BNL 51557
UC-70
(Nuclear Waste Management - TIC-4500)

ASSESSMENT OF MICROBIAL PROCESSES ON GAS PRODUCTION AT RADIOACTIVE LOW-LEVEL WASTE DISPOSAL SITES

Allen J. Weiss, Robert L. Tate III* and Peter Colombo

May 1982

BNL--51557

DE82 017804

*Cook College, Rutgers University, New Brunswick, New Jersey

NUCLEAR WASTE RESEARCH GROUP
DEPARTMENT OF NUCLEAR ENERGY
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
UPTON, LONG ISLAND, NEW YORK 11973

PREPARED FOR
UNITED STATES DEPARTMENT OF ENERGY
NATIONAL LOW LEVEL WASTE MANAGEMENT PROGRAM
UNDER CONTRACT NO. DE-AC02-76CH00016

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Drs. J. H. Matuszek and C. O. Kunz of the Radiological Sciences Laboratory, New York State Department of Health, for their valuable consultations and aid in acquiring documents containing pertinent data included in this report.

We also wish to thank Mrs. D. Thompson for her patience and skill in the preparation of this manuscript.

EXECUTIVE SUMMARY

Factors controlling gaseous emanations from low level radioactive waste disposal sites are assessed. Importance of gaseous fluxes of methane, carbon dioxide, and possibly hydrogen from the site, stems from the inclusion of tritium and/or carbon-14 into the elemental composition of these compounds. In that the primary source of these gases is the biodegradation of organic components of the waste material, primary emphasis of the study involved an examination of the biochemical pathways producing methane, carbon dioxide, and hydrogen, and the environmental parameters controlling the activity of the microbial community involved. Initial examination of the data indicates that the ecosystem is anaerobic. Hence, reaction sequences of importance are fermentation of carbonaceous substrates to fatty acids, alcohols, ammonia, carbon dioxide, and hydrogen. The fatty acids and alcohols are further metabolized to acetate plus carbon dioxide. With a sufficiently reducing environment, acetate, carbon dioxide and hydrogen are converted to methane by the methanogenic bacteria. As the result of the complexity of the pathway leading to methane production, factors such as substrate availability, which limit the initial reaction in the sequence, greatly affect the overall rate of methane evolution.

Although the methane and carbon dioxide production rate indicates the degradation rate of the organic substances in the waste, it does not predict methane evolution rate from the trench site. Methane fluxes from the soil surface are equivalent to the net synthesis minus the quantity oxidized by the microbial community as the gas passes through the soil profile. Methane metabolized within the soil profile will be converted to carbon dioxide, water and cell components. The carbon-14 entering cell components would remain within the soil for a period of time dependent upon the turnover rate of the cell carbon. Hence, biochemical transformations of methane, hydrogen and carbon dioxide as they pass through the soil profile above the trench are discussed.

Results of gas studies performed at three commercial low level radioactive waste disposal sites are reviewed. Methods used to obtain trench

and soil gas samples are discussed. Estimates of rates of gas production and amounts released into the atmosphere (by the GASFLOW model) are evaluated. Tritium and carbon-14 gaseous compounds have been measured in these studies; tritiated methane is the major radionuclide species in all disposal trenches studied. The concentration of methane in a typical trench increases with the age of the trench, whereas the concentration of carbon dioxide is similar in all trenches. Concentrations of tritium and carbon-14 measured in soil gases are compared to maximum permissible concentrations (MPC) for releases to unrestricted areas listed in Table II of 10 CFR Part 20.

Deficiencies in data involving quantities of gaseous products yielded within the trench, the amount leaving the ecosystem, and the duration of the biological production of these gases are noted. Also, further research is needed to determine the effect of various environmental parameters within the trench on gas production. These data will allow development of more effective trench loading procedures.

1. INTRODUCTION

The quantity and composition of the gaseous end products of biological degradation of carbonaceous compounds is determined by the basic chemical properties of the individual compound itself, i.e., whether it is a sugar, aromatic, protein, etc., and the physical and chemical properties of the environment of the microorganisms affecting the decomposition. A vast array of biodegradable compounds is buried in low level radioactive waste disposal sites. These include, but are not limited to, the cellulosic and lignin components of paper, wood, cotton and cloth; proteinaceous, lipoidal, and polysaccaride components of animal carcasses; aromatics of scintillation mixtures; and chelating agents, such as NTA, DTPA, and EDTA, which comprise decontamination solutions. Non-biodegradable organic compounds that are buried in large quantities include various plastic polymers. The list of nonbiodegradable organic compounds may be increased by a number of biodegradable substances which are rendered nonbiodegradable by the limiting environmental conditions. For example, human tissue is biodegradable, yet mummified remains exist for thousands of years. Because of the quantity and diversity of carbonaceous substrates in the waste material, limitations for microbial activity in low level radioactive waste sites are expected to result primarily from the chemical and physical parameters delimiting the ecosystem. These may include properties of the substrate, such as its solubility or physical location, as well as parameters associated directly with the physical environment (pH, aeration, moisture level, etc.).

The chemical and physical parameters have a highly selective effect on the nature of the biological activity expressed. Primary determination of the array of reactions available to the microbe for the metabolism of carbonaceous substrates results from the exclusion of free oxygen and depletion of the free oxygen trapped in the ecosystem. Thus, an anaerobic or oxygen-free environment is created. The microbial community metabolizing the waste material functions from a minimum of 3 feet to a depth of 40 to 50 feet below the soil surface. Thus, in non-water saturated situations, soil oxygen tensions (oxygen levels in the soil air) are limited by the

diffusion rate of oxygen through the soil matrix. With the saturated moisture levels constantly observed in some disposal sites (Maxey Flats, Kentucky, and West Valley, New York, for example) and periodically at other sites (Barnwell, South Carolina, and Beatty, Nevada), trench oxygen tensions would be further limited. Should oxygen reach the trench, through the trench caps or due to breaching of the trench wall by animals or other physical or biological actions, it would be rapidly depleted through the microbial oxidation of the readily degradable organic substances contained in the waste. Similar activities result in the rapid depletion of the oxygen trapped during waste burial. This process is not unlike that occurring when substrates with a high biological oxygen demand (BOD) enter a lake or stream.

Oxygen tension will determine the types of biological reactions that the microbe uses to degrade the waste substrate. Limitations upon the rate of the decomposition will be imposed by soil moisture level, pH, temperature, etc. These factors are discussed below.

An observation that is addressed at this point is that measurements of trench water redox potentials (E_h) suggest a greater potential for aerobic metabolism than is indicated by trench design and the nature of the products leaving the trench. For example, at Maxey Flats, Kentucky, E_h measurements of trench water samples ranged from -7 to 520 mV. Similarly, at West Valley, New York, this parameter ranged from -6.3 to 240 mV [1]. The conclusion that the in situ E_h is considerably lower than these values suggest is drawn from the detection of substantial methane levels in the trenches [2-7]. This methane results from the biological reduction of carbon dioxide or acetate to methane and, in the case of acetate, carbon dioxide. This process is termed methanogenesis and the unique group of bacteria which catalyze the reaction is the methanogens. Methanogens require extremely reducing conditions to grow and produce methane, where E_h values of approximately -200 mV to -1000 mV are necessary for metabolism and growth of the methanogen [8]. Since these bacteria are inactive at higher E_h potentials, production of methane in the trenches indicates a highly reduced or anaerobic environment. The oxidizing E_h potentials

measured in these trench waters likely result from oxygen transport to the trench, through the collection wells and from oxygen entering the samples during collection. Maintenance of the highly reduced E_h levels (needed for methanogenesis) during sampling is very difficult, in that at -330 mV, the oxygen concentration of the atmosphere is 10^{-76} atm, or one molecule of oxygen in 10^{56} liters of water at 25°C [8].

Hence, because of the physical placement of the waste material within the soil profile and the high BOD of this material, it is reasonable to conclude that the microbial transformations of the organic matter are anaerobic. The end products of the total decomposition of these waste materials anaerobically include methane and carbon dioxide. Copious amounts of methane are routinely produced in sanitary landfills by anaerobic digestion of organic materials in the waste. A gaseous intermediate in this metabolism, which has also been detected in trench gas, is hydrogen [2,3]. Methane, carbon dioxide, and hydrogen production in the trench ecosystem are the subject of this report. Topics to be discussed are i) nature of the biochemical reactions leading to gaseous end products, ii) factors limiting the rate of volatile gas formation, iii) transformation of methane and hydrogen as they pass through the soil profile, iv) field observations and measurements of gaseous releases, and v) major unanswered questions concerning methane and hydrogen evolution from trench waste sites.

2. BIOLOGICAL PRODUCTION OF HYDROGEN, METHANE, AND CARBON DIOXIDE

2.1 Hydrogen.

The presence of hydrogen in the trench ecosystem is important in that it serves as a substrate for methane generation and provides a vehicle for gaseous evolution of tritium from the trench as TH or T_2. Although the role of hydrogen in anaerobic decomposition processes is still little understood, several degradative processes have been shown to yield hydrogen amongst the products. The metabolism of Clostridium species (a group of anaerobic, spore forming bacteria) and many non-sporulating anaerobes yields hydrogen. These bacteria produce end products such as short-chain fatty acids, alcohols, ammonia, carbon dioxide and hydrogen through the anaerobic decomposition of cellulose and other carbohydrates, amino acids, purines and pyrimidines [9]. All of these products are found in organic low level radioactive waste leachates [1]. In this biochemical transformation, hydrogen, generally, is generated from reduced non-heme iron protein, ferredoxin, via hydrogenase action, but never from the direct oxidation of NADH (reduced nicotinimide adenine dinucleotide) [8].

Decomposition of fatty acids also occurs by β-oxidation. These fatty acids arise as intermediates in the decomposition of lipoidal materials and amino acids yielded by protein hydrolysis. Hydrogen can be released directly from β-oxidation, as is shown in the following example of butyric acid oxidation:

$$CH_3CH_2CH_2COO^- + 2H_2O \longrightarrow 2CH_3COO^- + 2H_2 + H^+ \quad (1)$$

Butyrate Acetate

Hydrogen can also be produced during the β-oxidation of fatty acids containing an odd number of carbon atoms. This is shown by the oxidation of propionic acid:

$$CH_3CH_2COO^- + 2H_2O \longrightarrow CH_3COO^- + 3H_2 + CO_2 \quad (2)$$

Propionate Acetate

The fate of the acetate so produced is varied. It can be reduced to ethanol, catabolized further to methane and carbon dioxide (see methane section) or leave the ecosystem unchanged. Should the acetic acid be reduced to ethanol, hydrogen can be formed by the reoxidation of the ethanol to acetate [10]:

$$CH_3CH_2OH + H_2O \longrightarrow CH_3COO^- + 2H_2 + H^+ \quad (3)$$

Ethanol Acetate

This reaction does not result in energy production for microbes unless the hydrogen is eliminated immediately. Such is the case with the microbial symbiosis which was formerly known as Methanobacter omilianski. This culture was originally felt to be comprised of a single bacterial species, which was capable of converting ethanol to methane and carbon dioxide. Further study in Wolfe's laboratory [10] demonstrated that the culture was comprised of two bacterial strains. One member of the association catabolized ethanol to acetate and hydrogen. This was designated the "S" organism. This organism is incapable of growth in the absence of the second organism, Methanobacter strain M.O.H., which removes the hydrogen that is inhibiting the growth of the "S" organism. The Methanobacter uses the hydrogen as an energy source during methanogenesis.

