

A NOVEL DETOXIFICATION APPROACH: PHOTO-OXIDATION OF VOLATILE ORGANICS IN GROUND WATERS OF PUERTO RICO

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ABSTRACT

Photocatalyst oxidation is an emerging remediation technology for the destruction of organic contaminants in our precious ground water resources. An experimental study was undertaken on the viability of utilizing UV (below 390 nm) photo-laser-anatase titanium dioxide (TiO₂) catalyst for reducing the concentrations of chloroform and carbon tetrachloride in spiked distilled water at the laboratory scale.

The study demonstrates the viability of utilizing the innovative UV-laser-anatase technology for the destruction of chlorinated solvents into environmental friendly end products. Low ppm level of catalyst loading was found to be optimum for the direct degradation of ppm levels of chloroform and carbon tetrachloride into low energy molecules. The data also suggest fast reaction kinetics where photo-catalytic oxidation of the test chemicals and reduction of metal ions may be taking place simultaneously.

Introduction

Industrialization of Puerto Rico has brought its adverse effects in the form of contamination of our precious underground water resources. Puerto Rico has nine known superfund sites. One of the worst known case is the Puerto Rico's Aqueducts and Sewer Authority (PRASA) drinking water supply wells in Barceloneta where the underground water resources got contaminated with the chlorinated hydrocarbons from the leaking buried tanks belonging to some of the industries established in the area. The revised Superfund Amendment and Reauthorization Act (SARA) of 1986 asks explicitly for permanent on-site clean up of the contaminated areas, and especially of the underground water resources which supplies potable water to the communities. Air stripping methodology under the Superfund program is being utilized to get rid of the contaminants from these wells. This approach is extremely expensive since the water is pumped out to the ocean, and also the volatile organic contaminants remain in the environment.

Heterogeneous photocatalysis oxidation by semiconductor powders¹ is an emerging new remediation technology for the destruction of volatile organic contaminants, and also for the effective removal of metals like iron and manganese from the contaminated ground water. In this innovative technology, organics are destroyed by photo-catalytic oxidation while metals are removed by reduction at the same time. Thus it becomes necessary to explore this efficient alternative to clean our underground contaminated water supplies with the aim of preserving the quality and quantity of our precious water resources.

Degradation of organic contaminants present in an aqueous suspension of titania

has been carried out with near-UV radiation^{2,3,4}. Ultraviolet radiation below 390 nm excites valence-bond electrons in photo-chemical stable TiO₂ (anatase) particles, and the resulting hydroxyl⁵ free radical species can either combine, produce thermal energy, or interact (oxidize) with the organic contaminants present in the external environment to produce environmentally friendly products⁷. Alternately, the electrons produced during this process can also reduce dissolved metals having proper reduction potential.

The propose of this study was to explore if photochemical oxidation^{6,7} destructive innovative technology (never used in Puerto Rico) may be utilized for regenerating our contaminated drinking water natural resources. Precisely, it involved the study on the viability of utilizing UV (below 390 nm) photo- laser-anatase titanium dioxide (TiO₂) catalyst for reducing the concentrations of chlorinated hydrocarbons, especially chloroform (CHCl₃) and carbon tetrachloride (CCl₄) in spiked distilled water at the laboratory scale.

Materials and Methods

Batch experiments were performed in a custom made (6x6x6") all quartz bath. The chlorinated solvents (CHCl_3 and CCl_4) and titanium dioxide catalyst, purchased from certified vendors, were of reagent grade quality. Deionized water having specific conductance of <3 umhos was used for preparing test solutions. One liter of the test solution containing known concentrations (ppm levels) of the chlorinated solvents and ferric chloride was placed into the quartz tank. The test solution was fortified with a known concentration of the photo-catalyst, and the contents of the reactor covered with a glass plate were magnetically stirred at a slow speed throughout the experiment. The solution was left to reach equilibrium (~10 minutes) before irradiation. After equilibration, a test sample was taken out for determining the total initial concentration of the analytes in the water sample. Before chromatographic analysis, the sample was filtered through 0.2 um sterile (Dualex, Millipore) filter using a laboratory syringe. A control setup was similarly prepared in a 2-liter Pyrex beaker.

The laser system for exciting the valence-band electrons in TiO_2 particles was an INNOVA-15 Argon ion laser capable of generating 9 W in "all-lines-UV" mode. Standard protocol for the utilization of the laser was followed before irradiating the test solution. The test sample was irradiated with the ultraviolet radiation below 390 nm at 3.5 W of output power for 100 minutes during each test run.

pH, dissolved oxygen content of the test solution was continuously monitored during the course of the experiment. Monitoring of the temperature of the test solution was of

prime concern since heterogeneous photo-catalytic degradation process is exothermic, and solubility of oxygen in water decreases with rise in temperature. A lower concentration of dissolved oxygen in the test solution will cause a decrease in the rate of electron withdrawal from the surface of the photo-catalyst, and thus reducing the oxidative capacity of the photo-catalyst. Standard laboratory pH, temperature and dissolved oxygen probes were used to monitor these parameters during the course of the experimental runs.

