Multimedia sampling for dioxin at a strip mine reclaimed with sludge from bleached kraft wastewater treatment

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ABSTRACT *Mead conducted a two-year dioxin testing program on strip-mined land being reclaimed with sludge from the wastewater treatment plant of its bleached kraft mill. Many different samples were analyzed for both 2,3,7,8-TCDD (or dioxin) and 2,3,7,8-TCDF (or furan). The study included biodiversity studies to determine the total environmental impact. The results indicate that the sludge is an excellent reclamation material that improves the biodiversity at the site. The trace dioxin in the sludge does not exhibit any significant migration or bioavailability when used for reclaiming strip mines. These findings differ from assumptions sometimes used in assessing the environmental risks of dioxin.*

KEYWORDS
Dioxins
Environmental control
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Landspreading
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Sludge
Waste disposal

In the late 1970s, the Chillicothe operation of the Mead Corp. embarked on research to determine a beneficial use for the sludge from its wastewater treatment plant. In cooperation with the Ohio State University and the Ohio Dept. of Natural Resources, it was determined that Mead's pulp and paper mill sludge could be effectively utilized as a soil replacement at abandoned strip mine sites (*1*).

In 1985, dioxin was discovered in sludges from the wastewater treatment plants of bleached kraft mills. This discovery has caused a shift in public policy concerning the development of programs regulating the beneficial landspreading of such sludge. In fulfillment of an agreement reached between the Mead Corp. and the Ohio Environmental Protection Agency, Mead undertook and completed a two-year multimedia dioxin testing program on a portion of strip-mined land that was being reclaimed with sludge from the wastewater treatment plant of its bleached kraft mill in Chillicothe, Ohio.

Here, we will discuss the results of the analyses, with emphasis on the results of the analysis of 2,3,7,8,-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8,-tetrachlorodibenzofuran (2,3,7,8-TCDF). Full documentation may be found elsewhere (*2*).

Background

At typical strip mine reclamation sites, sludge should be applied to the surface in a thin layer (average depth of 15 cm) and then incorporated into the top 15–45 cm of the spoil material that has been left behind after the mining was completed. In some sites, however, there are "gob" piles, and these sites are particularly difficult to reclaim. Gob consists of shale, low-grade to unmarketable coal, pyrite, and other minerals that are extracted with coal and left on the surface when the coal is cleaned. To reclaim these sites, it is necessary to apply the sludge to the surface and minimize the extent to which the sludge becomes incorporated with the gob.

In 1984, Mead began the reclamation of a site known as Broken Arrow. The Broken Arrow site is located in Jackson County, Ohio. It consists of approximately 190 hectares (470 acres) of gob. Broken Arrow had been ranked by the State of Ohio as the third worst abandoned strip mine site in the state because of its serious impact on the surrounding environment. The size and topography of the site made reclamation particularly difficult.

During late 1984 and 1985, Mead completed reclamation of approximately 40 ha of the total 190 ha to be reclaimed. In several areas, it was necessary to apply considerably more sludge than the normal 15 cm, in order to maintain a viable, long-term reclamation.

With the finding of dioxin in the wastewater treatment plant sludges of the industry's bleached mills, however, most reclamation activities using Mead's pulp and paper mill sludge were suspended in late 1985 pending review and program approval by the State of Ohio. In May 1987, approval was granted to Mead's Chillicothe operation to use its sludge for strip mine reclamation under the terms of a new general sludge management plan (*1*).

Because of the site's unique characteristics and the difficulties of reclamation, limited reclamation activities were allowed to continue at Broken Arrow pending review of the general sludge management plan. Ultimately, an approval separate from the plan was granted for the Broken Arrow site. Under the terms of this approval, Mead agreed to undertake an extensive sampling and monitoring study.

The purpose of this study was to determine the environmental impacts from the use of sludge at strip mine reclamation sites. Because sludge was surface-applied to substantial depths, the situation at Broken Arrow was determined to represent a worst case for the purposes of analysis.

