

## EVALUATION OF TECHNOLOGY FOR WASTES AND SOILS CONTAMINATED WITH DIOXINS, FURANS, AND RELATED SUBSTANCES

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### Summary

The objectives of the U.S. EPA Dioxin-Engineering program are: (a) to conduct basic/applied research on the behavior of 2,3,7,8-TCDD in contaminated soils, applying this knowledge to methods useful for the in-situ stabilization of such soils and investigating the viability of special organisms or chemical reagents for the destruction of this artifact and related toxic chemicals; and (b) to develop and evaluate, both in the laboratory and in the field, technologies for the detoxification, destruction, or control of PCDD-contaminated liquids and soils.

Resource levels for the program amount to \$3.3 million for 1984–1986 with an additional \$7.2 million from the Superfund to accelerate this program and provide quality assurance/control support to the data gathering and certification efforts.

In approximately one and one-half years, significant contributions have been made in the following areas:

- Sorption/desorption characteristics of 2,3,7,8-TCDD in contaminated soils have been investigated.
- In-situ stabilization techniques for soils are being evaluated.
- *Phanerochaete chrysosporium*, a white rot fungus, has shown the ability to degrade 2,3,7,8-TCDD in laboratory experiments.
- Shallow mines for contaminated soils have been evaluated and the concept appears technically and environmentally feasible.
- Field testing of the EPA Mobile Incineration System in Missouri is continuing. Destruction and removal efficiencies of >99.9999% were achieved; ash and scrubber water were delisted.
- Alkali polyethylene glycolate reagents are being studied and results are encouraging.

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### Introduction

On December 15, 1983, the U.S. Environmental Protection Agency (EPA) issued a national dioxin strategy for investigating, identifying, and cleaning up sites contaminated by dioxin (2,3,7,8-TCDD) [1]. Within the framework of this strategy was a plan that called for research to be conducted on the technical feasibility and economics of alternative methods for disposal and destruction of wastes and soils contaminated by dioxin.

To implement this strategy, EPA established seven categories (tiers) of

investigation and study ranging from the most probable contamination to the least. These are:

1. 2,4,5-Trichlorophenol (TCP) production sites and waste disposal sites.
2. Sites and associated waste disposal sites where 2,4,5-TCP was used as feedstock for pesticide products.
3. Sites and associated waste disposal sites where 2,4,5-TCP and its derivatives were formulated into herbicidal products.
4. Combustion sources such as municipal and hazardous waste incinerators, PCB transformer/capacitor fires, reactivation furnaces for spent granular activated carbon, boilers burning PCBs and pentachlorophenol (PCP)-treated wood, etc.
5. Sites where herbicides derived from 2,4,5-TCP have been and are being used on a commercial basis such as rights-of-way, rice fields, forests, certain aquatic areas, and pastureland.
6. Certain organic chemical and pesticide manufacturing facilities where improper quality control of certain production processes would have resulted in the formation of 2,3,7,8-TCDD.
7. Control sites where contamination of 2,3,7,8-TCDD is not suspected. These will be compared with known contaminated sites to form a background level for the strategy studies.

It is expected that 80–90 percent of the 2,3,7,8-TCDD contamination will be found in the first two categories. Cleanup activities in these areas are to be managed by the Agency's hazardous waste Superfund program.

## Discussion

The following projects were initiated in 1984 [2] and are herewith summarized:

### *Sorption/desorption of 2,3,7,8-TCDD in contaminated soils*

The environmental persistence and toxicity of 2,3,7,8-TCDD created an acute awareness of the need to clean up identified dioxin sites. Many investigators have documented the extreme immobility of TCDD and related chemicals, including some pesticides, in soils [3–6]; however, there have been no reported investigations dealing with the potential mobility of 2,3,7,8-TCDD in native, contaminated soils. Soil samples collected for this investigation were taken from an abandoned 2,4,5-T manufacturing facility and a scarp metal yard in New Jersey, and from horse arenas, roadways, and residential property in Missouri. These samples were contaminated with either chemical residues or waste oils containing 2,3,7,8-TCDD.