Five ml (triplicates) of the test sample was taken out of the quartz bath at ~20-minute interval for the quantification of the analytes. UV/Vis Spectrophotometric and 1-10 phenanthroline method was used to monitor the reduction in the iron concentration, and gas chromatographic peak area (standard methodology) was used to calculate the destructive efficiency of the experimental run for the organic analyte.

Results and Discussions

Metals have a continuum of electronic states whereas semiconductors possess a void energy region called the band gap where no energy levels are available to promote recombination of an electron and hole produced by the photo activation in the semiconductor solid. Once excitation occurs across the band gap, there is sufficient lifetime (nanoseconds) for the created electron-hole (e^-/h^+) pair to perform redox reactions⁹. A favorable feature of the semiconducting metal oxide is that photo generated holes have high positive oxidation potentials capable of oxidizing most organic compounds to carbon dioxide, water and mineral acids¹⁰.

Ultraviolet radiation below ~390 nm excites valance-band electrons in TiO_2 semiconductor particles suspended in aqueous phase. As shown in Figure 1, the resulting e^-/h^+ pairs can recombine, produce thermal energy, or interact with the contaminants to degrade them via oxidation-reduction reactions⁷. The holes react with water to produce high energy hydroxyl radicals. They are powerful oxidizers capable of attacking organic contaminants to produce environmental friendly low energy end-products. Also simultaneously, the electrons react with dissolved oxygen molecules to produce superoxide anions (also more hydroxyl radicals) capable of reducing metal ions having proper reduction potential.

Figure 2 demonstrates the chromatographic peak area data obtained on the oxidative destruction efficiency of laser irradiation runs carried out on individual test solutions containing 10-, 100- and 1,000 ppm levels of TiO_2 catalyst and each having 100 ppm of $CHCl_3$ and 50 ppm of ferric chloride. Reduction in the chromatographic peak area

was used to calculate the destructive efficiency of the test analyte. Irradiation of test solutions containing 100- and 1,000 ppm of the catalyst resulted in 100% and ~73% reduction in CHCl_3 concentration respectively within 80 minutes of irradiation time. High reduction in the analyte concentration in a short irradiation time reflects a fast oxidation reaction kinetics. This is supported by the data obtained with the 1,000 ppm catalyst test run where it was observed that the pH and dissolved oxygen content (Figure 3) of the test solution decreased within ~20-40 minutes of irradiating time. Also the temperature of the test solution increased from an initial value of ~22.8 °C to ~25.7 °C during ~100 minutes of irradiating time which may be attributed to the exothermicity of the fast reaction. The destruction efficiency for CHCl_3 reached ~83% after 100 minutes of irradiation time with the test solution containing 1,000 ppm of the catalyst. Only 36% reduction in the analyte concentration was observed with 10 ppm of catalyst loading for 100 minutes of UV-laser irradiation time. The results demonstrate that 100 ppm concentration level of the catalyst is optimum for the degradation of CHCl_3 utilizing UV laser radiation.

Similar results were obtained for the test solutions containing CCl_4 . Irradiation of individual test solutions (Figure 2a) containing 10- and 100 ppm of the catalyst and 100 ppm of CCl_4 and 50 ppm FeCl_3 demonstrated ~64% and ~80% reduction in the concentration of the test solvent respectively within ~120 minutes of irradiation time. Again this demonstrates that TiO_2 catalyst loading at 100 ppm level is optimum for the destruction of chlorinated solvents with UV laser radiation. Since it was observed that 100 ppm of the catalyst loading is optimum for the degradation of the chlorinated solvents, data obtained on the individual test solutions having similar concentration levels (100 ppm)

of CHCl_3 and CCl_4 and catalyst loading (100 ppm) are presented in Figure 2b. The purpose was to observe which of the two solvents degrade faster. Initially, CCl_4 concentration was found to be reduced by ~74% as compared to ~40% for CHCl_3 within ~40 minutes of the irradiation time. However, all of CHCl_3 degraded after ~80 minutes of irradiation time while it took ~100 minutes to degrade all of CCl_4 .

Gas chromatographs of the test samples taken out periodically after irradiation from the individual test solutions of both the solvents, and containing 100- and 1,000 ppm of the catalyst did not demonstrate the formation of intermediate (degradation) products suggesting direct destruction of the test analyte into environmental friendly compounds. However, chromatograms (mass spectrometer data) of the duplicate test runs containing 10 ppm of the catalyst demonstrated the formation of 2-propanone for both the solvents after ~100 minutes of irradiation time. The area under the chromatographic peak further increased by ~30% after ~120 minutes of irradiation time. This reflects that 10 ppm concentration level of the photo-catalyst is not optimum for the degradation of the CHCl_3 and CCl_4 .