Further sources of hydrogen result from the fermentation of various carbon sources. For example, glucose, a sub-unit of cellulose, is fermented by Clostridium pasteurianum to acetate, butyrate, carbon dioxide and hydrogen. Further discussion of this mode of carbon metabolism will be included in the subsequent report dealing with intermediary metabolism of various components of the biodegradable waste material.

These reactions indicate the wide variety of substrates and reactions that can produce hydrogen gas in the trench ecosystem. In all cases, tritium can substitute for one or both of the hydrogen atoms in the molecule. The fate of this hydrogen, once generated, is varied. Within the confines of the trench, the majority is likely to be used as a substrate for methanogenesis. Hence, any tritium atoms contained in the hydrogen molecule

would enter methane. Although recent studies [11,12] suggest at least a portion of the hydrogen atoms comprising methane may be derived from water, some apparently also arise from the hydrogen. Due to the mobility of the hydrogen gas, a portion would also be expected to enter the gaseous phase of the ecosystem, and thus diffuse from the confines of the trench. Because of the ubiquitous occurrence of aerobic hydrogen oxidizing bacteria [13], rapid oxidation of the hydrogen would be anticipated to occur as it passes upward through the soil profile. Therefore, little, if any, hydrogen gas would be expected to leave the soil environment. Perturbations of the ecosystem, which could result in rapid efflux of the gaseous phase from the trench, could cause hydrogen to enter the soil profile at a rate faster than it could be metabolized by the bacterial community. Also, active removal of trench waters from the ecosystem must be anticipated to contain measurable quantities of TH and T_2. Further field measurements of TH and T_2 fluxes from the surfaces of trench sites to document and quantitate evolution of tritium from the soil in this form are suggested.

2.2 Methane.

Production of methane within anaerobic ecosystems and the subsequent losses of the gas from these environments are common occurrences. Production of methane in sediment muds of lakes, the hypolimnion of deep lakes, swamps and bogs [14] is well studied. Ignition of methane evolved from swamps and bogs results in the pale blue elusive lights known as "will-o'-the wisp" [8]. More recently such lights have been termed UFO's. Methane production is common in living organisms. In a cow rumen, which contains approximately 100 liters of fermenting plant products, 200 or more liters of methane may be produced per day. About 8 to 10% of the carbon ingested by the animal is lost in this fashion [8]. An active methanogenic community is also found in heartwood of living trees located on poorly drained soils [15]. Current interest in methane generation has extended to studies of landfill sites [16,17], sludge digestion [18], and anaerobic fermentation of biomass for methane as a source of recoverable energy. Landfill sites have been studied as energy sources, as well as from the view of assessing the probability of ignition of accumulated methane.

In each of these examples, as is the case with methane generated in low level radioactive waste sites, the biological reactions involved with methane production are the same. A complex organic substrate must be decomposed to acetate, carbon dioxide, and hydrogen. These are the substrates used by the methanogens (Fig. 1). Since methane production is the end product of a long chain of substrate conversions, the intimate association of several species of bacteria, including the methanogen, is necessary. This obligatory association for the production of a product is termed a microbial consortium. For example, a consortium of several bacteria was demonstrated to decompose ferulic acid, a lignin derivative, to methane [19]. Similarly, cellulose is converted to methane and carbon dioxide by a consortium of Acetovibrio cellulolyticus, Desulfovibrio sp., and Methanosarcina barkeri [20].

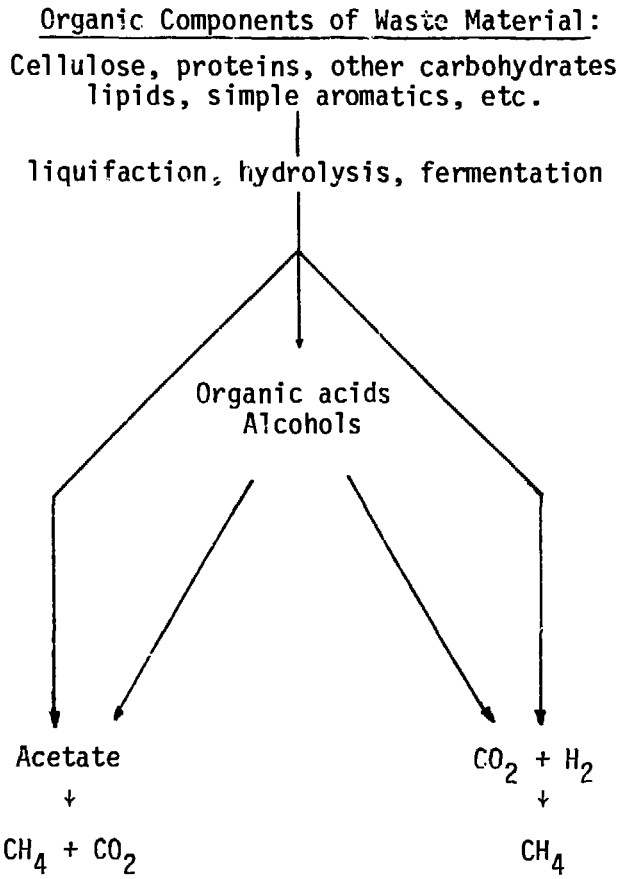

FIGURE 1. Transformations of Organic Waste Materials Leading to Methane Generation.

The methanogens comprise a unique group of bacteria, both structurally and biochemically [21], which are capable of oxidizing hydrogen for energy and using carbon dioxide as a final electron acceptor [14]. That is, hydrogen is oxidized and carbon dioxide is reduced to methane. Carbon dioxide may be used as the sole source of cell carbon. Thus, these microbes are considered to be true chemolithotrophic bacteria (they use inorganic substrates for carbon and energy sources) [14]. This property has been difficult to prove with some methanogens because of their slow growth rate [14]. Acetate is used as a methane precursor by several methanogens [18].

Once the carbon dioxide, hydrogen and acetate are formed within the ecosystem by the associated bacteria, methane is generated by the following reactions:

$$CO_2\ (aq) + 4\ H_2 \longrightarrow CH_4 + H_2O \qquad (4)$$

$$CH_3COO^- + H_2O \longrightarrow CH_4 + CO_2\ (aq) \qquad (5)$$

Other one-carbon substrates have been shown to be reduced to methane by some methanogens as follows:

$$4HCO_2^- + 4H^+ \longrightarrow CH_4 + 3CO_2 + 2H_2O$$

Formate (6)

$$4CH_3OH \longrightarrow 3CH_4 + CO_2 + 2H_2O$$

Methanol (7)

The hydrogen in methane, formed from carbon dioxide and hydrogen, may arise from hydrogen or water. Daniels et al. [11] recently demonstrated that with methane produced by Methanobacterium thermoautotrophicum, methane hydrogens are derived from water and not molecular hydrogen. Thus, in this case hydrogen solely is a source of electrons and energy for the microbes.

Functioning of methanogens in ecosystems, such as the low level radioactive waster disposal site, relies upon all the metabolic needs of the bacterial population being satisfied. As previously discussed, the high BOD of the organic matter and the trench placement within the soil profile suggests that the prime prerequisite for function of these bacteria is met;

that is, the environment is highly reduced. Besides hydrogen and carbon dioxide substrates, the microorganisms require a nitrogen source and in some cases growth factors, such as vitamins and amino acids. The methanogens studied thus far are capable of using ammonium as a nitrogen source [14,22]. Under the reducing atmosphere of the trench, this nutrient would not be anticipated to be limiting. Ammonium sources include the proteinaceous components of animal carcasses. Further studies are proposed to determine if adequate ammonium is found in the waste for complete biodegradation of the carbon substrates. Vitamins and other growth factors may or may not be required by the various species of methanogens [14]. The specific methanogens functioning in situ will reflect the co-factor supplying capacity of the associated microbial community. Thus, except for potential nitrogen limitation during long-term incubation of the trench waste, all nutrition requirements of the methanogens are apparently met.

Once formed, the methane can be quite mobile. The gas can escape from the trench through soil pores, cracks, or along channels produced by plant roots or animal activity. Methane has even been shown to escape from the ecosystems by transport directly through the plant. This was noted to occur with water lilies [23]. Importance is attributed to this mobility since tritium can be incorporated into the molecule. Tritiated methane fluxes have been recorded above waste disposal trenches, and will be discussed in a later section [2,4,5,6,7]. As will be discussed below, the quantity of tritium leaving the trench will be diminished by the oxidative activity of the methylotrophic bacteria within the soil profile. Hence, the quantity of tritiated methane reaching the atmosphere will be equivalent to that produced within the trench, minus the quantity oxidized by the bacteria within the soil profile.

2.3 Carbon Dioxide.

A discussion of gaseous evolution from trench sites would not be complete without consideration of carbon dioxide. The importance of discussion of carbon dioxide production relates to the fact that this gas serves

as a vehicle for ^{14}C transport from the ecosystem. Since total metabolism of carbonaceous substrate to one-carbon units leads to carbon dioxide, whether it is metabolized aerobically or anaerobically, the only factor of concern with carbon dioxide fluxes involves determination of the quantity of $^{14}CO_2$ lost from the ecosystem and the duration of the measurable production of $^{14}CO_2$ by the microflora. Considering the desirability of biodegradation of interred waste material, $^{14}CO_2$ fluxes are inevitable.

As was indicated above, carbon dioxide is an end product of both anaerobic and aerobic carbon metabolism. Anaerobic pathways leading to carbon dioxide as an end product were presented, in part, above. Carbon dioxide is produced 1) during methane synthesis from acetate, 2) from β-oxidation of odd-chain-length fatty acids, 3) from the fermentation of carbonaceous substrates, and 4) from demethylation reactions. Details of these reactions, which involve total catabolism of the substrates to carbon dioxide, will be presented in a subsequent report.

The migration of $^{14}CO_2$ from the trench ecosystem would occur by the same pathways as were discussed for methane. Since carbon dioxide is a terminal oxidation product of carbon, further heterotrophic catabolism would not occur as it passes through the soil profile. Transformations of importance would involve autotrophic incorporation into cellular material by autotrophic bacteria and plants. This process would delay the final exit of the component from the ecosystem, in that the ^{14}C would not be released from the cell until its demise and its degradation to carbon dioxide, water, and ammonium.

3. ENVIRONMENTAL LIMITATIONS TO GAS PRODUCTION

The major environmental parameters to be discussed herein that would limit gaseous end product synthesis in low level radioactive waste disposal sites are E_h, pH, temperature of the trench, and the accessibility of the biodegradable substrate to the active microbial community. Other parameters may prove to be important following further examination of the ecosystem, but evaluation of the data collected to date suggests that these four parameters are the major controls of the rate of biodegradation of organic waste material in low level radioactive waste disposal sites.

3.1 E_h.

As was indicated previously, methanogens must have an extremely reducing environment in which to grow and synthesize methane. Upon closing of the trench, such conditions would not be met. Thus, a portion of the time-delay before methane evolution is observed, results from the succession of microbial population necessary to establish the proper E_h.