The objectives of this study were to determine: (a) Partition coefficients ( $K_p$ ) for 2,3,7,8-TCDD in soils and correlative soil physicochemical parameters; (b) consistency of a  $K_{oc}$  (ratio of  $K_p$  to mass of organic carbon per mass of soil) value derived from soils used to a predicted value; and (c)

potential mobility of 2,3,7,8-TCDD in soils based on a one-dimensional, convective-dispersive, solute transport equation.

The  $K_p$  ranged from 0.3– $130 \times 10^5$  ml/g with a mean of  $18 \times 10^5$  ml/g. These values seem realistic compared to previous work suggesting that the  $K_p$  would be in the range of  $1-10 \times 10^5$  ml/g. Mean  $\log K_{oc}$  for the two batch methods and the intact cores were 7.39, 7.58, and 7.55; these values were within one standard deviation of a value of 6.95 predicted with data from previous studies [7,8].

2,3,7,8-TCDD was found to be more soluble in soils containing higher amounts of halogenated, semi-volatile compounds and organic contaminants in wastes, other than 2,3,7,8-TCDD. The presence of such organic contaminants may be more significant than soil properties in controlling solubility and movement of 2,3,7,8-TCDD in soil because the 2,3,7,8-TCDD partitions more strongly into other organic contaminants than into natural organic components (e.g., humic acids).

The solute transport model used and the data collected during the study were employed to predict that 2,3,7,8-TCDD would be essentially immobile in water percolating through the soils studied. Using worst-case conditions\* (i.e., continuous, saturated water flow in the soil and hydraulic conductivity of  $10^{-4}$  cm/s) and the highest and lowest values for partition coefficients, the model predicted that 2,3,7,8-TCDD movement rates would be between 12 and 163,600 y/ft (4 to 5,367 y/cm).

Using the mean  $K_p$  value for all soils, the movement rate would be 11,800 y/ft (388 y/cm) [7,8]. These rates, for all practical purposes, are so slow that movement of 2,3,7,8-TCDD in water percolating through the soil will be insignificant; other transport mechanisms, such as wind and water erosion, are likely to be significantly more important. What this translates into is a scenario where TCDD-contaminated soils that contain low levels of other soluble organic contaminants might be left in place with little more than surface soil stabilization employed to reduce or prevent particulate transport via rainfall or wind.

#### *In-situ stabilization techniques*

Under the January 14, 1985, dioxin listing rule [9], dioxin-contaminated soils have been classified as acutely hazardous materials that require special management procedures to prevent migration and reduce human exposure. At this time, an effective remedial technology is needed to prevent desorption or transport of polychlorinated dibenzo-*p*-dioxins (PCDD) from soil particles by either rainfall or wind.

The objectives of this investigation are: (a) to evaluate cost-effective fixa-

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\*Also assuming that the saturated zone of interest is homogeneous with constant hydraulic conductivity. (Of further interest here is what may occur with time to the "transported" 2,3,7,8-TCDD at lower depths where natural soil organic content (e.g., humic acids) may come into play relative to reabsorption of the 2,3,7,8-TCDD released through percolation and/or weathering processes.)

tion or stabilization techniques that can be used to immobilize dioxin-contaminated soils and serve as remedial technologies for dioxin-contaminated soils; (b) to evaluate these stabilization techniques in the laboratory to develop optimum soil/stabilizer proportions and mixing conditions using industry-standardization protocols and acceptance criteria and (c) to assess the probability of successful field implementation of these methodologies through evaluation of the ability of weathered, stabilized soil mixtures to inhibit transport of these soils.

Three Missouri sites were selected for evaluation of the feasibility of cementitious and asphaltic stabilization techniques:

- Minker site — a residential area with steep, sloping banks that drain into a nearby creek (2,3,7,8-TCDD = 700 ppb/sandy loam).
- Piazza Road — a roadside material (2,3,7,8-TCDD = 640 ppb/sandy loam).
- Sontag Road — a roadside material, but with a considerably greater percentage of fine particles (silt and clay) (2,3,7,8-TCDD = 32 ppb/sandy silty loam).

