Combined Ultrasonic-Oxidative Remediation of Aldrin and Dieldrin Soil Contamination

Final Draft

4/14/2009

PREPARED FOR:
UNIVERSITY OF FLORIDA
SOIL AND WATER SCIENCE DEPARTMENT
DISTANCE EDUCATION ENVIRONMENTAL TRACK
NON-THESIS MASTER'S DEGREE RESEARCH PROPOSAL
COURSE: SOS 6905

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List of Acronyms

µg/kg	micrograms per kilogram
µg/L	micrograms per liter
bgs	below ground surface
AOP	advanced oxidation process
CTL	cleanup target level
DO	Dissolved Oxygen
DPT	direct-push technology
ENCO	Environmental Conservation Laboratories, Inc.
EN Rx	Chemical oxidant provided by EN Rx, Inc.
FAC	Florida Administrative Code
FDEP	Florida Department of Environmental Protection
GCTL	groundwater cleanup target level
MACTEC	MACTEC Engineering and Consulting, Inc.
MDL	Method Detection Limit
Mg/kg	milligrams per kilograms
MSDS	material safety data sheets
OCP	organochlorine pesticide compounds
OWS	oil/water separator
OWSP	Oil Water Soakage Pit
ppb	parts per billion
ppm	parts per million
SCTL	soil cleanup target level
SOP	Standard Operating Procedures
SSO	Sustained Single Oxygen
TOC	top of casing

1.0 Executive Summary/Abstract

In this study, we investigated the combination of the proprietary EN Rx Advanced Oxidation Process with ultrasound treatment of aldrin- and dieldrin-contaminated soils. The target soils were obtained from a former pesticide application vehicle maintenance facility. A conventional ultrasonic bath was used for the treatment, with a similar setup on a water bath used for the non-sonicated samples.

Initial treatment consisted of preparing 1:1 mixtures of soil and oxidizer solution, followed by exposure to up to 80 minutes of ultrasonic activity. Control samples were run using one treatment or just water bath.

Further treatment consisted of samples allowed to continue reacting with the oxidizer for one week. Results showed that there is appreciably increased activity with the pre-sonicated samples to the limits of the experiment. An unexpected physical effect was also noted that seemed to forecast the increased activity.

2.0 Introduction

One of the most difficult problems in soil remediation is the ability to reach contaminants that are adsorbed onto the surfaces of very fine structures and sequestered within the nanoscale pores of clays and similar materials. This research attempted to combine methods to either release these compounds or to penetrate such fine material with agents that can remove and/or destroy them.

In 1939 Swiss chemist Paul Muller discovered DDT, which in its early days was hailed as a miracle for several reasons. It was a wide spectrum pesticide, seemed to have low toxicity to mammals, was persistent so it didn't have to be reapplied excessively, non-soluble so it didn't easily wash off, and was cheap and easy to apply. It was so effective at boosting crop yields that Muller was awarded the Nobel Prize in 1944[1]. Other organochlorine pesticides (OCPs) were subsequently developed such as chlordane, toxaphene, endrin, lindane, aldrin and dieldrin. Many of these persistent compounds may be present in soils, but the most toxic compounds found to a very high degree are aldrin and dieldrin, and since aldrin often epoxidizes to dieldrin in the environment, dieldrin is the target compound in the most difficult cases.

The log Kows of aldrin and dieldrin are greater than 5, which means they are highly likely to adsorb to soil particles and out of water solution. Being semi-volatile, those molecules near the surface will tend to vaporize, but do not seem to degrade much in direct sunlight. Dieldrin is one of the compounds that has been found distilled out of the atmosphere by pristine mountain snowcaps and detected in meltwaters where they are starting to become a problem[2]. The high log-Kow values also makes them lipophyllic and prime compounds for bioaccumulation in fish and other animal species far removed from their sources (BCF of 4,670)[3].

Dieldrin and aldrin (and to a lesser extent chlordane), besides having a high affinity for clay surfaces and spaces, are rather long somewhat spindly molecules, and as such have an ability to penetrate deeply into microporous molecular sieve-like structures of clay and clay-coated sand grains.[4] This makes them extremely unavailable for chemical or even biological activities, and it is believed their exit from such cavities is more a product of random diffusion.[5]

Because of this tight adsorption characteristic, this author believes that addition of an extra step, either simultaneously or preceding the application of the AOP might be of use. There has been a good deal of success with the use of ultrasonic waves in ex-situ soil-washing procedures and with AOPs in hydrocarbon remediation, and a limited success with in-situ ultrasonic and megasonic groundwater treatments[6]. Such high-energy sound waves can not only cause adsorption forces such as van der wals and electromagnetic attraction to loosen their grip, but also can generate hydroxyl radicals on their own directly from water molecules. There also is good evidence of their ability to dislodge material from surfaces, and the increase in rates of flow and diffusion within micropores, sometimes by a factor of a million. I propose the addition of distributed ultrasonic transducers into the treatment process to help dislodge the pesticide molecules form their labyrinthine enclosures where they can possibly reach the reactant molecules or even generate oxidants deep within the

nanopores of the clay matrices. This process was tested here on a bench scale in the laboratory, using source material from a contamination site in Florida.

3.0 Site Background

3.1 Site Background And Conditions

A former pesticide application vehicle maintenance facility is located in Orlando, Florida (see Figures 1 & 2). It is situated in an industrial park area, with a railroad track forming a southern boundary and a warehouse complex along the eastern edge. The slope of the site encompasses about a 2 1/2 foot drop towards the southeastern corner, where there is a small retention pond separated from the warehouse area by a grassy ridge, and a drainage ditch on the other side of this. Soil materials include a variety of fill materials such as coated sand, machine-compacted silty sand and suspected gravel overlying a confining clay layer. Original soil survey maps list the area as Smyrna Fine Sand. Currently another pest control company maintains a service facility here, but the legal obligations are falling upon the original owners.

In 1999 the original owners contracted to have the oil and water separator (OWSP) and associated piping removed (see Figure 3), and the floor drains were sealed with concrete. During the work an environmental assessment was carried out which revealed a high level of the major OCP contaminants aldrin and dieldrin in the upper layers of soil and in the groundwater surrounding the tank location (see Figure 4). Levels of dieldrin as high as 38 μg/L (parts per billion or ppb) have been detected in the monitoring well MW-1, placed at the location of the old OWSP[7].

