

Lee, Michael D., R. L. Raymond, Jr., and C. A. Nehrig. In Press. Source area bioremediation of chlorinated solvents with edible oil emulsion. To be presented at the In Situ and On-Site Bioremediation Seventh International Symposium, Orlando, FL, June 2-5, 2003.

SOURCE AREA BIOREMEDIATION OF CHLORINATED SOLVENTS WITH EDIBLE OIL EMULSION

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ABSTRACT: Groundwater in a sand and gravel aquifer beneath this active manufacturing facility was contaminated with high concentrations of 1,1,1-Trichloroethane (1TCA) and cis-1,2-dichloroethene (cDCE), and their degradation products including ethene and ethane. An acclimated anaerobic microbial population was present at the site, but was limited by the availability of carbon. Emulsified edible oil was injected into six points from 7.6 to 15.2 m below ground surface. The radius of migration of the substrate was as much as 7.6 m from the point of injection. Decreases in the parent compounds and increases in the daughter products including ethene and ethane were observed within the first month and a half after substrate addition. After 16 months, the average concentration of the total volatile contaminants had been reduced by 66%. However, substrate levels had fallen below the desired levels of 50 mg/L TOC in several wells. A second application of the emulsified substrate was injected into twelve 2.5 cm injection wells. Elevated total organic carbon levels were then observed throughout the treatment zone and stimulated further dechlorination. Degradation rates for the total volatile contaminants over the 762 day treatment period were as high as 268 $\mu\text{g/L-day}$ in a source zone well. 1TCA concentrations in this well have been reduced from 1,334 micromolar (μM) to 42.4 μM , a reduction of 97%. The overall average of total volatiles has declined by 82% over the 25 months since the emulsion was first injected.

INTRODUCTION: Slow-release substrates such as Regeneration's Hydrogen Releasing Compound (HRCTM), chitin, bark mulch, and edible oils last longer in the subsurface than soluble substrates and do not require installation, operation, and maintenance of a groundwater recirculation system (Lee et al. 2001). Substrates such as edible oil substrate or EOSTM will make it easier to distribute the substrate and can be less expensive than other substrates (Borden and Lee 2002).

Recent laboratory work has shown that anaerobic bioremediation may be applied to source areas with high concentrations of contaminants (Isalou et al. 1998, Yang and McCarty 2000, Yang and McCarty 2002). However, there is little supporting field data.

In August 2000, a pilot study was initiated to treat chlorinated volatile organic compounds (VOC) using in situ anaerobic bioremediation. The surficial deposit below the facility is primarily composed of interbedded sand, silt, gravel, and clay layers. Historical data indicates that anaerobic biodegradation is occurring at the site as evidenced by the presence of daughter products from the breakdown of tetrachloroethene (PCE) and trichloroethene (TCE) including cDCE, trans-1,2-dichloroethene (tDCE), vinyl chloride (VC), and ethene. 1TCA breaks down to 1,1-dichloroethene (1DCE), 1,1-dichloroethane (1DCA), chloroethane (CA), and ethane. However, VC and ethene can also be generated from the breakdown of the 1TCA, 1DCA, and 1DCE. Based on a

review of the site historical data, it appeared that the biological degradation process was limited by the availability of organic carbon.

The study area, which encompasses a triangular area roughly 28 m wide, 47.9 m long, and 18.2 m deep, underlies the drum storage area. At the start of the pilot test, total chlorinated contaminant concentrations in wells within the pilot area ranged from 457 to 539,000 $\mu\text{g/L}$. Generally, the contamination extends to approximately 27.4 m below ground surface (bgs) with the highest concentrations in the 6.1 to 15.2 m bgs zone.

The test area was injected with edible oil substrate or EOSTM in August 2000. The soybean oil is broken down into smaller organic molecules and hydrogen that are then used by the dechlorinating bacteria. VOC and substrate concentrations have been monitored seven times over a twenty-five month period at eight monitoring wells points (MW-14, MW-7, SMP-1, DMP-1, SMP-3, DMP-3, SMP-4, and DMP-4).