Initially, the primary microbial activity would be aerobic. The duration of this portion of the succession would depend upon the availability of the readily degradable waste materials to the microbial community. The nature of the biodegradable substrates buried suggests that this period would be of short duration. During the aerobic phase of the incubation, the available carbonaceous substrates would be metabolized by common aerobic biochemical pathways (Embden-Meyerhoff-Parnas pathway, tricarboxylic acid pathway, Entner-Douderoff pathway, etc.) to yield carbon dioxide, water, and ammonia. As free oxygen levels are depleted, fermentation of the carbonaceous substrates would become more prevalent. The final products would become short-chain fatty acids, alcohols, ammonia, carbon dioxide, and hydrogen.

During the aerobic period of trench development, free oxygen serves as the terminal electron acceptor for the microbes. The reaction involved is:

$$2H^+ + \frac{1}{2} O_2 \longrightarrow H_2O \qquad (8)$$

As oxygen tensions become limiting for aerobic microorganisms, i.e., the E_h declines, alternate electron acceptors are used by the microbes. One of the first compounds to be reduced is nitrate. These substrates are reduced to nitrous oxide and dinitrogen by the denitrifying bacteria via the following reaction sequence [24]:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (9)$$

During this process organic carbon is oxidized to carbon dioxide. A portion of the soil nitrate is also reduced to ammonia by anaerobic soil bacteria. Nitrate is used as a terminal electron acceptor in the absence of free oxygen at E_h values below 200 mV [8]. At 200 mV, the E_h is still too oxidizing for reduction of carbon dioxide to methane. As the nitrate is depleted, other electron acceptors are used by the more fastidious anaerobes, which become active. At E_h values of approximately -200 mV and less, sulfate is reduced to hydrogen sulfide. The sequence of reduction of the more common electron acceptors in the trench is: oxygen will be used before nitrate, which is reduced before sulfate, which precedes carbon dioxide reduction. These reductive processes are generally mutually exclusive within a single microenvironment. That is, methane will not be detected until the sulfate present is reduced to hydrogen sulfide. But, as the result of the size of the waste disposal trenches and the heterogeneity of the waste material itself, both sulfate reduction and carbon dioxide reduction could occur at different locations within the same trench. That is, the microbial succession would proceed at different rates at different locations within the same trench.

Electron acceptors may have an inhibitory effect on methane synthesis beyond their relationship to E_h. Balderston and Payne [25] examined the effect of general electron acceptors on methanogenesis in salt marsh sediments and with whole-cell suspensions of methanogens. Nitrate, nitrite, nitric oxide, nitrous oxide, and sulfite inhibited hydrogen-dependent methane syntheses. Their data suggest that this inhibition was not the result

of variation in E_h or substrate competition by the non-methanogenic bacteria present in the sample. Some compounds are inhibitory in situ in the environmental samples but not in pure culture. Martens and Berner [26] and Cappenberg [27] demonstrated sulfate inhibition of methanogenesis in marine and freshwater sediments, respectively. Cappenberg [28] suggests that the inhibition resulted from hydrogen sulfide production.

Inhibition of methanogenesis by compounds which would have no possible effect on E_h has also been shown to occur. Wood et al. [29] demonstrated inhibition of methanogenesis by methylene chloride, chloroform and carbon tetrachloride.

The E_h of the site must be maintained at less than about -200 mV for methane syntheses to be continuous. Saturation of the site with water makes this easier, in that the water slows diffusion of free oxygen into the site of microbial activity. Thus, in waste trenches such as those at Beatty, Nevada, where intermittent flooding of the trench is observed, E_h levels are likely higher between flooding events than the minimum necessary for carbon dioxide reduction. During these periods, hydrogen and carbon could leave the site as volatile amines and fatty acids rather than as methane and hydrogen. Further research is needed to clarify this point.

3.2 pH.

The law of tolerance states that biological reactions have a maximum and a minimum value for a limiting parameter beyond which the reaction does not occur and an optimum level of the limiting agent at which the reaction proceeds at maximum velocity [31]. Such is the case for the effect of pH on methanogeneses. Generally, the optimum pH range for methanogenesis is 6.7 to 7.4. The most restrictive pH range is below 6.0 and above 8.0 (especially if free ammonium is present in the ecosystem) [Paul Smith, personal communication].

Analyses of trench waters at several disposal sites suggest that the disposal trenches are generally within the 6.0 to 8.0 pH range. At Maxey

Flats, Kentucky, 34 of 45 trench water samples were between 6.0 and 8.0. Similarly, 5 of 9, 11 of 12, and 1 of 2 trench water samples were between 6.0 and 8.0 at Barnwell, South Carolina, West Valley, New York, and Sheffield, Illinois, respectively [1]. Because of the heterogeneity of the trench environment, methane synthesis could still be occurring in those trenches with pH values outside the optimum range. This is possible because islands of more ideal conditions than the trench water samples suggest, most likely exist.

Generally, it may be concluded that because of the large heterogeneous environment represented by the trench and the capability of substrate movement within the trench via water movement, pH must be limiting the rate of methane generation in these sites, but it does not preclude its occurrence. Further studies are needed 1) to relate trench water pH and the rate of methane synthesis, and 2) to determine if variation of waste composition and placement within the trench could be used to maintain the pH at levels more conducive to methanogenesis.

3.3 Temperature.

Methanogeneses has a temperature optimum of 35 to 42°C, with a range of activity from 4 to 45°C [14]. Because of the placement of wastes within the soil profile, the temperature range *in situ* would be expected to be reasonably constant and within the range for methane syntheses to occur. The temperature is below the level necessary for optimum methane production. Temperature measurements of trench waters substantiate these conclusions. Temperature ranges of 10.7 to 22.5°C, 10.2 to 13.6°C, 8.5 to 10.0°C, and 13 to 19.5°C were detected for Maxey Flats, Kentucky; West Valley, New York; Sheffield, Illinois; and Barnwell, South Carolina, respectively [1].

Because of the nature of the ecosystem, little can be done to bring the temperature closer to the optimum level for methanogeneses. Future decisions may involve discussions of site location in warmer climates and placement of waste within the trench to maximize use of biologically produced heat.

3.4 Substrate Availability.

For a microorganism to degrade organic waste material to methane, carbon dioxide, water, and ammonium as terminal end products, not only must the microbe have the requisite metabolic capacities, but it must be in a position to apply these capabilities to the substrate. This latter process may be limited or even precluded by the chemical structure of the substrate or its water solubility. A chemical must be water soluble to be metabolized by the microbial community. These limitations are of particular importance in estimating the rate of methane generation, in that methane synthesis is the final reaction in a long chain of biochemical conversions. Thus, rate limitations early in the biodegradation pathway will have severe effects on the rate of final product evolution.

The chemical structure of the substrate may limit enzymic action through steric hindrance [32]. The substrate molecule may contain chemical groups which retard or prevent the interaction of the microbial enzymes and the substrate. Since this is an inherent property of the biochemicals comprising the waste material, knowledge of the possibility merely provides an explanation of the rate of methanogenesis and a suggested hypothesis for leaching of partially degraded aromatic compounds from the trench. Generally, steric hindrance is not a problem with the cellulosic components of paper and cotton waste materials or in the biodegradation of animal remains.

Of greater importance from the view of site management, is the fact that biodegradation is limited by the physical structure of the waste substance and the chemical properties of the environment in which it is placed. For example, encasement of biodegradable substances in concrete or placement of waste materials in highly acid or toxic environments will prevent microbes from degrading them. Solutions to these barriers to biodegradation involve either neutralization of the chemical toxicity or diffusion of the substrate from the limiting site. That is, the biodegradable substance may leach from the concrete and then be degraded. These problems require examination of the techniques of waste placement within the trench

and determination of the desirability of biodegradation of specific waste substances. Retarded biodegradation would mean that methane evolution, and hence tritium loss, from the trench would occur over a longer time frame.

Of more interest in explaining the slow conversion of biodegradable materials as paper goods and natural fiber cloths to methane and carbon dioxide is the limited surface area of the waste material. For a microorganism to decompose an organic compound, it must be rendered water soluble. This is accomplished in part by weathering and is completed through enzymic cleavage of the carbonaceous compounds. Weathering of the waste material allows the breaking of the paper into smaller pieces. This increases the surface area and hence the number of sites available for microbial attack. As the surface area increases, so does the probability of the microbial exoenzymes reaching the sites of their activity. Practical implications of this process are limited due to the improbability in increased shredding of the waste material to increase surface area prior to burial. The slow increase in surface area under natural conditions explains in part the delay in methane generation following trench closing.

4. TRANSFORMATIONS OF GASEOUS PRODUCTS LEAVING THE TRENCH

Although methane is a terminal metabolic product within the trench ecosystem and hydrogen may be totally consumed by biochemical processes occurring in the trench, both gases may diffuse to the soil layers over the trench and eventually to the atmosphere. The quantity of these gases entering the atmosphere above the trench is not proportional to the quantity synthesized within the trench because of the ubiquitous occurrence of methane and hydrogen oxidizing bacteria within the aerobic soil ecosystem.

Methane is oxidized by methylotrophic microorganisms. These are a group of microorganisms capable of growing on compounds that contain no carbon bonds and of assimilating carbon as formaldehyde or as a mixture of formaldehyde and carbon dioxide [33]. Aerobic methyltrophs are predominantly aerobic gram-negative bacteria. The bacteria are divided into two groups based on morphology and the nature of their carbon assimilation pathways. Fungi and yeasts have also been isolated with this methane oxidizing capacity [34].

The hydrogen oxidizing bacteria comprise 28 species belonging to 15 genera. These organisms are numbered amongst the common soil bacterial genera of Alcaligenes, Pseudomonas, Flavobacterium, Xanthbacter and Nocardia. These are chemolithotrophic bacteria in that they oxidize hydrogen for energy and reduce carbon dioxide to carboyhydrate. Generally, they are facultative lithotrophs in that they can use alternate energy and carbon sources [33].

The importance of the methylotrophic bacteria in reduction of methane fluxes from anaerobic ecosystems was demonstrated by Higgens et al. [33] when they stated, "About half of the substantial, but not precisely known, proportion of total carbon degraded by anaerobic microflora is converted to methane. The amount of hydrocarbon released into the atmosphere, however, represents only about 0.5% of the total carbon turnover." Similarly, the amounts of radioactive methane emanating from the surface of trenches at the Maxey Flats, Kentucky, and West Valley, New York, disposal sites

compared to their concentrations in the trenches, have been shown to be reduced by more than two and three orders of magnitude, respectively [4,5,7]. The concern for the estimation of the quantities of methane and hydrogen oxidized by the soil microflora above the waste disposal trench stems from the role of this process in reduction of tritium and carbon-14 released to the atmosphere. Further study is suggested to determine the extent of methane and hydrogen transformations by the aerobic soil microflora above the trench waste material.