It is thought that since these levels can rise and fall with the groundwater levels, the dieldrin is being leached into the groundwater from the soil during periods of rain and subsequent higher water levels. (See Figure 5)

4.0 Selection of Remedial Technologies

The most direct and straightforward method used to clean up soil is to remove it, then transport to either a specialized treatment center or to a special landfill depository. For the cleanup of remaining contaminated soil and the groundwater on the site, there are a number of available technologies that are useful depending on the conditions at the sites as well as the ultimate cleanup goals to be met. These methods include various degrees of chemical oxidation, reductive dehalogenation, bioremediation and phytoremediation. The resources describing the various methods for cleaning up OCP-contaminated soils are listed in the endnotes, with some general reviews for oxidative methods.[8,9,10,11,12]

Treating the contamination by reductive dehalogenation requires the addition of sulfur or metal based reagents, but this is generally less acceptable to State regulators. Phytoremediation is ruled out due to the industrial use of the primary site, since the owners wish to continue doing business on the site. Bioremediation was also

considered, which utilizes bacteria to process the pesticides[13]. The fact that it is still not a rapid or complete method to remove chlorinated pesticides eliminates this as a method[14].

The chemical oxidation alternatives are the only current practical technologies in many instances for performing in-situ pesticide cleanup of soil and water. Since chlorinated organics are very stable compounds, the more chlorine saturation per molecule, the harder it is to get them to react with an oxidizer. Advanced Oxidation Technologies are any systems that produce hydroxyl radical, one of the strongest oxidizers known. There are a number of these techniques available, and the most common methods are Fenton's-type reactions (using hydrogen peroxide and iron), persulfate oxidation, permanganate oxidation, ozone, hydrogen peroxide, ultraviolet light, EN Rx proprietary two-part system, and combinations of some of these.[15]

The hydrogen peroxide and persulfate oxidation systems were examined for one of these sites, as these are two of the least expensive means of generating advanced oxidations. However, the reagents active very quickly, generate excess heat and finish their reactions in a matter of hours, thereby not having time to penetrate deeper into the soil matrix and give lasting residual effects (see Figure 5). Persulfate would also leave excess sulfate in the ground which is more troublesome than the slight excess of sodium and chloride that EN Rx would leave.

The methods which introduce sulfur or metals were eliminated due to State objections as mentioned above, and ultraviolet light and ultrasound are considered more appropriate for ex-situ systems. The EN Rx system was compared with another leading system called Regenox by the Regenesis company (www.regenesis.com), which utilizes hydrogen peroxide activated by iron in solution. They claim to have a slower activation rate than typical Fenton's reagents, which is advantageous by way of eliminating heat which can cause deformation of the soil structure. Besides the addition of iron to the ground, the system was found to be less reactive than EN Rx, more dangerous to handle, not as long lasting for residual action (30 days), and at approximately $60,000 for a single treatment at the site would be twice the cost to utilize.

EN Rx has the advantages of introducing no heavy metals or other objectionable end products underground, has a slow activation rate to allow further penetration after injection and longer residual action (up to 90 days), has a surfactant component to allow further penetration as well as some coating loosening, is safer and easier to apply, and has the best price for treatment at about $30,000 for the first study site. The treatment can be performed as an injection as well as an in-place pump-and-treat to reach additional groundwater, soil and sediments below the area where the soil has been removed.

EN Rx can be formulated in two ways: with hydrogen peroxide as the oxygen source, or with a slightly more expensive singlet-oxygen source, SSO. This proprietary ingredient generates an oxidizing solution that is claimed to be as strong as fluorine, as seen in the following table:

Oxidant	Oxidation Potential, eV
Fluorine	3.1
EN Rx Compound	3.1
Fenton's Reagent	2.8
Ozone	2.1
H_2O_2	1.7
Chlorine	1.4

4.1 Assessment And Effectiveness Of EN Rx

The chemox treatment system chosen for this pesticide site was looked at for reliability, efficiency, ease of use, cost, speed of remediation, residual compatibility, and State of Florida acceptance. EN Rx was chosen because there is no metal addition as with a Fenton's reagent, the redox potential was higher than any other competing system, thereby giving it a better chance for success, it operates at ambient pH levels without mineral acidification being necessary, the addition of an organic surfactant allows some 'loosening' of the soil absorbed OCPs[16], and the slow activation and release of the hydroxyl oxidant permits the treatment to penetrate farther into the soil matrix. The State of Florida's permission to use the system requires the tracking of sodium and chloride, the two administered chemical species in high initial concentration in the treatment, which should be eventually diluted to acceptable levels as time passes and rain events provide fresh water to the ground.

4.2 Special Equipment Or Techniques For This Proposed Bench Test

I proposed the following bench-scale test for this research project: The assumption is made that soils being treated, whether they are *in situ* or *ex situ*, will need to be saturated in order to pass adequate amounts of ultrasound into the matrix. To this end I devised a bench scale test apparatus (Figures 7 & 10) which provides a number of equally-sized soil samples to be treated with both EN Rx and ultrasound.

The apparatus consists of an ultrasonic cleaning bath and a support stand holding a Plexiglas plate supporting up to eight 125-mL Erlenmeyer reaction flasks. These flasks have been chosen for the best possible transmission of ultrasound from the bottom of the bath to the sample through a flat surface. They were stoppered loosely to allow any off-gassing of water vapor, O_2 or CO_2 produced by the reactions. Because ultrasonic baths cause an increase in temperature, the control samples were kept in a water bath with a temperature maintained to that of the ultrasonic bath by means of a recirculating pump.

Because of the affinity of the target compounds for the soil structure and possibly the glass containers, extra steps were taken to insure that each sample for analysis had been initially weighed accurately, and the reaction flask was submitted as the sample container itself. Further details of the experimental setup were coordinated

with ENCO to provide the most consistent results possible. Quantitative laboratory techniques were used throughout the procedures.

4.3 Calculations

Reaction of organochlorine pesticides with advanced oxidizers (in this case from sodium peroxide) will proceed to "mineralization" as follows:

$$C_xH_yCl_z + Na_2O_2 \rightarrow CO_2 + H_2O + Na^+Cl^-$$

For the oxidation to proceed to completion, all oxidizable material in the sample must be reacted. The vast majority of oxidizable material in this sample is going to be the TOC, as determined in the initial sample set. For the Swale 0-4' sample used, the TOC by the Walkley Black Method was reported as 2000 mg/Kg dry, equivalent to 0.2% carbon. In comparison, the total OCPs determined were less than that by a factor of at least 200. Therefore, an excess of oxidizer was determined using this organic carbon figure. As calculated using methane as the organic and hydrogen peroxide as the oxidant, the balanced equation is:

$$CH_4 + 4\ H_2O_2 \rightarrow CO_2 + 6\ H_2O$$

Since 4 moles peroxide must be used to oxidize one mole of carbon, the concentration of peroxide in the reactant must be approximately 4 times that or 0.8 %.