MATERIALS AND METHODS: Figure 1 is a schematic of the biotreatment system showing the monitoring wells and the injection locations within the treatment cell. The initial pilot bioremediation system consisted of seven injection points spaced about 4.6 to 6.1 m apart. In this injection event, the substrate was distributed throughout the vertical extent of the treatment area by a Geoprobe® rig. The Geoprobe® pushed a drivepoint to about 15.2 m bgs. The drill rod was pulled back 0.6 m to inject the fluids under pressure with a Rupe pump. The rod was then withdrawn 1.2 m and additional fluid was injected. This process continued until about 6.7 m bgs. In addition to pressure injection of the emulsion followed by injection of chase water to disperse the substrate, natural groundwater flow has dispersed the substrate. Another injection point received a direct injection of soybean oil. Total organic carbon (TOC) levels after the emulsion injection ranged from 39 to 23,500 mg/L.

Additional substrate containing soybean oil, a surfactant mix, a quick release substrate package, sodium bromide (a tracer), and activated carbon-treated water was injected in months 17 and 19 with a low pressure injection system to inject substrate into the treatment area with twelve injection wells (injection points 8-19). Twelve 2.5 cm wells installed to 16.8 m or 18.2 m bgs. Eight of the wells were spaced 2.3 m apart in a line. Two additional wells were placed on either side of the line. All of the wells had 6.1 of PVC blank riser and 10.7 to 12.2 m of PVC screen (0.02 slot) respectively. The wells were installed using the GeoprobeTM direct-push method.

RESULTS: Table 1 shows the initial concentrations of electron acceptors and TOC in mg/L and chlorinated ethenes and chlorinated ethanes in μM after the first injection of the EOSTM in August 2000. The percent change in the concentrations between then and the last sampling point (1/8/02 for wells MW-14 and MW-7 and 10/2/02 for the remaining wells) is also presented. Positive changes indicate that the concentrations of the analyte have decreased. A negative change indicates that the concentrations have increased. In a number of cases, the contaminants were not detected in the initial samples collected after emulsion injection or in the samples collected after twenty-five months. In these cases, the percent change was calculated using the analyte detection limit and the percent changes are designated as greater than (>) or less than (<) the calculated change. Figure 2 shows the concentrations of chlorinated ethenes and chlorinated ethanes on a micromolar basis and TOC over time for wells SMP-1 and SMP-3.

