



WATER RESOURCES RESEARCH GRANT PROPOSAL

Title. Dechlorination of PCBs, CAHs, Herbicides and Pesticides in Soils, Sludges, DNAPLs and Bulk with Na/NH₂ Ca/NH₃ at Ambient Temperature

Focus categories. TS, GW, TRT

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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/NH₃ or Ca/NH₃) 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, DOE's 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 pentachlorophenol.

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/NH₃ or Ca/NH₃ 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 (¹⁰⁴ or ¹⁰⁵) 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/NH₃ 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/NH₃ 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/NH₃ or Ca/NH₃ solutions into DNAPLs, or slurrying soils in liquid NH₃, appears reasonable. Ammonia retained by the soils as NH₄⁺ ions can serve as a fertilizer component.

Benefits Expected from Ca/NH₃ 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 PCBs⁷ and PCB-contaminated soils⁸ (as received clay, loam, sandy soils containing up to 30% water) can be decontaminated in liquid ammonia slurries when treated with either Na/NH₃ or Ca/NH₃. PCB-destruction efficiencies >99.9% were achieved in 30 sec. at room temperature.^{7,8} The products were biphenyl and CaCl₂. 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-pollutants) rapidly and in the presence of water? Demilitarization activities have emphasized existing problems with nitro and nitrate compounds (explosives), nitration factory soil contamination, and propellant residues.^{11,12} All of these might be reduced rapidly by Na/NH₃ or Ca/NH₃. Several model nitroaromatics have been very rapidly and quantitatively reduced using Na/ethylenediamine in our labs in 1994-95.¹³ The major goal is to develop solvated electron chemistry (e.g. Na/NH₃, Ca/NH₃) 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 (CCl₄, CHCl₃, CH₃CCl₃, Cl₂C = CCl₂) 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).

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.

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/NH₃ 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/NH₃ 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/NH₃ or Na/NH₃ 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 (NH₃ boils far lower than any other component of these systems). Ammonia recycle will be possible unless some unforeseen 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 105 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. $e^-(s) + H_2O \rightarrow \frac{1}{2}H_2 + \cdot OH$) 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 ($t_{1/2} = \sim 100$ msec)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 $t_{1/2} = \sim 300$ 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 msec versus transfer to H₂O to give $\frac{1}{2}H_2$ (in 20% H₂O/80% NH₃) in ~ 100 sec. One can estimate that chloroorganics might reduce $\sim 10^7$ to $\sim 10^8$ 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 unforeseen role. Therefore, research needs to be carried out on a variety of systems (as proposed herein).

Economics. As the chlorocarbon is dechlorinated in Na or Ca/NH₃, 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.