I. Soil data giving the ranges of dioxin and furan over the four semi-annual sampling events

Site and type of sample	Concentration, parts per trillion	
	Dioxin	*Furan*
Area 1		
Surface	1.77 - 7.99	16.0 - 51.5
Subsurface	< 0.23 - 397	0.60 - 34.2
Deep subsurface	< 0.25 - 2.08	0.24 - 9.92
Area 2		
Surface	< 2.95 - 9.59	32.1 - 58.1
Subsurface	< 2.97 - 4.00	20.6 - 31.7
Deep subsurface	< 0.92 - < 3.93	< 1.0 - 4.0
Area 4		
Surface	5.16 - 7.72	36.2 - 49.6
Subsurface	4.23 - 9.83	38.4 - 46.1
Deep subsurface	1.17 - 7.03	8.1 - 29.7
Area 7		
Surface	< 0.28 - 13.10	1.7 - 44.4
Subsurface	< 0.10 - 7.09	< 0.1 - 30.1
Deep subsurface	< 0.10 - 3.70	< 0.2 - 16.6
Control Site I		
Surface	< 0.17	< 0.18
Subsurface	< 0.86	< 0.16
Deep subsurface	< 0.11	< 0.52
Control Site II		
Surface	1.82	7.65
Subsurface	< 0.95	4.93
Deep subsurface	< 0.65	< 0.44
Control Site III		
Surface	< 0.21	< 0.38
Subsurface	< 0.32	< 0.31
Deep subsurface	< 0.25	< 0.39

Surface = 0-2.5 cm deep, core composite.
Subsurface = 2.5-15.0 cm deep, core composite.
Deep subsurface = 15.0-30.0 cm deep, core composite.

Design of study

The ecological media that were sampled included mixtures of sludge and soil, earthworms, terrestrial and aquatic vegetation, small field rodents, and lake and stream sediments.

The sludge/soil sampling plan included surface and subsurface sludge/soil samples. These samplings were made to determine the extent to which vertical translocation of TCDD and TCDF was occurring.

Terrestrial vegetation samplings, consisting of grasses and forbs, were analyzed to study the possibility of TCDD and TCDF uptake into these vascular plants. Earthworms were chosen because they are known to bioconcentrate TCDD and TCDF.

The field rodents, mostly field mice (*Peromyscus*), were the mammals chosen because they are among the least transient, which makes them a vital link in the food chain, and because they burrow in soil.

After the first round of four sampling events, aquatic vegetation and frogs (*Rana*) from a small lake on the site, Lake Adams, were added to the study. The purpose for this addition was to determine if bioaccumulation was taking place and whether there were any deleterious effects on these aquatic organisms.

Finally, sediment samples were obtained from a stream known as Flint Run, which flows by the site. Samples were taken upstream, adjacent, and downstream of the Broken Arrow reclamation site. Also, during the fourth round of sampling, silt samples from bank run-off and lake sediment collections were taken at the Lake Adams sampling site. All of these samples were obtained to determine if erosion was causing translocation of the TCDD and TCDF.

Throughout the two-year study, 228 samples were analyzed for TCDD and TCDF. In addition to the study components chosen for TCDD and TCDF analysis, the population density of vegetation, the biomass of samples, the age distribution of field mice, and the species identity were determined.

Selection of the sampling site

Four different areas were chosen within the reclamation site. Though there were a number of different areas, these particular ones were chosen because they represent a variety of regrowth times elapsed since the initial reclamation. These areas had been reclaimed and seeded during the following time periods:

- Area 1: Oct. 1984 through Nov. 1985
- Area 2: Summer 1986
- Area 4: Oct. 1984 through Nov. 1985
- Area 7: Autumn 1986.

Three control sites were found outside the reclamation area. The first control site location (Site I) was chosen because of its similarity to the original Broken Arrow strip mine site. It consisted of sparse vegetation except along a power company's right-of-way. Many of the first-round control samples for soil, vegetation, and mouse catches were taken in or near this clear-out.

A second control site (Site II) was established when it was determined that the vegetation at Control Site I was not representative of the vegetation at the test site and mouse catches were too few to allow for a sufficient sample size to meet analytical requirements.

A third control site (Site III) was used for soil samples and field rodents when TCDD and TCDF was detected at Control Site II. Upon further study of the history of land use at Control Site II, we discovered that this area was previously a railroad right-of-way. Consequently, the TCDD and TCDF might have resulted from railroad ties being treated with pentachlorophenol.

The initial lake control site (Lake Site I) also had to be changed to a different location (Lake Site III) when it was found that species diversity was not as great at the original control site as it was at the test site.

Sampling procedures

Grid sampling method

A literature review was conducted to determine the most appropriate sampling procedures to use (*2*). Based on this review, a grid sampling method was chosen.

Square grids measuring 10 m × 10 m were laid out in each of the four previously selected reclamation areas and the control site. From this grid, two sectors were selected from each area for sampling. The sectors were selected on the basis of topography, geographic separation, vegetation homogeneity, and sludge uniformity. Similarly, at the control site, sectors were chosen for comparison if they had topography, soil conditions, sun exposure, and vegetative cover similar to the reclaimed areas.