EN Rx states that their SSO is equivalent, on a weight per weight basis, to 35% hydrogen peroxide solution. Therefore, the concentration of the SSO reagent must be at minimum 0.8% ÷ 0.35 = 2.3%. By doubling this concentration it was hoped to have plenty of excess reagent to consume all carbon and organochlorine compounds within the samples, yet not make it overly reactive and tending to develop excess gas and heat. An example was presented by the engineers of a remediation site where the client had insisted upon a 6% mixture (against the advice of the manufacturer), which subsequently caused excess heating in the mixing vessel and overpressurized the injection system. Therefore, rounding up, a value of 5% was determined appropriate for this experiment.

4.4 Procedure

Two sources of aged pesticide-laden, somewhat clayey soils from the site, one from near the hottest well MW-1, and one from the swale area, were each well-mixed, and separate samples sent to the lab for analysis by EPA method 8081A. Organic content was determined as TOC to offset the reagent consumed by carbon. During the time before the results were known, the apparatus was constructed and set up.

A 5% solution of EN Rx reagent was prepared as follows: 25.00 grams of SSO reagent was slowly added to DI in a 500 mL flask with stirring. After dissolving, 10% of that amount, or 2.50 grams of the activator Synergist

D was added and dissolved. DI was added to bring up to volume, and then allowed to stand for 2-3 hours to begin activation. EN Rx reagent was used at a dosage considered adequate to adequately treat any pesticide or organic carbon (which will also consume reagent), and to minimize foaming due to the effect of the sonication. Various parameters such as temperature, pH, conductivity, DO, and ORP was measured in the oxidizer liquid at regular intervals (Figures 8 and 9). Loss of oxidizing activity as indicated by these measurements may call for increased dosing in future studies.

Equivalent samples of approximately 30 grams were weighed to the nearest 0.01 gram and then added to each 125 mL glass Erlenmeyer flask. 25 mL EN Rx was added to select treatment vessels to simulate a well-saturated soil, and 25 mL distilled water was added to each non-reagent sample. One flask had no reagent or other treatment except warming, to act as full control. Some of the sample vessels were then suspended in the ultrasonic bath to provide an initial 2.5, 10, or 80-minute continuous ultrasound treatment and resultant warming. All the samples were swirled at 5-minute intervals to maintain adequate reagent contact.

The 2 flask holders were able to hold 8 samples each, so the full setup was as follows:

SAMPLE #	1	2	3	4	5	6	7
Reagent added	-	-	-	-	EN Rx	EN Rx	EN Rx
Initial treatment	Warming + swirling	Ultra sound 2.5 MIN.	Ultra sound 10 MIN	Ultra sound 80 MIN.	-	-	-
Label	FULL CONTROL	2.5 MIN. ULTRA-SOUND ONLY	10 MIN ULTRA-SOUND ONLY	80-MIN. ULTRA-SOUND ONLY	2.5 MIN. EN Rx-ONLY	10 MIN EN Rx-ONLY	80-MIN. EN Rx-ONLY

SAMPLE #	8	9	10	11	12	13
Reagent added	EN Rx	EN Rx	EN Rx	EN Rx	EN Rx	EN Rx
Initial treatment	-	Ultra sound 2.5 MIN.	Ultra sound 10 MIN	Ultra sound 80 MIN.	-	Ultra sound 80 MIN.
Label	80-MIN. EN Rx-ONLY (DUPLI-CATE)	2.5-MIN. ULTRA-SOUND + EN Rx	10-MIN. ULTRA-SOUND + EN Rx	80-MIN. ULTRA-SOUND + EN Rx	1-WEEK EN Rx-ONLY	1-WEEK ULTRA-SOUND + EN Rx

The setup allows three types of controls for the soil sample: Untreated except by warming, oxidizer and warming only, and ultrasound with warming only. The remaining flasks will have each soil sample receiving extended lengths of oxidizer treatment time. See figures 10 and 11.

At the end of the treatment period, a small amount (5 mL) of pesticide-grade methanol was added to consume excess oxidizing reagent and stop further reactions.

4.5 Analyses

Samples were sent to ENCO Laboratories in Orlando for analyses of OCPs in soils by EPA Method 8081A. Extraction procedure 3550C was performed prior to analysis. Although this is an ultrasonic digestion and extraction method, there is not expected to be any degradation of analytes because this is carried out in solvents over a very short period of time.

Samples were analyzed by a modified 8081A method, yielding results as if for a saturated sediment. The result was expressed according to the dry weight of the original approximately 30-gram sample mass.

The data from the full control was used as a baseline for the analytical results. The EN Rx only control shows the amount of remediation to be expected with the chemical alone, and the sonication control will tell if any of the contaminants are being degraded by this method alone. There are remediation methods that rely on the generation of hydroxyl radical by ultrasound, but in this research we will attempt to minimize this to give preference to the expected microstreaming and mixing effects of lower intensity and lower frequency ultrasound. Another effect to watch for is any soil structure degradation which will make the end product less usable even if OCP contaminants can be removed.

4.6 Research Results

Results from the lab were received and tabulated (Figure 12). Due to difficulties with providing precise 2.5 and 10 minute treatment intervals on selected flasks, and given the variation in experimental results on these samples, only the 80-minute and 1-week treatment sample results were used (Figures 13 & 15). The planned re-treatment of two flasks after one week proved difficult to ensure similar reaction conditions as the first week, so it was decided not to run these flasks for analysis. Supernatant was saved from each flask for future analysis, but in the results all combination treatment flasks were treated equally so this was deemed not to be a major factor.

Results from these controls and the various multiple treatment setups were tabulated and plotted for each of the conditions varied in the tests. Conclusions were drawn from the controls to determine the amount of pesticides that may have diffused out of the soil matrix from being treated over that time period, concerning the efficiency of the EN Rx at attacking pesticide adsorbed onto the soil matrix, and the additional benefit from the addition of sonication to the treatment.

4.7 Conclusions

It can be seen from the analytical results that there seems to be a definite advantage in using ultrasound prior to or in conjunction with EN Rx. The reduction of target analytes after 80 minutes of ultrasound with reagent is around 26%, and after ultrasound-treated material is left for a week in the reagent, the reduction averages 44%, much greater than the week-long reagent-only treatment at around 19%.

An unexpected observation was made that may shed light on the fact that ultrasound-treated soil continues to lose pesticide much faster after only 80 minutes of sonication. In the photographs of the week-long samples (Figure 14), a large amount of foam appears for a few days that does not appear in the un-sonicated flasks. It may be that the initial sonication has 'scrubbed' the soil particles cleaner, allowing them to react with the slowly-generated oxidizer more quickly than those not so treated. This will have implications in designing any large-scale remediation process, in that sonication will only be an initial or repeated treatment, instead of a much more involved (and expensive) continuous treatment.

