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# Byproduct Formation During the Reduction of TCE by Zero-Valence Iron and Palladized Iron

by Liyuan Liang, Nic Korte, J.D. Goodlaxson, Jay Clausen, Quintus Fernando, and Rosy Muftikian

## Abstract

**T**richloroethene (TCE) was reduced with zero-valence iron and palladized iron in zero-head-space extractors. Progress of the reaction in these batch studies was monitored with purge-and-trap gas chromatography and a flame ionization detector. When a 5 ppm initial concentration of TCE reacts with zero-valence iron, approximately 140 ppb of vinyl chloride persists for as long as 73 days. The concentration of vinyl chloride (approximately 10 ppb) remaining with palladized iron is approximately an order of magnitude less than when zero-valence iron is the reductant. These data suggest that volatile byproducts may be under-represented in other published data regarding reduction with zero-valence metals. These results also demonstrate that the reduction of TCE with palladized iron (0.05 percent palladium) is more than an order of magnitude faster than with zero-valence iron. With a 5:1 solution-to-solid ratio the TCE half-life with zero-valence iron is 7.41 hours, but is only 0.59 hours with the palladized iron.

## Introduction

The use of zero-valence metals for reduction of chlorinated solvents such as trichloroethene (TCE) has been an area of significant recent research (Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994). The proposed method has great attraction because the reactive media, iron filings, are relatively inexpensive. Moreover, remedial systems can be designed that rely on a passive funnel and gate approach (Starr and Cherry 1994) that would minimize the cost of operation and maintenance.

Published results to date have focused on the disappearance of the primary compound. As noted by Gillham and O'Hannesin (1994), "an exhaustive study of degradation products has yet to be performed." The degradation products are an important issue because of the potential formation of products that are toxic yet not degraded, or the production of a byproduct that, while degraded in part, persists in sufficient quantities to violate ground water standards. An example of the former is the lack of reactivity of dichloromethane (Gillham and O'Hannesin 1994). For example, a long-term column study demonstrated that carbon tetrachloride is rapidly dechlorinated to chloroform, which slowly degrades to dichloromethane where the reaction, for all practical purposes, stops (Matheson and Tratnyek 1994). Toxic byproducts from the degradation of TCE include vinyl chloride and the various dichloroethene isomers. There is no doubt that a

permeable iron barrier would cause a significant reduction in the contaminant mass at a TCE spill. However, as a consequence of the low maximum contaminant level (MCL), the reduction of TCE may yet result in an unacceptable level of vinyl chloride.

Evaluating production and removal of byproducts is difficult because of the volatility of the compounds under study. Recent research at Oak Ridge National Laboratory (ORNL) has focused on the handling of water and soil samples contaminated with volatile organic compounds (VOCs) such as TCE and vinyl chloride (Gu et al. 1995; West et al. 1995; Siegrist et al. 1997). These studies have shown that the leakage of VOCs from containers, though generally recognized, can be quite severe, and that rigorous precautions are required to ensure there are no losses of volatile contaminants. An example of leakage from a 40-mL vial is shown in Figure 1. Considering that vinyl chloride's vapor pressure (2600 mm Hg) is more than 40 times that of TCE (60 mm Hg) (Barbee 1994), loss of vinyl chloride when conducting batch experiments is a potential problem.

The concern regarding loss of byproducts is also based on the fact that researchers in the field have not typically reported a high mass balance for carbon as indicated by reported values of 73 percent (Orth and Gillham 1995) and approximately 90 percent (Sivavec and Horney 1995). Chloride mass balances near 100 percent have been reported (Haitko and Baghel 1995), but an excellent mass balance does not necessarily mean that vinyl chloride is not above acceptable levels.

In this paper, we report results of batch studies performed with zero-headspace extractors (ZHEs). The ZHEs prevent losses due to leakage (Siegrist et al. 1997). Also presented in this paper is a comparison of results from zero-valence iron and palladized iron. Palladized iron has been shown to dechlorinate TCE more rapidly and to also be effective for otherwise recalcitrant compounds such as dichloromethane (Muftikian et al. 1995; Korte et al. 1995). Batch experiments provided a convenient means for comparing the reduction reactions to determine whether there are differences in byproduct formation when using zero-valence iron or palladized iron.