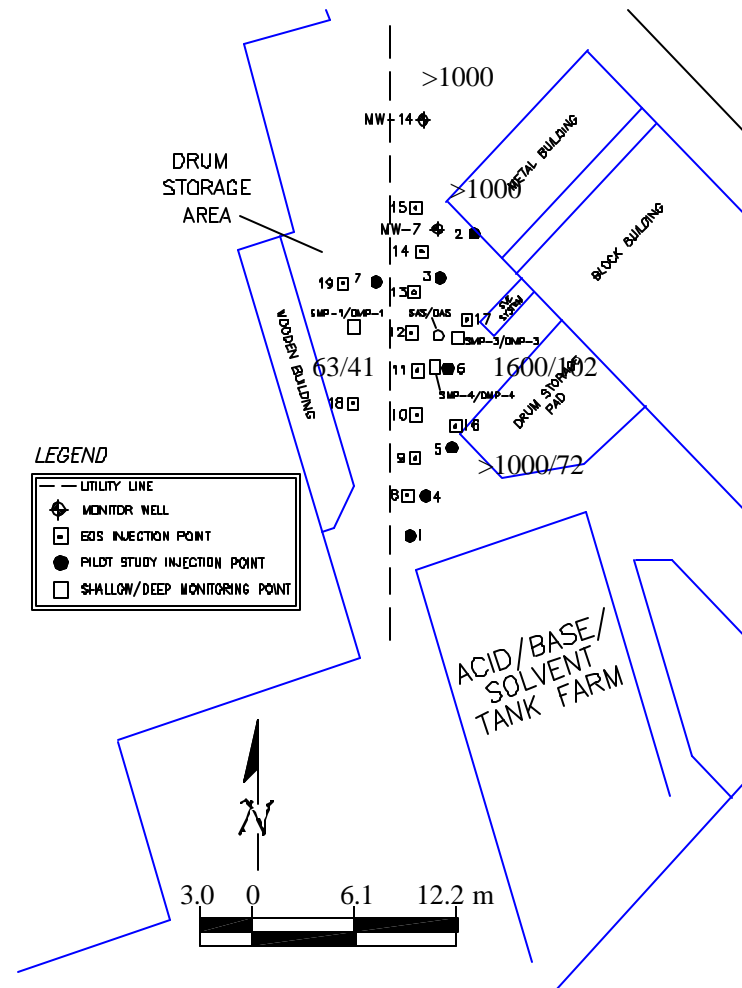


Figure 1. Treatment Cell and TOC Distribution 4/02/02

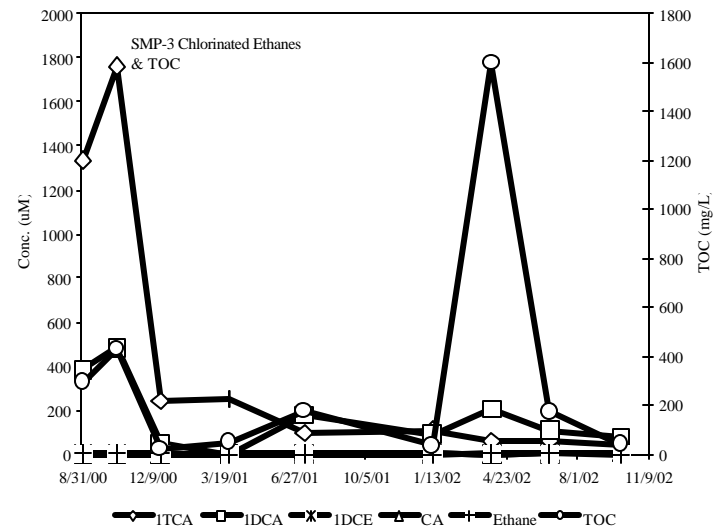
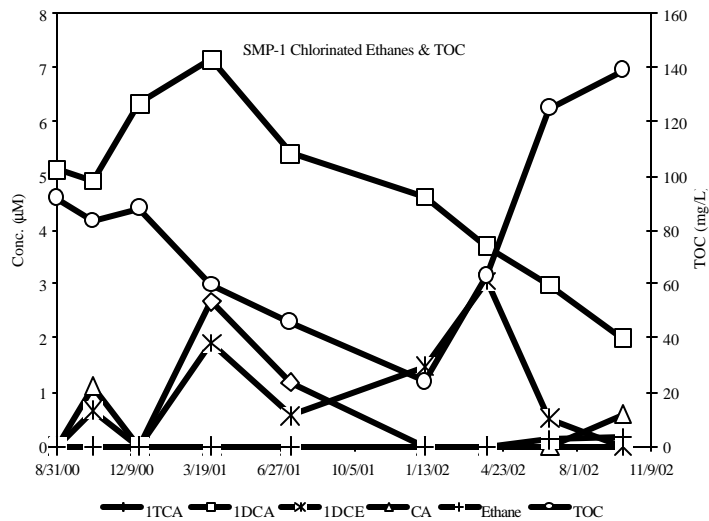
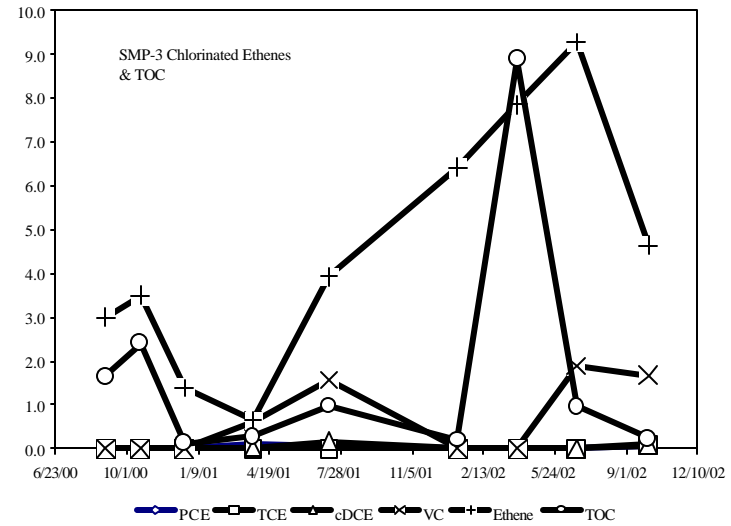
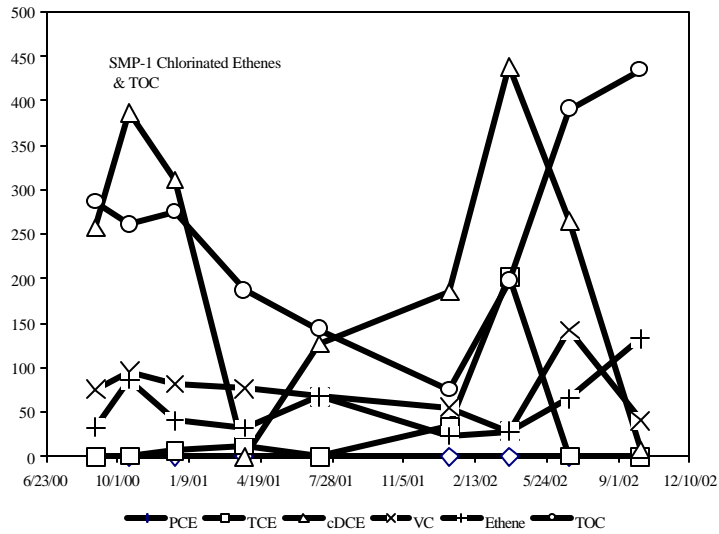