Before sampling, sludge/soil pH and porosity tests were conducted, and photographs were taken of the sectors to be sampled. Also, for the purposes of earthworm sampling, a 1-m^2 sampling subsector was randomly selected from within the larger 100-m^2 sector.

The following are the specific sampling techniques employed in each area and control site for each of the media sampled.

Sludge/soil mixture sampling

A single sample point was randomly selected for core sampling in each of the 100-m^2 sectors. Representative 50-cm^2 samples were composited from the core for three different-depth horizons. These three samples were designated surface, subsurface, and deep subsurface.

Vegetation sampling

Samples of vegetation were collected from each of the previously selected sectors. The vegetative cuttings were made from the soil surface up to the apex of the plant.

The samples were separated and identified as to which species were dominant. The samples were either weight composited (for the first sampling period) or separated into dominant and nondominant species (in the subsequent three sampling periods). The dominant species were kept separate for individual analysis, and the nondominant species were weight composited.

Earthworm sampling

Multiple attempts were made at obtaining earthworms from each of the 100-m^2 sampling sectors. The soil from several randomly selected subsectors (1 m × 1 m × 0.3 m) was hand sifted for earthworms. It was necessary that at least 50.0 g of earthworm biomass be collected for each composite sample to produce valid analytical results (*3*). However, because of a lack of earthworms at the sites, it was not possible to meet this minimum.

Small field mammal sampling

In initial sampling efforts, randomly placed traps within the 100-m^2 sampling sectors did not produce satisfactory results as measured by the trap success rate. By closely checking the sampling areas, we found evidence of mouse runs. Traps were then placed near these mouse runs and baited with a mixture of peanut butter, oatmeal, and bacon bits. The location of each trap was marked with red plastic tape for ease in retrieval. Each morning, the traps were checked for captures. The method provided a capture success rate of 15% per trap night, approximately two times the success rate of a similar study (*4*).

The captured rodents were collected and tagged as to the location of capture and as to genus. If possible, they were determined to be juvenile, intermediate in development, or adult.

Aquatic (lake) sampling

The aquatic samples consisted of lake bank vegetation, aquatic vegetation, and frogs collected in and near Lake Adams. Samples were obtained using appropriate sampling methods (*2*).

In addition to these samples, during the fourth round of sampling, two silt screens were constructed across drainage ways into Lake Adams. These were used to capture silt running off the reclaimed area (Area 1) into the lake.

Sediment samples from the lake were also obtained. These samples were collected at a depth of 0.5 m from the water's surface and approximately 3 m out from the water's edge.

Stream sediment sampling

Sediment samples were obtained upstream, adjacent, and downstream of the Broken Arrow strip mine reclamation site from a stream (Flint Run) which flows by the site. The sampling method employed was similar to that used for the lake sediment sampling.

General handling and analysis

Chemically sterile conditions were maintained throughout each sampling event. To prevent potential contamination from one site to another, all sampling equipment was washed with water and then acetone prior to reuse.

II. Vegetation data for dioxin and furan

Sample site	*Dioxin, parts per trillion*				*Furan, parts per trillion*			
	Summer 1987	*Spring 1988*	*Autumn 1988*	*Summer 1989*	*Summer 1987*	*Spring 1988*	*Autumn 1988*	*Summer 1989*
All species								
Area 1	<5.45	...	...	...	<2.03	...	...	...
Area 2	<2.71	...	...	...	<1.09	...	...	...
Area 4	<8.07	...	...	...	<6.47	...	...	...
Area 7	<2.82				<4.21			
Area 1, 2, 4, 7								
By dominant species								
Orchard grass (*dactylis*)	...	<0.40	...	<0.22	...	<0.36	...	0.81
Tall red fescue (*festuca*)	...	<0.22	...	<0.16	...	<0.23	...	0.55
Common lambsquarter (*chenobium*)	...	<0.35	<0.32	...	...	<0.31	1.95	...
Goldenrod	...	...	<0.19	...	...	...	<0.60	...
Common milkweed (*asclepias)*	...	...	<0.33	...	...	...	2.07	...
Long leaf aster (*bidens*)	...	...	...	<0.21	...	...	...	0.84
By nondominant species								
Yellow sweet clover, milkweed evening lychnis, foxtail Queen Anne's lace	...	<0.41	...	...	...	<0.55	...	...
Wild daisy, wooly mullein, boneset, grasses	...	...	<0.41	...	...	...	<0.73	...
Golden, timothy, white sweet clover, mullein	...	...	...	<0.13	...	...	...	<0.54
Control Site I								
Butterfly weed, spotted joepye weed, sneezeweed, yarrow, mountain mint, black-eyed susans	<2.04	...	...	<0.12	<1.59	...	...	0.66
Control Site II								
By dominant species								
Goldenrod (*solidago*)	...	<0.21	<0.24	...	...	0.60	1.41	...
Yellow and white sweet clover	...	<0.37	...	...	...	<0.22	...	...
Tall red fescue	...	<0.81	...	...	...	<0.39	...	...
By nondominant species								
Milkweed, alsike clover, yarrow, Queen Anne's lace,	...	<0.36	...	...	...	<0.31	...	...
Common lambsquarter, grasses	...	...	<0.37	...	...	...	<1.06	...