## Experimental Batch Studies

The data presented in this paper were obtained from batch studies using ZHEs (Associated Design and Manufacturing Co., Alexandria, Virginia). Figure 2 is a schematic diagram of a ZHE. The reagents are contained in Section 1, and headspace is excluded by forcing the piston up with pressurized gas.

In these batch experiments, 25 g of 40-mesh iron filings (Fisher Scientific, Pittsburgh, Pennsylvania) were added to the ZHEs, which contained 125 mL of an aqueous solution (nominally 2 mg/L of TCE). A solution without the addition of the iron filings was prepared in a ZHE as a control. The ZHEs were mounted on a rack

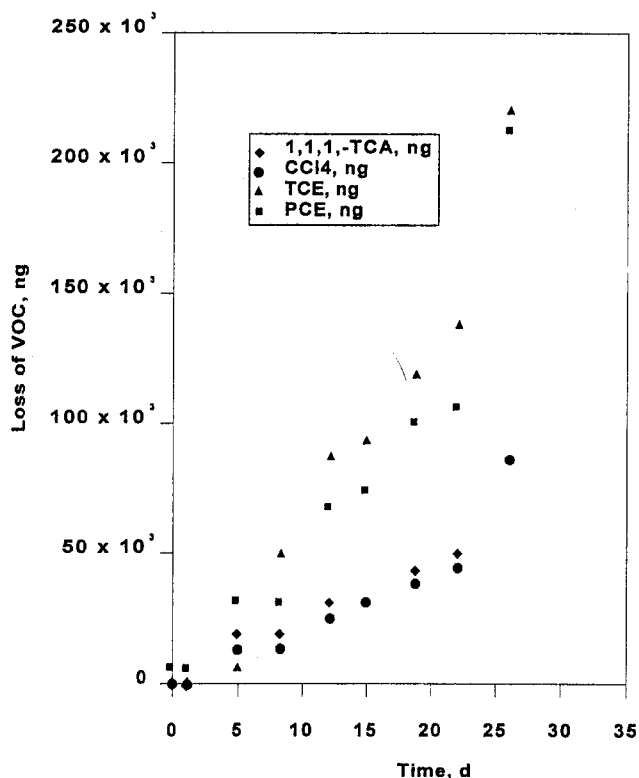


Figure 1. Mass of VOCs escaping from a 40-mL VOA vial with an adaptor cap and 10 mL of a high-level aqueous solution of VOCs. Source: Siegrist et al. 1997.

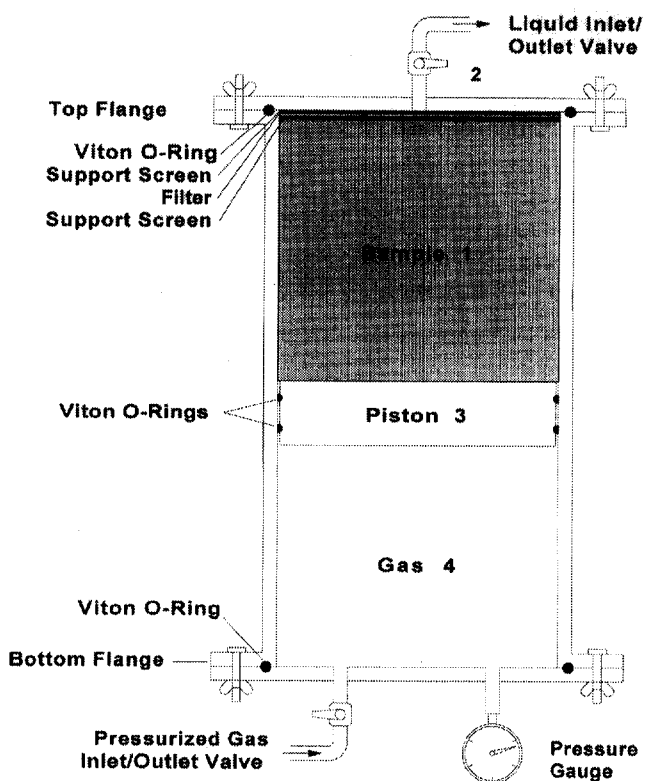


Figure 2. Schematic diagram of a zero-headspace extractor.

and rotated at 30 rpm. Samples were collected at various intervals without exposing the fluid to the atmosphere.