Efforts were focussed on the fate of dissolved oxygen and pH during irradiation of test solution. In a typical run with a test solution containing 100 ppm of CHCl_3 , 50 ppm of FeCl_3 and 1,000 ppm of the catalyst, it was observed (Figure 3) that the initial ~20 minutes of irradiation time act as an incubation period since the dissolved oxygen content of the test solution was found to be almost constant within the first 20 minutes. It was found to decrease from ~7.42 ppm from the ~20 minutes of irradiation time to ~7.12 for ~40 minutes of laser irradiation. This decrease reflects that oxygen molecules are being

consumed as the reaction velocity increases. It was expected since the electrons produced by laser irradiation and adsorbed on the surface of the photo-semiconductor reduce dissolved oxygen molecules (electron acceptor) in aerated water into superoxide anions and produce more hydroxyl radicals to oxidize CHCl_3 at a much faster rate. Superoxide anions, in turn, may carry out photoreduction of metal ions having appropriate potential.

Similarly, pH of the test solution (Figure 3) decreased from its initial ~ 3.52 to ~ 3.39 after ~ 20 minutes of irradiation time. This reflects that the holes (h^+) produced by photo activation in the semiconductor solid particles in the initial stages may be reacting with water molecules to produce hydroxyl radicals and hydrogen ions (H^+). A slight reduction in pH (more acidic) is attributed to these H^+ ions in the initial stages. pH of the test solution demonstrates a small uniform increase after ~ 20 minutes of irradiation time. As the photo-reaction velocity increases, CHCl_3 is oxidized to CO_2 and water, and ferric ions (as ferric chloride) are reduced to ferrous ions (as ferrous hydroxide). These hydroxide ions may be responsible for the slight increase observed in the pH value after ~ 20 minutes of irradiation time.

The photoreduction of Fe(III) to Fe(II) was observed to increase at a steady rate. Visual change in the intensity of the test solution color during irradiation was noticeable qualitatively. Initial attempts to quantify these results were made using calorimetric method. Selective color development at 500 nm can be observed with high sensitivity and selectivity due to chelate formation of Fe(II) with 1,10-phenanthroline. Results are not included since only preliminary data is available.

Conclusions

1. Results obtained has demonstrated that the anatase titanium dioxide photo catalyst-laser system is very efficient for the degradation of chloroform and carbon tetrachloride (CHCl_3 and CCl_4) into environmental friendly end products.
2. Catalyst loading at 100 ppm is found to be optimum; the destruction efficiency of test solvents at 100 ppm levels in the test solutions was found to reach as high as 100 percent within ~80-100 minutes of laser irradiation (below 390 nm).
3. Gas chromatographic data of the test solutions containing 100- and 1,000 ppm of the catalyst did not demonstrate the formation of intermediate (degradation) products suggesting direct destruction of the test analyte into low energy molecules.
4. Change in the color intensity of the test solutions (visual observation) during irradiation suggests a fast reaction kinetic where oxidation of the organic solvent and reduction of Fe(III) is taking place simultaneously at a steady state.