All samples were composites.

After appropriate field processing, all collected samples were wrapped in aluminum foil and placed in plastic Lock-Tite bags. The samples were coded, labeled, and logged. All samples, except the sludge/soil samples, were placed in iced coolers for temporary holding in the field. At the end of each day's collections, all animal samples were frozen. All other samples were refrigerated.

At the end of each sampling round, all samples collected were transported, along with the chain of custody documentation, to Wright State University for analysis for 2,3,7,8-TCDD and 2,3,7,8-TCDF.

Throughout this work, sampling procedures were modified as necessary and in accordance with good scientific principles to reflect site specific conditions. All modifications have been carefully documented elsewhere (*2*).

Results

Mixtures of sludge and soil

Table I lists the ranges of 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in the soil/sludge mixtures collected at the site. (For all tables, the less-than sign, ">," indicates that the analytical result was below the detection limit represented by the number following the symbol.) The concentrations of TCDD and TCDF decreased with increasing depth.

There was no evidence of vertical translocation within the sludge/soil column.

Terrestrial vegetation

In **Table II** are the results from the analysis for TCDD and TCDF of terrestrial vegetation samples collected from the site. No vegetation sample collected during this study contained detectable amounts of TCDD. TCDF was detected in samples collected from both the reclaimed areas and the control sites.

As the table shows, vegetative biomass, population density, and diversity were higher on the reclaimed site than on the control sites. Vegetation samples showed no detec-

III. Field mouse data for dioxin and furan

Sample site	Dioxin, parts per trillion Summer 1987	Spring 1988	Autumn 1988	Summer 1989	Furan, parts per trillion Summer 1987	Spring 1988	Autumn 1988	Summer 1989
Area 1	<2.54	...	...	...	<3.45	...	...	...
Area 2	<1.01	...	...	...	<1.00	...	...	...
Area 4	<3.76	...	...	...	<1.86	...	...	...
Areas 1, 2, 4, 7								
Adult males	...	<0.29	<0.15	<0.14	...	<0.30	<0.20	0.28
Adult females	...	<0.83	<0.16	0.21	...	1.62	<0.16	0.46
Juveniles and intermediates	...	<0.72	<0.18	<0.40	...	<0.30	<0.15	<0.34
Control Site I								
Both sexes*	<1.51	<3.26	...	<0.20	<0.68	...	...	...
Males	...	...	...	...	...	<0.30	...	<0.28
Females	...	<0.87	...	<0.12	...	...	...	0.18
Control Site I								
Males	...	...	<0.12	...	...	...	<0.11	...
Females	...	...	<0.15	...	...	...	<0.11	...

All samples were composites.
*Mice were not differentiated according to gender.

table uptake of TCDD, indicating no absorption or translocation of TCDD from the roots to the aerial parts of the plants.

Small concentrations of TCDF were found in the samples, half of which were from the control sites. This finding indicates other sources of TCDF in the area unrelated to the use of the mill sludge.

Earthworms

All areas proved to be void of any form of earthworms with the exception of one sample obtained during the first round of the study. This sample was from Area 1 near the banks of Lake Adams. Three small earthworms were found in that 0.3 m^2 of sample; however, the sample was well below the 50 g required for analysis.

A literature review revealed that these results are similar to those of other researchers who have studied the existence of earthworms on reclaimed strip mine sites (*2*).

This finding discounts an important pathway by which TCDD and TCDF can enter the environment.

Mammals

In **Table III** are the results of TCDD and TCDF analysis of the field mouse samples. There was a good distribution of males to females and of juveniles to adult mice at the test site. The mice captured at the test site were higher in body mass and population than at the control sites.