The palladized iron was prepared according to the method presented by Muftikian et al. (1995). In this method, an aliquot of the 40-mesh iron filings was

treated with 6 N HCl, followed by a thorough rinse with distilled and deionized water (Milli-Q water system, Millipore, Bedford, Massachusetts). Palladium was then plated on the iron filings at a loading of approximately 0.05 percent.

TCE was dissolved in water with the aid of a sonicator. The TCE solutions contained 1 mM of  $\text{NaHCO}_3$  as a means of simulating the carbonate content of a natural water. The pH of the TCE solutions was also adjusted with HCl to approximately 6.5.

Sampling and analysis of TCE and its products were performed as follows. At selected time intervals, 5-mL aqueous samples were collected from the ZHEs and immediately injected into a purge-and-trap concentrator (Tekmar 3000, Tekmar, Cincinnati, Ohio). Samples from the concentrator were analyzed for reaction byproducts by gas chromatography (GC) (HP-5890 Series II, Hewlett-Packard, Wilmington, Delaware) with a flame ionization detector (FID). The initial oven temperature was 30°C, and ramped to 150°C. The detector temperature was 300°C and the carrier gas was helium with a flow rate of 7 mL/min. The GC was equipped with a 0.53-mm capillary column (DB-624, J&W Scientific, Folsom, California).

Experiments were also performed with  $^{14}\text{C}$ -labeled TCE. The labeled samples were analyzed with a scintillation counter (Packard 2000 CA, Packard Instrument Co., Downers Grove, Illinois). These experiments were designed to evaluate the physical loss of TCE in the experimental apparatus (ZHEs). The same experimental conditions were maintained as for the unlabeled samples, except that a small fraction of  $^{14}\text{C}$ -labeled TCE was introduced into the TCE solution. Samples were collected for simultaneous GC analysis and scintillation counting. For the latter, 9 mL of the scintillation cocktail Ecolume (ICN Biomedicals Inc., Irvine, California) were added to 1 mL of sample.

## Results

### Persistence of Byproducts

Figure 3 presents typical results for the reaction of iron filings with TCE. The control showed no loss of TCE. The ethene content increased rapidly as the TCE was degraded. It should be noted that it was not possible to distinguish ethene from ethane with the experimental apparatus available. Thus, these two compounds are reported as total C2 in Figures 3 and 4, which present the formation and persistence of the byproducts. During the length of this experiment, the cis-1,2-DCE began to decline, but the vinyl chloride persisted. Trans-1,2-DCE was not detected. Experiments with an initial TCE concentration of 5 ppm were performed for as long as 73 days. Under those conditions the cis-1,2-DCE decreased to less than 10 ppb, but the amount of vinyl chloride stabilized at approximately 140 ppb on day three and remained constant throughout the experiment.

Figure 4 presents the same experiment as in Figure 3, except palladized iron was used to accomplish the dechlorination. As with the untreated iron, vinyl

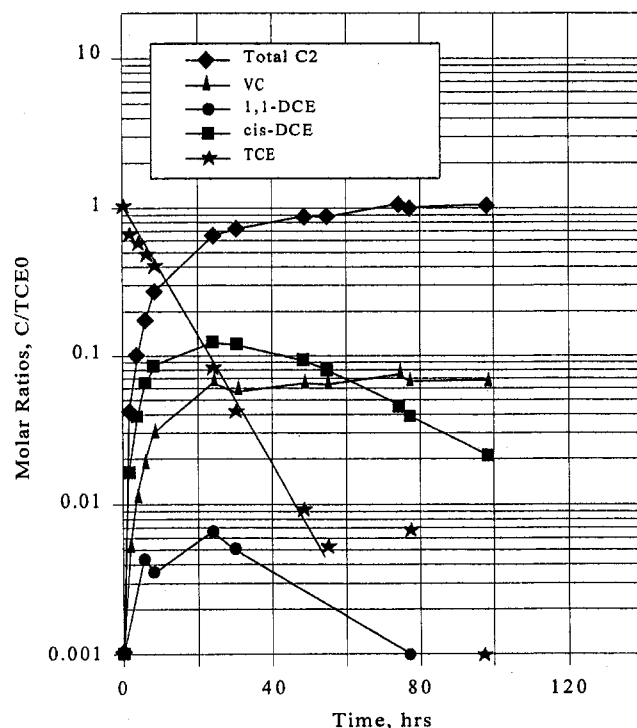


Figure 3. Kinetics and byproduct distribution from TCE degradation by zero-valence iron. Initial pH was 6.5. Initial TCE concentration was 17.4  $\mu\text{M}$  (2.3 ppm). The solution was buffered with 1 mM  $\text{NaHCO}_3$ ; 25 g of iron filings (Fisher, 40 mesh) was added to 125-mL solution. C2 includes ethene and ethane.

