

CHEMICAL AND BIOLOGICAL ANALYSIS OF A HAZARDOUS WASTE DISPOSAL SITE

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A hazardous waste disposal site located in central Oklahoma was studied during summer, 1974. The waste materials delivered to this site included oil-based products, organic solvents, ink, paint, and miscellaneous acids, bases, and salts. Selected chemical and biological parameters of the site were measured to provide a basis for evaluating this particular disposal operation and to provide recommendations for developing, managing, and regulating future sites.

The need for proper disposal of toxic chemical and biological materials that pose real or potential danger to the environment has been recognized only recently. Governmental agencies are currently evaluating existing laws and recommending additional statutes to regulate the management of such waste materials (1, 2, 3).

Extensive efforts in technology and management have provided various proposals for economical methods of waste disposal (4, 5). The assessment of human health problems related to hazardous waste disposal (6) has received less attention.

Basic information regarding the environmental impact of existing hazardous waste disposal sites is important if proper consideration is to be given to establishing future legal guidelines in this area.

This study was initiated in late 1973 to determine certain chemical properties of the waste materials as they occur in the disposal lagoons of a hazardous waste disposal site in central Oklahoma. The surrounding vegetation and soils were examined to provide an assessment of the impact of the hazardous wastes on the immediate environment.

MATERIAL AND METHODS

Site Location and Operation

In fall, 1972 a privately owned and operated hazardous waste disposal site was established in central Oklahoma. The site, in McClain County, Oklahoma, approximately 1.2 km west of Criner, is located on a gently sloping hilltop that lies on the boundary of two geologic units, the El Reno Unit and the underlying Hennessey Unit (7). The soils range from dark brown clayey fine sand and silt to reddish brown silty clay with permeability properties from 1.906×10^{-8} to 5.793×10^{-8} cm sec⁻¹. The underlying materials are unconsolidated clays, clayey sand and clayey silts to a depth of 3-4 in with consolidated clayey shale below (Hardege, personal communication).*

The vegetation of the disposal site is dominated by *Aristida oligantha* Michx. and *Cynodon dactylon* (L.) Pers. Most of the species encountered are indicative of disturbance areas in central Oklahoma (8).

The natural surface drainage system begins 50-100 m west of the hilltop area and is interrupted by two small farm ponds before joining the north fork of Criner Creek. This ultimately enters the Washita River some 20 km downstream.

The 2-ha disposal site consists of several discrete lagoons (Figure 1). The primary lagoon (I) received raw wastes including grease emulsions, oil refinery wastes, rubber products, silicone sludge, and miscellaneous acids, bases, and salts. The aqueous fraction of the primary lagoon was drained into the secondary lagoons (II & III).

A sprayer system installed on the dike west of the main lagoon was used to enhance evaporation. On favorable days with southerly winds the aqueous fraction from

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*Data supplied by R. N. Hardege from a report to Hardege by Standard Test and Engineering Co., Oklahoma City, File #57, Lab #5605.

the secondary lagoons was pumped through the sprayer with a maximum capacity of $300,000 \text{ l} \cdot \text{day}^{-1}$. A large portion of the mist settled into the main lagoon but a substantial amount drifted northward for a considerable distance. During early summer, 1974, high water levels from spring rains, poor evaporation conditions and continued disposal of wastes increased the risk of overflow. To relieve this danger the operator took precautionary measures that resulted in a thorough mixing of the contents of the primary and secondary lagoons.

Printer's ink and similar wastes were segregated in lagoons IV and V. The northernmost lagoons (VI-IX) were used primarily for highly volatile substances such as paint thinners, strippers and other organic solvents. Cyanide materials were buried in the area north of the lagoons.

The basic operation involved the reduction of volume of the waste materials by evaporation and the subsequent burial of solids and precipitates accumulated in the lagoons by landfill procedures (area X, Figure 1).

The initial intent of this study was to develop a comparison of chemical compositions among the various lagoons. However, due to alterations in management by the owner we confined our investigation to the main lagoon.

Chemical Analysis

Chemical analysis of the water and the sediment of the main lagoon was performed on samples collected throughout the summer. These were taken from the edge of the lagoon except for one series which were taken from a fiberglass boat from the middle of the lagoon.

Qualitative analysis for cations were performed on the aqueous fraction according to Margolis (9). The following quantitative determinations according to standard methods for water analysis (10) were made: phenol, nitrite nitrogen, ammonium nitrogen, COD, pH, chloride, phosphate, and residue. Aqueous and sediment samples were digested for atomic absorption spectrophotometric determinations of various metals by adding two g of sample to 40 ml 50% HNO_3 ; the mixture was heated gently and filtered through acid-washed glass wool and made to 100 ml volume (11).