5. MEASUREMENTS OF GASEOUS RELEASES

5.1 Introduction.

Gas studies were performed at three of the six commercial low level radioactive waste disposal sites during the period 1976-1978. The first was an exploratory study performed at West Valley, New York, in June 1976 by personnel from USGS, NYGS, and N.Y. State Health Department, to confirm the possibility that ^{3}H and ^{14}C wastes buried at the site might escape as gaseous species [2,3,7]. Samples of gas were obtained during the process of driving well points into Trenches 2, 3 and 5 for collection of trench water. The samples were taken as soon as methane was detected in gas escaping from the well. An air sample was also taken over a fracture in the cap of Trench 3. Additional gases were collected at West Valley during sampling periods in 1977 and 1978. In August 1978, a limited study was conducted at the Beatty, Nevada, disposal site [6,35], and in December 1978, a similar study was made at Maxey Flats, Kentucky [4,5].

The terms "trench gas" and "soil gas" used in this report refer, respectively, to those gases that are present within the trench cell, and those that emanate from the trench caps into the atmosphere.

5.2 Field Collection Procedures.

5.2.1 West Valley, New York - 1976.

Trench gas samples were collected from well points 2-1A, 3-1A, 5-1A, and 5-3A (Figure 2) [7] at depths between 3m and 5m below the surface of the ground during well driving operations. The trench gas was taken from the outlet line of the compressor used to draw trench gas through the well point. The outlet line was connected to an evacuated sampling cylinder and then filled to approximately 100 psi. For a one-liter cylinder, this procedure took approximately 10 seconds.

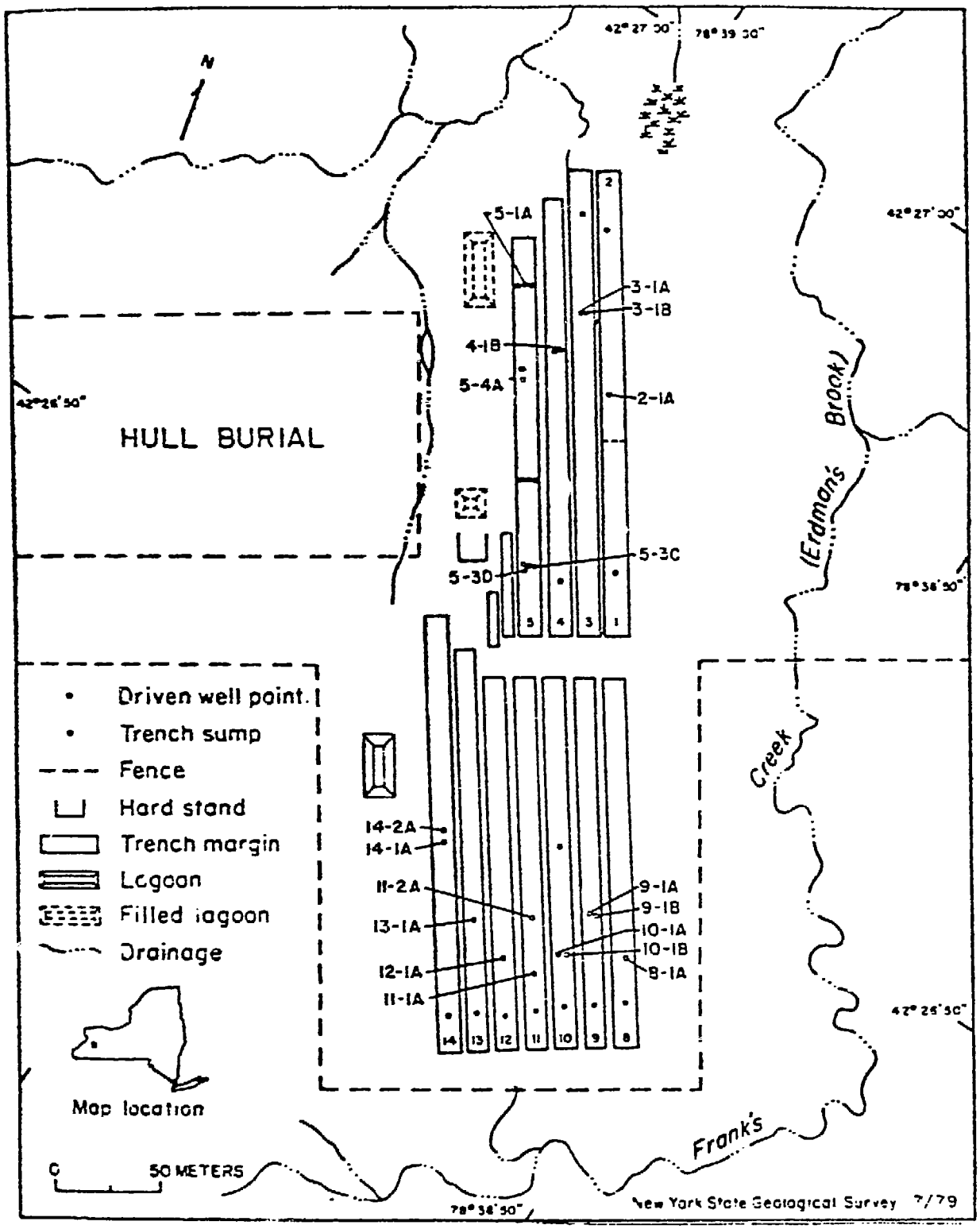

Figure 2. Locations of Trench Gas Collection Wells at the West Valley, New York, Disposal Site [7]

The soil gas emanating from the fracture in Trench Cap 3 was pumped into a 16-liter cylinder from beneath a plastic tarpaulin that was placed over the fracture. The edges of the tarpaulin were dug into the trench cap, and air trapped beneath the tarpaulin was pumped out, prior to an overnight accumulation of soil gas.

5.2.2 West Valley, New York - 1977-1978.

Trench gas samples were obtained in 1977 and 1978 during installation of additional well points into trenches (Figure 2) [7]. A total of 37 trench gas samples were collected through various pipes in the trench caps.

Seven field air samples were also collected from above various trenches for comparison with trench gases. Air samples were pumped into cylinders from one inch above the surfaces of Trenches 5, 9, 11 and 14, and from five feet above Trenches 5 and 14.

Flux boxes were installed over a fractured section on Trench 5, over an unfractured section on Trench 5, and over an unfractured section on Trench 9. These boxes were intended to measure the escape of radioactive gases through the trench cap, and to measure trench cap permeability in order to assess the potential for release of gases into the atmosphere. This technique proved to be unsuccessful, since extensive surface fractures in the caps allowed large quantities of air to flow into the boxes despite efforts to seal against air infiltration [7]. However, flux box techniques were subsequently successfully employed in measuring venting rates and estimating the production rates of methane gas in the Fresh Kills Landfill, where production rates are orders of magnitude higher [16].

5.2.3 Beatty, Nevada - 1978.

Compressed and uncompressed gas samples were collected from observation wells, sump wells, accumulation canisters, and from settlement cracks in the trench caps at the Beatty, Nevada, site by personnel from Dames and Moore.

Sump Wells are points that penetrate into the trench solid waste cell.

Observation Wells are wells that are located between trenches.

Accumulation Canisters are standard open head 55-gallon steel drums, fitted with two ports, and inverted over the surface of the ground. The rim of the drum is sealed to the soil with Thompson's Waterseal, a water-emulsified polymer sealant. One port is used for sampling; the other port allows for consistent flushing of the accumulated air out of the sampling port.

Compressed samples were obtained by pumping gas through Neoprene hose that was lowered into the well points or connected to accumulation canisters. The gas samples were delivered into evacuated 20-pound propane cylinders.

Uncompressed samples were collected into 15-liter, five-layer bags, which exhibit minimal gaseous diffusion through the walls [6].

A total of 12 compressed and 11 uncompressed gas samples were obtained from locations shown in Figure 3 [6].

During the same period in August 1978, personnel from USEPA also obtained samples from several trench wells and monitoring wells. These gas samples were analyzed by EPA laboratories in Las Vegas and Montgomery, and the results communicated to the Nuclear Engineering Company, Inc. (NECO). These EPA results are included in the Dames and Moore report prepared for NECO, which compares trench and soil gas data at the Beatty, Nevada, disposal site [35].

5.2.4 Maxey Flats, Kentucky - 1978.

Samples of soil gas and trench gas were collected by personnel from Dames and Moore at the Maxey Flats site during December 1978, using the

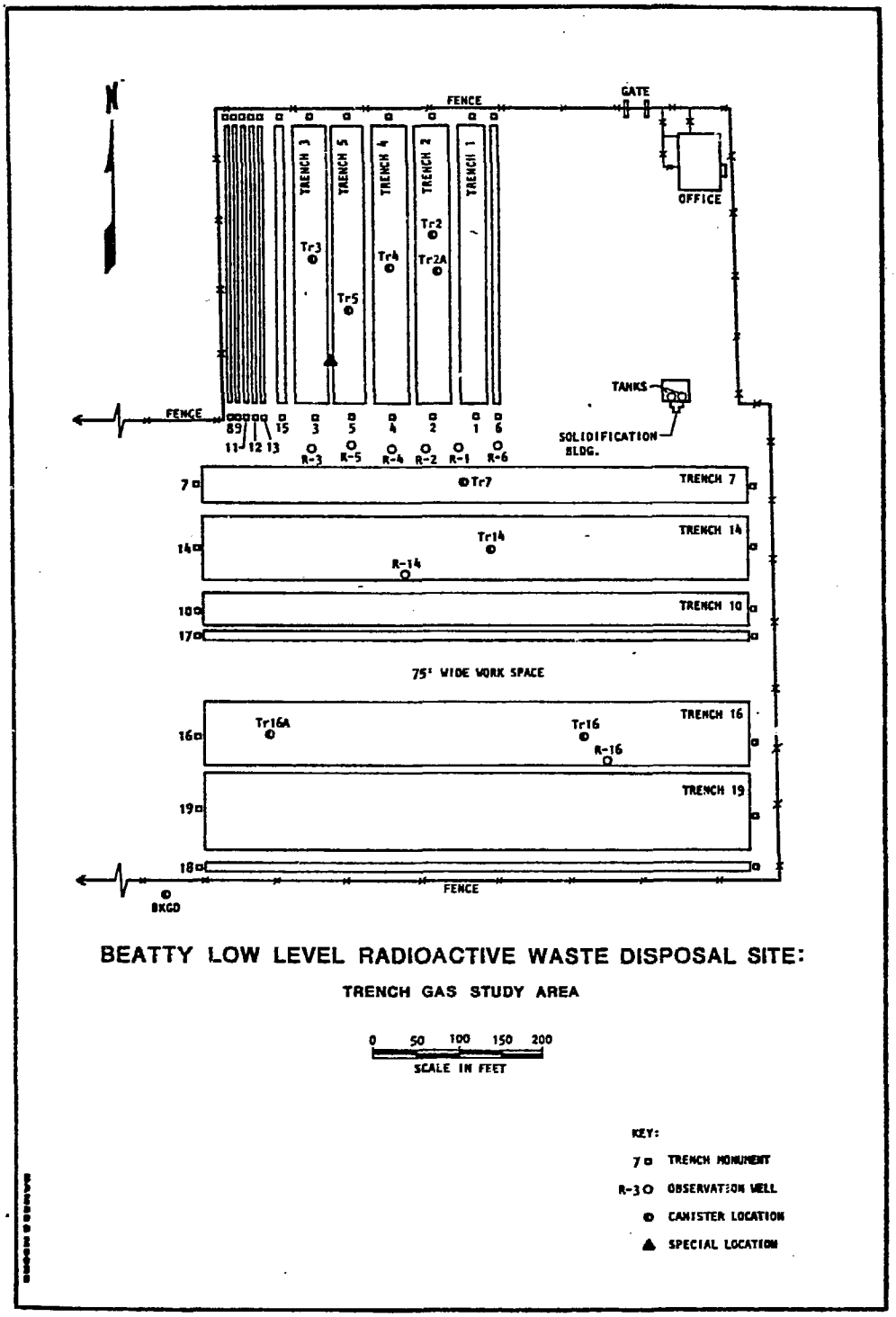

FIGURE 3. Locations of Observation Wells and Canister Emplacements at the Beatty, Nevada, Disposal Site[6]

