

Fate and Remediation of 1,2,3-Trichloropropane

Paul G. Tratnyek (tratnyek@ebs.ogi.edu) and Vaishnavi Sarathy
(Oregon Health & Science University, Portland, OR)
John H. Fortuna (Geosyntec Consultants, Oakland, CA)

ABSTRACT: 1,2,3-trichloropropane (TCP) has been used in a variety of chemical production processes, in agricultural chemicals, and as a solvent, resulting in point and non-point source contamination. The chemical properties, and the relatively few studies that have focused on the fate or remediation of TCP suggest that TCP—while very recalcitrant in general—can be degraded by biotic and abiotic processes under favorable conditions, including some of those employed for in situ chemical oxidation (ISCO) and in situ chemical reduction (ISCR). In general, TCP exhibits little or no reaction with mild reductants (including construction-grade Fe^0) but is dechlorinated by strong reductants (like palladized nano- Fe^0). Similarly, strong oxidants like activated peroxide or persulfate give favorable rates of degradation but a mild oxidant like permanganate does not. Aerobic and anaerobic biodegradation have been observed in laboratory studies, but the rates are comparatively slow, and definitive evidence for biodegradation in the field is still lacking.

INTRODUCTION

1,2,3-Trichloropropane (TCP) has been used in a variety of chemical production processes and agricultural chemicals including widely used soil fumigants. The primary cause for concern at contaminated sites is spills associated with its use as a solvent (paint and varnish removal, cleaning and degreasing, etc.). TCP has been detected in more than three hundred drinking water wells in California (<http://www.cdph.ca.gov/certlic/drinkingwater/Pages/123TCP.aspx>). Despite TCP's relatively widespread use, very little data is available on its occurrence in the environment, and few studies have addressed its environmental fate or potential methods for its remediation. The chemical properties and available toxicity data (Kielhorn et al., 2003) suggest that sites where contamination by TCP is significant will pose challenges for clean-up that are at least as severe as those associated with other dense chlorinated solvents.

Currently, there are no state or federal maximum contaminant levels (MCL) defined for TCP. The EPA does, however, have a reference dose (RfD) of 0.006 mg/kg-day, based on a non-cancer endpoint (<http://www.epa.gov/ncea/iris/subst/0200.htm>), and TCP has been designated as “reasonably anticipated to be a human carcinogen” (National Toxicology Program, 2005). Among other advisories, NIOSH considers TCP as a potential occupational carcinogen, and has set recommended exposure levels (REL) at 10 ppm (<http://www.cdc.gov/niosh/81-123.html>). NIOSH also considers 100 ppm of TCP in air to be an immediate danger to life and health. California has currently set their notification (action or reporting) levels by the most precautionary criteria. The California Department of Public Health has a notification level of 0.005 ppb for TCP in drinking water, which is much lower than the corresponding level for TCA (trichloroethane) or TCE (trichloroethene).

VOLATILIZATION AND PARTITIONING

A summary of the physical properties of TCP (along with carbon tetrachloride, CT, and TCE, for comparison) is given in Table 1. The Henry's constant (H), the octanol-water partition coefficient (K_{ow}), and the soil-sorption coefficient, (K_{oc}) measure partitioning between air/water, organic matter/water, and soil/solution phases, respectively.

TABLE1. Physical properties of 1,2,3-trichloropropane, as compared to carbon tetrachloride (CT), and trichloroethylene (TCE).¹

Property	1,2,3-TCP	CT	TCE	Notes
Vapor Pressure	3.1	99.3	131.5	Torr (mm Hg) @ 25° C
Henry's Constant	2.94	286	93.7	$\times 10^{-4}$ atm m ³ mole ⁻¹ @ 25° C
Solubility	1.75	0.8	1.1	g/L @ 20° C
log K_{oc}	1.99	2.04	126	
log K_{ow}	1.98 – 2.54	2.64	2.42	

¹(Kielhorn *et al.*, 2003) and other sources.