The effectiveness of neutralization-precipitation treatments on the waters was examined. Aqueous samples that had been adjusted to various pH levels with 0.1N NaOH were analyzed by atomic absorption spectrophotometry for selected metals.

The hydrocarbon content of the air was determined in November, 1973, and in late July, 1974, with a Century System Vapor Analyzer calibrated with methane (12).

Plants and Soils

Biomass was estimated from nine 0.5-m^2 circular quadrats in late June, 1974. The living materials was clipped at ground level, separated as to species, oven-dried at 60 C for 24 h and weighed on an analytical balance.

The metal content of the soil and of the aerial portions of several of the major species was determined by atomic absorption spectrophotometry. Plant samples were collected from 49 locations within and surrounding the disposal site. The total area sampled was approximately 10 ha. Soil samples, 0-15 cm depth, were taken from 15 of the 49 locations.

The plants were oven-dried at 60 C for 24 hr and subsequently ground to pass through a 40-mesh screen. Triplicate samples of 0.200 g of ground plant material were digested in 10 ml of an acid mixture of 1.5 parts conc. H_2SO_4 : 2.0 parts conc.

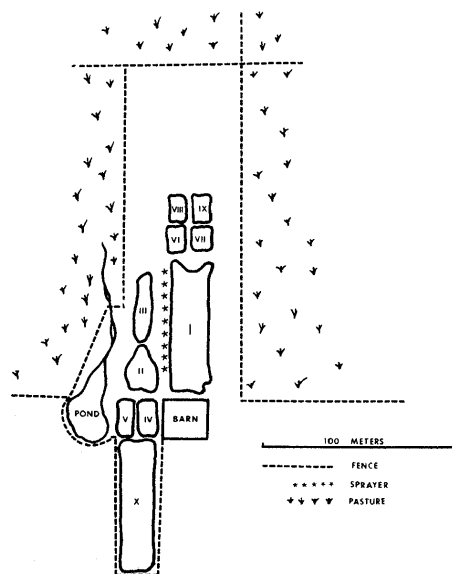


FIGURE 1. Map of lagoons at the disposal site. (See text for further description.)

HClO₄: 7.5 parts conc. HNO₃. The digestion mixture was gently heated until clear. It was then cooled, diluted, and filtered through acid-washed glass wool. The filtered solution was made to 25 ml volume. The resulting solutions were analyzed on a Perkin-Elmer Model 303 atomic absorption spectrophotometer for Cd, Co, Cr, Cu, Fe, Hg, Pb, and Zn, following the procedures of Perkin-Elmer Corp. (11).

The soils were air-dried and all visible organic matter was removed. The dried soil was ground in a soil mill to pass through a 0.5-mm sieve. Duplicate samples of 2.00 g air-dried soil were digested in 40 ml 50% (v/v) HNO₃. Following digestion the solution was filtered and made to 100 ml volume for analysis.

Microorganisms

Samples were drawn from each of the pits during the months of May, June, and July for the isolation and identification of microorganisms. In addition, a sample which had been collected in November, 1973 and stored in a closed container in the laboratory was examined for the presence of microorganisms. A 0.2-ml aliquot of each sample was streaked on plates of Difco Sabouraud agar. Also a 0.2-ml aliquot was introduced into 10 ml thioglycolate broth to encourage growth of anaerobes. The inoculated media were incubated at 25 C and checked for growth after 24 hr and 76 hr.

The effect of waste water contamination of river water was examined with respect to changes in the total number of microorganisms and BOD. Fifteen liters of water from the Washita River near Maysville, Oklahoma, was placed in each of six 20-l. carboys. These were placed in the laboratory where they received approximately 2,000 lux illumination at 50 C. An air line was connected to each carboy to insure that the system was well aerated. Pit liquid was added to achieve final dilutions of 10⁻², 10⁻³, 10⁻⁴, 10⁻⁵, and 10⁻⁶. The control received no pit liquid. BOD and total organisms counts were taken weekly for 4 weeks. BOD was performed without seeding (10).

RESULTS

Chemical Analysis

Qualitative analysis of the primary lagoon waters indicated the presence of the following cations: Fe^{+2, +3}, Ni⁺², Cr⁺³, Ca⁺², Pb⁺², Cu⁺², Cd⁺², Zn⁺², and NH₄⁺. Tests were negative for the following: Ag⁺, Hg^{+1, +2}, BiO⁺, AsO⁺, SbO⁺, Sn⁺⁴, Mn⁺², Co⁺², Al⁺³, Ba⁺², Sr⁺², and Mg⁺².

