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Project Summary

Field and Laboratory Evaluation of Petroleum Land Treatment System Closure

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The objectives of this research were to measure and interpret the effect of surface soil changes on the underlying soil and the quality of runoff water from petroleum landfarms undergoing simulated closure. Four landfarm waste/soils were studied for chemical transformations in the greenhouse with one of the same sites tested in the field for runoff quality and waste stabilization. The results obtained at the field site closely paralleled the greenhouse results for the same refinery. The field results over two years showed insignificant downward migration of the organics and heavy metals studied. On the basis of aggregate measures of organics, several compound groups of organics, as well as specific organic species, the closure period of two years in this study allowed significant reductions in waste/soil concentrations. These reductions leveled off or became more slowly changing in the second year of the study. No substantive leaching was observed for inorganic or organic parameters measured in both the greenhouse and the field studies associated with this project. Vegetation improved runoff quality. Some adverse effects on seed germination and vegetation establishment were observed with soil/waste mixtures in greenhouse studies.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, 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

Land treatment is the treatment and stabilization of wastes applied to the soil-vegetation complex by biological, chemical, and physical processes. In considering the closure of a hazardous waste land treatment system the U.S. Environmental Protection Agency (EPA) has stressed the importance of controlling migration of constituents into ground water along with release of airborne particulates (EPA 1981). The primary focus of this project was the behavior of petroleum land treatment systems in the closure period. That is, after active use for treating typical petroleum refinery sludges or wastes, use of the land application area is discontinued. During this period, shortly after discontinuing use, practices are employed which in the context of RCRA are referred to as site closure. Closure activities continue until certain environmental standards are achieved at which time a post-closure period begins.

In the context of closure, the EPA (1981) established certain objectives:

1. control the migration of leachate from the zone of active incorporation into ground water;
2. control the release of contaminated runoff to surface water;
3. control the release of airborne particulate contaminates; and
4. comply with the standards established for food-chain crops.

Further, a series of techniques or approaches were suggested for achieving these objectives (EPA 1981).

1. "no action" provided the (closure) plan is acceptable from the human health viewpoint and is environmentally sound,
2. the establishment of a permanent vegetative cover, i.e., *in-situ* conversion to usable land,
3. the capping of the landfarm area with a layer of material which will control infiltration and wind and water erosion, i.e., a landfill-type closure, and
4. the removal and landfilling the zone of incorporated waste.

As a part of the decision-making process leading to the specific research project objectives, these four techniques were evaluated in some detail in a literature assessment (Kendall, et al., 1981). The report concluded the following:

1. There were four principal approaches to design and management of a closed site.
2. These approaches and the respective total five year costs for a standard site were:
    a. no-action on site but with runoff collection and monitoring ($143, 000)
    b. vegetation establishment and runoff collection and monitoring ($193,000)
    c. establish an impermeable clay cap ($707,000)
    d. removal of surface soil to an approved landfill ($1,516,000)
3. A well managed petroleum land treatment area achieving substantial assimilation of waste constituents would not be expected to pose major closure difficulties.

The major research objective of this project was to measure and interpret the surface soil zone changes in relation to the quality of runoff water from petroleum landfarms undergoing simulated closure. The experimental effort was directed at measuring the changes in the composition of four petroleum landfarm waste/soil mixtures over a two-year closure period in the greenhouse. Simultaneously, one of these waste/soil mixtures was monitored at the original landfarm and runoff liquid samples collected to measure this aspect of land treatment site closure.

Secondary objectives adopted for the study included sampling two immediately lower soil zones at the field site for constituent migration. In addition, a limited evaluation relating to establishing a grass vegetation on a closed land treatment area was conducted.

Materials and Methods

Four sites for the greenhouse study were selected. In general, petroleum land treatment areas are operated with rates of application

1. established to optimize oil waste treatment, or
2. to largely obviate extended closure periods.

Since the majority of petroleum land treatment systems use the former operating mode, a single field site was selected to reflect these practices. The field site would provide over an extended period of time the opportunity to measure changes in the surface conditions. A rainfall simulator was used to produce runoff liquid from nearly identical events spaced over approximately six-month periods for 2.5 years. At the location chosen multiple test plots were established within vegetated and non-vegetated waste amended areas and non-vegetated control areas.