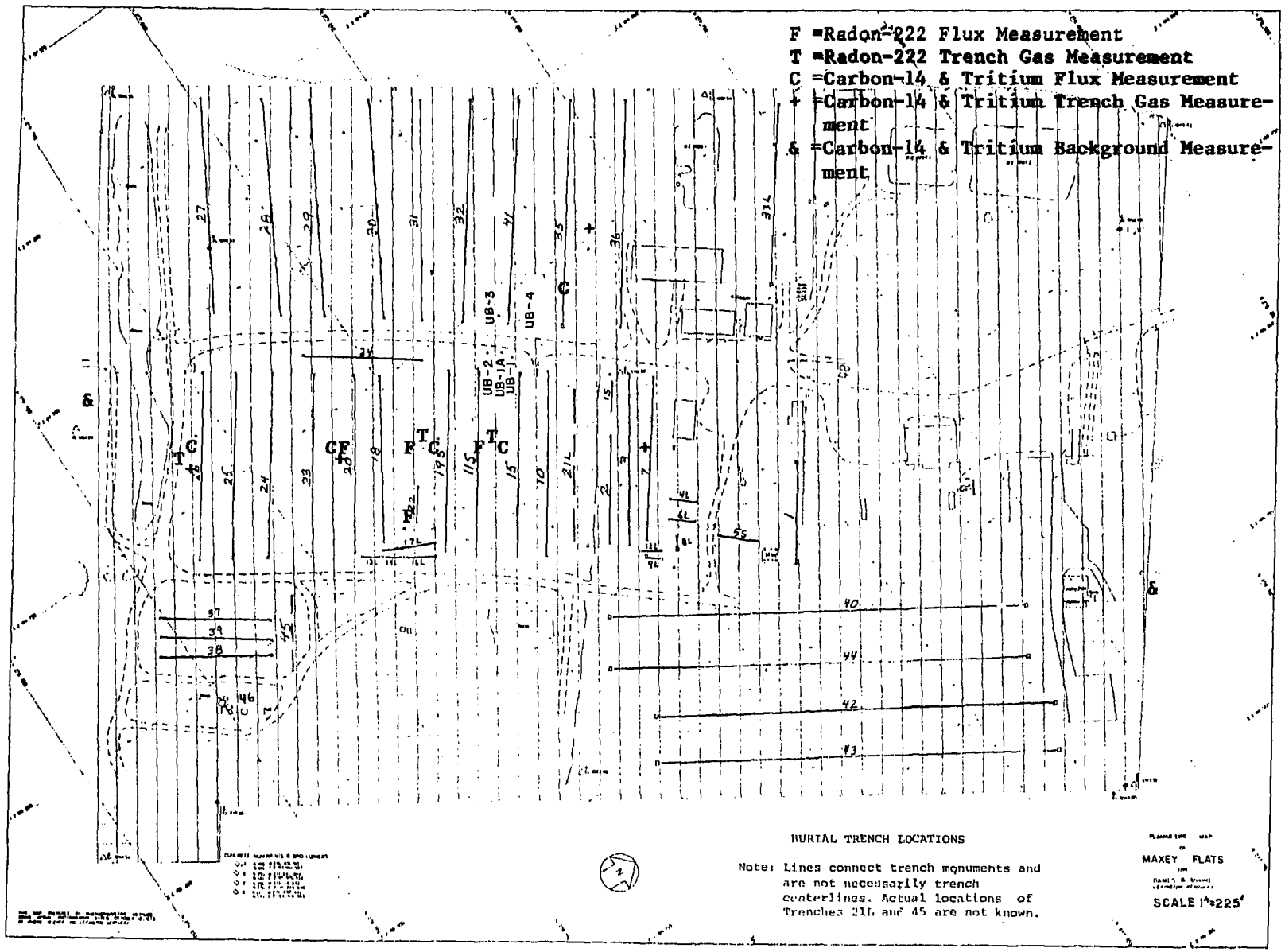

FIGURE 4. Locations of Gas Sampling Points at the Maxey Flats, Kentucky, Disposal Site (adapted from Figure 3.1 of Ref. [5])

same techniques employed at Beatty. Accumulation canisters were used to collect soil gas for flux measurements of gases emanating from Trenches 11S, 18, 20, 26 and 35 (Figure 4) [5]. The canisters accumulated these emanations for approximately 20 hours prior to being transferred into 20-pound propane cylinders.

Trench gas samples were obtained from the bottom of the sumps of Trenches 7, 11, 18, 26 and 35 by compressing the gases into 20-pound propane cylinders, as described earlier.

5.3 Analytical Results.

5.3.1 West Valley, New York.

5.3.1.1 Trench Gas Samples: The collected gases were separated and purified using gas chromatographic techniques; the activity levels were measured by internal gas proportional counters. By using these techniques, the concentrations of various radionuclides in specific chemical species were obtained [7]. The results of these analyses are summarized in Tables 1 and 2. Table 1 shows the concentrations of ^{3}H and ^{14}C labeled compounds corresponding to trench gas samples obtained from locations indicated in Figure 2; Table 2 shows the percent abundance of the various gas species in each trench gas sample. The radionuclide species include: ^{3}HH, $^{14}CH_4$, $^{3}HCH_3$, $^{14}C(HC)^*$, $^{3}H(HC)^*$, $^{14}CO_2$, ^{14}C (total), and ^{3}HHO. Concentrations of the radionuclides are given in $\mu Ci/cm^3$; the numbers in parentheses are the percentage errors reported for the measurements.

Table 3 contains the analyses of the field air samples collected one inch and five feet above the soil cover.

The following observations derived from the trench gas analyses are presented [7]:

---

*HC - as hydrocarbons above methane (C_2H_6, C_3H_8, and C_4H_{10})

TABLE 1

Radionuclide Concentrations in Trench Gas Samp
from West Valley, New York [7]
($\mu Ci/cm^3$ ± % error in parentheses)

Well #	Date	^3HH	$^{14}CH_4$	$^3HCH_3$	$^{14}C(HC)^a$	$^3H(HC)^a$	$^{14}CO_2$	$^{14}C(Total)$	^3HHO
2-1A	6/08/76	1.3E-6 (9)	5.5E-6(17)	1.3E-4(17)	1.1E-6(33)	2.5E-6(32)	2.2E-6(45)	6.7E-6(22)	8.1E-7 (7)
3-1A	6/08/76	8.2E-6 (6)	2.0E-5(10)	2.5E-4(12)	4 E-7(50)	2.9E-5(10)	9 E-7(44)	1.5E-5 (6)	2.0E-6 (3)
3-1B	9/77	2.4E-7(43)	1.0E-5 (6)	4.0E-4 (5)	<1 E-7	3.3E-5 (5)	1.0E-6(17)	8.6E-6 (5)	6.9E-7 (8)
3-1A	9/77[b]	<6 E-8	5.4E-7(14)	1.7E-5 (5)	<1 E-7	4.0E-6 (9)	<2 E-7	7.4E-7(12)	--
4-1B	9/77[b]	2.1E-6 (8)	4.2E-6 (7)	4.6E-5 (6)	1.3E-7(77)	2.6E-5 (5)	2.3E-6 (6)	--	8.6E-7 (5)
#4[c]	4/25/78	2.8E-7(16)	1.4E-7(21)	3.7E-6 (8)	3.5E-8 (7)	4.9E-6 (5)	1.1E-6(19)	--	2.8E-7(14)
4-1B	4/25/78	3.6E-7(25)	5.2E-6 (5)	1.0E-4 (5)	3.2E-8(63)	2.6E-5 (5)	1.6E-6(14)	--	9.9E-7 (6)
5-1A	6/03/76	5.3E-7(15)	6.4E-6(14)	4.8E-4(10)	<2 E-7	4.7E-5(11)	7.4E-6(20)	2.6E-5(27)	1.7E-7 (6)
5-3A	6/07/76	--	9.6E-5(13)	1.6E-3(10)	--	--	4.8E-6 (6)	--	7.1E-8(10)
5-4A	9/77	1.1E-6(12)	1.8E-5 (6)	5.0E-4 (5)	6.2E-7(19)	4.7E-5 (5)	1.1E-5 (6)	2.7E-5 (5)	9.9E-6 (3)
5-3C	9/77	1.9E-7(20)	2.3E-5 (5)	6.9E-4 (6)	2.4E-7(49)	3.0E-5 (5)	4.5E-6 (6)	2.4E-5 (5)	--
5-3D	9/77	2.1E-6 (8)	1.7E-5 (5)	5.0E-4 (5)	2.1E-6 (8)	2.3E-5 (7)	1.3E-5 (5)	2.0E-5 (5)	1.1E-6 (5)
5-2C	9/77	5.1E-7 (9)	3.5E-5 (5)	7.9E-4 (5)	2.7E-7(32)	4.7E-5 (5)	7.6E-6 (3)	3.3E-5 (5)	--
5-3D	4/25/78	1.6E-6(11)	1.2E-5 (5)	4.4E-4 (5)	2.9E-7(12)	7.2E-5 (5)	4.1E-6 (8)	2.4E-5 (5)	3.6E-7(11)
8-1A	6/14/77	3.4E-6 (8)	1.2E-5 (6)	7.7E-4 (5)	2.2E-7(33)	2.9E-4 (5)	1.5E-5 (5)	2.1E-5 (6)	5.3E-6 (4)
8-1A	9/77	1.8E-6 (8)	1.4E-5 (5)	7.3E-4 (5)	1.8E-7(24)	8.8E-5 (5)	1.1E-5 (5)	3.4E-5 (5)	4.4E-6 (3)
8-1A	4/26/77	2.5E-6 (7)	1.0E-5 (5)	5.7E-4 (5)	1.9E-7(17)	4.6E-5 (5)	1.4E-5 (7)	1.9E-5 (6)	4.8E-8 (3)
9-1A	6/14/77	8.3E-7(10)	1.9E-6 (6)	4.0E-4 (5)	8 E-8(53)	1.8E-4 (5)	1.5E-5 (5)	1.7E-5 (5)	3.8E-6 (4)
9-1B	6/16/77	2.3E-6(17)	1.7E-7 (7)	2.9E-4 (5)	<3 E-7	2.1E-4 (5)	2.4E-5 (5)	1.8E-5 (5)	1.3E-5 (3)
9-1A	9/77	3.4E-6 (7)	1.5E-6(13)	2.6E-4 (5)	1.1E-7(56)	7.1E-5 (5)	4.6E-6 (5)	8.0E-6 (7)	2.3E-6 (4)
9-1B	9/77	2.6E-6 (8)	1.7E-6 (9)	3.8E-4 (5)	<9 E-8	6.1E-5 (5)	7.4E-6 (5)	9.7E-6 (5)	9.5E-7 (6)
9-1B	4/26/78	5.8E-7(26)	1.9E-6 (6)	4.1E-4 (5)	1.2E-7(18)	7.6E-5 (5)	2.1E-5 (5)	3.1E-5 (7)	5.2E-7 (9)
10-1A	6/14/77	6.1E-6 (6)	9.8E-7(18)	7.6E-4 (5)	8.7E-7(22)	5.5E-4 (5)	1.9E-5 (5)	1.3E-5 (6)	2.6E-6 (4)
10-1B	9/77[b]	1.8E-7(46)	1.7E-7(35)	8.2E-5 (5)	<1 E-7	1.0E-5 (6)	<2 E-7	3.7E-7(27)	--
10-1A	9/77	4.6E-6 (5)	5.5E-7 (5)	1.6E-3 (5)	5.6E-7(14)	3.5E-4 (5)	1.1E-5 (5)	1.5E-5 (5)	2.0E-6 (3)
10-1A	4/25/78	1.7E-5 (6)	8.4E-7(15)	1.9E-3 (5)	5.1E-7(14)	2.6E-4 (5)	1.3E-5 (6)	1.7E-5 (5)	2.4E-6 (4)
11-1A	6/15/77	--	<4 E-7	2.6E-4 (5)	<3 E-7	1.6E-4 (5)	1.9E-5 (6)	1.9E-5 (5)	3.7E-6 (4)
11-2A	6/16/77	1.3E-5 (6)	<2 E-6	9.1E-4 (5)	<8 E-7	5.1E-4 (6)	1.7E-5 (5)	1.3E-5 (5)	1.7E-5 (3)
11-2A	9/77	7.3E-5 (5)	4.5E-6 (6)	9.6E-4 (5)	3.3E-6 (6)	3.0E-4 (5)	8.7E-6 (5)	1.3E-5 (5)	1.1E-6 (5)
11-2A	4/26/78	3.1E-5 (5)	3.1E-6 (5)	8.9E-4 (5)	8.7E-7 (5)	2.9E-4 (5)	7.3E-6 (9)	2.2E-5 (6)	9.1E-6 (3)
12-1A	6/15/77	6.6E-7 (5)	4.1E-7(28)	2.3E-4 (5)	<3 E-7	1.6E-4 (5)	3.6E-6 (6)	3.4E-6 (6)	1.8E-6 (5)
12-1A	9/77	1.2E-5 (5)	5.2E-7(17)	2.5E-4 (5)	6.2E-7(14)	2.0E-4 (5)	5.3E-6 (5)	5.2E-6 (5)	2.8E-6 (4)
12-1A	4/25/78	2.6E-6(28)	4.8E-7(15)	2.5E-4 (5)	3.3E-7(33)	1.2E-4 (5)	2.9E-2(24)	2.9E-6 (7)	7.7E-7 (7)
13-1A	6/15/77	1.1E-6(23)	1.1E-6 (6)	8.0E-5 (5)	<6 E-8	5.0E-5 (5)	1.2E-6(11)	1.8E-6 (7)	2.0E-5 (3)
14-1A	6/16/77	2.2E-6 (7)	9 E-8(50)	6.4E-5 (5)	<9 E-7	3.7E-5 (5)	7.7E-6 (6)	7.7E-6 (5)	4.1E-6 (4)
14-2A	6/16/77	9.1E-6(11)	1.3E-7(67)	8.6E-5 (5)	9 E-8(60)	6.4E-5 (5)	1.4E-5 (5)	1.5E-5 (5)	3.1E-6 (4)
14-2A	9/78	3.4E-7(18)	<2 E-7	1.5E-5 (5)	<2 E-7	7.4E-6 (8)	2.0E-6(13)	2.3E-6 (7)	--