Figure 2. Chlorinated Ethene and Chlorinated Ethane Micromolar Concentrations and TOC for Monitoring Wells SMP-1 and SMP-3

TABLE 1. Initial Concentrations and Percent Change Between 9/1/00 and 1/8/02 or 10/2/02

Compound Last Sampled	Units	MW-14 8/31/00	% Change 1/8/02	MW-7 8/31/00	% Change 1/8/02	SMP-1 8/31/00	% Change 10/2/02	DMP-1 8/31/00	% Change 10/2/02
Methane	mg/L	0.044	-18195	0.66	-665	3.4	24	8.2	69
Iron	mg/L	55.2	-405	2.22	-490	19.8	38	88.5	95
Sulfate	mg/L	5470	92	104	-813	236	43	29600	96
TOC	mg/L	23500	89	38.8	96	91.7	-52	299	80
PCE	µM		0	<0.0024	0	<0.096	0	<0.0024	0
TCE	µM	<0.0065	0	<0.0065	>-218	<0.026	0	<0.0065	<-88
cDCE	µM	<0.0098	0	0.49	82	257	97	0.52	-152
tDCE	µM	<0.014	0	<0.014	>-56	<0.56	0	<0.014	<-211
VC	µM	<0.028	>-9786	0.63	73	75	46	3.0	4
Ethene	µM	1.5	-109	2.3	-75	33	-299	20	23
1TCA	µM	0.11	-10456	<0.0041	0	<0.16	0	<0.0041	0
1DCA	µM	1.3	-11090	1.2	-58	5.1	61	0.93	-351
1DCE	µM	<0.011	>-51519	<0.011	0	<0.43	0	<0.011	0
CA	µM	0.24	-3112	4.0	-51	<1.1	48	51.0	99.5
Ethane	µM	1.7	6	<0.20	>-1033	<0.20	23	<0.20	<72
Sum VOAs (w/o gases)	µg/L	396	-4529	490	-33	30598	88	12436	93

Compound Last Sampled	Units	SMP-3 9/1/00	% Change 10/2/02	DMP-3 9/1/00	% Change 10/2/02	SMP-4 9/1/00	% Change 10/2/02	DMP-4 9/1/00	% Change 10/2/02
Methane	mg/L	0.10	-640	0.39	-695	0.45	-633	0.18	-4678
Iron	mg/L	50.6	80	60.4	36	76.2	-1357	48.2	67
Sulfate	mg/L	286	-95	124	-868	933	92	133	-69
TOC	mg/L	294	86	98.2	-105	73.6	-4900	43.7	-79
PCE	µM	<0.48	>88	<0.097	0	0.080	-184	<0.0024	0
TCE	µM	<1.3	>98	<0.26	0	<0.0065	0	<0.0065	0
cDCE	µM	<2.0	>96	<0.39	>96	1.5	81	<0.0098	0
tDCE	µM	<2.8	>99	<0.56	>98	<0.014	0	<0.014	-41
VC	µM	<5.6	<70	17	94	2.8	83	<0.028	-209
Ethene	µM	3.0	-55	15.4	-28	7.9	99	8.9	44
1TCA	µM	1334	97	148	99	24	95	0.42	>99.5
1DCA	µM	386	80	53	24	41	100.0	0.30	-163
1DCE	µM	<2.2	>-60	1.6	96	1.1	99.7	<0.011	0
CA	µM	<5.1	>-54	83	-61	19	62	38	-34
Ethane	µM	1.3	72	0.19	-356	<0.20	<55	<0.20	<82
Sum VOAs (w/o gases)	µg/L	218600	93	32164	59	9376	87	2689	-27