Values of the waste water composition (Table 1) obtained at various times throughout the summer indicated minimal fluctuation. In most cases there were minor increases in concentration as would be expected from continued disposal and evaporation. The quantitative determinations confirm the expected accumulation of the poorly soluble metals in the sediment layer (Table 2).

Precipitation of dissolved metals occurred around pH 11, effectively reducing the concentration by 95-99% for the various metals tested.

The hydrocarbon content, expressed as CH₄, in the air in November, 1973 shows that within a zone <10 m from the lagoons the concentration averaged 15 ± 6 ppm. However, when volatiles were being disposed the level increased to 80 ppm. The concentration normally diminished to <1 ppm at 100 m downwind from the lagoon. By July, 1974, high temperatures had vaporized nearly all the hydrocarbons so that the hydrocarbons in the air were negligible.

TABLE 1. Concentrations of various constituents found in waste water of the primary lagoon.

| | \bar{X} | Min. | Max. |
|-----------------------------|-----------|------|-------|
| pH | 2.0 | 1.5 | 2.9 |
| Phenols ppm | 2.1 | 2.0 | 2.5 |
| Nitrite N ppm | 446 | 425 | 780 |
| Ammonium N ¹ ppm | 126 | -- | -- |
| Chloride ¹ ppm | 140 | -- | -- |
| Phosphate ppm | <0.01 | 0.00 | <0.03 |
| COD ¹ ppm | 5962 | -- | -- |
| Residue ¹ ppm | | | |
| volatile suspended | | | |
| solids | 127 | | |
| non-volatile suspended | | | |
| solids | 319 | | |
| total suspended | | | |
| solids | 446 | | |
| volatile dissolved | | | |
| solids | 5295 | | |
| non-volatile dissolved | | | |
| solids | 14015 | | |
| total dissolved | | | |
| solids | 19310 | | |
| total volatile | | | |
| solids | 5422 | | |
| total non-volatile | | | |
| solids | 14334 | | |
| total solids | 19756 | | |

¹Single determination

Plants and Soils

There is obvious damage to plant life in a zone varying from 1-25 m in width surrounding each of the holding lagoons. The leaf margins and the exposed stem apices of all species found in the zone were brown and curled by mid-June. Their condition deteriorated as the summer progressed. A few American elm (*Ulmus americana* L.) trees which are located 20-25 m NW of one lagoon were severely affected. By July most of the leaves had fallen from these trees. The presumed cause of the damage is the high level of volatile hydrocarbons emanating from the lagoons. Concentrations of hydrocarbons at times reached 80 ppm in this zone.

The presence of heavy metals in the vegetation poses a potentially serious problem. The spraying operation used to enhance evaporation of the aqueous layer of the lagoons causes a mist to drift some distance from the lagoon. Chromium, because it is normally present at extremely low concentrations in the soils and the vegetation of central Oklahoma, provides an excellent means of assessing the effect of the sprayer system with respect to the distribution of metals. Data from 17 points in a zone north of the sprayer system were used to obtain a least-square exponential regression equation that describes the concentration of Cr as a function of distance from the sprayer (Figure 2). A more complete picture of the spatial distribution of Cr is provided in the Symap (13) display (Figure 3). The influence of the prevailing southerly winds is apparent.

Comparisons of various components showed that in all cases, except that of Pb, the vegetation had much higher maximum levels of metals than did the pit solution (Table 2). Also, the plants had higher concentrations than the soil (Table 3). However, linear regressions indicated no statistically significant correlation between the levels in the plants and the soil. From these data and from on-site observations it appears that the plants are receiving the metals primarily by intercepting the mist with their aerial parts rather than by uptake processes from the soil.

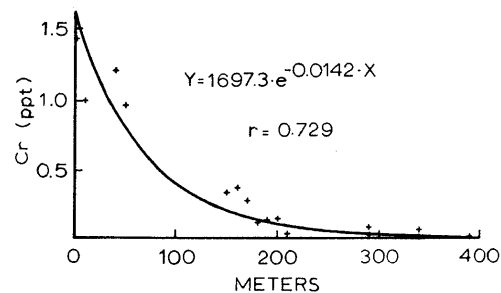


FIGURE 2. Least-square exponential regression of Cr concentration in vegetation and distance north of the lagoons.