[a] As hydrocarbons above methane (C_2H_6, C_3H_8, and C_4H_{10})

[b] Apparent air leakage into sample

[c] Sump in trench - poor communication between sump and trench gas

TABLE 2
Composition of Trench Gas Samples
from West Valley, New York [7]
(% Composition)

Well #	Date	N_2	O_2	Ar	CO_2	CH_4	H_2
2-1A	6/08/76	62.0	0.2	0.7	10.4	26.7	<0.03
3-1A	6/08/76	67.0	0.7	0.8	2.8	28.7	0.3
3-1B	9/77	76.8	5.4	1.0	1.8	15.1	--
3-1A	9/77[a]	79.0	16.4	1.0	1.5	2.1	--
4-1B	9/77[a]	80.1	13.8	1.1	1.7	3.3	--
#4[b]	4/25/78	89.9	2.6	1.1	6.3	0.2	--
4-1B	4/25/78	86.8	2.7	1.0	2.5	6.7	--
5-1A	6/03/76	63.6	3.5	0.7	10.3	21.8	<0.4
5-3A	6/07/76	25.8	0.1	0.4	4.5	68.3	0.8
5-4A	9/77	78.9	1.6	1.0	8.2	10.1	--
5-3C	9/77	81.5	3.1	0.8	2.9	11.7	--
5-3D	9/77	81.0	3.4	0.9	3.6	11.2	--
5-2C	9/77	83.2	2.7	0.9	3.2	10.1	--
5-3D	4/25/78	81.8	0.1	1.1	3.3	13.8	--
8-1A	6/14/77	79.1[c]	16.2	0.9	2.0	1.8	--
8-1A	9/77	75.2	1.4	1.0	12.2	10.3	--
8-1A	4/26/77	80.5	1.8	0.9	9.1	7.6	--
9-1A	6/14/77	87.2	2.6	0.9	7.4	1.8	0.05
9-1B	6/16/77	82.5	1.3	1.1	12.6	2.5	--
9-1A	9/77	82.5	11.7	0.9	3.8	1.2	--
9-1B	9/77	81.8	6.4	1.1	8.7	1.9	--
9-1B	4/26/78	85.1	0.3	1.0	10.8	2.6	--
10-1A	6/14/77	89.0	2.7	1.0	6.1	1.1	0.2
10-1B	9/77[a]	79.9	19.4	0.8	0.4	0.1	0.2
10-1A	9/77	83.5	5.4	1.2	8.6	1.3	--
10-1A	4/25/78	87.6	1.9	1.0	8.3	1.2	--
11-1A	6/15/77	86.9	8.8	0.9	3.2	0.3	--
11-2A	6/16/77	93.5	2.2	1.0	2.8	0.6	--
11-2A	9/77	92.5	2.4	1.2	3.1	1.1	--
11-2A	4/26/78	90.8	4.3	1.0	3.1	6.7	--
12-1A	6/15/77	89.7	3.5	0.9	5.4	0.6	--
12-1A	9/77	86.5	2.1	1.2	9.4	0.9	--
12-1A	4/25/78	87.8	3.1	1.1	7.3	0.7	--
13-1A	6/15/77	90.8	2.5	0.9	5.5	0.3	--
14-1A	6/16/77	88.4	4.8	0.9	5.6	0.3	--
14-2A	6/16/77	89.5	3.1	0.9	6.1	0.3	--
14-2A	9/78	78.9	19.4	0.8	0.8	0.1	--

[a] Apparent air leakage into sample

[b] Sump in trench - poor communication between sump and trench gas

[c] Possible air leakage into mass spectrometer sample

TABLE 3

Radionuclide Concentrations in Field Air and Soil Gas Samples
Above Trench Soil Covers at West Valley, New York [7]
($\mu Ci/cm^3 \pm$ error in parentheses)

Over-Trench	Date	^3HH	$^{14}CH_4$	$^3HCH_3$	$^{14}C(HC)$[a]	$^3H(HC)$[a]	$^{14}CO_2$	^3HHO
14 (1 in.)	6/15/77	-	<8 E-8	<2 E-7	-	-	<1.6 E-7	-
11 (1 in.)	6/15/77	-	<1.1 E-7	<1.4 E-7	-	-	<1.3 E-7	-
9 (1 in.)	9/21/77	-	<3 E-8	<1.0 E-7	-	-	-	-
5 (1 in.)	9/21/77	-	<5 E-8	<1.7 E-7	-	-	-	-
9 (1 in.)	4/26/78	<6 E-8	<1.4 E-8	7 E-8(83)	-	-	<1.3 E-7	-
5 (5 ft.)	4/26/78	-	<1.3 E-12	8 E-13(51)	-	-	<4 E-11	2.5 E-12(17)
14 (5 ft.)	4/26/78	-	<9 E-13	4 E-12(34)	-	-	<1.3 E-11	< 4E-13
3 (Over-fracture)	6/04/76	<1.3 E-9	7 E-7(11)	1.1 E-7(10) [b]	-	-	6.7 E-9(12)	-
5 (F) Flux Box[c]	9/21/77	4.1 E-9(40)	3.3 E-7(5)	9.0 E-6(5)	1.1 E-8(21)	1.1 E-6(5)	4.1 E-7(7)	<1.6 E-9
5(UF) Flux Box[d]	9/21/77	<3 E-10	9.1 E-8(5)	2.3 E-6(5)	<2 E-9	4.8 E-7(5)	9.3 E-7(5)	1.2 E-8

[a] As hydrocarbons above methane (C_2H_6, C_3H_8, and C_4H_{10})

[b] Total methane in gas sample < 0.02%

[c] Fractured

[d] Unfractured

- $^{3}HCH_3$ is the major radionuclide specie in all trenches studied.

- Intratrench variations in radionuclide activity between sampling locations is slight (disregarding those samples showing obvious air contamination).

- Variations in concentration of specific species over periods of one to two years may be due to random breaching of containers by corrosion, and by changing conditions within the trench that will alter bacterial decomposition.

- The concentration of stable CH_4 in the trench increases with the age of the trench, whereas concentrations of CO_2 are similar for all trenches. The equilibrium concentration of 6% for CO_2 appears to be established a few years after trench closure.

- In any particular trench the specific activity of ^{14}C is similar for the $^{14}CH_4$ and $^{14}CO_2$ fractions in the trench gas and the total ^{14}C in the trench water. This is expected, since $^{14}CH_4$ and $^{14}CO_2$ are produced by decomposition of carbonaceous material in the trench water.

- In the older trenches (1 through 5), the specific activity of tritium for trench water and methane are in good agreement. In the newer trenches (8 through 14), the specific activity of tritium in trench water is somewhat less than in the older trenches, whereas the specific activity of tritium in the methane fraction is one to two orders of magnitude higher in the newer trenches.

5.3.1.2 Flux Box Samples: Although the flux box technique proved unsuccessful in measuring trench cap permeability and release rates of radioactive gases, some conclusions could be made from analyses of methane and CO_2 collected in the flux boxes.

- The depletion of $^{14}CH_4$, $^{3}HCH_3$ and stable methane relative to $^{14}CO_2$ indicates that methane is lost in passing through the trench cap.

- Substantial aerobic decomposition in the trench caps is indicated by the decrease in specific activity of ^{14}C as $^{14}CO_2$ in the flux box.

- The relatively high percentage of stable CO_2 relative to stable CH_4 in the flux boxes also indicates CO_2 production in the trench caps. Approximately 5% CO_2 with no measurable radioactivity was observed in the flux box over Trench 9.