Future studies will have to address the issues of frequency, power, and other variables to give the optimum sonic streaming and mixing parameters. Additionally, aluminum foil ultrasound efficiency testing may be done with the sonicators prior to the main EN Rx reaction runs to determine optimum levels without incurring excessive hydroxyl generation, agglomeration and/or soil structure degradation.

Further avenues of research will incorporate other means of increasing diffusion rates while soils are exposed to AOPs, based on recent advances in electrokinetic soil treatments[17,18,19,20]. Although the majority of these methods rely on removing contaminants through electrostatic motility forces, I foresee advantages to using alternating currents to move either the contaminants in and out of pore structures, or to transport the EN Rx-generated hydroxyl radicals themselves.

4.8 Acknowledgements

The author is extremely grateful for the support of Laboratory Manager Matthew Foti, Russ Erikson, and the rest of the analytical team at Environmental Conservation Laboratories, Inc. in Orlando, Florida. Also instrumental in the success of this study were the scientists and engineers at MACTEC E & C, Newberry Florida in Eric Arenberg, Ed Kellar, Lance Robinson, Chris Mickler and others, and the assistance of Professors Kizza, Lena Ma, Dr. Bloomquist, and Dr. Jawitz at the University of Florida. Additional thanks goes to K. Pace , E. Piatt and of course my highly supportive wife Sara.

5.0 Appendices

5.1 Figures

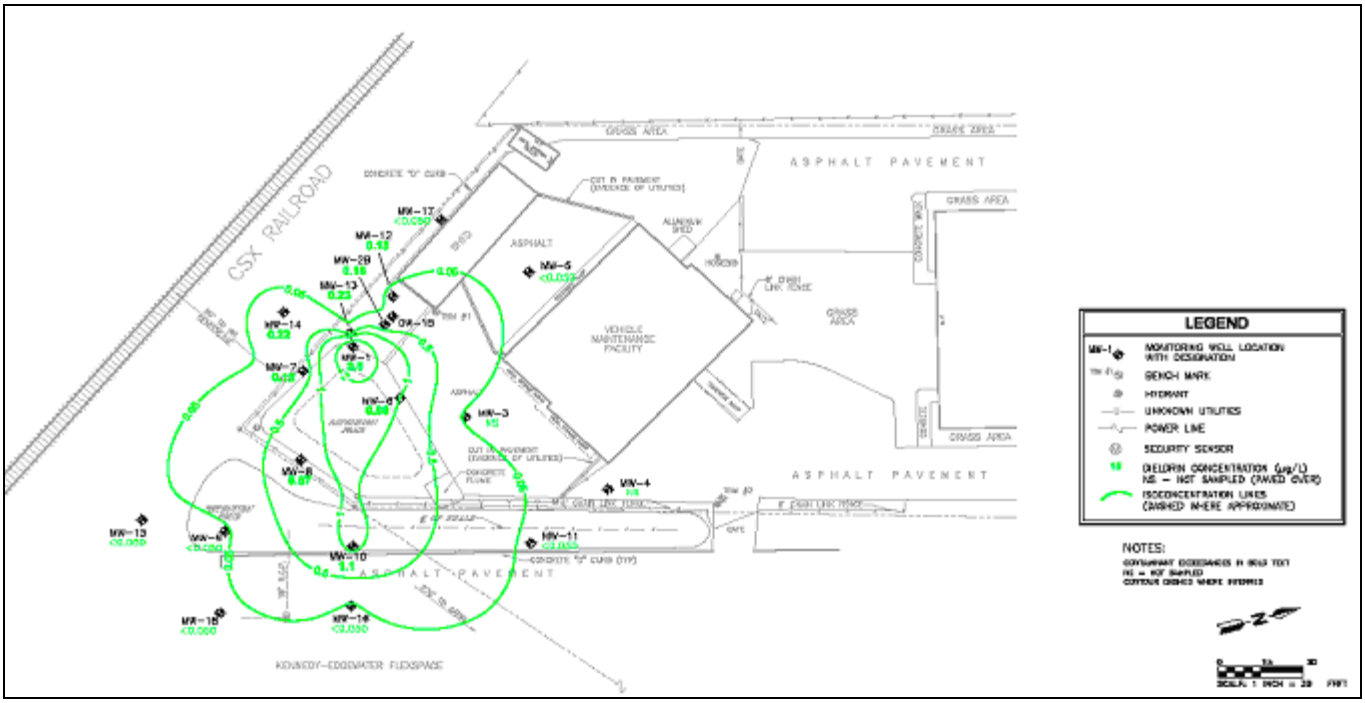

Figure 16: Groundwater Dieldrin plume at site

Figure 17: Google Earth aerial photograph of site, showing continued use as vehicle maintenance facility