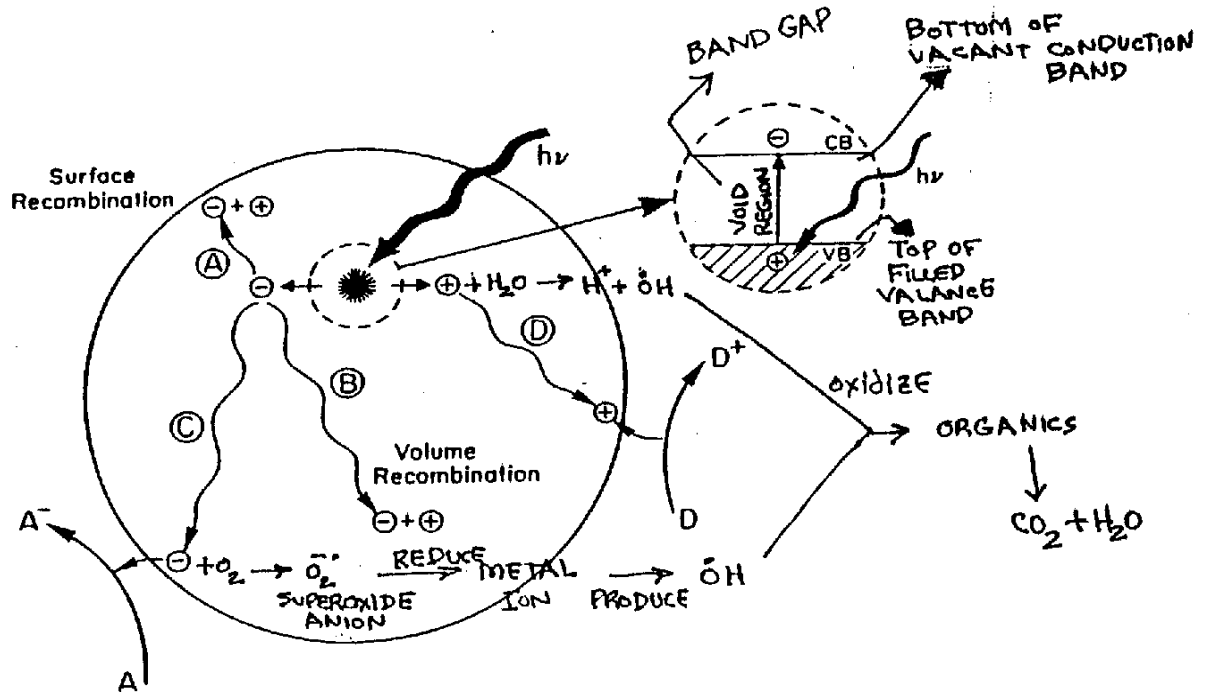
Student Participation/Presentations

An under-graduate student (José Luis Ramirez) from the Department of Chemistry was involved in running the experiments under the supervision of the investigators. The results of the work has been presented in several meetings and forums including Puerto Rico-EPSCoR and 212th National Meeting of the American Chemical Society in Orlando, FL.

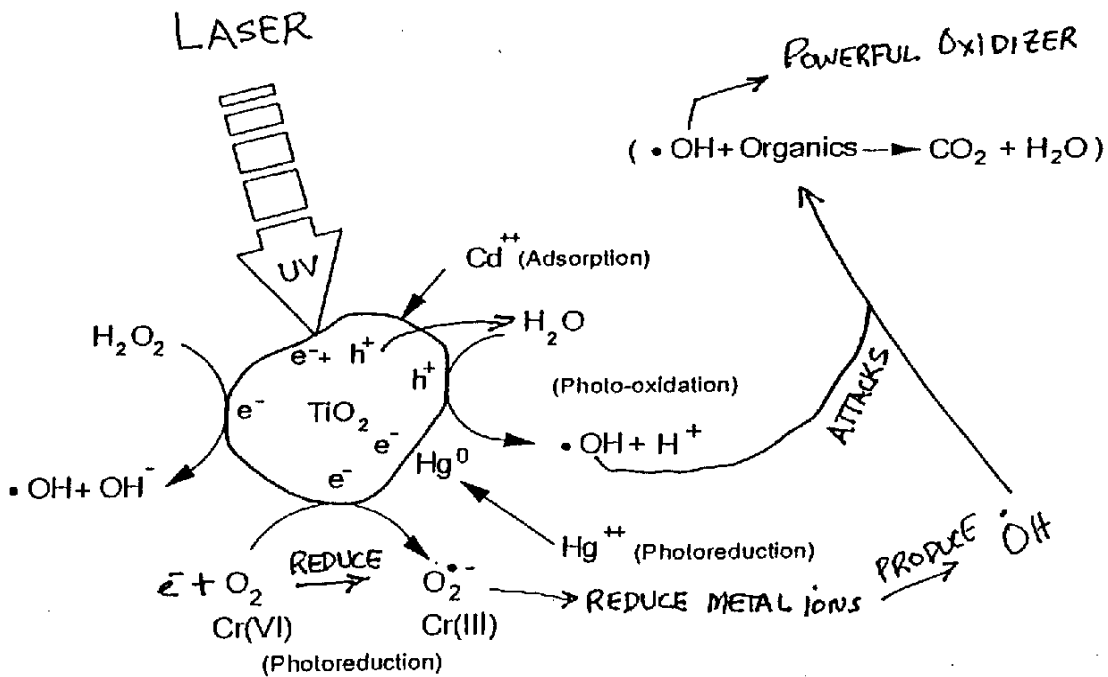
LITERATURE CITED

1. Vincenzo, A., Loddo, V, Palmisano, L.,and Schiavello, M., "Performance of Heterogeneous Photocatalyst Systems: Influence of Operational variables on Photoactivity of Aqueous Suspension of TiO₂", Journal of Catalyst, 1995, 153, 32-40.
2. Zeltner, W.A., Hill Jr, C.G., and Anderson, M.A.,"Supported Titania for Photodegradation", pp 21-28, CHEMTECH, May 1993.
3. Low, G.K-C, McEvoy, S.R., and Matthews, R.W., Environ. Sci. Technol. 1991, 25, 460.
4. D'Oliviera, J.-C, Al-Sayyed, G, and Pichat, P., Environ. Sci. Technol. 1990, 24, 990.
5. Fox, M.A., Acc. Chem. Res. 1983, 16, 314.
6. Prairie, M.R., Evans, L.R., Stange, B.M., and Martinez, S.L.,"An Investigation of TiO₂ Photocatalysis for the Treatment of Water Contaminated with Metals and Organic Chemicals", Environ. Sci. Technol. 1993, 27, 1776.
7. Prairie, M.R., Stange, B.M., and Evans, L.R.,"TiO₂ Photocatalysis for the Destruction of Organics and the Reduction of Heavy Metals", Proceedings from the 1st International Conference on TiO₂ Photocatalytic Purification and Treatment of Water and Air, London, Ontario, November 1992.
8. Standard Methods for the Examination of Water and Wastewater, 14th ed., American Public Health Association, Washington DC 1975.
9. Linsebigler, a. L., Lu, G., and Yates Jr., J. T.,"Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected results", Chem. Rev. 1995, 95, 735-758.
10. Zang, Y., Crittenden, J. C., Hand, D.W., and Perram, D.L., Environ. Sci. Technol. 1994, 28, 435.