Cement specimens were formulated at optimum moisture, but with varying cement contents, and tested for freeze/thaw susceptibility, and 7-day unconfined, comprehensive strength. Significant quantities of specimen loss occurred during the two sequential weathering processes, followed by the aqueous leaching procedure. Percent by weight degradation of the solid soil/cement specimens into disassociated particles ranged from 6–18% for Minker, 13–16% for Piazza Road, and 16–27% for Sontag Road, under the rigorous laboratory procedures employed. Differences in settling rates between soil/cement disassociated particles and native, unstabilized soil observed during the leaching process, suggest that the former contain a very low percentage of “erodable” silt- and clay-sized particles (<50  $\mu\text{m}$  diameter).

These experiments indicate a strong possibility that the leachate concentration may be limited by the decreased aqueous solubility of 2,3,7,8-TCDD in the range of 2–3 ppt in the leachate from the matrix [10,11].

For the emulsified asphalt stabilization tests, a cationic, slow-setting emulsion (CSS-1h) was chosen as the grade of asphalt to be used because a low-setting emulsion is recommended for mixed-in-place applications when a dense-graded aggregate is encountered such as in Missouri soils. After mix design work was completed on Minker and Piazza Road sites, it became apparent that emulsified asphalt per se would not provide an effective method for stabilization of the test soils. As a result, calcitic lime — calcium hydroxide — was employed to modify the soil prior to asphalt addition, thus reducing the effective surface area of the soil to be coated and the subsequent reduction in swell characteristics improved the properties of the compacted soil/asphalt mixtures exposed to water; curing or pozzolanic action takes place within the soil and contributes additional strength to the soil/asphalt matrix. Therefore, addition of 1.5% lime dramatically improved the per-

formance of soil/asphalt specimens when the SS-1h, a nonionic, slow-setting emulsion, was substituted for the CSS-1h emulsified asphalt previously employed.

Nine percent residual asphalt (RA) was chosen as the optimum asphalt percentage, which includes a safety factor of 0.5% RA. In addition to compacted specimens for each soil, triplicate soil/asphalt/lime mixtures from the Minker site were formulated but left uncompacted to evaluate the leaching potential and acceptability of this alternative. This option is currently being investigated because a keen interest has been expressed to evaluate an option in which a temporary in-situ stabilization effort is subsequently followed by soil/stabilizer removal and thorough stabilization at an off-site facility. It is anticipated that this approach would provide an excellent dust palliative prior to excavation and removal of the contaminated soil. Particle size analyses on uncompacted mixtures as well as non-associated particles from compacted specimens are awaiting completion. Preliminary observations suggest that the asphalt/lime combination has acted effectively to flocculate the fine particles and reduce the percentage of "erodable" particles ( $<50 \mu\text{m}$ ) relative to the native soil and will be effective as an interim remedial measure for solidification of dioxin-contaminated soils and concomitant mitigation of further environmental pollution. Leaching experiments with these specimens are complete and the extracts were subjected to GC/MS analysis. Examination of leachate concentration data from these stabilized soils revealed that the dioxin levels were not statistically different from those obtained for the corresponding unstabilized soils. This was true for leachates from both the parent soil-cement specimens, as well as for the disassociated particulate material. However, the absence of dioxin at detectable levels in virtually all soil-asphalt leachates implied that soil stabilization effectively reduced solubilization of the dioxin contaminant [11].

Capital costs were estimated for the emulsified asphalt for a  $340 \text{ m}^3$  volume (12-ft. wide  $\times$  1000-ft. length  $\times$  1-ft. depth =  $444 \text{ yd.}^3$ ) and amounted to  $\$5\text{--}10/\text{m}^3$  compared to  $\$11\text{--}13/\text{m}^3$  for portland cement for a  $284 \text{ m}^3$  volume (10-ft. width  $\times$  1000-ft. length  $\times$  1-ft. depth =  $370 \text{ yd.}^3$ ). When health and safety costs are considered, an increase of  $\$4\text{--}8/\text{m}^3$  must be included [11].

