



Project Summary

Report on the Feasibility of APEG Detoxification of Dioxin-Contaminated Soils

Albert Klee, Charles Rogers, and Thomas Tiernan

This project was designed to verify, in proof-of-principle studies, the efficacy of newly developed chemical reagents to destroy 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) dissolved in a solvent (toluene) and in contaminated soil samples from two locations in Missouri.

The study demonstrated that alkali-based polyethylene glycol reagents under ambient conditions can completely destroy, within 48 hours, 510 nanograms of TCDD dissolved toluene. Also, in laboratory studies, the APEG reagents significantly reduced, within 21 days, the 330 ppb of TCDD in a Missouri soil by 25 percent with a single APEG application and 68 percent with two APEG applications.

Although this study accomplished its proof-of-principle objective, further research is required to establish optimal methods for applying APEGs to TCDD, PCBs, and other toxic halo-organics in contaminated soils and waste materials.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The full report describes proof-of-principle studies conducted to determine the ability of newly-developed chemical reagents to destroy 2,3,7,8-tetrachlorodibenzo-p-dioxin (referred to in the full report simply as TCDD) in contaminated soil samples from two locations in

Missouri. These novel reagents are based upon the reaction of alkali metals or their hydroxides with polyethylene glycols or their derivatives. For convenience, we refer to these reagents generically as APEGs. The code used for specific reagents is comprised of the following:

- K for potassium
- M for monomethyl polyethylene glycol ether (absence indicates that the ordinary form of polyethylene glycol was used)
- A number indicating the average molecular weight of the glycol

For example, KM-350 indicates a reagent made from reacting potassium (metal or hydroxide) with a monomethyl polyethylene glycol ether of average molecular weight 350, and K-120 indicates a reagent made from reacting potassium (metal or hydroxide) with a polyethylene glycol of average molecular weight 120.

Phase I

Two APEGs were involved in the first phase of these studies, K-400 and K-120. These reagents were used both with "neat" solutions of 510 nanograms TCDD (i.e., solutions containing TCDD dissolved in toluene; no soils were present) and with soils from two locations in Missouri, Denny Farm and Timberline Stables. The organic chlorine contents of these two soils were, respectively, 1380 ppm and 15.3 ppm; their TCDD contents were, respectively, 330 (± 33 ppb) and 277 (± 28 ppb).

With regard to the "neat" solutions, the K-120 destroyed 510 nanograms of TCDD

within a 2-day period. The results with K-400, however, were indeterminate, because this reagent was prepared using a 66% aqueous KOH solution and was therefore not miscible with the toluene solution of TCDD.

The percent reduction in TCDD from the original levels in the soil samples is shown in Table 1. The TCDD reduction data varied cyclically throughout the 4 weeks of the tests, with the samples showing an anomalous final TCDD reduction at 28 days, lower than that observed after 7 days. Furthermore, the variability of replicate analyses was quite high; in some cases the variability, expressed as a coefficient of variation, was as high as 40%.

Table 1. Percent Reduction from Initial TCDD Levels

	Timberline		Denny	
	K-400	K-120	K-400	K-120
7 days	45%	46%	nm	51%
28 days	35%	38%	12%	5%

nm = not measures.

Phase II

A series of supplementary experiments involving alterations in sample preparation and analytical procedure was conducted to discover the source of this high variability, and perhaps, to explain the anomalous 7- versus 28-day results. The results are summarized as follows:

1. There was no statistical evidence that exhaustive Soxhlet extraction, even with fresh solvent and with extraction times of up to 32 hours, extracted more TCDD than bottle extraction with extraction times of no more than 3 hours.
2. Although statistically significant differences do exist between "unconditioned" and "conditioned" soils (the term "conditioning" is used here to describe the addition of HCl, potassium hydroxide, or polyethylene glycol to the soil sample, followed by analysis for TCDD), the size of these differences is relatively unimportant. The following averages illustrate the differences found (the glycol used had an average molecular weight of 400 and is referred to as PEG-400 in the listing below:

Unconditioned:	292 ppb
With HCl:	302 ppb
With KOH:	313 ppb
With PEG-400	317 ppb

Thus, neither the individual components of the reagent itself nor the quench chemical used in the analytical procedure (i.e., the HCl) appreciably affects the amount of TCDD released from a soil sample during analysis. Furthermore, this observation is valid regardless of the period of time, up to 8 hours, that the chemicals are in contact with the soil.

3. There is no measurable time effect, up to 8 hours, on the recovery of the internal standard (37-Cl-labeled dioxin) after addition to the sample. Thus, the amount of time (up to 8 hours) that samples stand after the internal standard is added does not affect the precision of the results.
4. During these supplementary experiments, the precision of the analyses increased dramatically over that observed in the first series. Since the soil samples in the supplementary series were considerably more homogeneous than in the first (in the supplementary series the samples were sieved, intermixed, and ground in a ceramic ball mill containing Borundum grinding media, whereas in the first series the samples were sieved and intermixed only), it was concluded that inadequate sample preparation was the main cause of the anomalous results shown in Table 1. It is now clear that the TCDD is not uniformly distributed throughout the soil samples; therefore, it is imperative that soil samples be thoroughly homogenized before they are subjected to treatment with APEG reagents in laboratory studies.

Phase III

As a consequence of the Phase II supplementary studies, a final series of experiments, essentially designed as a repetition of Phase I, was conducted. However, during the interim between Phase I and Phase III of this study, new APEG reagents were tested that appeared to be much more reactive than K-120. Thus, K-120 was replaced by one of these new reagents, that is, KM-350, in this last phase. In addition, the K-400 reagent used in Phase III was prepared directly from KOH pellets rather than the 66% aqueous KOH solution used in Phase I. Only Denny Farm soil was used in the Phase III experiments. The results (in percent reduction in TCDD from the original level in the Denny Farm soil) are

shown in Table 2. The anomalies in the apparent decrease of the TCDD level of K-400 treated sample at day 14 were found not to be statistically significant.

Table 2. Percent Reduction from Initial TCDD Levels

	Denny Farm Soil	
	K-400	KM-350
1 day	8%	15%
7 days	19%	27%
14 days	16%	36%
21 days	25%	42%
28 days	22%	43%

To test the effect of a multiple application of an APEG reagent, a sample of Denny Farm soil was treated with K-400 and, 12 days later, a second application was made. Table 3 summarizes the percent reduction in TCDD observed, along with a repetition of days 14 and 21 in the single application data of Table 2 for comparison:

Table 3. Percent Reduction in Starting TCDD Levels

	Denny Farm Soil Treated with K-400	
	Single Application	Repeat Application
14 days	16%	56%
21 Days	25%	68%

The results of this study clearly indicate that APEG reagents can, under certain laboratory conditions, significantly reduce the levels of TCDD in contaminated soils. Future work must, however, concern itself with the following questions:

- What is the toxicological significance of by-products of APEG-dioxin reactions in soils?
- Can additives be found (surfactants, wetting agents, etc.) to increase and accelerate the contact between the reagent and TCDD that is tightly-bound to soil particles and other materials commonly found in soils?
- Are there other processes (radio-frequency heating, photolysis, etc.) that can enhance the use of APEG reagents on contaminated soils?
- What are the optimal methods for applying APEGs to soils and maintaining the integrity of the site (prevention of water influx, etc.) during the reaction period?