FIGURE 1



Schematic photoexcitation in a solid followed by deexcitation events.
(HETEROGENEOUS PHOTOCATALYSIS)



Examples of some basic chemical reactions that can occur on a particle of TiO_2 suspended in contaminated water and illuminated with ultraviolet radiation.

FIGURE 2
GAS CHROMATOGRAPHIC DATA
PHOTO-OXIDATION OF CHLOROFORM
(Oxidative Destruction Efficiency)
100 ppm CHCl₃ - 50 ppm FeCl₃

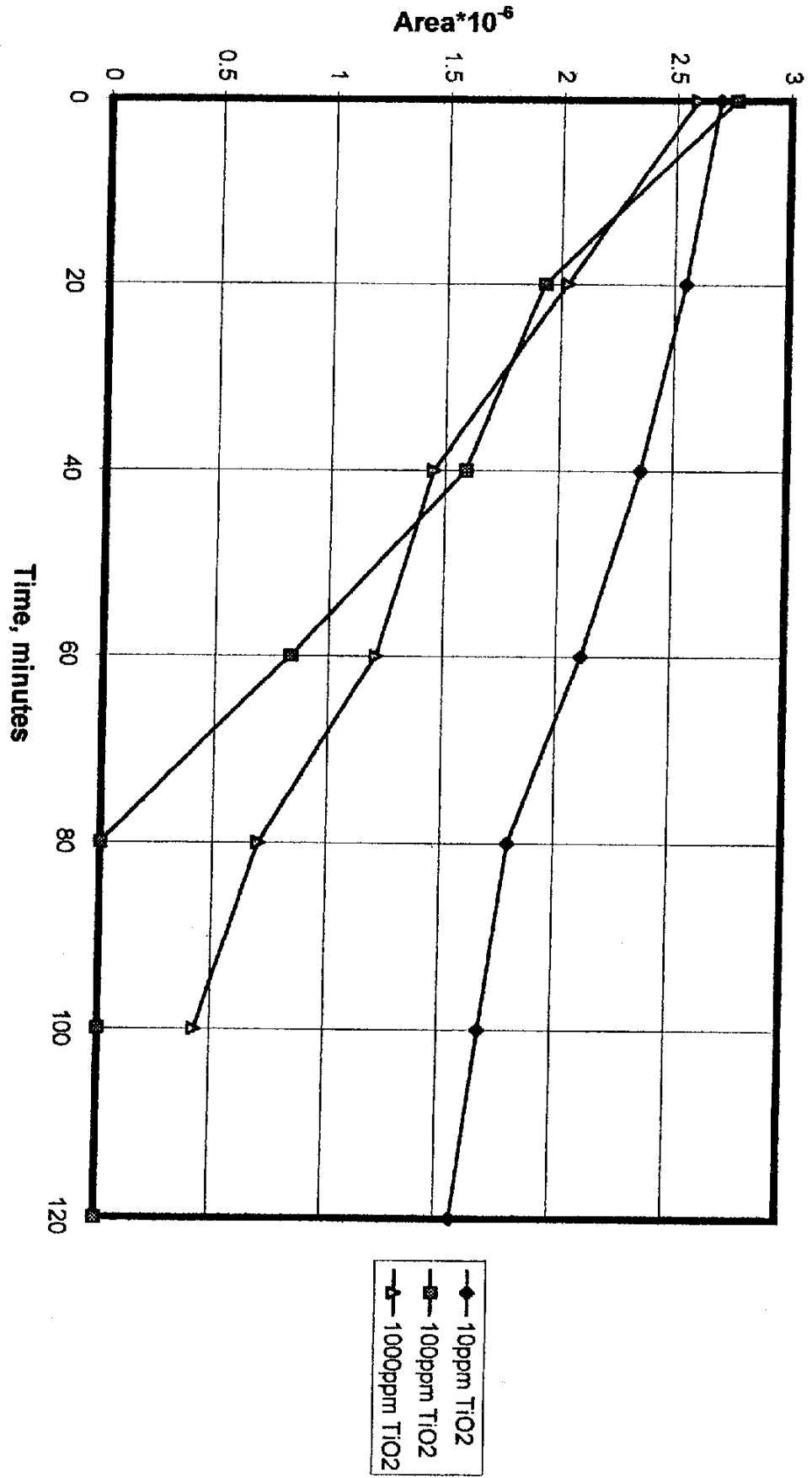


FIGURE 2a
GAS CHROMATOGRAPHIC DATA
PHOTO-OXIDATION OF CARBON TETRACHLORIDE
(Oxidative Destruction Efficiency)
1000 ppm CCl₄, -50 ppm FeCl₃