5.3.1.3 Well-Point Experiments (GASFLOW Model): Bulk permeability of trench caps and estimates of rates of gas production and gas release were obtained by Lu and Matuszek at West Valley by measuring the pressure differential between trench gas and the atmosphere and applying an empirical model, GASFLOW, to the field data. The model considers the system to consist of two reservoirs, the atmosphere and the void volume in the trench, separated by a permeable trench cover. Gas produced in the trench from microbial degradation of the wastes produces gas pressures greater than atmospheric pressure. As atmospheric pressure changes, the pressure differential between trench gas and the atmosphere causes air to flow into, or gas to flow out of, the trench.

Experimental Procedure - The experimental procedure involves measuring changes in the pressure differential caused by changing atmospheric pressure and pumping gas in or out of the trench. Two well points penetrating the cover and open to the trench gas are required, so that one can be used to monitor trench gas pressures with pressure differential transducers, while the second is used to change the pressure differential. All other openings in the trench cover must be sealed. The pressure differential can be altered by pumping water out of the trench, pumping gas out of the trench or pumping air into the trench. Trench gas samples are also collected for mass spectrometric and radiochemical analyses to obtain the

molecular and radionuclide concentrations used to estimate release rates.

Where only one well point was available to measure trench gas pressures, an adaptation of the GASFLOW model was developed by Kunz and Lu to estimate gas production rates, by monitoring the pressure differential as it modulates in concert with changes in atmospheric pressure. This is referred to as the Static Model [16].

Mathematical Model - The GASFLOW models are discussed in detail in References 37, 7 and 16. The Darcy-flow equation is used to measure the cap permeability coefficient from measurements of pressure differentials between the atmosphere and trench gas under various conditions. "The removal of a known volume of water (or gas) provides a way to measure indirectly the sum of the air flowing into the trench and gas production in the trench." [37].

When the pump is on, removing gas (or water), and the atmospheric pressure is constant, the observed trench gas pressure decreases. As the atmospheric pressure becomes greater than trench gas pressure, atmospheric air is drawn into the trench through the trench cap. An equilibrium point will be reached when the trench gas pressure drops to the level, where water (or gas) is being removed at the same rate that air is being drawn into the trench, and gas is being produced anaerobically in the trench. When the pump is turned off at constant atmospheric pressure, the rate at which gas leaves the trench is equal to the rate of gas production. If this equilibrium can be established, the cap permeability and the volumetric gas production rate can be obtained from the Darcy equations.

Equilibrium may not be reached during the period of observation due to variations in barometric pressure and experimental difficulties in controlling the pumping rate. The GASFLOW model was developed to compute trench gas behavior and to determine flow rates under non-equilibrium conditions, by fitting calculated pressure differentials to those observed in the field.

Results - Cap permeability coefficients, volumetric gas production rates, and void volumes were calculated for Trenches 3, 5, 8, 9, 10, 11 and 12 from the period between October 1977 to July 1978. The trench gas pressures calculated with GASFLOW closely reproduced the observed values. The model proved to be consistent regardless of whether air was pumped in or gas was pumped out.

Estimation of the volume of gas released to the environment depends upon the values obtained for cap permeability, which can vary seasonally with climatic changes. Estimates of gas released to the environment for seven trenches at West Valley ranged from 1.9×10^9 to 4.4×10^9 cm^3/yr. These volumes correspond to approximately 1 to 8 curies per year of $^3HCH_3$ released to the atmosphere from a typical trench at West Valley. The rate of production and rate of release of stable methane is 1 to 2 orders of magnitude higher in the older trenches. Since the specific activity of tritium in the methane fraction is 1 to 2 orders of magnitude higher in the newer trenches, the rate of release of tritium as $^3HCH_3$ is similar for all trenches.

Conclusions - The GASFLOW model appears to provide reasonable estimates of ^3H and ^{14}C release rates from disposal trenches that have a relatively high degree of permeability. Since the trench covers for all shallow land burial sites in the United States are prepared from excavated material, it is assumed that this model will be applicable to them.

5.3.2 Beatty, Nevada.

Gas determinations included: gas composition, tritium and carbon-14 concentrations, and tritiated water vapor (^3HHO). Gas composition determinations were made by gas chromatographic techniques. The results of these analyses are summarized in Table 4, which shows the gas compositions of trench and soil gas samples obtained from observation wells, sump wells, and canisters shown in Figure 3 [6]. Tritium and carbon-14 concentrations are reported as $\mu Ci/cm^3$.

TABLE 4

Radionuclide Concentrations and Gas Compositions

of Trench and Soil Gases at Beatty, Nevada [6]

Location	N_2 (% Vol.)	O_2 (% Vol.)	CO_2 (ppm)	CH_4 (ppm)	Trace H_2O (mg/L)	Gaseous Tritium ($\mu Ci/cm^3$)	^3HHO ($\mu Ci/cm^3$)	Gaseous C-14 ($\mu Ci/cm^3$)
Background	78	22	300	10	1.95	<1.4 E-10	5.52 E-8	<9.01 E-11
Trench Gas								
Observation Well R-1	78	20	1860	7.7	2.81	2.68 E-7	8.22 E-8	5.90 E-8
Observation Well R-2	78	17	8100	19	2.74	5.68 E-9	3.08 E-8	3.60 E-8
Observation Well R-3	74	15	1270	41	2.55	4.73 E-8	2.93 E-8	3.04 E-8
Observation Well R-6	78	22	600	7	--	2.11 E-7	--	1.46 E-9
Sump Well Tr-14	76	21	530	16	2.88	9.86 E-8	5.52 E-6	2.59 E-8
Sump Well Tr-16	64	17	2200	9.8	3.59	9.82 E-9	9.35 E-8	8.56 E-9
Soil Gas								
Canister Tr-2	73	21	300	5.1	1.77	<1.4 E-10	5.18 E-8	<9.0 E-11
Canister Tr-3	77	22	300	7.1	2.11	1.99 E-7	1.90 E-8	2.21 E-10
Canister Tr-4	76	21	300	6.5	2.08	1.17 E-7	7.55 E-8	1.35 E-10
Canister Tr-5	73	21	300	6.5	2.02	7.75 E-8	1.27 E-8	5.27 E-9
Canister Tr-14	79	21	300	6.5	2.02	1.53 E-7	3.72 E-8	5.41 E-10
Canister Tr-16	78	22	300	7.3	2.58	1.98 E-7	1.62 E-8	8.11 E-10

In the six canister samples, there did not appear to be any significant amounts of CO_2 and CH_4. In the observation and sump well samples, CO_2 was present in concentrations ranging from 530 to 8100 ppm. Slightly elevated methane concentrations were present in the trench gas samples; none was detected in the soil gas samples. Comparison of these gas data with those of West Valley indicates that organic decomposition at the humid West Valley site is much more significant than at the arid Beatty site.

Elevated concentrations of carbon-14 were present in the trench gas samples (observation and sump wells). However, reduced carbon-14 concentrations were observed in the soil gas samples. Similar concentrations of carbon-14 are present in the observation wells and the trench sumps, which indicates that lateral diffusion of carbon-14 may be taking place beneath the facility [36]. A similar situation is observed for gaseous tritium and tritiated water vapor.

Comparison of the small amounts of data obtained by the EPA sampling of gases at Beatty with the Dames & Moore data shows no pattern of consistency; some of the Dames & Moore analyses are higher than the others, and sometimes the analyses from the two EPA laboratories did not agree [35].

5.3.3 Maxey Flats, Kentucky.

Gas composition and radionuclide concentration analyses of trench and soil gas samples were made by the same analytical procedures used for the Beatty gas samples. Gas composition determinations were made by gas chromatographic techniques; gaseous tritium and carbon-14 were radiochemically separated and analyzed by liquid scintillation counting. The results of these analyses are summarized in Table 5, which shows the gas compositions of trench and soil gas samples obtained from wells and canisters from locations shown in Figure 4 [5]. Tritium and carbon-14 concentrations are reported as $\mu Ci/cm^3$.

The methane concentration in the trench gas sample from Trench 18 sump was above the lower explosive limit (LEL) as determined with a Gas Scope, a

TABLE 5

Radionuclide Concentrations and Gas Compositions

of Trench and Soil Gases at Maxey Flats, Kentucky [5]

Location	N_2 (% Vol.)	O_2 (% Vol.)	CO_2 (ppm)	CH_4 (ppm)	Trace H_2O (mg/L)	Gaseous Tritium ($\mu Ci/cm^3$)	^3HHO ($\mu Ci/cm^3$)	Gaseous C-14 ($\mu Ci/cm^3$)
Background								
North Fence	77	22	98	2	0.95	4.18 E-8	2.48 E-9	N.D.[a]
South Fence	77	22	168	2	2.11	1.28 E-8	8.33 E-9	N.D.
Trench Gas								
Tr-7 Sump	77	22	148	2	1.48	1.29 E-8	6.31 E-9	N.D.
Tr-11S Sump	77	22	470	114	2.60	1.58 E-8	1.48 E-8	4.95 E-11
Tr-18 Sump	78	20	12000	6720	2.56	1.12 E-7	2.25 E-8	7.88 E-8
Tr-26 Sump	77	22	29	2	2.22	1.58 E-7	7.77 E-9	2.57 E-10
Tr-35 Sump	77	22	186	8	1.38	1.61 E-8	2.25 E-9	N.D.
Soil Gas								
Tr-11S	77	22	255	1	1.04	2.84 E-9	8.67 E-10	N.D.
Tr-18	77	21	2580	12	1.33	9.01 E-10	6.42 E-10	4.50 E-11
Tr-20	78	22	881	1.4	1.47	1.13 E-8	2.59 E-9	N.D.
Tr-26	77	22	819	2	2.12	5.81 E-9	4.95 E-10	N.D.
Tr-35	77	22	1410	4	2.83	9.50 E-9	1.80 E-9	N.D.

[a] N.D. - Not detected

methane monitoring instrument made by Mine Safety Appliance. All other trench gas samples taken from the sumps were below the LEL of 2% methane. The trench gas from Trench 18 was therefore indirectly sampled by accumulation in a canister placed over the sump, resulting in some dilution with ambient air. Trench 18 had the highest amounts of CO_2, CH_4, tritium, and carbon-14 of the trenches sampled at Maxey Flats. Except for Trench 18, concentrations of carbon-14 measured in the trench sumps were similar to those measured in the soil gas.

5.4 Discussion.

Tritium and carbon-14 gaseous compounds have been measured in trench and soil gas samples at the three low-level disposal sites investigated. The concentrations in methane and carbon dioxide are orders of magnitude higher at West Valley, while the levels at Maxey Flats are comparable to Beatty. It would be expected that microbial activity at the humid West Valley site would produce more methane and carbon dioxide than at the arid Beatty site, but the observation that the levels of carbon-14 in soil gas are approximately the same at Beatty and Maxey Flats (humid site) is noteworthy. The observation that gaseous tritium and tritiated water vapor in soil gas samples at Beatty are higher than at Maxey Flats may be caused by (1) the higher evapotranspiration at Beatty, (2) by the higher permeability of the trench covers at Beatty, or (3) by the differences in atmospheric pressure at the time the samples were obtained.