Chlorinated Ethene Results. In the monitoring wells within the treatment cell, cDCE, VC, and ethene are the predominant chlorinated ethenes with little of the parent compounds, PCE or TCE, being detected. tDCE is a minor product. The highest concentrations of chlorinated ethenes were initially detected in SMP-1 and DMP-3.

TCE concentrations have increased in wells DMP-1 and MW-7 (through the last sampling point for this well in January 2002; the emulsion was found in wells MW-7 and MW-14 in subsequent sampling events and the wells were not sampled). The increases may be a result of dissolution of PCE and subsequent biodegradation to TCE, dissolution of TCE from a source zone, or an inadequate supply of substrate. TCE concentrations in SMP-1 increased from $<0.26 \mu\text{M}$ on 8/31/00 to a maximum of $202 \mu\text{M}$ on 4/2/02. However, TCE concentrations in SMP-1 declined greatly between 4/2/02 and 10/2/02 to $<0.0055 \mu\text{M}$ as VC and ethene increased; the dechlorination was attributed to the increased substrate availability in this area. There were increases in cDCE concentrations in well DMP-1. cDCE concentrations peaked in SMP-1 in April 2002 at $439 \mu\text{M}$, but then declined to $7 \mu\text{M}$ as of 10/2/02. cDCE concentrations have declined in wells MW-7 and SMP-4 by between 81 and 82%. VC concentrations have increased in wells MW-14 and DMP-4. Decreased VC levels have been observed in wells MW-7 (through 1/8/02), SMP-1, DMP-1, SMP-3, DMP3, and SMP-4 with reductions of 4 to 94%.

Ethene concentrations have increased in wells MW-14 (through 1/8/02), MW-7 (through 1/8/02), SMP-1 (through 10/2/02), SMP-3 (through 10/2/02), and DMP-3 (through 10/2/02) from the initial levels observed on 8/31/00-9/1/00. Ethene concentrations for the other three wells of the treatment area were lower than measured initially in September 2000. The continued presence of ethene in all of the wells in the treatment area shows that complete dechlorination of the chlorinated ethenes is occurring.

The addition of soybean oil emulsion has resulted in an increase in intermediate and final daughter products from the chlorinated ethenes in treatment area wells MW-14, MW-7, SMP-1, SMP-3, DMP-3, and DMP-4.

Chlorinated Ethane Results. There is also evidence for biodegradation of the chlorinated ethanes. Wells DMP-1, SMP-3, DMP-3, and SMP-4 had the highest total chlorinated ethane concentrations. 1TCA was the primary chlorinated ethane contaminant in wells SMP-3 and DMP-3. Reduced products such as 1DCA, CA, and ethane predominated in wells MW-14, MW-7, SMP-1, DMP-1, SMP-4, and DMP-4.

Well SMP-3 has shown a 97% ($1,334 \mu\text{M}$ to $42.4 \mu\text{g/L}$) reduction in the 1TCA concentrations. 1TCA levels in wells SMP-3, DMP-3, SMP-4, and DMP-4 have dropped by 95 to 99.5 percent. Between 24% and 80% reductions in the 1DCA concentrations were observed in DMP-3 and SMP-3, respectively. However, increased 1DCA concentrations have been noted in MW-14 (through 1/8/02), DMP-1, and DMP-4. When substrate levels were elevated after the second application of EOSTM, the 1TCA and 1DCA concentrations dropped. Large reductions in the 1DCE concentrations have been observed in wells DMP-3 (96%) and SMP-4 (99.7%), but 1DCE increased in MW-14 (through 1/8/02) and SMP-3. CA concentrations have declined by 99.5% in DMP-1 (51 to $0.24 \mu\text{M}$) and by 62% in SMP-4, but increased in MW-14, MW-7, SMP-3, DMP-3, and DMP-4. Based upon these results and laboratory studies currently underway with an anaerobic culture derived from the site groundwater, direct utilization of 1TCA and 1DCA may be occurring in addition to the reductive dechlorination reaction where

daughter products such as CA are produced and degraded. Degradation products CA and ethane levels are elevated in wells MW-14, MW-7, SMP-3, DMP-3, SMP-4, and DMP-4. Acetic acid has been reported as a byproduct of 1TCA degradation (Lee and Davis 2001). Alternatively, sulfides generated from the reduction of sulfate may be reacting abiotically with the 1TCA and 1DCA (Gander et al. 2002).