The data in Table 1 suggest that TCP, while volatile, will be considerably less prone to volatilization than comparable chlorinated solvents. It has been reported, however, that purging of an aqueous TCP solution gave first-order removal with a rate constant = $2.99 \times 10^{-2} \text{ min}^{-1}$ (Lin *et al.*, 1993), which is sufficiently fast ($t_{1/2} = 24 \text{ min}$) for treatment.

The volatility of TCP suggests that some of what is released to the environment will contaminate the atmosphere. This has led to some interest in the oxidation of TCP—and related chlorinated propanes—by gas phase free radicals. Reported second order rate constants include $4.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\bullet\text{OH}$ (Mu and Mellouki, 2001) and $1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\bullet\text{Cl}$ (Voicu *et al.*, 2001). These translate to relatively short atmospheric lifetimes (on the order of days).

DEGRADATION PATHWAYS AND KINETICS

There are few studies that include detailed information on the pathways (or kinetics) of TCP degradation in water or soil, and the few that are available (esp. Focht, 1994; Hunter, 1997; Pagan *et al.*, 1998) do not provide complete coverage of the full range of possible remedial alternatives. However, drawing from the four studies cited above, other studies where TCP was included among other contaminants (Anderson *et al.*, 1991; Klausen *et al.*, 2003; Pagan *et al.*, 1998; Peijnenburg *et al.*, 1998), and a few studies on closely related model compounds [e.g., 1,2-dichloropropane (Löffler *et al.*, 1997)], we have summarized in Figure 1 the routes of degradation that appear to be most promising for remediation of TCP.