#### *White rot fungus: Phanerochaete chrysosporium*

Biotreatment systems using microorganisms for the degradation of toxic and refractory organopollutants hold the promise of being an efficient and economical means of detoxifying contaminated water, soils and sediments. Few organisms, however, have shown the ability to degrade organohalide pollutants. In general, organohalides are poorly soluble in water and are adsorbed to particulate matter thus making them even less susceptible to microbial attack. Pollutants of interest, such as 2,3,7,8-TCDD, are often present in the parts per million range or less.

Microbial enzymes, which may be able to degrade organohalide pollutants,

do not function effectively at very low substrate concentrations. Microbial strains especially adapted to grow on organohalide pollutants have only shown limited effectiveness. Because the chemical substances are present in such low concentrations, these strains may not be able to compete effectively with other microorganisms in a biotreatment system.

The basic objective of biodegradation research is to identify, develop, and test microorganisms capable of degrading highly toxic and refractory organohalide pollutants, more specifically at 2,3,7,8-TCDD-contaminated sites.

Research performed over the last ten years has not yet produced successful biodegrading organisms suitable for detoxification of 2,3,7,8-TCDD. Recent interest, however, has focused on a unique hydrogen peroxide-dependent oxidase secreted by the white rot fungus, *Phanerochaete chrysosporium*. *P. chrysosporium* and related fungi (there are between 1,600—1,700 species of wood-rotting fungi in the class *Basidiomycetes*) have the ability to recycle carbon bound within lignin. This enzyme system has proven effective in degrading lignin, a highly complex, chemically resistant, non-repeating heteropolymer. In cultures (10 ml) containing 1.25 nmol of the 2,3,7,8-TCDD substrate, 27.9 pmol were converted to  $^{14}\text{CO}_2$  in 30 days (2.23% metabolism) increasing to 49.5 pmol in 60 days (3.96% metabolism) [12,13]. Similar, but even more effective results, were observed with other organohalides including lindane, DDT, 3,4,3',4'-tetrachlorobiphenyl, 2,4,5,2',4,5'-hexachlorobiphenyl, 4,5,6-trichloroguaiacol, 3,4,5,6-tetrachloroguaiacol, and 2,4,6-trichlorophenol [12—14].

*P. chrysosporium* is a highly successful competitor in nature, especially when the carbon source consists of wood, wood byproducts or other lignin containing materials. Thus, if wood chips or sawdust, for example, are used as the carbon source in biotreatment systems, competition by non-lignin degrading organisms is likely to be minimal. Because degradation is promoted by nitrogen starvation rather than by the presence of substrate, low levels of organopollutants do not repress the biosynthesis of enzymes required for their degradation.

Of special significance for the degradation of organohalides is the fact that *P. chrysosporium* has the demonstrated ability to dehalogenate and degrade chlorobenzene derivatives and to cleave aromatic rings.

The *P. chrysosporium* enzyme system may be field tested in a small number of plots during the summer of 1987 at one of the contaminated sites in Missouri. These experiments may be considered as extensions of the ideally conducted tests in the laboratory and may indicate whether a full field evaluation in the future.

#### *Shallow mines as repositories for dioxin-contaminated soils*

The State of Missouri contains a large number of underground mines of various types, including shallow and deep, active and inactive, limestone, sandstone, lead, and iron varieties. If contaminated soil is removed from the

numerous dioxin sites in Missouri during remedial action cleanup operations, certain abandoned mines have the potential to be used as secure facilities for the placement of contaminated material.

It is assumed that it would not be necessary to subject the dioxin-contaminated soil to a stabilization process before placement in a mine because research on the desorption characteristics of 2,3,7,8-TCDD has shown it to be essentially non-mobile (mean value based on partition coefficient determination — 388 y/cm) [7,8]. However, some type of containment would be necessary (i.e., steel vaults (dumpsters), barrels, or polypropylene bags).

The objective of this project was to evaluate the feasibility of utilizing abandoned mines located in or near Missouri as repositories for dioxin-contaminated soils. This study addressed the many diverse factors that required consideration before the mine storage concept could actually be implemented.

The types of mines available in Missouri have been investigated. Twenty-nine mines, ranging in physical condition from abandoned and collapsing to excellent warehouse quality, were selected for study and 20 of these sites were visited. Aerial reconnaissance of mine sites was performed. Geological and hydrogeological conditions were extensively reviewed. The Missouri Department of Natural Resources, the University of Missouri (Rolla) School of Mines, and EPA Region VII staff were involved in the project from the onset.