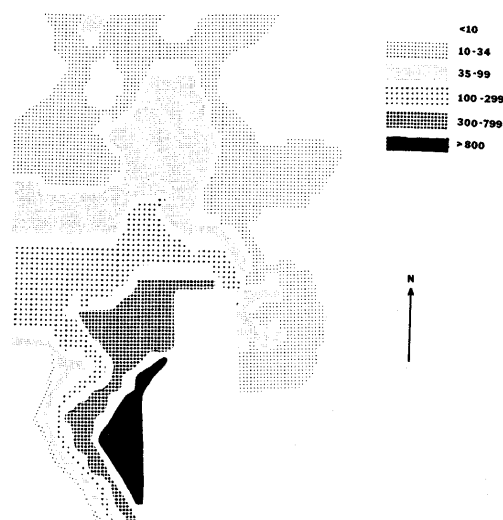


FIGURE 3. Symap display of Cr in vegetation surrounding the disposal site. (See Figure 1 for cartographic comparisons.)

TABLE 2. Concentration ($\mu\text{g/g}$) of metals in lagoon vegetation and soil.

| | Cd | Cr | Cu | Fe | Pb | Zn |
|-------------------------|------------------------|--------------------------|--------------------------|-------------|-------|-------------|
| Lagoon ¹ | | | | | | |
| Solution | 4.8 | 19.4 | 33.5 | 72.5 | 1.3 | 23.5 |
| Sediment | 7.3 | 372.8 | 1722.0 | 959.1 | 192.6 | 545.1 |
| Vegetation ² | 23.1-54.5 ⁴ | <0.1-1323.2 ¹ | 21.4-1225.3 ¹ | 201.4-831.6 | <0.1 | 92.9-1273.3 |
| Soil ³ | 1.4-3.8 | 2.9-43.5 | 0.1-15.2 | N.D. | <0.1 | 22.8-204.8 |

¹Single determination

²Range for 49 samples

³Range for 15 samples

⁴Represents dietary levels toxic to animals (17)

Different concentrations of metals were found among the species tested. Of the species that occurred in more than 10 of the sampling locations, rank in order of decreasing Cr content was: *Ambrosia psilostachya* D.C., *A. oligantha*, *C. dactylon* and *Rudbeckia hirta* L. Attempts to correlate metal content with the measured surface areas of mature plants as well as with the height of the plants failed to yield a statistically significant correlation.

The biomass of the nine quadrats ranged from 49 g•m⁻² to 546 g•m⁻² with a mean of 111.0 g m⁻². The biomass tended to increase with distance from the lagoons. However, the trend was not statistically significant for the degrees of freedom available. The large amount of continued disturbance near the lagoons due to vehicles, and farther away due to grazing, made further measure of biomass seem unwarranted.

Microorganisms

Five species were isolated from the November, 1973 sample. Two of these, a yeast and a bacterium, were not capable of growing in media containing 5% or more pit liquid. A fungus, *Cephalosporium* sp. (red colonies on SAB agar), grew slowly in concentrations up to 75% pit liquid while a *Penicillium* sp. and *Cephalosporium* sp. (black colonies on SAB agar) grew well in 75% pit liquid. No isolates were obtained from any of the summer samples.

Preliminary studies regarding the effect of the pit liquid on the microbial populations of natural water systems indicated that the waste waters would have to be diluted more than a millionfold before the general toxicity became negligible (Table 4).

Management Problems and Recommendations

Central Oklahoma receives 80.3±18.0 cm annual precipitation and has an average yearly evaporation potential of approximately 150 cm (14). The oil layer of the primary lagoon traps the rainfall and prevents evaporation. The current spraying operation is useful in eliminating or reducing this trapped water as well as the water from disposed wastes. However, this results in the dispersal and the accumulation of metals in the surrounding vegetation and ultimately in the soil. On a long-term basis the practice of spraying would result in the essentially permanent contamination of a large area.

Alternative management procedures such as incineration, carbon sorption, chemical oxidation and neutralization are costly and technologically complex (3, 15). The cost of neutralizing the wastes at this site to pH 7 with CaO at 1974 bulk rate prices is \$13.70/m ton, while neutralization-precipitation at pH 11 is \$19.35/m ton. This treatment cost represents a substantial increase over the current charge for disposal of \$5.25-\$7.85/m ton. Neutralization-precipitation presents another difficulty in that the precipitate formed from a volume of the waste occupies about 40% the original fluid volume, which would fill the lagoon rapidly.