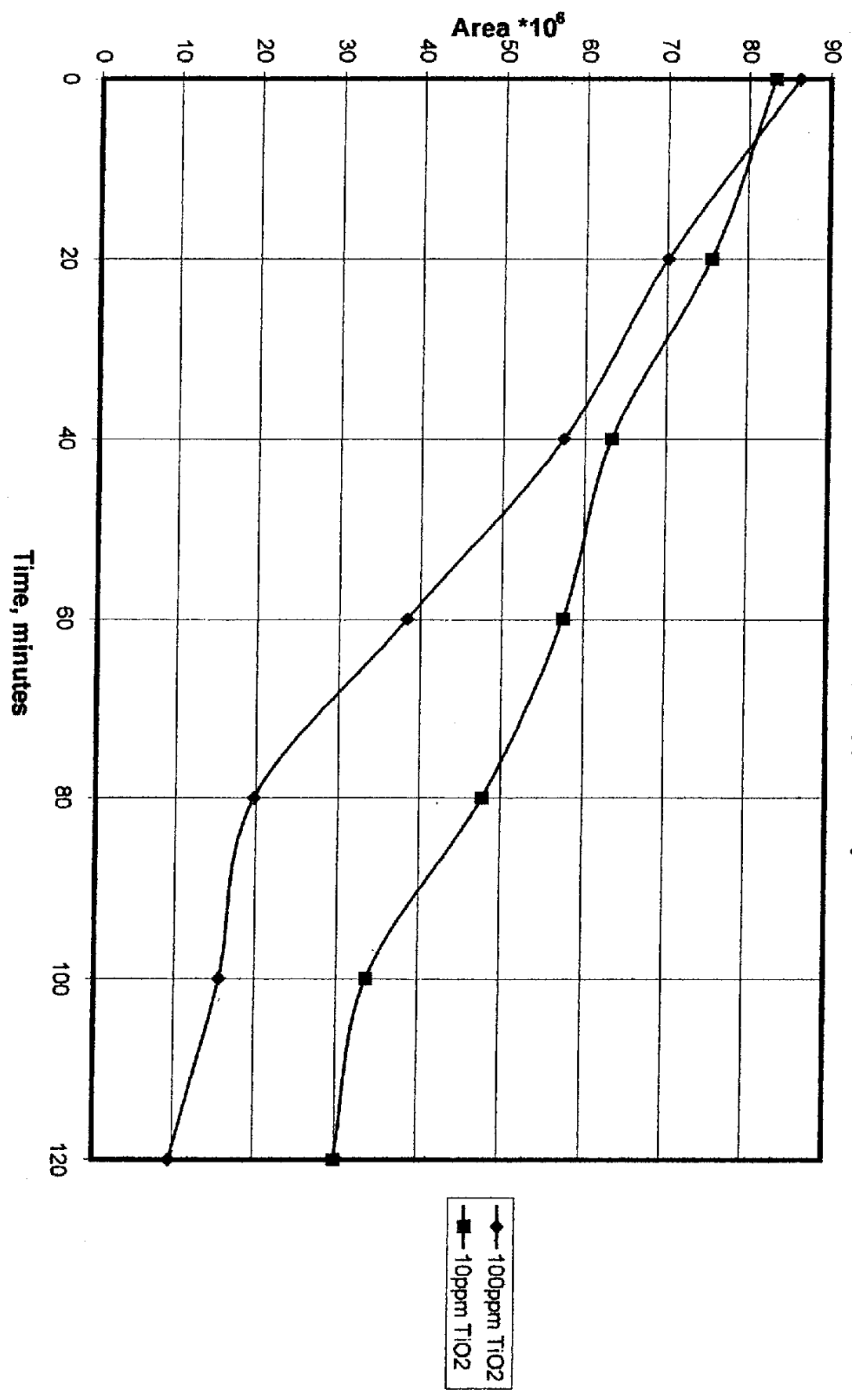
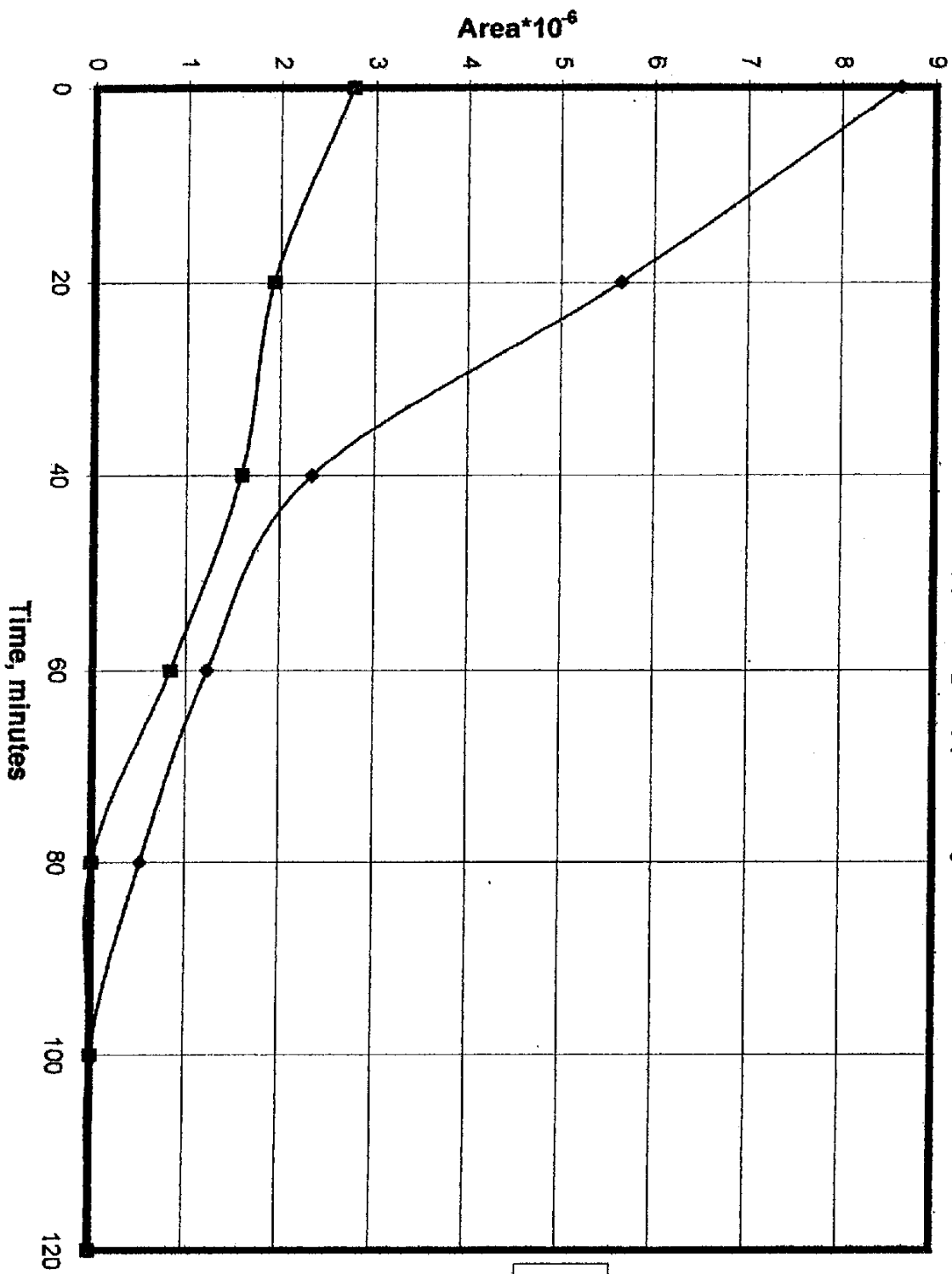
