been used alone and with $NaBH_4/NiCl_2$ systems.[27,29,30] The complete dechlorination of PCBs to biphenyl[29] ^{3}-Lindane[30] and pentachlorophenol[31] using $NaBH_2(OCH_2CH_2OCH_3)_2/NiCl_2$ at 68°C was also achieved at MSU. This latter work was chemically very promising. However, the costs associated with using $NaBH_4$ or $NaBH_{4-x}(OR)_x$ rule out the very large scale application of this chemistry, thereby, confining its use to higher cost nitch areas or to use on smaller neat samples. In recent studies we have directly dechlorinated PCBs with cheaper $NaBH_4$ in high boiling solvents.[32] However, this method would not be applicable to *in situ* application.

Detoxification by dechlorination continues to be one major focus in both industrial and academic laboratories. The Industrial and Engineering Chemistry Division (of the ACS) recently sponsored several special symposia “Emerging Technologies in Hazardous Waste Management V,” Sept. 27-29, 1993 and VI, Sept. 19-21, 1994 in Atlanta, GA and VIII, Sept. 9-11, 1996 in Birmingham, AL. These symposia featured a large number of papers devoted to problems and technologies associated with chloroorganic wastes and contamination. The numerous papers on bioremediation of soils, that were contaminated with chlorinated organics, reviewed a litany of unsolved

problems and barriers. Sessions on chemical treatments of chlorinated wastes reviewed promising catalytic reductive dehalogenations,[33] hydrodechlorinations[34,35,36] and photooxidations,[34,37] but **none of these had easy application to soils, sludges or DNAPLs.**

This proposal advocates the reductive dehalogenation using **solvated electrons**. Solvated electrons are formed on dissolving Li, Na, K, Ca etc. into liquid ammonia or other amines and these media have long been used to reduce organics. This class of reductions, known as the **Birch reduction**[38-42] has been **known for 80 years and employed routinely on a commercial scale** in the pharmaceutical industry. Chloroorganic compounds are reduced at high rates. This chemistry has never been applied to environmental (soil, sludge, DNAPL) cleanups because the assumption has always existed that the solvated electron would react rapidly with water. This would consume, stoichiometrically, the solvated electron causing the cost to be prohibitive. *Studies in our laboratory*[7,8] *(and at Commodore Solutions Inc.*[9,10]*) have now shown that the reduction of water is much slower than that of chlorinated aromatic compounds*. Therefore, even wet PCB-tainted soils may be rapidly dechlorinated without undue consumption of the reducing agent. Can this also be achieved for PCBs in sludges or chlorinated aliphatic compounds (CAHs), organic nitro and nitrate residues, etc. in the environment?

The solvated electron is the ultimate reducing agent. It is an *extremely* powerful dehalogenating agent. Solutions of solvated electrons reduce carbonyl groups, alkynes, quaternary ammonium salts, aromatic rings (to cyclohexadienes or cyclohexenes), nitriles, imines and they cleave C-N, C-O, C-S, N-N, N-O, C-halogen, P-halogen and other bonds.[38-42] Thus it was never imagined that such reductions could be selective in soils, sludges, etc. Typically, electron transfer to chlorinated organic compounds generates a radical anion which can eject a chloride and then pick up a proton. This process is repeated until the reduction is compete. The dehalogenation of chlorobenzene is shown in equation (2) where hydrogen is ultimately substituted for chlorine and chloride ion remains in solution. Kennedy, Stojanovic and Shuman demonstrated that all the halogens were stripped from 19 different pesticides in Na/NH_3 solutions when analytical grade samples of each pesticide was used (examples included Atrazine, DDT, Dalapon, Diuron, Paraquat, 2,4-D, 2,4,5-T and Trifluralin).[43]

Can a process known since 1914 be novel today? Although solvated electron solutions had proven highly effective in the treatment of analytical-grade halogenated organic compounds, their application to soils and sludges contaminated with these same compounds was simply never tried because of the highly heterogeneous nature of soils. Typically large amounts of water, oxygen, and iron are present which can interfere with solvated electron chemistry.[40,44,45] Both oxygen and iron catalyze the reaction of the metal with the ammonia, producing the metal amide. Thus, the presence of so many constituents competing for solvated electrons led to the universal assumption that this chemistry should be carried out in clean, anhydrous media for a specific substrate's reduction. The 1989-1993 fundings from our lab (and those of Commodore Solutions, Inc.)[7,8,12,13] showed that PCBs could be rapidly destroyed in wet soils using Ca/NH_3 or Na/NH_3 at ambient temperature. This was possible due to enormous rate of R-Cl

reduction versus that of water or soil functional groups. We believe this has set the stage for environmental remediation of **PCBs, CAHs,** chlorinated pesticides and herbicides and possibly organonitro and nitrate contaminants.

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