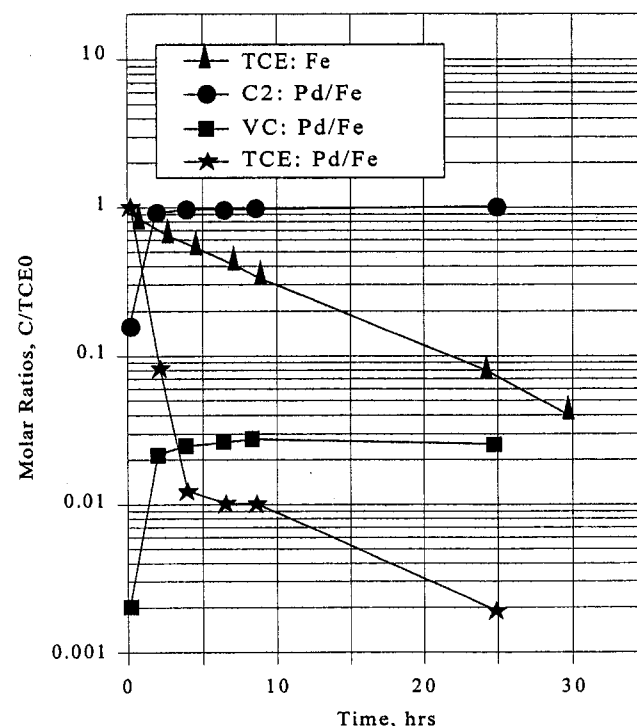


Figure 4. Kinetics and byproduct distribution from TCE reduction by palladized iron. Reduction of TCE with iron alone is shown as  $\blacksquare$ . The conditions were TCE = 15.3  $\mu\text{M}$  (2 ppm),  $\text{NaHCO}_3$  = 1 mM, pH = 6.5. 25 g palladized (0.05 percent) iron (iron is from Fisher, 40 mesh) in 125 mL of solution. C2 is a combination of ethene and ethane.

chloride that formed during the reaction with the palladized iron persisted for as long as the experiment was continued. In contrast to the untreated iron, the persistent concentration of vinyl chloride was an order of

magnitude less, averaging approximately 10 ppb for the experiments performed under these conditions. It is important to note that no DCE isomers were observed with the palladized iron, while both 1,1-DCE and cis-1,2-DCE were observed during the reaction with untreated iron. If DCE isomers are produced during the reaction with palladized iron, they were degraded to nondetectable levels prior to collection of the first sample.

### Mass Balance

Carbon mass balance was initially attempted by means of  $^{14}\text{C}$ -TCE. However, as shown in Figure 5, both control and treated samples lost TCE. Parallel analyses by GC did not indicate any loss from the control samples. The loss of  $^{14}\text{C}$ -TCE, therefore, apparently occurred in the scintillation cocktail after removal of sample from the ZHEs. The greater leakage from the treated samples (Figure 5) is attributed to the escape of the more volatile byproducts, such as vinyl chloride, ethene, ethane, and the DCEs. Consequently, experiments with labeled TCE were discontinued. Problems with labeled TCE have been reported previously (Gu et al. 1995).

As shown in Figure 5, the concentration of TCE without addition of iron remained constant in the ZHEs for the duration of the experiments. Unfortunately, the carbon balance for the reaction in the ZHEs was hampered by the inability to separate ethene and ethane. Ethane has a higher response factor with the FID detector, although it is believed to be present in lower concentrations than ethene. In addition, separate GC analyses indicated that the ratio of ethane to ethene increased with time. With calibration performed with ethene, the carbon mass balance was greater than 100 percent. The overestimation of total carbon increases with time because the ethane-to-ethene ratio increases. Keeping in mind that the carbon mass balance is slightly greater than 100 percent, after 24 hours the