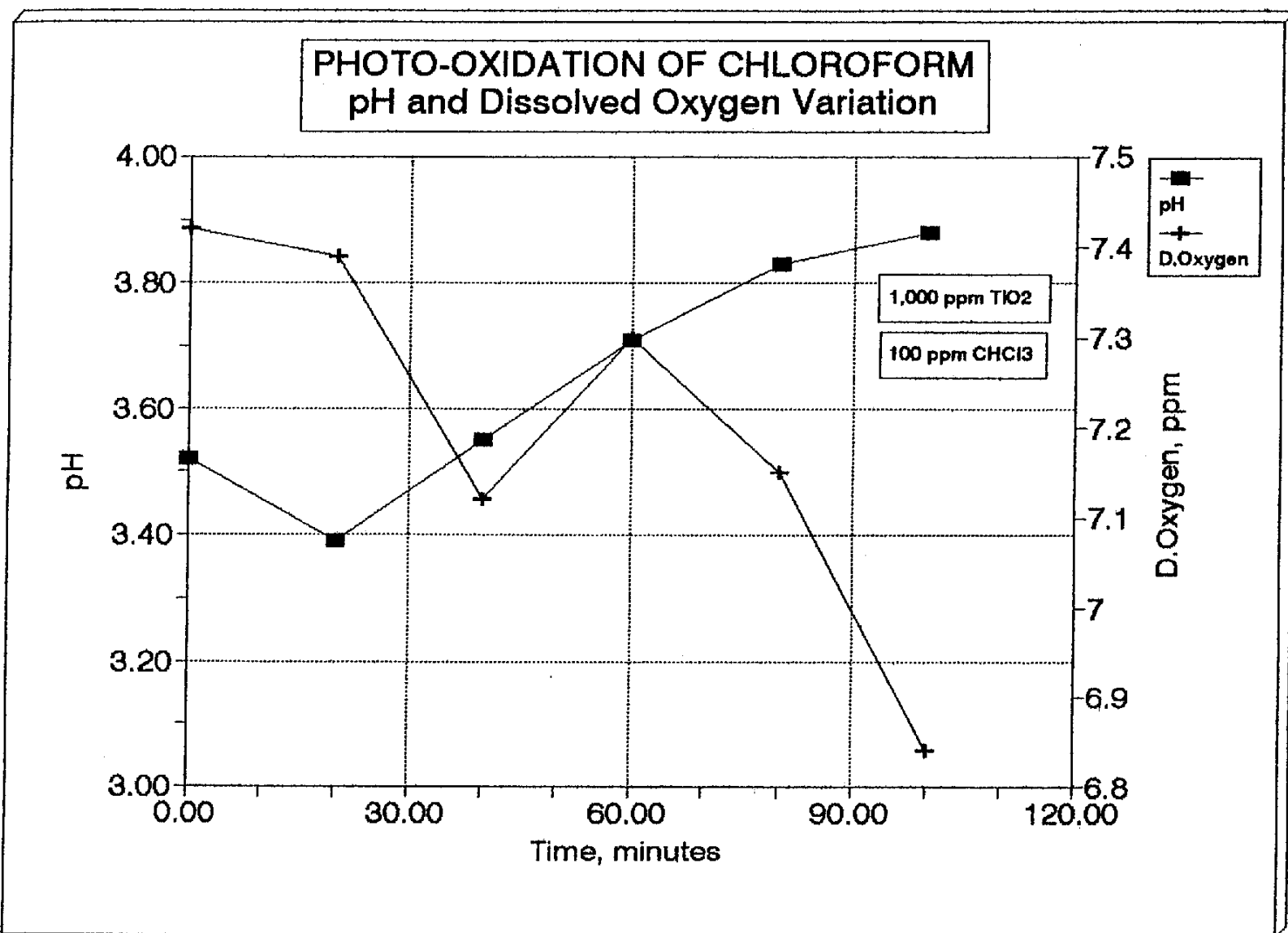