At present, one of the most economical approaches to managing aqueous hazardous waste materials is to rely on evaporation to reduce the volume (15). Figure 4 depicts a simple, stylized disposal site that would enhance evaporation and not present the environmental hazards of spraying. In this scheme the oil-based materials would be retained in a lagoon which minimizes the surface-to-volume ratio, thereby reducing the volume of rainwater trapped and allowing the drainage of the trapped rainwater.

TABLE 3. Concentrations of metals (µg/g) in soil and vegetation from 15 locations near the lagoons.

| Metal | $\bar{X} \pm \text{S.E.}$ | | |
|-------|---------------------------|-------------|-----------------|
| | Plant | Soil | R _{xy} |
| Cd | 33.5 ± 1.9 | 2.5 ± 0.2 | -0.138 |
| Cr | 268.4 ± 95.5 | 15.6 ± 2.8 | -0.248 |
| Cu | 261.5 ± 81.7 | 6.1 ± 1.0 | 0.170 |
| Zn | 398.1 ± 71.8 | 55.1 ± 11.1 | -0.259 |

TABLE 4. Plate counts and BOD for Washita River water following the addition of toxic wastes.

| Final dilution of waste water | 10 ⁻² | 10 ⁻³ | 10 ⁻⁴ | 10 ⁻⁵ | 10 ⁻⁶ | Control |
|----------------------------------------------|------------------|------------------|------------------|------------------|------------------|---------|
| Initial plate count (× 10 ⁻³) | 12 | 15 | 18 | 42 | 16 | 62 |
| Plate count after 1 wk (× 10 ⁻³) | 2.4 | 0.4 | -- | -- | -- | 8.2 |
| Initial BOD | 30 | 10 | 4.9 | 8.5 | 6.1 | 8.8 |
| BOD after 1 wk | 8.9 | 4.9 | 6.6 | 3.9 | 3.3 | 1.2 |

The aqueous-waste and the volatile-waste lagoons would be constructed to maximize surface-to-volume ratio to enhance the evaporation process. In addition, the aqueous waste would be pumped up slope and allowed to trickle over a black plastic tarp to increase evaporation. As before, cyanide compounds would be buried separately.

Current law regarding point-source of pollution from agricultural wastes (16) requires disposal structures capable of withstanding a 10-year 24-hr rainfall (5.5 inches for Central Oklahoma). Similar regulations are likely to be imposed for hazardous waste sites in the near future. With this in mind, an emergency retaining dike should be a required feature of any disposal site.

DISCUSSION

The impact of the disposal site on the surrounding environment, at this time, is primarily a result of construction and maintenance. One exception is the deleterious effect the volatile hydrocarbons have had on vegetation near the lagoons. Tree species show the effect at a greater distance from the lagoons, apparently being more susceptible because of intrinsic intolerance to hydrocarbons or because they received higher doses of the rising vapors. At this particular site damage due to hydrocarbons is of no real consequence.

Although, to date, no substantial environmental impact has occurred, a clear potential for danger exists from the accumulation of heavy metals in the surrounding landscape and from the possible escape of wastes into the watershed.

One task facing the public and legislative bodies is the formulation of guidelines and laws that regulate the licensing and provide for rigorous monitoring of the operation of disposal sites. These regulations should be designed to insure against the imposition of unwarranted environmental damage to the surrounding landscape and associated watersheds.

It should be noted that prior to the establishment of disposal sites the hazardous waste materials were being discarded in municipal land fills and in rural areas along roads and in gullies. There existed the ever-present danger of stream and groundwater contamination. Therefore, any provisions and restrictions placed on the disposal operator should be designed so the operation of the site remains economically attractive.

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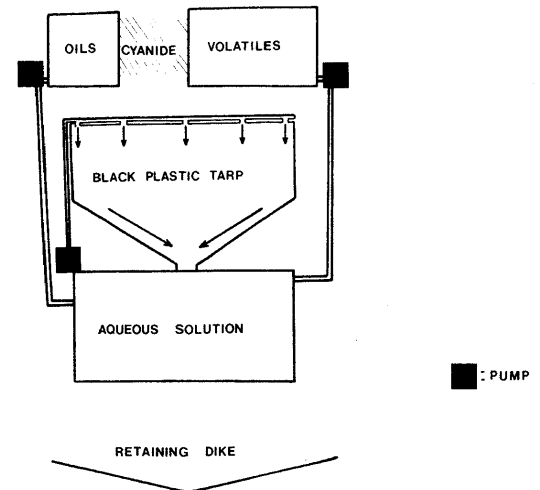


FIGURE 4. Stylized disposal site featuring a black tarp to enhance evaporation.

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