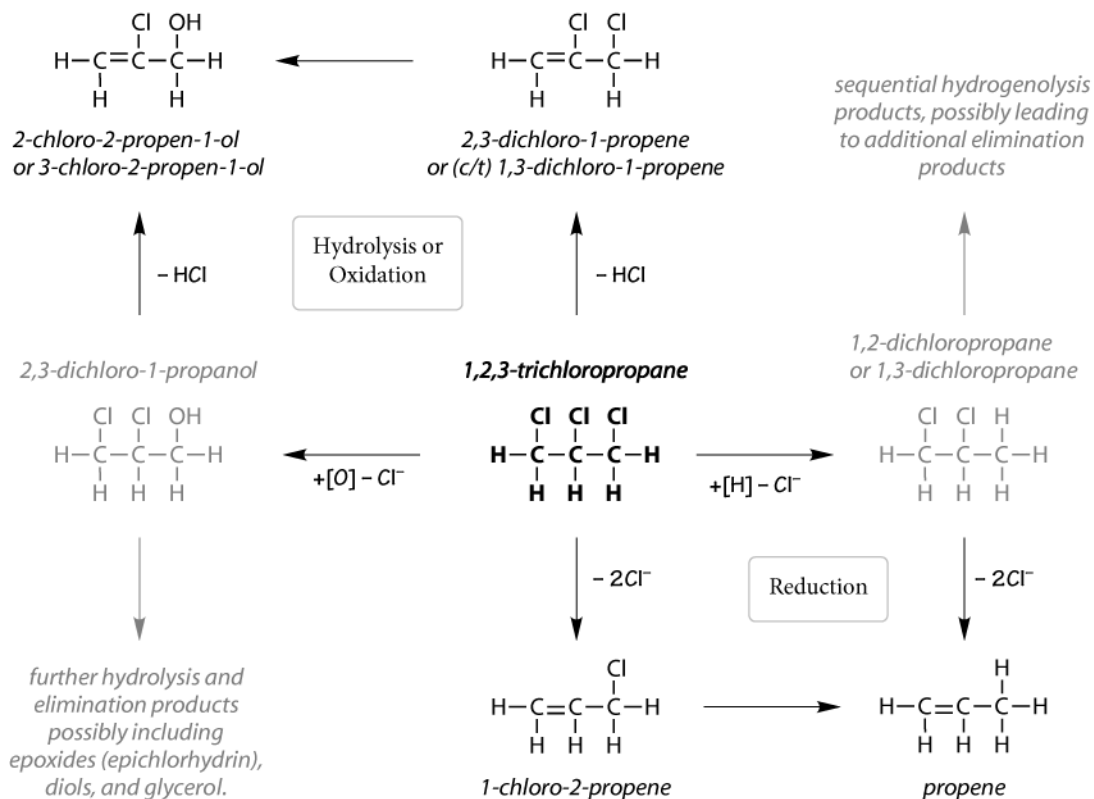


FIGURE 1. Summary of anticipated, primary reaction pathways for degradation of TCP. Oxidation, hydrolysis, and hydrogenolysis are represented by the horizontal arrows. Elimination (dehydrochlorination) and reductive β -elimination) are shown with vertical arrows. [O] represents oxygenation (by oxidation or hydrolysis), [H] represents reduction. Gray indicates products that are likely to be of lesser significance.

Hydrolysis of TCP has been shown to occur by both neutral and base-catalyzed pathways (Pagan et al., 1998), with the neutral pathway being too slow to be of consequence and the base-catalyzed pathway being fast only at rather high pHs. For example, $t_{1/2}$ is thousands of years at pH 7 and 15°C (during natural attenuation), but 0.1 days at pH 8 and 90°C (as might be achieved during in situ thermal remediation).

Under reducing conditions, hydrogenolysis or reductive β -elimination (dichloroelimination) of TCP are possible. The former, however, is not expected to be facile (as with any haloalkane that has only one chlorine per carbon) but the latter might be comparatively favorable with appropriate reductants. This is consistent with available data for laboratory batch and column tests. We have found negligible degradation of TCP by conventional and nano-sized Fe^0 (ZVI) in well mixed batch reactors, although palladization does give significantly accelerated rates, as do alternative zero-valent metals like zinc (not shown).

Two detailed studies with ZVI-containing columns have reported limited degradation of TCP (Focht, 1994; Klausen et al., 2003). In the first (Focht, 1994), the rate of TCP disappearance was found to increase with increasing percentage of iron used, up to a half-life of 3 hours with 100% iron (corresponding to a surface area to volume ratio of

8 m²/L). It was hypothesized that sorption onto the iron, or onto impurities such as carbon, contribute to disappearance, although the extent of this contribution was not determined. In the second column study (Klausen *et al.*, 2003), TCP appeared to be degraded only in the initial 10% of each column, with a half-life of over 1000 days, which is much slower than what was observed for TCE in the same column.

Studies of chemical oxidation of TCP have found it to be moderately reactive: e.g., feasibility testing with iron-activated H₂O₂ gave, $t_{1/2} \approx 1.5$ days (Hunter, 1997) and we have found that heat-activated persulfate gives $t_{1/2} \approx 2\text{-}4$ hr (not shown) but reaction with permanganate is negligible. It has also been reported the O₃/H₂O₂ give satisfactory oxidation of TCP, although the kinetics of this reaction were not presented (Dombeck and Borg, 2005). Of course, it is not meaningful to make direct comparisons between the rates of these advanced oxidation process because of variability in the dose of oxidant, degree of activation, and other operating conditions of these tests. In future work, we hope to develop the data for making more general comparisons among these possible treatments by chemical oxidation.

Biodegradation of TCP, in general, seems to be very slow, but a few detailed laboratory studies have documented both aerobic and anaerobic biodegradation. A series of papers by Bosma and others focus on the hydrolysis of TCP catalyzed by organisms expressing haloalkane dehalogenase enzymes (Bosma and Janssen, 1998; Bosma *et al.*, 2002). They defined the kinetics, pathways, and some of the molecular biology of this process, and had some success engineering bacteria to enhance this activity. The motivation was, in part, to develop a biotechnology that could recycle TCP-containing waste from the manufacture of epichlorhydrin (Parales *et al.*, 2002), but there is no indication that this approach could be used for in situ remediation. Recent work, in fact, has reported that TCP hydrolysis by the haloalkane dehydrogenase in a related bacterium is the slowest ever measured by microcalorimetric assay (Monincová *et al.*, 2007). In anaerobic microcosms (Löffler *et al.*, 1997), TCP was found to be less reactive than (and inhibitory to) biodegradation of 1,2-dichloropropane (1,2-DCP).