Figure 18: Excavated drains at site

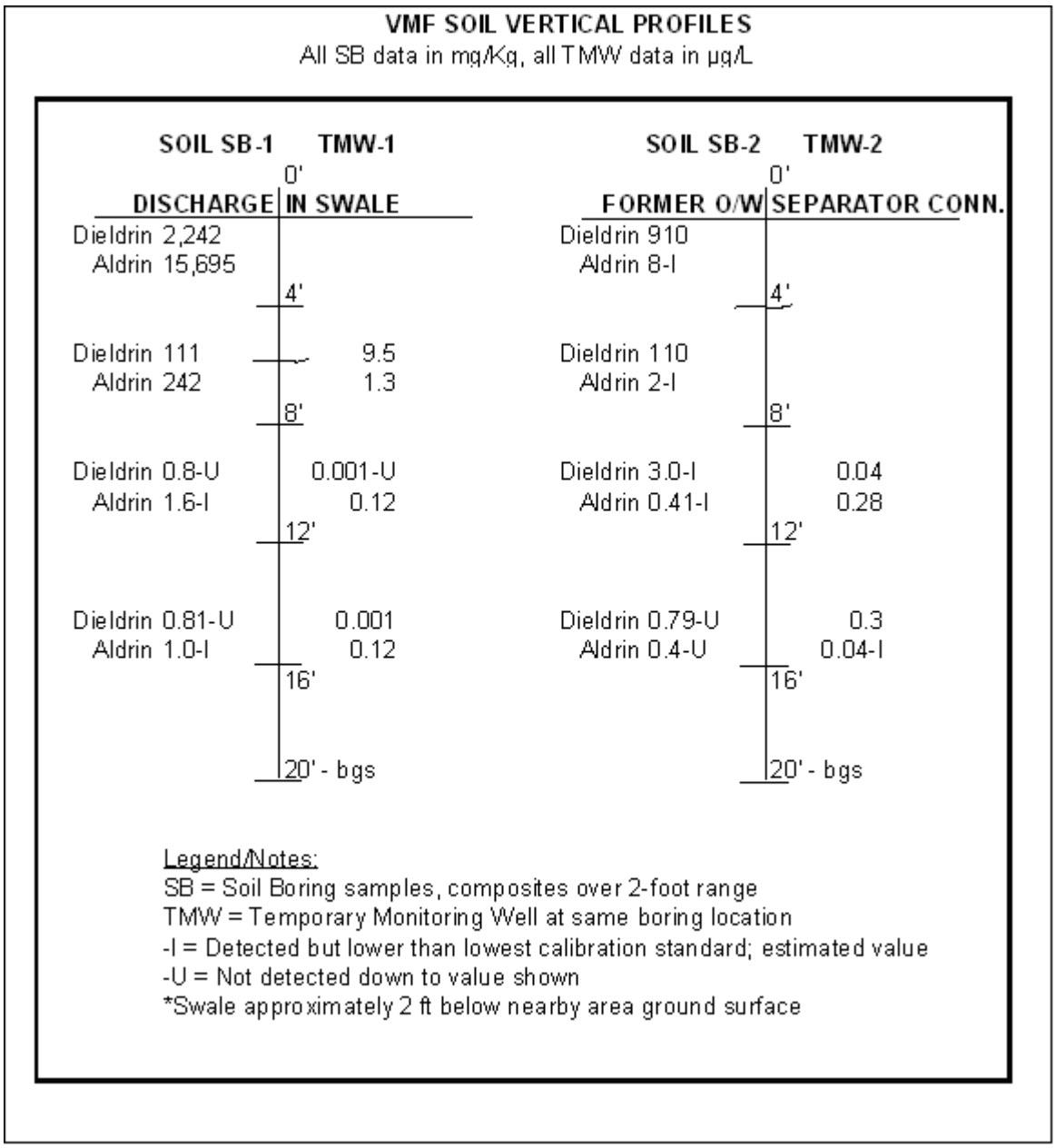

Figure 19: Soil and water analysis at two 'hottest' locations on site

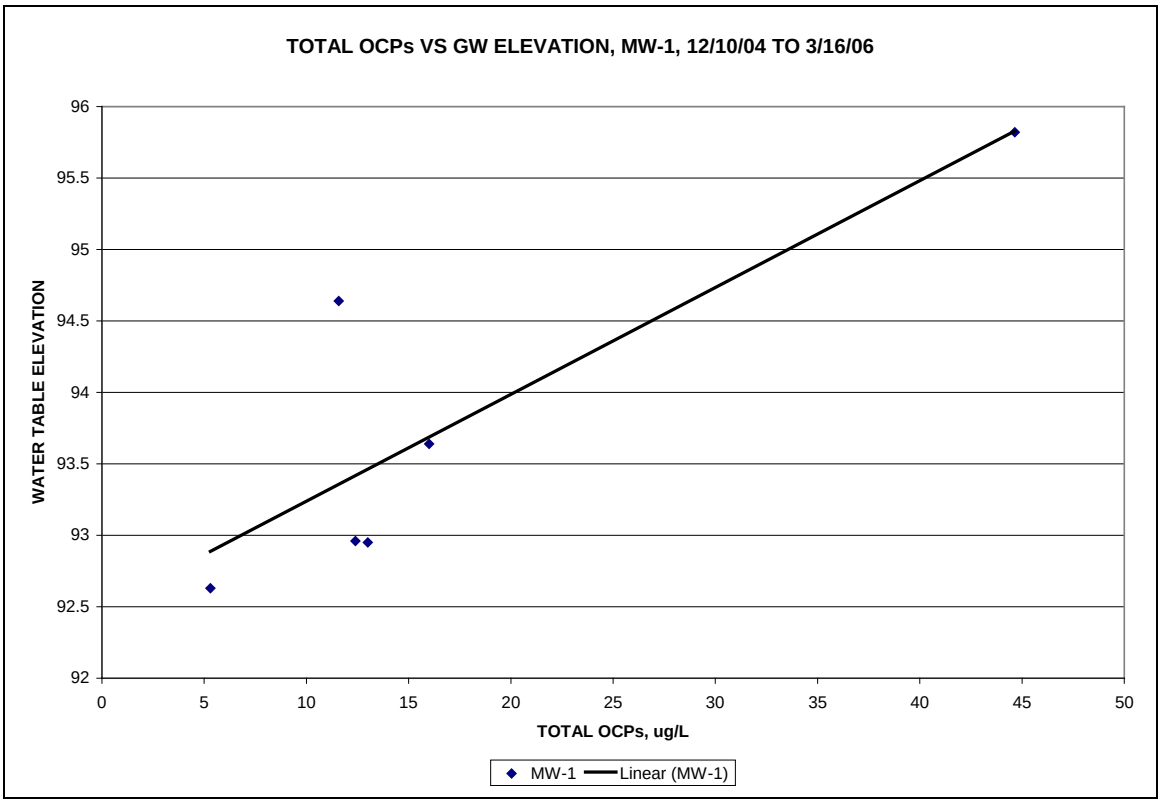

Figure 20: Possible correlation of pesticides in groundwater with change in water table elevation