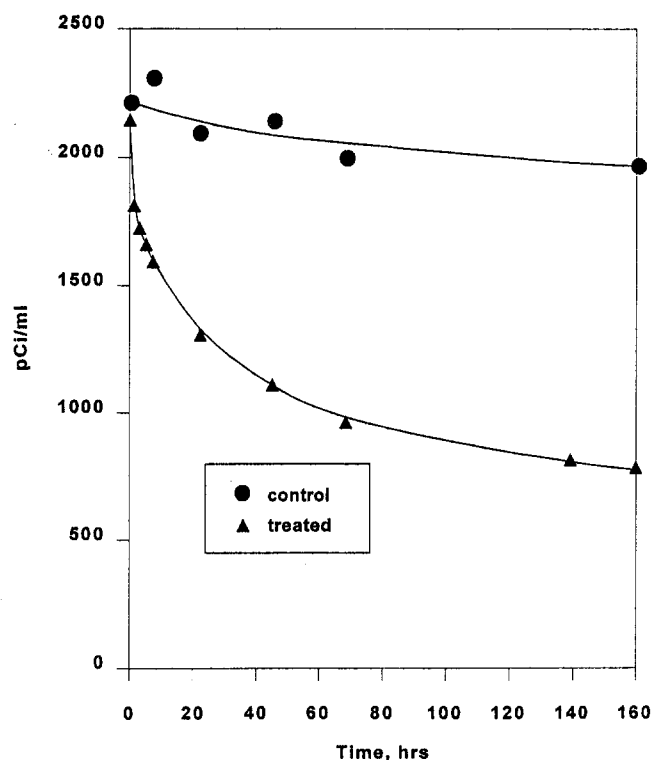


Figure 5. TCE analysis with  $^{14}\text{C}$  tracer with scintillation counting. Experiment was conducted with 10 g iron filings (Fisher, 40 mesh) in 50-mL TCE solution. The solution contained 1 mM  $\text{NaHCO}_3$ , 71.6  $\mu\text{M}$  (9.4 ppm) TCE.  $^{14}\text{C}$  tracer was added to the TCE solution. The initial pH was 6.5.

byproduct mixture contained approximately 12 percent cis-1,2-DCE, 8 percent vinyl chloride, and <1 percent of 1,1-DCE.

### Half-lives

The data in Figures 3 and 4, which compare results from experiments that used similar amounts of vinyl chloride, cis-DCE, and trans-DCE as starting materials, were used to calculate half-lives for the reductive dechlorination of TCE (Table 1). The TCE half-life with

**Table 1**  
Observed Rate Constants for Chlorinated Ethenes in the Presence of Iron Filings

Compound	Initial Concentration		Observed Rate, Hour <sup>-1</sup> for Zero- Valence Iron	Half-Life
	$\mu\text{M}$	mg/L		
Vinyl chloride <sup>a</sup>	25.0	1.56	0.0107	64.7
cis-DCE	28.6	2.8	0.0196	35.2
trans-DCE	27.3	2.6	0.0504	13.7
TCE	26.3	3.5	0.0931	7.41
			Rate (hour <sup>-1</sup> ) palladized iron	
TCE	15.58	2	1.17	0.59

<sup>a</sup> Dissolved in methanol

Note: 200 g/L of Fisher 40-mesh (327 m<sup>2</sup>/L) iron filings, 1 mM bicarbonate solution.  
Initial pH = 6.5

untreated iron was 7.4 hours, which compares reasonably well with other reported values from batch reactions (Gillham and O'Hannesin 1994; Sivavec and Horney 1995) conducted under somewhat different conditions. For palladized iron, the TCE half-life under the same experimental conditions was 35 minutes. The more rapid reaction is consistent with the observation that chlorinated intermediates were less persistent with time.

## Conclusion

The results presented in this investigation have shown that ZHEs are excellent vessels for batch studies of reductive dechlorination of volatile compounds. Experiments relying on containers that are not leak-proof have a significant potential of underpredicting the formation and persistence of byproducts. This study has shown that the formation and persistence of vinyl chloride from zero-valence metal reduction may be a more significant problem than previously realized. Finally, this study demonstrates that the use of palladized iron results in a reaction that is an order of magnitude or more faster than zero-valence iron. Similarly, the concentration of vinyl chloride that persists in a long-term batch study with palladized iron is also an order of magnitude less than with zero-valence iron.

**Editor's Note:** The use of brand names in peer-reviewed papers is for identification purposes only and does not constitute endorsement by the authors, their employers, or the Ground Water Publishing Co.