The above studies of TCP degradation have reported about a half-dozen products, most of which are not entirely diagnostic for any one degradation pathway. For example, hydrolysis gives dichloropropenes (Pagan *et al.*, 1998), which are further hydrolyzed to chloropropanol, while oxidation with activated H₂O₂ gives the same products (as intermediates), which then are further oxidized to 1,3-dichloropropanone, chloroacetic acid, and formic acid (Hunter, 1997). Another example is that while reduction of TCP might involve some hydrogenolysis (to sequentially dechlorinated propanes), both ZVI column experiments discussed above (Focht, 1994; Klausen *et al.*, 2003) yielded mainly propanes and propenes, which probably arise by reductive β -elimination and/or base-catalyzed dehydrochlorination. We have tried to incorporate some of the overlap between the products formed by the various degradation pathways in Figure 1.

TREATMENT IN THE FIELD

From public records on contaminated sites in the U.S., the first attempts at TCP remediation appear to have been at the Del Monte Oahu Plantation and the Burbank Operable Unit of the San Fernando Valley Superfund Site. At both of these sites, groundwater remediation was by extraction and treatment with granular activated carbon (GAC). However, TCP only has a low to moderate adsorption capacity for GAC, therefore requir-

ing large treatment systems and higher costs. Pump and treat remains the most commonly-cited remedial technology for TCP.

Recent efforts to remediate TCP contamination in the field have focused on chemical oxidation or reduction of TCP. Dombeck et al. (Dombeck and Borg, 2005) present evidence of TCP degradation using an advanced oxidation processes (involving O_3/H_2O_2) in bench-scale tests. At the MacKenzie Chemical Superfund site, in situ ozone sparging was not effective at remediating TCP in groundwater, but more recent efforts with base-catalyzed persulfate look promising (Mark Granger, U.S. EPA, Personal communication). Geosyntec has conducted bench-scale tests and in situ field treatability studies using a number of different amendments for the remediation of TCP-impacted groundwater. The results of two case studies are discussed below.

Case Study I. At an agricultural chemical retail and distribution facility in Northern California, soil and groundwater are impacted by nitrate and fumigant compounds including TCP and 1,2-DCP. Site investigation activities identified an above-ground tank farm as the source of the impacts (Figure 2). In 2000, Geosyntec implemented a pilot test in the vicinity of the former tank farm for remediation of VOCs in shallow groundwater. Hydrogen Release Compound (HRC[®]) was injected into the shallow groundwater zone to promote anaerobic reductive dechlorination of TCP and other compounds. HRC[®] was injected into a sand layer at 20-30 ft bgs (below ground surface) that comprises the shal-

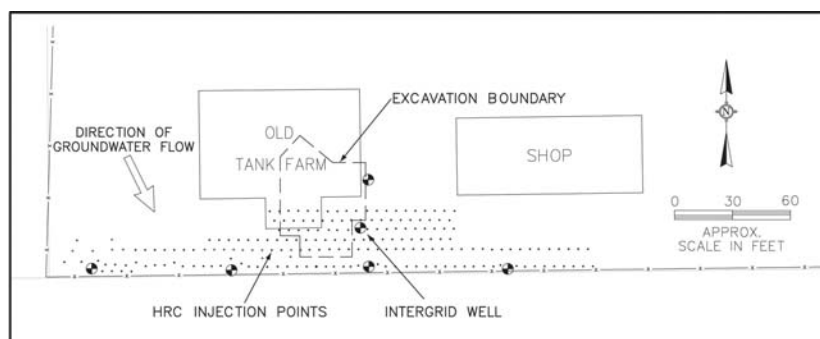


FIGURE 2. Site plan showing former tank farm, area of soil excavation, and injection point locations.

low aquifer at the site. At the time of the pilot test, concentrations of TCP and 1,2-DCP in shallow groundwater were approximately 4,000 $\mu\text{g/L}$ and 1,000 $\mu\text{g/L}$ respectively.