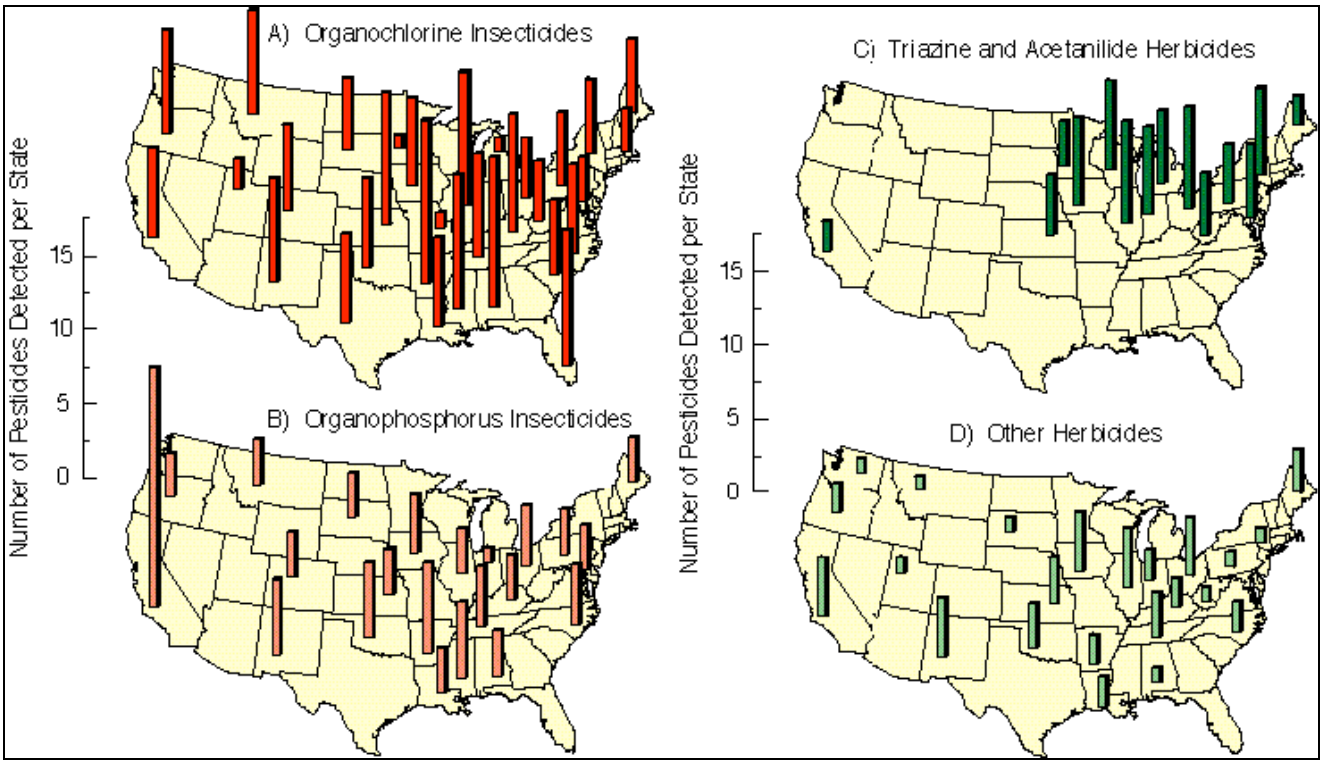

Figure 21: Map of various pesticide contamination detections by state across the country

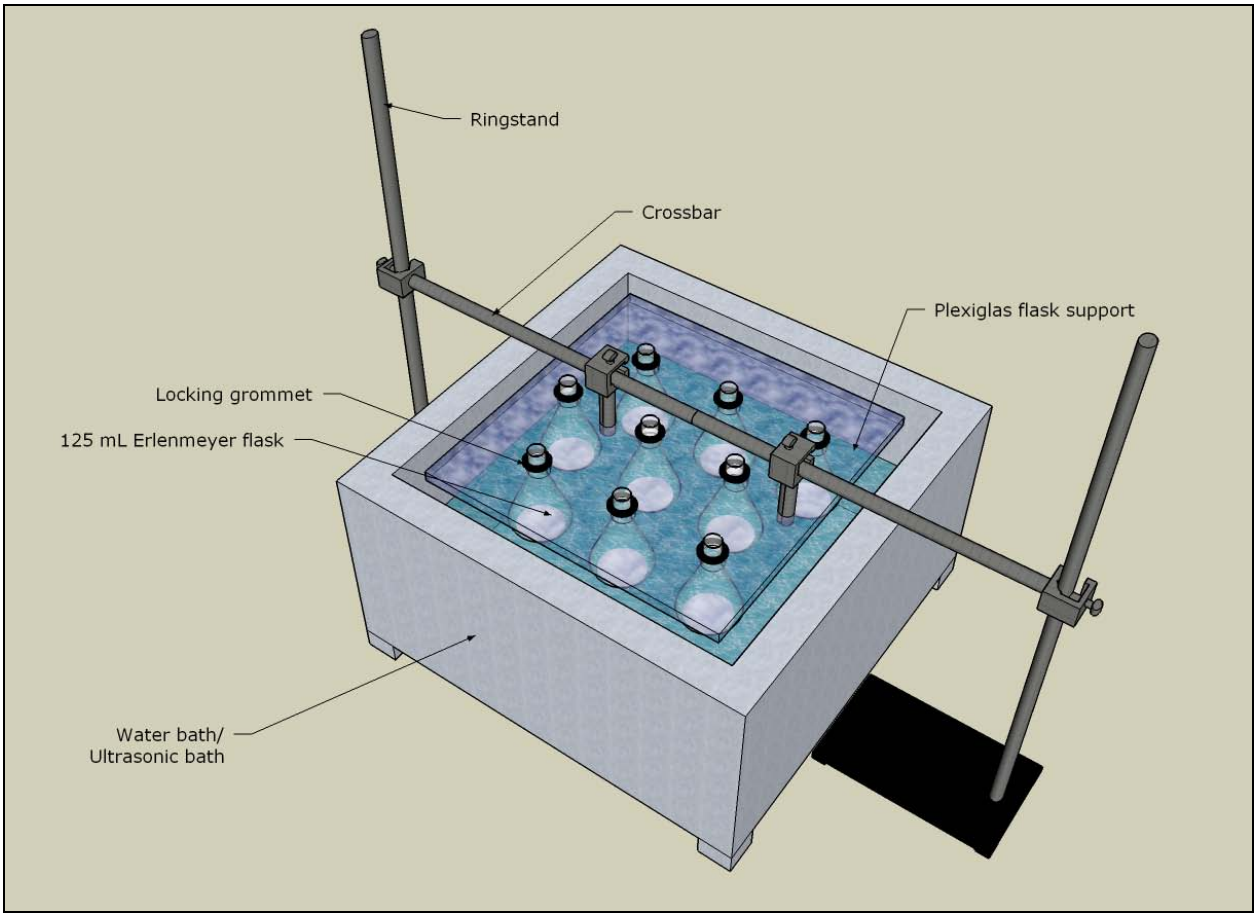

Figure 22: Experimental setup

EN Rx REAGENT MONITORING									
Batch #	Date prepared	Date measured	Age of batch	Temperature	Specific Conductance	DO, Percent Saturated	DO, mg/L	pH	ORP, mV
3	4/2/2009	4/3/2009	1	24.7	41797	500.4	35.67	10.54	3.4
3	4/2/2009	4/5/2009	3	24.2	43715	363.1	25.92	10.3	12.9
1	3/21/2009	3/26/2009	5	24.61	41695	402.8	28.79	10.26	-11.5
2	3/26/2009	4/1/2009	6	23.25	42005	199.3	14.57	10.57	0
2	3/26/2009	4/3/2009	8	24.47	42205	150	10.52	10.6	7.6
1	3/21/2009	4/3/2009	13	24.52	42150	124	8.88	10.57	10.4
Above recorded with a YSI Model 556 multiparameter water monitoring meter									
Notes: Flask #24 after EN Rx treatment 3 days.									
ORP suppression due to high pH									