The landfarm conditions studied were broadened by adoption of a parallel greenhouse investigation. Four petroleum landfarms with areas available for closure were selected to collect surface soils for experimentation. One of these was the field location so that some comparative relation could be developed between greenhouse and field information. Such multiple site experiments in a greenhouse were much less costly than equivalent field studies. In the greenhouse the variables of vegetated waste/soil, non-vegetated waste/soil, and non-vegetated control soil were used in an analogous fashion to the field. However, only the soil changes over time were investigated in the greenhouse, with runoff liquid studies confined to the larger field study.

From the general experimental system described above, samples were taken at approximately six-month intervals over a period of two years from the implementation of closure status corresponding to the summer of 1982. These samples consisted primarily of surface waste/soil material or runoff liquid with some vegetation samples also taken. For the primary samples, the chemical constituents selected for analyses were chosen to reflect both the agronomic and environmental requirements of the closure approaches investigated. These parameters were in three groups:

1. macro- and supplementary nutrients and conditions important to vegetation growth;
2. metals—the most prevalent criteria for judging long-term closure status; and
3. organic parameters reflecting aggregate measures of organics and oil, specific groups representing fractions of petroleum-related wastes, and specific compounds.

For the secondary objectives, the same field and greenhouse soils were used. Samples of the soil directly below the zone of incorporation were taken in the field and greenhouse and soil samples from a third lower depth were taken from the field. These additional mid- and lower-depth samples were analyzed for a subset of the parameters characterizing the upper soil. This subset of parameters were thus a measure of migration under field and greenhouse conditions. In addition, a germination study was instituted to assess the feasibility of establishing vegetation during the land treatment closure period.

Results

Behavior of Aggregate Organics

Three measures of aggregate organic concentrations were used to establish the initial conditions and closure period behavior:

1. total organic carbon (TOC);
2. oil and grease (O&G); and
3. total chromatographable plus gravimetric organics (TCO+GRV).

An initial decrease followed by an asymptote in aggregate organic parameter concentration is characteristic of general organic behavior in soil. However, the basis for the organics asymptote could not be determined from this research. The asymptote was in all cases considerably above the level of control soils.

Behavior of Fractions of the Total Organic Extract

The organic material extracted from the waste/soil mixtures was split into a group (TCO) with a boiling point generally lower than 303°C and a group (GRV) with a boiling point above this temperature. Each of these two groups was fractionated into the additional subcategories:

1. aliphatics (LCH);
2. aromatics (LCA); and
3. polar species (LCX).

For the high boiling group (GRV) the aliphatic and aromatic losses were 3,000 to 20,000 mg/kg soil (6 to 40 mt/ha) and 3,000 to 10,000 mg/kg soil (6 to 20 mt/ha), respectively. The lower boiling group (TCO) evidenced a greater percentage loss, but on a mass basis was 1,000 to 2,000 mg/kg soil (2 to 4 mt/ha) for aliphatics and 500 to 2,000 mg/kg soil (1 to 4 mt/ha) for aromatics.

Behavior of Inorganics

Over the experiment duration the total metals were analyzed in waste/soil mixtures and in the control soils. The controls were unchanged over these two years. No differences between waste/soils with or without vegetation were found for total metals. Examinations of total metals concentrations over the two years show that no changes occurred. That is, the experiment consistency was such that the expected conservation of total inorganic constituent concentrations was achieved. As with total metals, the control soil soluble inorganics were found to have remained essentially unchanged over the two-year experiment.

Comparison of Behavior of Constituents in Greenhouse Waste/Soil Mixtures with Field Waste/Soil Mixtures

Only a single landfarm soil was available for a direct comparison of the constituent assimilative phenomena under both field and greenhouse conditions. The control soil in the greenhouse plots and at the field site are essentially the same throughout the two-year study for all of the measures of aggregate organics. For the waste/soil mixtures, it was found that the TCO, GRV, TOC, and the fractions of LCH, LCA, and LCX were essentially the same between greenhouse and field experiments (within data variability). There were only two dates in which directly comparative data on the fractions (LCH, LCA, LCX) were available. The similarity of field and greenhouse concentrations continued over the span of two years, thus the mass losses (kg/ha-yr) were similar.