During 2001 and 2002, the property owner removed the tank farm and excavated over 2,500 tons of impacted soils. Soil was excavated to the depth of the water table, approximately 18–20 feet bgs. Confirmation samples from the base of the excavation in the saturated zone contained TCP at concentrations up to 6,500 micrograms per kilogram ($\mu\text{g/kg}$) and 1,2-DCP at concentrations up to 3,200 $\mu\text{g/kg}$. Maximum concentrations were detected at the down-gradient (southern) edge of the excavation, in the area of the HRC[®] pilot test (Figure 2).

Subsequent quarterly groundwater monitoring demonstrated the effectiveness of the pilot-scale field test (Figure 3). As shown in this figure, TCP concentrations in the intergrid well declined significantly by early 2002, and in 2004 Geosyntec implemented the

full-scale groundwater remedy by conducting additional injections in the vicinity of the tank farm and along the property boundary (Figure 2). By 2005, TCP was non-detect (<0.005 µg/L) in the intergrid well.

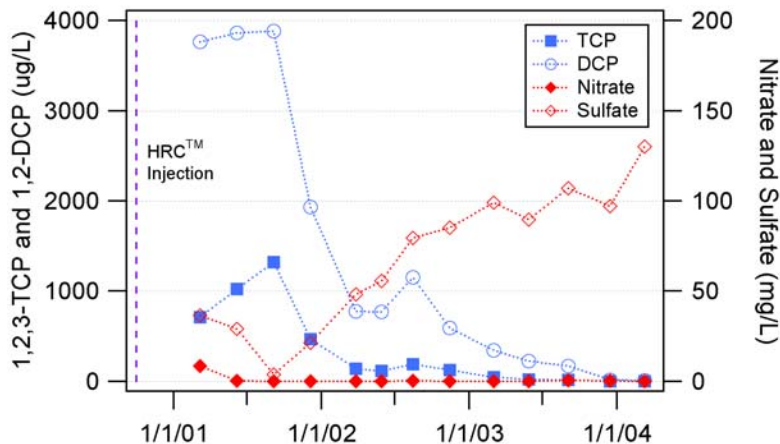


FIGURE 3. Quarterly monitoring results for HRC™ treated site.

Case Study II. Subsequent to the success at the above site, Geosyntec conducted HRC® pilot testing at a similar site with similar groundwater chemistry, but results were not as favorable. At the second site, only a small transient TCP reduction was observed, and the concentrations quickly rebounded to pre-injection conditions. The site-specific factors responsible for successful reduction of TCP at one site and lack of TCP reduction at the second site have not been identified. Based in part on these disparate results, we conducted bench-scale studies at a third site prior to field testing, as described below.

The subject site is an operating retail agricultural chemical distribution center in the Northern San Joaquin Valley. Site operations consist of storing, blending, and distributing bulk liquid fertilizers, and storing pre-packaged pesticides prior to sale. Shallow groundwater at the site occurs in a sandy zone approximately 45–90 ft bgs, and is impacted by the fumigant compounds 1,2-DCP, TCP, and ethylene dibromide (EDB). Maximum concentrations of these constituents in site wells were approximately 1,400 µg/L, 150 µg/L, and 50 µg/L, respectively.

In 2004, Geosyntec collected saturated soil and groundwater samples from the shallow aquifer in the area of highest TCP concentrations and sent them to SiREM Laboratories (SiREM) in Guelph, Ontario, Canada to perform bench-scale biotreatability and zero-valent iron (ZVI) studies to promote reductive dechlorination of VOCs. SiREM constructed eight sets of microcosms, including three control sets (anaerobic sterile control, non-amended control, ZVI non-amended control), one set for each of the three electron donors, one enhanced with the microbial consortium KB-1®, and one for ZVI. Tested electron donors were HRC®, emulsified soybean oil (EOS), and chitin. All treatments and controls were constructed in triplicate (24 total microcosms). The study period was approximately four months. Samples were collected from the control and treatment microcosms after the first three weeks, and then every five to six weeks thereafter for

analysis of target compounds. The ZVI microcosms were sampled at more rapid frequency compared to biodegradation microcosms.