Figure 23: 5% EN Rx solution measurements

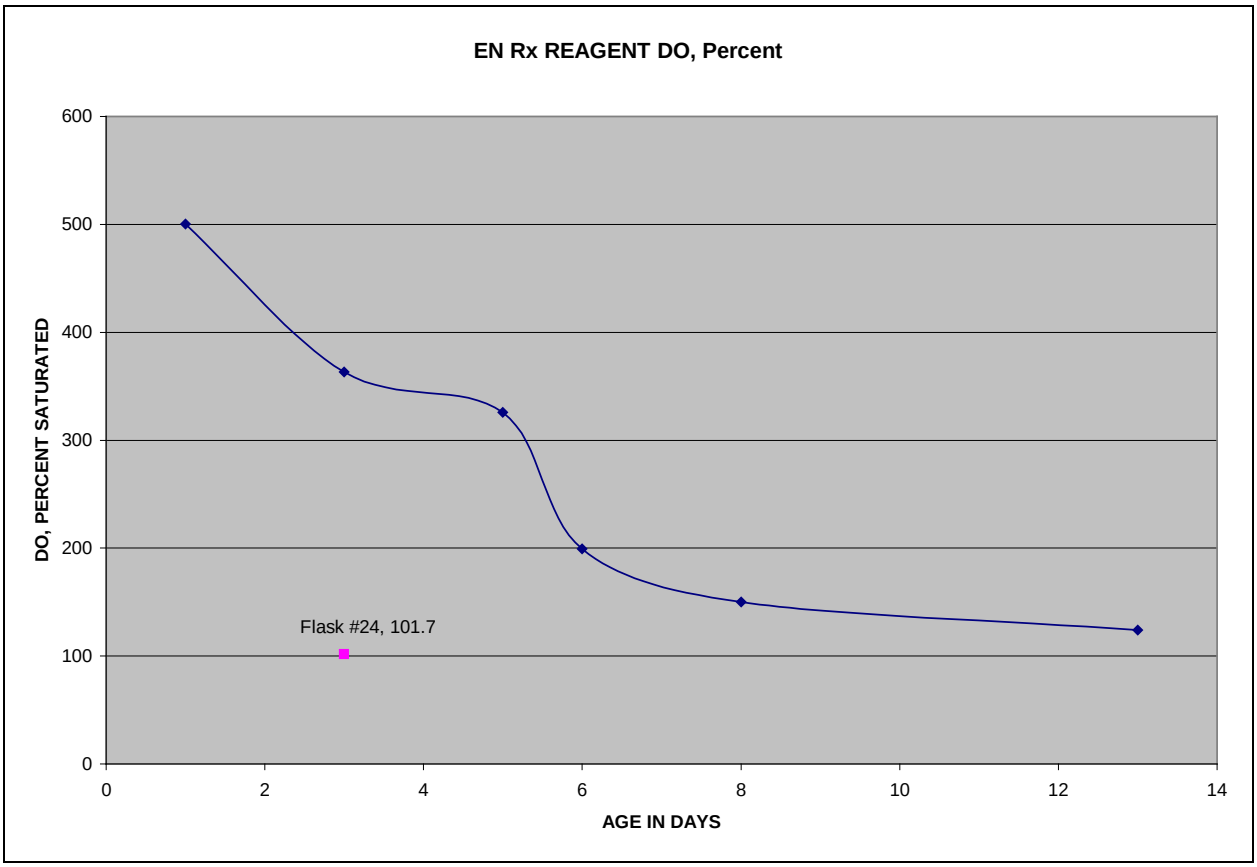

Figure 24: Change in DO in pure 5% EN Rx solution over time, plus one measurement taken in a treated flask

Figure 25: Reaction in progress in ultrasonic bath, note control (no EN Rx) on left

Figure 26: View of samples after 80 minutes treatment; ultrasound on left

LABORATORY RESULTS									
TREATMENT	#	ALDRIN	DIELDRIN	ALDRIN+ DIELDRIN	% ALDRIN + DIELDRIN REDUCTION	CHLORDANE α	CHLORDANE γ	CHLORDANE α + γ	% CLORDANE α + γ REDUCTION
FULL CONTROL	1	0.34	0.98	1.32	NA	0.68	0.34	1.02	NA
2.5-MIN. ULTRASOUND ONLY	2	0.28	0.90	1.18	10.6%	0.61	0.33	0.94	7.8%
10-MIN. ULTRASOUND ONLY	3	0.27	0.87	1.14	13.6%	0.59	0.32	0.91	10.8%
80-MIN. ULTRASOUND ONLY	4	0.31	0.93	1.24	6.1%	0.66	0.33	0.99	2.9%
2.5-MIN. EN Rx-ONLY	5	0.33	0.82	1.15	12.9%	0.52	0.27	0.79	22.5%
10-MIN. EN Rx-ONLY	6	0.43	0.96	1.39	-5.3%	0.60	0.33	0.93	8.8%
80-MIN. EN Rx ONLY	7	0.25	0.84	1.09	17.4%	0.57	0.32	0.89	12.7%
(DUPLICATE)	8	0.27	0.83	1.10	16.7%	0.57	0.31	0.88	13.7%
2.5-MIN. ULTRASOUND + EN Rx	9	0.22	0.70	0.92	30.3%	0.48	0.27	0.75	26.5%
10-MIN. ULTRASOUND + EN Rx	10	0.24	0.75	0.99	25.0%	0.53	0.28	0.81	20.6%
80-MIN. ULTRASOUND + EN Rx	11	0.23	0.73	0.96	27.3%	0.50	0.26	0.76	25.5%
1-WEEK EN Rx ONLY	12	0.31	0.75	1.06	19.7%	0.55	0.28	0.83	18.6%
1-WEEK ULTRASOUND + EN Rx	13	0.19	0.54	0.73	44.7%	0.38	0.19	0.57	44.1%