FIGURE 2b
GAS CHROMATOGRAPHIC DATA
PHOTO-OXIDATION OF CHLORINATED SOLVENTS
(OXIDATIVE DESTRUCTION EFFICIENCY)
100 ppm TiO₂-50 ppm FeCl₃



◆ 100ppm CCl₄
■ 100ppm CHCl₃

FIGURE 3



SYNOPSIS

Project Number: 03

Start: 06/95
End : 05/96

Titles: A Novel Detoxification Approach: Photo-oxidation of Volatile Organics in Groundwater - Phase I

Investigators: Mehta, Narinder K. and Hernández, Samuel

Focus categories: GW, TRT, WQL

Congressional District: N/A

Descriptors: Photo-oxidation, Detoxification, Groundwater Quality, Oxidation

Problem and research objectives: (a)

Contamination of our ground water resources has forced us to explore innovative and efficient alternatives to clean our underground contaminated water supplies. The objective of this research was to explore if photochemical oxidation technology may be utilized for regenerating the chlorinated solvent contaminated water at the laboratory scale.

Methodology: (b)

Heterogeneous photocatalysis oxidation was carried out using UV (<390 nm) photo-laser-anatase titanium dioxide catalyst. Organics are destroyed by photo-chemical oxidation while metals are removed by reduction at the same time.

Principal findings and significance: (c)

The study demonstrated the viability of utilizing UV-laser-anatase oxidation technology for the destruction of chloroform and carbon tetrachloride in aqueous phase in a short time. Complete destruction of the chlorinated solvents was achieved with low ppm of catalyst loading which reflects that the regenerated water may be utilized with minimum post-treatment.

Publications and professional presentations: (d) (Include a list of the locations where copies of all publications and manuscripts may be obtained.)

1. EPSCoR Technical Meeting on Scientific and Technological Research in Puerto Rico: A Key Element for Economic Development, May 24-25, 96, Ponce, Puerto Rico.
2. 212th National Meeting of the American Chemical Society, Undergraduate Research and Successful Student Affiliate Chapter Activities, August 25-29, 96, Orlando, FL.

M.S. theses: (e) (List titles, authors, and institutions.)

None

Ph.D. dissertations: (List titles, authors, and institutions.)

None

TRAINING ACCOMPLISHMENTS

<u>Field of Study</u>	<u>Academic Level</u>			<u>Total</u>
	<u>Undergraduate</u>	<u>Master's Degree</u>	<u>Ph.D. Degree</u>	
Chemistry	1			1
<u>Engineering:</u>				
- Agricultural				
- Civil				
- Environmental				
- Soils				
- Systems				
- Other *	1			1
Geology				
Hydrology				
Agronomy				
Biology				
Ecology				
Fisheries, Wildlife and Forestry				
Computer Science				
Economics				
Geography				
Law				
Resources Planning				
<u>Other (specify)</u>				
	2			
	TOTAL:			

* Less than 5 students in any one field of study.