Results of treatability testing for TCP are shown in Figure 4. All of the biotreatability study microcosms showed nitrate reduction at varying rates of the study period. However, none of the biotreatability or bioaugmentation studies significantly degraded the sulfate or target organic constituents of concern (CoCs). High sulfate concentrations (>2000 mg/L) were detected in samples, which may have contributed to the lack of organic CoC degradation. Results of the ZVI study showed that all target organic CoCs and nitrate were capable of being degraded by this amendment. EDB degradation was 100% complete by day 3 of the study. At the conclusion of the study (35 days), 1,2-DCP had decreased by 40%, 1,2,3-TCP had decreased by 80%, and nitrate was 100% degraded. Ethane and ethene concentrations, which increased rapidly over the first three days of testing, were also an indication of volatile CoC degradation under anaerobic conditions.

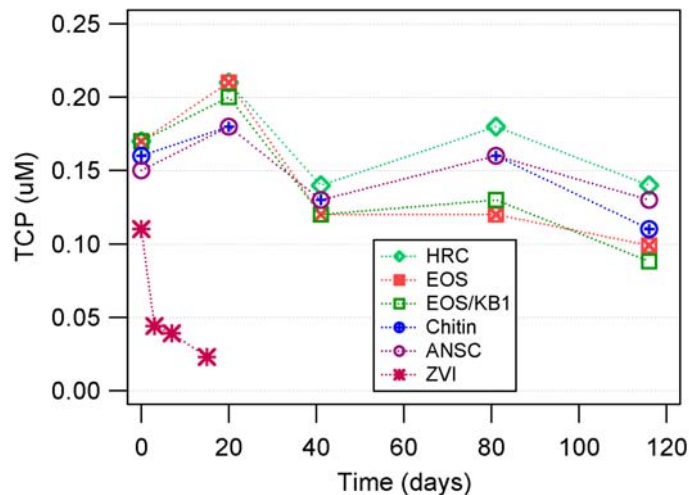


Figure 4. Results of treatability tests with TCP-contaminated groundwater/soil.

Based on the results of the bench-scale study, a granular ZVI-chitin mixture (Adventus EHC™) was selected as the application for the in-situ pilot test. In bench-scale testing, chitin was found to help prevent formation of ammonia during nitrate reduction. In October and November 2006, approximately 2600 pounds of EHC™ was injected into the shallow groundwater zone during a field-scale pilot test at the site. After a year of performance monitoring, there has been very little change in aquifer geochemistry and CoC concentrations in samples from performance monitoring wells. Although these results are preliminary, they suggest that kinetics of CoC reduction with EHC™ in the field pilot test are significantly slower than those observed in the laboratory ZVI microcosm. Performance monitoring is ongoing at the site.

CONCLUSIONS

While TCP can be degraded by hydrolysis, elimination, oxidation, and reduction, controlled studies in the laboratory show that all of these processes are relatively slow compared to most other CoCs: e.g., hydrolysis/elimination require high temperatures or

pH; reduction requires activated/strong reductants like palladized nano Fe⁰, and oxidation requires activated processes mediated by hydroxyl or sulfate radical. Biodegradation proceeds by similar pathways, including reduction under anaerobic conditions and oxidation under aerobic conditions (with elimination reactions apparently being relatively less prominent), but those processes can be slow compared with other, relevant CoCs. There is some as yet unexplained differences between bench-scale and field-scale tests of TCP remediation scenarios, suggesting that there are factors affecting the rate of TCP degradation that are not yet understood.

ACKNOWLEDGMENTS

Parts of the work described here was supported by a grant (ER-1457) from the Strategic Environmental Research and Development Program (SERDP). Contributors to Geosyntec's work in this area include Arnab Chakrabarti and Carolyn Kneibler.