Figure 27: Laboratory results

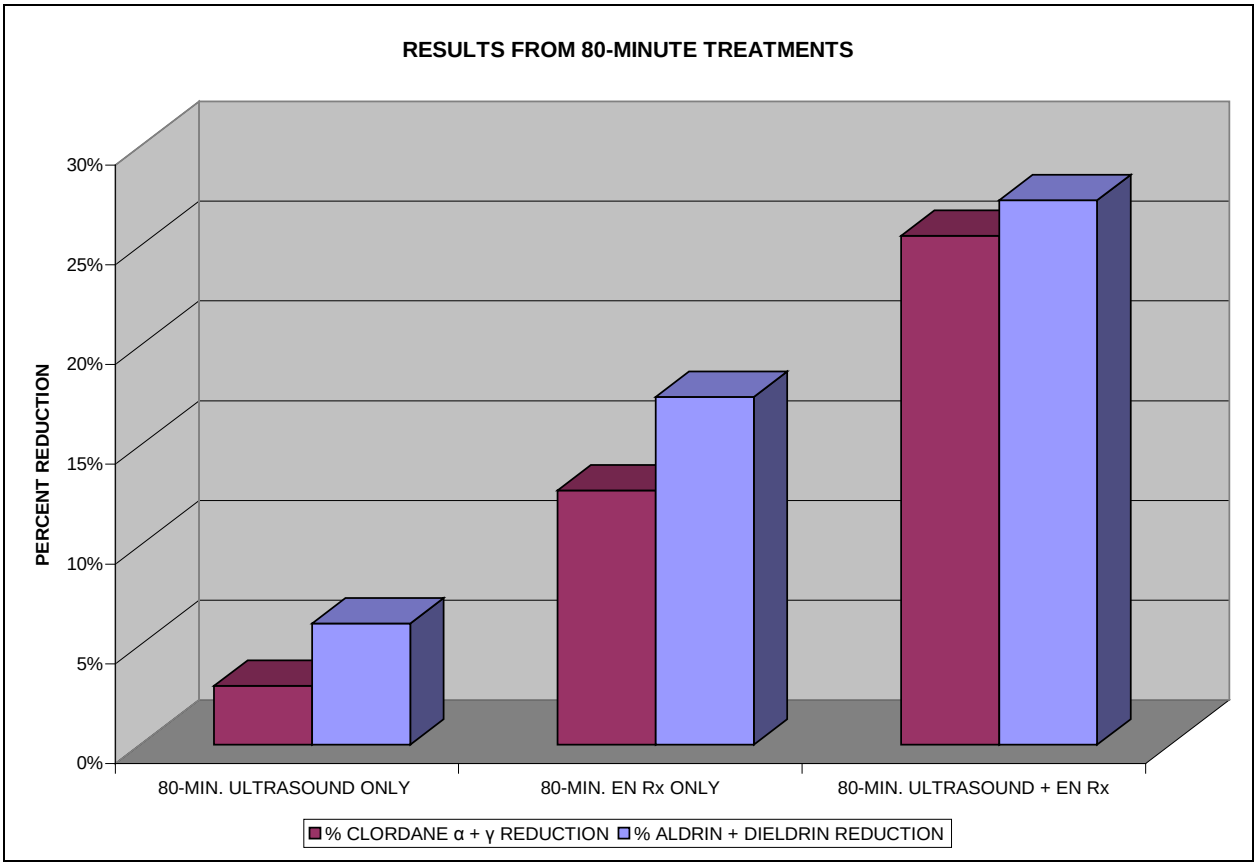

Figure 28: Results for various 80-minute treatments

Figure 29: Sequence of unexpected reaction foaming; from upper left, after 2, 3, 5, and 7 days respectively

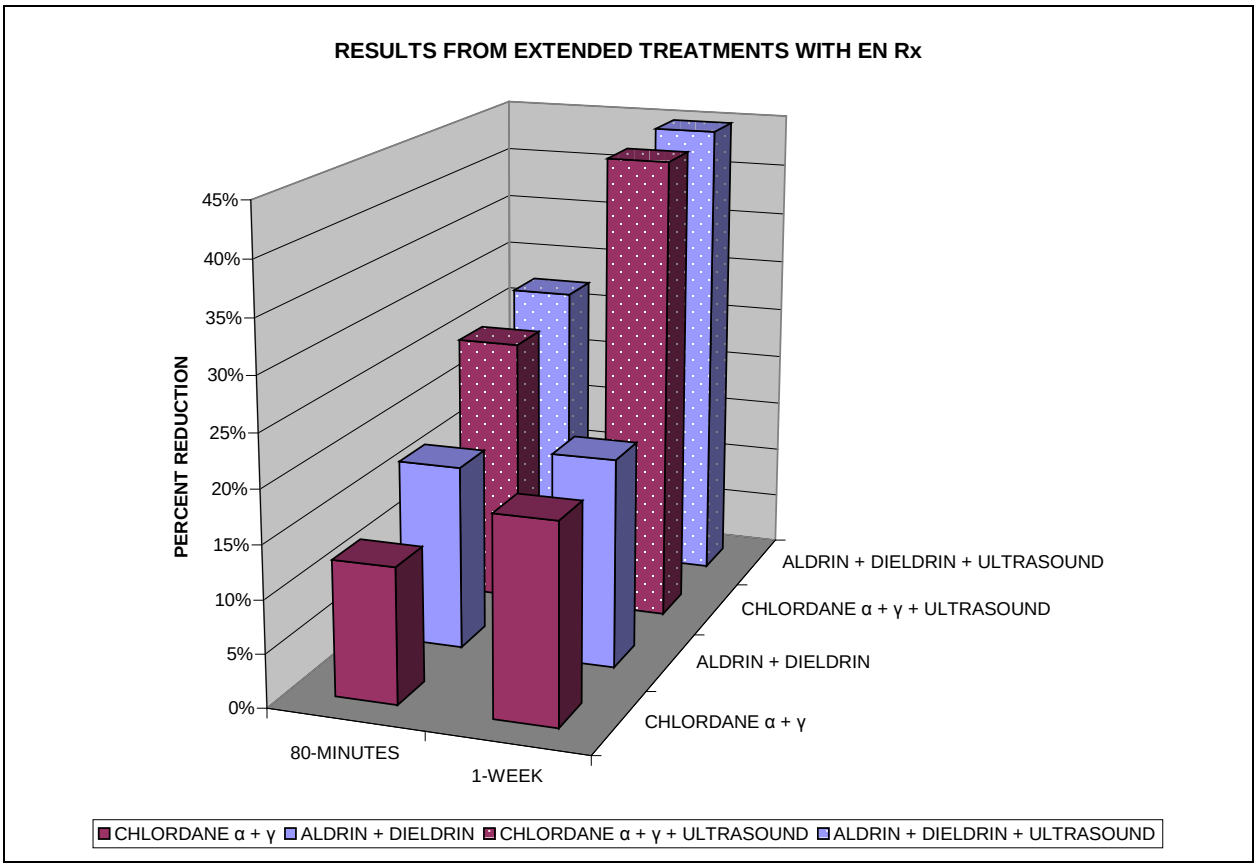

Figure 30: Results for various 80 minute and 1-week treatments

5.2 Lab Reports

Please see attached PDFs

5.3 End Notes

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