There were no observable external abnormalities of any mice after a continuous exposure of 30 generations (minimum) during the test period from 1987 through the summer of 1989.

There was no significant uptake and no apparent bioaccumulation of TCDD found in the mice. Of the twelve composite mouse samples (61 individuals) analyzed, only one mouse sample, collected during the fourth round of sampling, was found to contain any detectable TCDD. The amount detected, 0.2 ppt, was below the analytical limit of detection for the samples collected during the earlier phases of the study and well below the soil/sludge concentrations in the areas.

Similarly, there was no significant uptake and no apparent bioaccumulation of TCDF found in the mice. A total of four mouse samples were found to contain TCDF (one of which was from a control site).

Aquatic life

Table IV summarizes the TCDD and TCDF results from the aquatic studies. Some of the bank vegetation and aquatic vegetation contained detectable amounts of TCDF. Silt samples from run-off into the lake and sediment samples from the lake itself did not have detectable amounts of TCDD or TCDF.

All frog samples were found to have detectable concentrations of TCDF, but only one frog sample was found to contain TCDD (below 1 ppt).

There were no observable physical abnormalities noted in any of the aquatic samples.

Based on analyses of silt and lake sediments, there was no evidence of translocation of TCDD or TCDF from the reclaimed areas due to erosion or run-off.

Stream sediments

Table V is a summary of the results from sampling sediments from Flint Run. Detectable amounts of TCDD and TCDF were found at varying times in samples taken upstream, adjacent, and downstream of the site. However, it was as likely to find detectable amounts of TCDD and TCDF upstream of the site as it was to find them adjacent or downstream of the site.

There has been no plausible explanation found for this observation. However, it seems to support the belief that there are in the area other trace sources of TCDD and TCDF that are unrelated to the mill sludge.

IV. Lake sampling data for dioxin and furan

Sample site	Dioxin, ppt Spring 1988	Dioxin, ppt Autumn 1988	Dioxin, ppt Summer 1989	Furan, ppt Spring 1988	Furan, ppt Autumn 1988	Furan, ppt Summer 1989
Lake Adams						
Frog (*Rana*)	<0.46	<0.32	1.36	<0.97	1.88	1.61
Algae (*Rhizoclonium*)	<0.43	...	<0.17	3.67	...	<0.54
Terrestrial bank plants (cattails and rushes)	<0.35	<0.63	<0.18	<0.33	1.52	1.37
Silt runoff into lake	...	...	<0.10	...	...	<0.37
Lake sediment	...	...	<0.16	...	...	<0.14
Lake Control Site I						
Frog (*Rana*)	<0.55	<0.32	...	<0.74	<0.77	...
Algae (*spirogyra*) and pondweed (*Potamogeton*)	<0.99	...	...	<0.49	...	...
Terrestrial bank plants (cattails and rushes)	<0.55	<0.17	<0.13	<0.32	<0.54	<0.13
Lake Control Site II						
Algae (*spirogyra*) and pondweed (*Potamogeton*)	...	...	<0.25	...	...	<0.55

All samples were composites.

Conclusions

The results of this study indicate that the dioxin in the sludge from Mead's Chillicothe bleached kraft mill does not exhibit any significant translocation or bioavailability when used for reclaiming strip mines. These findings are different from the assumptions that have sometimes been used as the basis of public policy in environmental risk assessments on dioxin. The results from this study should be carefully considered prior to the development of programs regulating the beneficial landspreading of sludge from the wastewater treatment plants of bleached kraft pulp mills.☐

V. Stream sediment sampling for dioxin and furan, ppt

Sample date	Upstream TCDD	Upstream TCDF	Adjacent TCDD	Adjacent TCDF	Downstream TCDD	Downstream TCDF
August 1987	<0.58	2.53	2.07	18.4	<0.32	0.45
October 1987	0.74	<0.94	<0.35	<0.21	<0.17	<0.29
December 1987	<1.31	<0.38	<0.20	<0.22	<0.22	<0.38
April 1988	1.12	2.88	<0.17	<0.27	<0.17	<0.70
October 1988	<0.54	<0.68	<0.77	3.72	<0.55	<0.70
December 1988	4.55	0.64	2.45	<0.59	<0.20	0.58
March 1989	<0.57	<0.39	<0.15	<0.14	<0.26	<0.48
May 1989	<0.50	<0.39	1.04	4.34	<0.18	<0.28
August 1989	<0.26	0.51	<0.31	<0.27	<0.52	3.59
November 1989	<0.30	0.41	<0.13	0.29	<0.14	0.56

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