Specific selection criteria were employed to determine which mines would be considered for review and evaluation. These included:

- Isolation from the surface environment and human contact.
- Reduction in the likelihood of inadvertent intrusion.
- Adequate confinement from secondary leakage problems.
- Surroundings that were chemically compatible with and thus would not corrode the waste forms or containers.
- Disposal areas that could easily be accessed for reconditioning and monitored.
- Location above the local watertable to prevent flooding and groundwater intrusion.
- Those mines located within a reasonable distance to problem areas.
- Selection limited to only mines already known to the Missouri Department of Natural Resources, Division of Geology and Land Survey.

Based on these criteria, a total of 29 mines was investigated [15]. Shallow, underground limestone/dolostone mines were found to offer distinct technical advantages over all other types of underground mines, i.e., sandstone, lead-zinc, iron, and coal. These advantages principally are related to dryness, structural stability, potential size, location, and accessibility factors. The overall cost of developing a facility was found to be affected primarily by the contaminated soil packaging container and mine packing arrangement. Packaging options evaluated included rectangular steel vaults, steel drums, and woven polypropylene sacks (supersacks). Supersacks

also are considerably less expensive than metal drums (plastic drums were not used in cost estimates), and metal drums are less expensive than metal vaults. Supersacks allow more soil to be stored in the same available space than the other packaging systems. Three different spatial arrangements for packing the containers in a mine were evaluated.

The project will expand beyond the concept of using existing mines to explore the concept of developing a new mine for storage purposes. Preliminary engineering, economic, and regulatory evaluations were prepared. Development of a new mine for storage purposes compared favorably with rehabilitation of an existing, inactive mine. Per unit costs for dioxin-contaminated soil were developed. Total capital costs for an existing 20,000 yd.<sup>3</sup> (15,290 m<sup>3</sup>) mine range from \$225–275/yd.<sup>3</sup> (\$172–210/m<sup>3</sup>), including waste handling costs, which average one-third of the latter estimates; annual operating and maintenance (O&M) costs amount to \$7/yd.<sup>3</sup> (\$5.4/m<sup>3</sup>) [15]. Estimated capital costs for excavation, containerization, and interim storage in pole barns range from \$754–1008/yd.<sup>3</sup> (\$577–771/m<sup>3</sup>) for three Missouri sites.

The EPA Office of Research & Development (ORD) will recommend that a small, existing shallow limestone mine be utilized to evaluate not only packaging concepts under a statistically suitable experimental design, but to identify and resolve permit issues for this type of activity. The research study will develop data regarding effectiveness of packaging methods, monitoring techniques, transportation, and will include hydrogeological assessment of the mine.

### *Mobile incineration*

As a result of the verification of 44 dioxin-contaminated sites within the State of Missouri, there became a need to initiate a field evaluation of a thermal destruction process sufficiently advanced and laboratory tested that would, in effect, be capable of achieving a Destruction and Removal Efficiency (DRE) of 99.9999% and hence remediation of a significant number of these sites.

The objectives of this research and evaluation program were: (a) to improve and facilitate the permitting process; (b) to establish that permit conditions of 99.9999% DRE and delisting guidelines for dioxins and other hazardous waste components could consistently and reliably be met; (c) to develop site-specific risk assessment methods; (d) to document the economics of the process; (e) to develop and put into practice an aggressive and positive community relations program; and (f) to demonstrate to the public that dioxin-containing wastes and contaminated soils could be safely processed and thereby open the marketplace to the private sector for use of equivalently effective technologies.

In 1983, trial burns were conducted in Edison, NJ, on RCRA-listed surrogates, including dichlorobenzene, trichlorobenzene, tetrachlorobenzene, Aroclor 1260, and tetrachloromethane (CCl<sub>4</sub>) [16]. After a solids feed sys-



tem was installed and tested in December 1984, additional laboratory tests were conducted by IT Corporation in Knoxville, TN. Currently, the mobile incinerator is installed at the Denney Farm site near McDowell, MO, where "cold" and "hot" tests were conducted using clean soil and soil contaminated with surrogates similar to those employed in the earlier liquid waste tests ( $\text{CCl}_4$  and hexachloroethane). Tests using dioxin-contaminated liquid wastes and soil verified the DRE and the effectiveness of the control devices. Interim delisting guidelines were established and analyses were conducted on ash, treated soils, filter materials, and process/quench water to ascertain if the guidelines were attainable.