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## Biographical Sketches

**Liyuan Liang** received a B.S. in civil engineering from Northeastern University and an M.S. and Ph.D. in environmental engineering from California Institute of Technology. Currently she is a principal investigator and the leader of the Environmental Engineering Group at Oak Ridge National Laboratory (Environmental Sciences Division, Oak Ridge, TN 37831). Dr. Liang has been conducting research in environmental chemistry for the last 10 years in the areas of particle dynamics in natural water and subsurface environments, equilibrium and kinetics of adsorption/desorption of metals and organic contaminants at solid/aqueous interface, chemical speciation in aqueous systems, and redox-transformation and fate of organic and inorganic contaminants.

**Nic Korte** received a B.S. in chemistry from the University of Illinois in Champaign-Urbana and an M.S. in analytical chemistry from the University of Arizona, Tucson, Arizona. Currently he is restoration technology manager at Oak Ridge National Laboratory (Environmental Sciences Division, Grand Junction Office, 2597 B 3/4 Rd., Grand Junction, CO 81503). Korte's primary research interest is studying the fate and effect of trace species in the environment. He has more than 15 years experience in planning and conducting field investigations at hazardous waste sites. He also serves as an adjunct faculty member at Mesa State College in Grand Junction, Colorado. Korte is a certified hazardous materials manager and a certified ground water professional.

**J.D. Goodlaxson** is an analytical chemist with the Environmental Engineering Group at Oak Ridge National Laboratory (Environmental Sciences Division, Oak Ridge, TN 37831). He received a B.S. in biology with a chemistry minor from the University of Wisconsin-Stevens Point. His research interests include adsorption/desorption of heavy metals onto solid organic matrixes and redox-transformation of organic contaminants in aqueous systems.

**Jay L. Clausen** is a hydrogeologist/geochemist with Lockheed Martin Energy Systems Inc. (761 Veterans Ave., Kevil, KY 42053). He received a B.S. in geology from the University of Nebraska-Omaha and an M.S. in geological sciences from the University of Maine in 1987 and 1990, respectively. Clausen's interests include evaluation of innovative technologies for sampling, analysis, characterization, and remediation, and the fate and transport of contaminants and geochemistry of ground water systems. Clausen is a registered professional geologist in Kentucky.

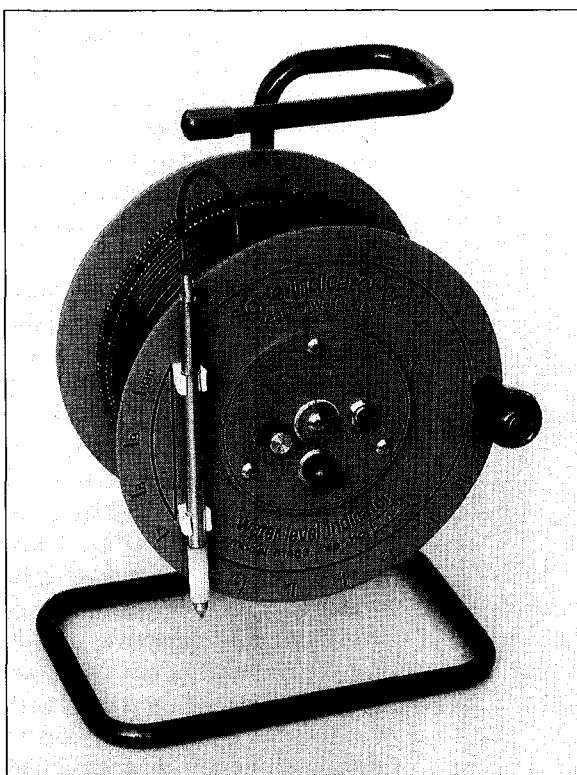
**Quintus Fernando** is professor of chemistry, forensic science, and toxicology in the Department of Chemistry at the University of Arizona, Tucson, Arizona. His research interests include trace metal analysis in environmental and biological samples using x-ray emission spectroscopy, and the synthesis, structure, and reactivity of metal complexes. He has published more than 200 papers on these topics.

**Rosy Muftikian** is at present a predoctoral student in the Chemistry Department at the University of Arizona, Tucson, Arizona. She received a B.S. and an M.S. in chemistry from California State University, Northridge. Her research interests include studies on remediation of toxic organic and inorganic compounds in the environment. Of special interest are the halogenated aliphatic saturated and unsaturated compounds.

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