Sum of VOAs. The sum of the concentrations including chlorinated ethenes, chlorinated ethanes, and other compounds in each well was calculated excluding the final degradation endproduct gases, ethene and ethane. The sum of the VOAs has declined by up to 93% in DMP-1 with large decreases in SMP-1 (88%), SMP-3 (93%), DMP-3 (59%), and SMP-4 (87%). The sum of VOAs has increased by 4529% in MW-14 through 1/8/02 as the contaminated groundwater displaced during injection came back into the well and potentially as VOCs adsorbed into the oil were released. Increases in the sum of VOAs were also observed to a lesser degree in MW-7 (-33 through 1/8/02) and DMP-4 (-27%). The overall average of the sum of the volatiles has declined by 82% over the course of the treatment. This average includes the wells sampled on 10/2/02 and the two wells (MW-7 and MW-14) last sampled on 1/8/02. Increased biodegradation rates are expected as substrate limitations are overcome with the second injection of substrate. A first order degradation half-life of 462 days was calculated for the average total volatile contaminants within the treatment cell.

Substrate Distribution. The TOC distribution in April 2002 after the second application of the emulsion is shown in Figure 1. The TOC concentrations ranged from 41 mg/L in DMP-1 to 1,600 mg/L in SMP-4. Wells MW-7, MW-14, and SMP-4 contained the emulsion in April 2002 and were not sampled. These wells are shown as having >1000 mg/L TOC. Fifty mg/L TOC should provide sufficient carbon to support dechlorination and other electron accepting processes such as methanogenesis and sulfate-reduction. TOC levels increased in all wells as a result of the February-April 2002 injection event.

Electron Acceptor Results. As the microbes break down the emulsion, sulfate would be depleted and the concentrations of iron and methane would increase. The predominant electron acceptor in the groundwater in September 2000 was sulfate with concentrations that ranged from 104 mg/L in MW-7 to 29,600 mg/L in DMP-1. Sulfate concentrations have declined from the initial concentrations in wells MW-14 (92% through 1/8/02), SMP-1 (43%), DMP-1 (96%), and SMP-4 (92%) as would be expected with consumption of the oil emulsion. However, sulfate levels have increased in MW-7 (though 1/8/02), SMP-3, DMP-3, and DMP-4 over the course of the project. Total iron concentrations within the treatment area in October 2002 ranged from 4.2 mg/L in DMP-1 to 1,110 mg/L in SMP-4, which indicated that iron is also an important electron acceptor. Total iron concentrations have increased in three of the eight wells in the treatment area. The drop in dissolved iron concentrations in the other wells may be due to precipitation of the ferrous iron with sulfide produced from the utilization of sulfate. During the most recent sampling event in October 2002, methane was detected in all wells with methanogenic conditions (>1,000 µg/L) in MW-14 (though 1/8/02), MW-7 (though 1/8/02), SMP-1, DMP-3, SMP-4, and DMP-4. Methane concentrations have increased in six wells in the treatment area between September 2000 to January 2002 or October 2002.

DISCUSSION: Conditions continue to be favorable for accelerated anaerobic biodegradation of the chlorinated solvents at the site based upon the following positive results from the project to date including:

- decreases in the parent compound concentrations observed in many wells, particularly the large drops in the 1TCA and 1DCA concentrations in wells SMP-3 and DMP-3
- increases in the daughter products including final products ethene and ethane in many of the wells
- good distribution of substrate and its consumption
- prevalence of reducing conditions based upon the removal of sulfate and the production of dissolved iron and methane
- total contaminant concentrations have decreased by an average 82%.
- the average concentrations of the parent compound 1,1,1-trichloroethane has decreased by 96%

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