Results of the recently completed, four dioxin test burns were compiled from more than 15,000 pages of analytical data and reviewed for quality assurance/control by EPA's Environmental Monitoring Systems Laboratory in Las Vegas, NV, prior to final report distribution for Agency peer review in late June 1985 and Agency Science Advisory Board (SAB) review in September 1985. Table 1 summarizes the results of the dioxin trial burns conducted during the period February 26–April 9, 1985 [17]. The dioxin trial burns were successful with DREs exceeding 99.9999%. During these tests, 1.75 kg of 2,3,7,8-TCDD, contained in 6,625 liters of liquids and over 40 tonnes of soil, were destroyed.

Particulate emission permit limitations ( $<180 \text{ mg/Nm}^3$  at 7%  $\text{O}_2$ ) were achieved in three of four test runs. The fourth run exceeded the prescribed limit slightly, possibly due to the accumulation of submicron-sized particles in the air pollution control system. The observed CO emission values (1.3–7.7 ppm) are equivalent to those from the best available incineration technologies and are indicative of very complete combustion (combustion efficiency (C.E.s) = 99.993–99.999%).

Finally, the treated soil (ash) and process wastewater from the incinerator were analyzed for a series of specific constituents considered as likely contaminants and were shown to meet interim delisting guidelines established by the Office of Solid Waste (OSW) (see Table 2). These materials, therefore, have been "delisted" from RCRA designation after a prescribed public comment period of 30 days, based on a prediction that these byproducts would not pose a hazard to human health or to the environment. The basis for this prediction was that data obtained from the trial burns demonstrated that the incineration system's byproducts met applicable guidelines for being nonhazardous.

As of February 6, 1986, about 2 million pounds (865,000 kg) of dioxin-contaminated solids (including soil, drums, and trash) and approximately 18,000 gallons (68,000 l) of dioxin-containing liquid wastes have been processed since February 1985. Total materials remaining include about 625,000 pounds (28,400 kg) of solids and 44,000 gallons (16,600 l) of liquid wastes. Operations were suspended on February 6, 1986, due to exhaustion of funds.

ORD currently is preparing, with OSWER financial support, to conduct

TABLE 1

Results of dioxin trial burns in Missouri [17]

Parameter	Permit limit	Test number				
		2-2 <sup>a</sup>	2-3	2-4	2-5	3-1, -2, -3 <sup>b</sup>
Rotary kiln Temp. (°C)	760-1040	845	826	902	918	852
Secondary Temp. (°C)	1120-1315	1153	1199	1194	1199	1187
Ret. time (s)		2.5	3.2	2.5	2.6	-
O <sub>2</sub> (vol.%)	>4	7.96	6.61	6.44	6.42	5.4
CO (ppm <sub>v</sub> )	<100(6 min)	7.7 <sup>e</sup>	1.3	2.3	2.5	6.8
CO <sub>2</sub> (vol.%)		10.9	11.3	11.4	11.1	-
C.E. (%)		99.993	99.999	99.998	99.998	-
TH (ppm <sub>v</sub> )		0.1	0.5	0.5	0.9	-
NO <sub>x</sub> (ppm <sub>v</sub> )		139	132	126	166	-
Liquid waste feed Total flow (pound/h)		233	236	234	247	-
TCDD (ppm)	<400	249	357	264	225	-
TCDD (g/h)	<27.2	26.3	38.3	28.0	25.2	-