Oil and grease (organics extracted by trichlorotrifluoroethane) was consistently higher in soil concentration at the field location when compared to the waste/soil mixture kept in the greenhouse. Between field and greenhouse experiments, this O&G difference is small when compared to the concentration differences between waste/soil and control soils.

In overview of soluble and total inorganics, there was a similarity between comparable field and greenhouse conditions. The field differences between waste/soil mixtures versus control soils remained the same as previously described for the greenhouse plots.

Environmental Impacts During Field Closure

Vertical Migration—Samples were collected at the 25- to 50-cm depth in the field as representative of the first zone to evidence any leaching from the upper waste/soil mixture. Examination of the total inorganics, soluble inorganics and the aggregate organic parameters revealed no consistent increase at the lower depth over the two-year closure period.

Runoff—During the course of the field experiments five simulated rainfall events were conducted to obtain runoff samples. In these rainfall simulations the precipitation intensity was constant. However, the preconditions of the soil (moisture content) were determined by the climatic rainfall pattern and thus could not be controlled.

In the phenomena contributing to the transport of chemical constituents from rainfall impinging on the land surface there are two counterbalancing effects that determine the response of an area containing a waste and the corresponding control soil. These are:

1. the relative surface soil concentration of a specific chemical parameter between the landfarm area and the control area; and
2. the effect of waste on the infiltration/runoff mechanism relative to the control area without waste.

The higher the ratio of a constituent concentration in the surface soil of a waste treated area to that of the control location, the greater the possibility that the runoff liquid chemical concentration from the waste application plots would exceed that of the control plots.

In an effort to depict the nonlinear relation between the various waste constituent concentrations in the surface soil and that in the runoff liquid a comparison was made, Figure 1. The ratio of waste/soil concentration to control soil concentration was diagrammed versus the same ratio measured in runoff liquid. As can be seen from Figure 1, the very high surface zone levels were not reflected in a similar elevation above control for the runoff impact. Note the soil ratio is a logarithmic scale. As the character of the waste/soil surface zone approaches that of the control soil the runoff concentrations also are essentially the same as that from control plots. One can conclude that very large ratios of surface soil concentrations of a chemical to that of the control soil are needed to have a major impact on runoff liquid concentrations during landfarm closure.

Conclusions and Recommendations

The following summary statements apply to the results of this two-year simulation of petroleum landfarm closure in the greenhouse and on field plots.

1. Field results at a closed refinery land treatment (LT) system closely paralleled the results obtained in a greenhouse simulation of closure using soil/waste obtained from the same refinery. This being only one comparative study, no firm conclusion can be drawn as to whether the green house studies using soil/waste mixtures from three additional refineries would adequately predict full-scale results at the respective locations. However, it can be concluded that greenhouse simulation studies, which have advantages in terms of cost and controlled environment may be an important aspect of full-scale closure evaluation at a LT system; and at such time that results are statistically comparable, emphasis might be shifted to the greenhouse studies at a considerable cost savings. It can also be concluded that the results of this study for one refinery operation suggest that future comparative greenhouse/field studies will show the predictive usefulness of the greenhouse, leading hopefully to the emphasis being placed on greenhouse simulation with periodic field confirmation.
2. Based on two years of data collected at one land treatment closure site, closures having similar conditions of waste soil and climate will have insignificant downward migration of the organics and heavy metals studied.