REFERENCES

- Anderson, T.A., J.J. Beauchamp, and B.T. Walton. (1991) Fate of volatile and semivolatile organic chemicals in soils: Abiotic versus biotic losses. *J. Environ. Qual.* 20(2), 420-424.
- Bosma, T., and D.B. Janssen (1998) Conversion of chlorinated propanes by *Methylosinus trichosporium* OB3b expressing soluble methane monooxygenase. *Appl. Microbiol. Biotechnol.* 50(1), 105-112.
- Bosma, T., J. Damborsky, G. Stucki, and D.B. Janssen. (2002) Biodegradation of 1,2,3-trichloropropane through directed evolution and heterologous expression of a haloalkane dehalogenase gene. *Appl. Environ. Microbiol.* 68(7), 3582-3587.
- Dombeck, G., and C. Borg. (2005) Multi-contaminant treatment for 1,2,3 trichloropropane destruction using the HiPOx reactor. In *Proc. 2005 NGWA Conf. on MTBE and Perchlorate, 26-27 May 2005, San Francisco, CA.*
- Focht, M.R. (1994) Bench-Scale Treatability Testing to Evaluate the Applicability of Metallic Iron for Above-Ground Remediation of 1,2,3-Trichloropropane Contaminated Groundwater. Thesis. University of Waterloo,
- Hunter, F. (1997) Fenton's treatment of 1,2,3-trichloropropane: chemical reaction by-products, pathways, and kinetics. In *Proc. Int. Symp. Chemical Oxidation: Technology for the Nineties* Vol. 6, Technomic, pp. 50-71.
- Kielhorn, J., G. Könecker, C. Pohlenz-Michel, S. Schmidt, and I. Mangelsdorf. (2003) 1,2,3-Trichloropropane. World Health Organization, Geneva.
- Klausen, J., P.J. Vikesland, T. Kohn, D.R. Burris, W.P. Ball, and A.L. Roberts. (2003) Longevity of granular iron in groundwater treatment processes. *Environ. Sci. Technol.* 37(6), 1208-1218.
- Lin, D.P., C. Falkenberg, D.A. Payne, J. Thakkar, C. Tang, and C. Elly. (1993) Kinetics of purging for the priority volatile organic compounds. *Anal. Chem.* 65(8), 999-1002.
- Löffler, F.E., J.E. Champimi, K.M. Ritalahti, S.J. Sprague, and J.M. Tiedje. (1997) Complete reductive dechlorination of 1,2-dichloropropane by anaerobic bacteria. *Appl. Environ. Microbiol.* 63(7), 2870-2875.
- Monincová, M., Z. Prokop, J. Vévodová, Y. Nagata, and J. Damborsky. (2007) Weak activity of haloalkane dehalogenase LinB with 1,2,3-trichloropropane revealed by X-ray crystallography and microcalorimetry. *Appl. Environ. Microbiol.* 73, 2005-2008.

- Mu, Y.J., and A. Mellouki. (2001) Rate constants for the reactions of OH with chlorinated propanes. *Phys. Chem. Chem. Phys.* 3(13), 2614-2617.
- National Toxicology Program (2005) 11th Report on Carcinogens. U.S. Department of Health and Human Services, National Institutes of Health, Bethesda, MD,
- Pagan, M., W.J. Cooper, and J.A. Joens. (1998) Kinetic studies of the homogeneous abiotic reactions of several chlorinated aliphatic compounds in aqueous solution. *Appl. Geochem.* 13(6), 779-785.
- Parales, R.E., N.C. Bruce, A. Schmid, and L.P. Wackett. (2002) Biodegradation, biotransformation, and biocatalysis. *Appl. Environ. Microbiol.* 68(10), 4699-4709.
- Peijnenburg, W.J.G.M., L. Eriksson, A. de Groot, M. Sjöström, and H.H. Verboom. (1998) The kinetics of reductive dehalogenation of a set of halogenated aliphatic hydrocarbons in anaerobic sediment slurries. *Environ. Sci. Poll. Res.* 5(1), 12-16.
- Voicu, I., I. Barnes, K.H. Becker, T.J. Wallington, Y. Inoue, and M. Kawasaki. (2001) Kinetic and product study of the Cl-initiated oxidation of 1,2,3-trichloropropane (CH₂ClCHClCH₂Cl). *J. Phys. Chem. A* 105(21), 5123-5130.