<b>Solids feed</b>						
Total flow (pound/h)	< 2000	1158	1163	2068	1322	973
TCDD (ppb)		101	382	1010	770	-
TCDD (g/h)		0.05	0.24	0.95	0.46	-
<b>Stack</b>						
<b>Emission rate:</b>						
TCDD <sup>c</sup> (mg/day)		< 0.169	< 0.127	< 0.031	< 0.064	-
<b>Particulates</b>						
(mg/Nm <sup>3</sup> at 7% O <sub>2</sub> )	< 180	134.3	147.3	145.6	201.5	-
DRE (%)	> 99.9999	> 99.99997	> 99.99999	> 99.99999	> 99.99998	-
<b>Bromine emission rate<sup>d</sup></b>						
(pound/h)		-	-	-	-	< 0.26
R.E. (%)	> 99	-	-	-	-	> 99.0

TCDD = 2,3,7,8-TCDD; C.E. = combustion efficiency; R.E. = removal efficiency; DRE = destruction and removal efficiency; TH = total hydrocarbons.

<sup>a</sup> Test 2 - liquid feed: dioxin-contaminated TCP still bottoms; solids feed: TCP still bottoms + contaminated soil.

<sup>b</sup> Test 3 - liquid feed: fuel oil; solids feed: dioxin-contaminated/brominated naphthalene-contaminated lagoon sludge; combined results for three one-half hour runs.

<sup>c</sup> No TCDD detected at detection limits in effect; hence, emission rates denoted are detection limits and not measured quantities.

<sup>d</sup> In three test runs conducted on February 20-21, a CCl<sub>4</sub>/methanol mixture (33/67 wt.%) was fed at 480 pound/h (chlorine feedrate = 147 pound/h) with stack gas HCl emission rate = 0.071-0.156 pound/h for a HCl R.E. = 99.89-99.95%; RCRA permit required HCl emission rate < 4 pound/h and R.E. = > 99%.

<sup>e</sup> In this test, there resulted a CO excursion of 282 ppm for 168 s, but limit was met overall.

TABLE 2

MDNR<sup>a</sup> and EPA delisting parameters (for trial burn only)

## A. Per 40 CFR 261 Subpart C

	Ash (treated soil)	Scrubber waste liquids
Ignitability	N.A. <sup>b</sup>	N.A. <sup>c</sup>
Corrosivity	pH = 2.0–12.5	pH = 2.0–12.5
Reactivity	Not reactive with water	Not reactive with water
EP Toxicity	As per 40 CFR, 261.24, Table 1, and App. II, except mercury <sup>d</sup>	ICP scan—heavy metals, except mercury as per Table 1 <sup>d</sup>

## B. Specific substances

Toxic constituent	Concentration	
	Ash	Scrubber water
Dioxins/Dibenzofurans <sup>e</sup>	1 ppb	10 ppt
2,3,4-Trichlorophenol	100 ppm	10 ppm
2,3,5-Trichlorophenol	100 ppm	10 ppm
2,4,6-Trichlorophenol	1 ppm	50 ppb
2,5-Dichlorophenol	350 ppb	15 ppb
3,4-Dichlorophenol	100 ppm	10 ppm
2,3,4,5-Tetrachlorophenol	1 ppm	50 ppb
2,3,4,6-Tetrachlorophenol	1 ppm	50 ppb
1,2,4,5-Tetrachlorobenzene	100 ppm	10 ppm
1,2,3,5-Tetrachlorobenzene	100 ppm	10 ppm
Hexachlorophene	200 ppm	5 ppm
Polychlorinated biphenyls	2 ppm	1 ppm
Benz(a)pyrene	5 ppm	10 ppb
Benz(a)anthracene	5 ppm	10 ppb
Chrysene	50 ppm	1 ppm
Dibenzo(a,h)anthracene	5 ppm	10 ppb
Indeno(1,2,3-c,d)pyrene	5 ppm	10 ppb
Benz(b)fluoranthene	5 ppm	10 ppb

<sup>a</sup> Missouri Department of Natural Resources.<sup>b</sup> The ash would not be ignitable after having passed through a kiln and having reached approximately 750°C at the time of discharge.<sup>c</sup> The scrubber waste liquid, water, is not considered ignitable.<sup>d</sup> Analysis will be for the following metals; arsenic, barium, cadmium, chromium, lead, nickel, selenium, silver.<sup>e</sup> Weighted average of TCDDs/TCDFs, PCDDs/PCDFs, and HxCDDs/HxCDFs using toxicity weighting factors (in this case, P denotes penta).