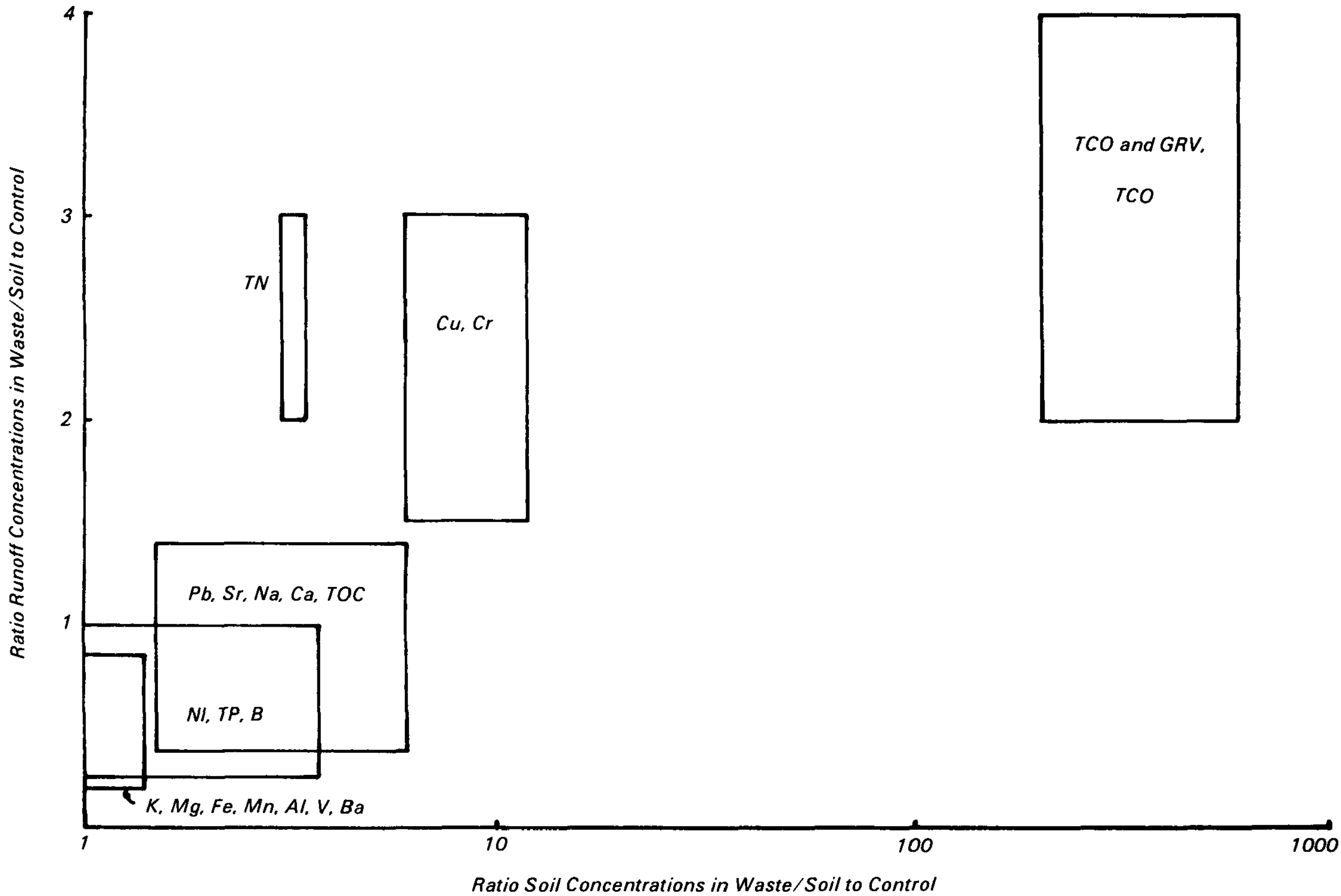

Figure 1. *Relation of surface soil and runoff concentrations.*

3. Based on field results at one refinery for two years, grass vegetation (as opposed to no vegetation) will improve runoff water quality by controlling migration of eroded particulate material contaminated with organic and inorganic constituents originating from the waste/soil mixture.
4. Based on greenhouse results representing four refinery land treatment systems and three native grasses, preliminary testing of soil/waste mixtures and different grasses is recommended to identify adverse effects that may result from incomplete germination and/or grass kill.
5. Based on controlled greenhouse studies of two-years duration, the zone of soil/waste mixture for land treatment closure will exhibit essentially no change in total extractable organics and in solubilizable and total metals; the mixture will also exhibit an asymptotic decline with time to above background levels in oil and grease and in total chromatographable organics (i.e., boiling point $\leq$300°C).
6. For the 10 RCRA Appendix VIII polynuclear aromatic hydrocarbons (PNAs) analyzed in field and greenhouse studies, the expected levels in the surface soil/waste mixtures (similar to those investigated) will be $\leq$5 ppm. These levels may be expected to decrease over two years by $\leq$80%.

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The complete report, entitled "Field and Laboratory Evaluation of Petroleum Land Treatment System Closure," (Order No. PB 86-130 564/AS; Cost: $16.95, subject to change) will be available only from:
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