experimental test burns at its Combustion Research Facility (CRF) near Pine Bluff, AR. The wastes to be investigated include: Occidental Chemical Corporation (OCC) Hyde Park non-aqueous phase leachate (NAPL) and Love Canal sludge (both from sites in the Niagara Falls, NY, area); Vertac Chem-

ical Corporation still bottoms from Jacksonville, AR; and Tennessee Valley Authority (TVA), Muscle Shoals, AL, Herbicide Orange. The test burns will generate valuable combustion data for presentation at public hearings where the merits and effectiveness of private-sector-developed mobile or transportable incineration units can be discussed. (Hyde Park NAPL volumes are in excess of 300,000 gallons (113,200 l); Vertac has several thousand drums of still bottoms from 2,4,5-TCP, 2,4,5-T, and 2,4-D production; and TVA has 21 drums of Herbicide Orange, one with 5.6 ppm 2,3,7,8-TCDD.)

Additional research may be conducted using a variety of composite sludges from wood treating waste lagoons containing creosote, pentachlorophenol, dioxins, furans, copper and zinc naphthalenates and arsenicals, inorganics, etc. The intention of future operations with the mobile incineration system is more to encourage commercialization of on-site cleanup technologies than it is to employ the system consistently for cleanup activities. As a result of the EPA experiences and operating information amassed, the private sector will likely design and construct improved, more reliable, larger capacity, and lower cost systems of equivalent performance for use in routine cleanup operations.

#### *UV photolysis/APEG chemical detoxification*

Chemical destruction of PCDDs within Missouri soils may represent a practical method for reducing widespread contamination. Laboratory tests, conducted at EPA HWERL-Cincinnati, have shown the ability of newly developed chemical agents termed APEGs (alkali polyethylene glycolates) to destroy 2,3,7,8-TCDD in solution and within a limited number of contaminated Missouri soils.

The ultimate objective of the APEG program is to develop reliable and cost-effective techniques for the destruction and/or detoxification of toxic halogenated organics, including 2,3,7,8-TCDD, present in contaminated soils at dumpsites, in roadbeds and horse arenas that have been coated with dioxin-containing waste oils. The specific objective is to determine the performance and cost effectiveness of APEG reagents singly and in conjunction with UV irradiation at ambient conditions in the field.

Laboratory proof-of-principle experiments using 1,2,3,4-TCDD show that this isomer in soil may be chemically dechlorinated to levels below 1 ppb in soil [18]. The dechlorination is accomplished by addition of APEG reagents, and in some instances dimethylsulfoxide (DMSO), to the soil allowing the reagent mixture to extract and dechlorinate the 1,2,3,4-TCDD at temperatures from 70 to 170°C. Three methods of application are currently under investigation in the laboratory: in-situ; heated in-situ; and slurry; the latter involving reagent recovery and recycle [19-21].

Costs of chemicals (APEG) are estimated \$1000/acre/1-cm penetration. Capital costs for a 160 yd<sup>3</sup>/day (122 m<sup>3</sup>/day) slurry process with reagent recovery are estimated at \$2.25 million, which includes \$0.75 million for an on-site GC/MS/MS trailer unit. Given these preliminary estimates and the fact

that field evaluation tests must be conducted, it appears that applicability of this technique is limited to open, flat areas similar to dioxin-contaminated horse arenas, where minimal vegetation exists. Data from soil borings at Times Beach, MO, demonstrate almost complete adsorption of 2,3,7,8-TCDD within the upper 23 cm soil thickness and an interesting chromatographic effect when concentration of 2,3,7,8-TCDD (143 to 2 ppb range) is plotted against soil depth [4]. Total organic carbon (TOC) (117 to 6 ppm range) adsorption paralleled that of 2,3,7,8-TCDD except that removal occurred in the upper 5 cm. Given this information, chemical detoxification of contaminated soils will be limited by depth of penetration. In other words, the upper 30 cm (12 in.) soil thickness is the depth of concern and detoxification will be limited to that depth. Any remaining 2,3,7,8-TCDD below this depth is assumed to be immobile based on desorption experiments discussed previously.

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