The concentrations of tritium and carbon-14 measured in soil gas compared to maximum permissible concentrations (MPC) for release to unrestricted areas listed in Table II of 10 CFR Part 20 are a factor of 200 below MPC for tritium and a factor of 190 below MPC for carbon-14 [36]. These calculations were based on the maximum tritium and carbon-14 concentration observed at the Beatty facility, viz., 2×10^{-7} $\mu Ci/cm^3$ gaseous tritium and 5.27×10^{-9} $\mu Ci/cm^3$ carbon-14. MPC values of 4×10^{-5} $\mu Ci/cm^3$ and 1×10^{-6} $\mu Ci/cm^3$ for submersion doses were used for tritium and carbon-14, respectively. The same comparisons for the highest tritium and

carbon-14 soil gas emanations measured at Maxey Flats (1.1×10^{-8} $\mu Ci/cm^3$ [tritium] and 9×10^{-7} $\mu Ci/cm^3$ [carbon-14]) indicate less than MPC releases for each radionuclide. The highest emanations measured at West Valley, in the flux boxes above Trench 5, were a factor of 4.4 below MPC for tritium and a factor of 1.1 below MPC for carbon-14. The actual concentrations in unrestricted areas would be much less due to atmospheric dispersion. Emanation rates are expected to be considerably less than the 25 mrem/yr whole body criteria proposed at the facility boundary [36].

Additional field studies should be performed to verify these preliminary investigations, taking into consideration the effects of differences in site climate, soil conditions, and measurement techniques.

6. ASSESSMENT OF RESEARCH NEEDS

Evaluation of the state of research involving the analyses of gaseous product evolution from low level radioactive waste disposal sites indicates data needs relating to 1) the quantity of gaseous loss from the ecosystem, 2) the duration of significant carbon-14 and tritium fluxes from the soil, 3) factors limiting complete biodegradation of the organic waste material, and 4) production of incompletely reduced or oxidized carbon compounds (such as amines or volatile acids) from trenches with insufficiently reducing E_h values for methanogeneses to occur. These data will be useful in assessing long term problems with trench sites and in evaluating alternative procedures for trench site location and construction. Specific data deficiencies are listed below:

1) Field studies of the quantity of gaseous products yielded within the trench and the proportion of those compounds leaving the soil surface are obligatory to determine the extent of biodegradation occurring within the ecosystem and the quantity of carbon-14 and tritium retained in the aerobic biomass in the upper layers of the soil profile. These data will allow a more accurate assessment of the duration of measurable carbon-14 and tritium fluxes from the site. As many physical and chemical parameters of the trench site at the time of flux determination should be measured, so that trench design can be evaluated.

2) From the non-flooded sites, evolution of carbon-14 and tritium as volatile acids and amines must be assessed. These data should also be collected periodically at the flooded sites. Importance is attributed to this portion of the project in that, should the E_h of the ecosystem rise, significant fluxes of these gases must be expected.

3) A major variable which controls biological activity in trenches is the pH. Highly acidic or alkaline pH values will severely retard

biodecomposition. pH variation and gaseous evolution from the trench should be specifically studied with the objective of maximizing trench design capabilities to minimize pH inhibition or biological activity.

4) Examine procedures of trench loading to develop procedures which will minimize physical barriers to microbial decomposition of the waste material.

5) Quantify methane and hydrogen oxidation within the soil profile. A portion of the oxidation products of these reactions will be fixed into soil biomass and organic matter. The loss of the carbon-14 and tritium so fixed from the environment will be delayed. Some of these compounds have long turnover times in the ecosystem, and hence long term difficulties could be postulated.

REFERENCES

1. Weiss, A. J. and P. Colombo, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites," NUREG/CR-1289, BNL-NUREG-51143, Brookhaven National Laboratory (March 1980).

2. Husain, L., J. M. Matuszek, J. Hutchinson and M. Wahlen, "Chemical and Radiochemical Character of a Low Level Radioactive Waste Disposal Site," in Management of Low-Level Radioactive Waste, 2, pp. 883-900, M. W. Carter et al., Eds., Pergamon Press, New York, (1979).

3. Lu, A. H. and J. M. Matuszek, "Solute and Gas Transport from Radioactive Waste," Trans. Am. Nucl. Soc., 30, pp. 94-95 (1978).

4. Clancy, J., O. Oztunali, H. Tuchfeld and T. Von Arsdale, "Maxey Flats Facility Studies Progress Report No. 2, January-March 1979," Dames and Moore (May 1979).

5. Clancy, J., H. Tuchfeld and G. Re, "Mass Balance Study of Maxey Flats Low-Level Waste Disposal Site, Task 5 Report, Evaporator Effluent and Trench Gas Studies," Dames and Moore (April 1980).

6. Clancy, J., "Trench Gas Study at the Beatty Low-Level Radioactive Waste Disposal Site," Dames and Moore (October 1978).

7. Matuszek, J. M., C. O. Kunz, J. A. Huchinson and W. E. Mahoney, "Studies of Trench Gas at a Low-Level Radioactive Waste Burial Site, West Valley, New York, Chemical and Radiochemical Analyses and Migration Studies," Report submitted to U. S. Environmental Protection Agency, Office of Radiation Programs, New York State Health Dept., Albany, N. Y., (August 1979).

8. Zehnder, A.J.B., "Ecology of Methane Formation," in Water Pollution Microbiology, 2, pp. 349-375, R. Mitchell, Ed., John Wiley and Sons, Inc., New York (1978).

9. Thauer, R. K., K. Jungermann and K. Decker, "Energy Conservation in Chemotrophic Anaerobic Bacteria," Bacteriol. Rev., 41, pp. 100-180 (1977).

10. Bryant, M. P., E. A. Wolin, M. J. Wolin and R. S. Wolfe, "Methanobacillus omelianskii, a Symbiotic Association of Two Species of Bacteria," Arch. Mikrobiol., 59, pp. 20-31 (1967).

11. Daniels, L., G. Fulton, R. W. Spencer and W. H. Orme-Johnson, "Origin of Hydrogen in Methane Produced by Methanobacterium thermoautotrophicum," J. Bacteriol., 141, pp. 694-698 (1980).

12. Francis, A. J., S. Dobbs and R. F. Doering, "Biogenesis of Tritiated and Carbon-14 Methane from Low-Level Radioactive Waste," Nuclear and Chemical Waste Management, 1, pp. 153-159 (1980).

13. Bowien, B. and H. G. Schlegel, "Physiology and Biochemistry of Aerobic Hydrogen Oxidizing Bacteria," Ann. Rev. Microbiol., 35, pp. 405-452 (1981).

14. Zeikus, J. G. and J. C. Ward, "The Biology of Methanogenic Bacteria," Bacteriol. Rev., 41, pp. 514-541 (1977).

15. Zeikus, J. G. and J. C. Ward, "Methane Formation in Living Trees: A Microbial Origin," Science, 184, pp. 1181-1183, Washington, D. C. (1974).

16. Kunz, C. O. and A. H. Lu, "Methane Production Rate Studies and Gas Flow Modeling for the Fresh Kills Landfill," New York State Department of Health, ERDA Report 80-21 (1980).

17. Perron, C. H., "Refuse Conversion to Methane," Symposium paper, Energy Biomass Wastes, 4, pp. 509-525 (1980).

18. Smith, P. H., "The Microbial Ecology of Sludge Methanogenesis," Dev. Ind. Microbiol., 7, pp. 156-160 (1966).

19. Healy, J. B., Jr., L. Y. Young and M. Reinhard, "Methanogenic Decomposition of Ferulic Acid, A Model Lignin Derivative," Appl. Environ. Microbiol., 39, pp. 436-444 (1980).

20. Laube, V. M. and S. M. Martin, "Conversion of Cellulose to Methane and Carbon Dioxide by Triculture of Acetovibrio cellulolyticus, Desulfovibrio sp., and Methanosarcina barkeri, Appl. Environ. Microbiol., 42, pp. 413-420 (1981).

21. Balch, W. E., G. E. Fox, L. J. Magrum, C. R. Woese and R. S. Wolfe, "Methanogens: Reevaluation of a Unique Biological Group," Microbiol. Rev., 43, pp. 260-296.

22. Bryant, M. P., S. F. Tzeng, I. M. Robinson and A. E. Joyner, Jr., "Nutrient Requirements of Methanogenic Bacteria," Adv. Chem. Ser., 105, pp. 23-40 (1971).

23. Dacey, J.W.H. and M. J. Klug, "Methane Efflux from Lake Sediments Through Water Lilies," Science, 203, pp. 1253-1255 (1979).

24. Knowles, R., "Denitrification," in Soil Biochemistry, 5, pp. 323-369, E. A. Paul and J. N. Ladd, Eds., Marcel Dekker, Inc., New York (1981).

25. Martens, C. S. and R. A. Berner, "Methane Production in the Interstitial Waters of Sulfate-Depleted Marine Sediments," Science, 185, pp. 1167-1169, Washington, D. C. (1974).

26. Balderson, W. L. and W. J. Payne, "Inhibition of Methanogeneses in Salt Marsh Sediments and Whole Cell Suspensions of Methanogenic Bacteria by Nitrogen Oxides," Appl. Environ. Microbiol., 32, pp. 264-269 (1976).

27. Cappenberg, T. E., "Interrelations Between Sulfate-Reducing and Methane-Producing Bacteria in Bottom Deposits of a Fresh Water Lake, I. Field Observations," Antonie van Leeuwenhoek, J. Microbiol. Serol., 40, pp. 285-295 (1974).

28. Cappenberg, T. E., "A Study of Mixed Continuous Culture of Sulfate-Reducing and Methane-Producing Bacteria," Microbiol. Ecol., 2, pp. 60-72 (1975).

29. Wood, J. M., F. S. Kennedy and R. S. Wolfe, "The Reaction of Multihalogenated Hydrocarbons with Free and Bound Reduced Vitamin B_{12}," Biochem., 7, pp. 1707-1713 (1968).

30. Wolfe, R. S., "Microbial Formation of Methane," in Adv. Microbial. Physiol., 6, pp. 107-146, A. H. Rose, Ed., Academic Press, New York (1971).

31. Dommergues, Y. R., L. W. Belser and E. L. Schmidt, "Limiting Factors for Microbial Growth and Activity in Soil," in Adv. Microbiol. Ecol., 2, pp. 49-104, M. Alexander (Ed.), Plenum Publishing Corp., New York (1978).

32. Alexander, M. and B. K. Lustigman, "Effect of Chemical Structure on Microbial Degradation of Substituted Benzenes," J. Agr. Food Chem., 14, pp. 410-413 (1966).

33. Higgins, I. J., D. J. Best and R. C. Hammond, "New Findings in Methane-Utilizing Bacteria Highlight Their Importance in the Biosphere and Their Commercial Potential," Nature, 286, pp. 561-564 (1980).

34. Hanson, R. S., "Ecology and Diversity of Methylotrophic Organisms," Adv. Appl. Microbiol., 26, pp. 3-39 (1980).

35. Clancy, J. and O. I. Oztunali, "Comparison of Trench and Soil Gas Data at the Beatty Low-Level Radioactive Waste Disposal Site," Dames and Moore (May 1979).

36. U. S. Nuclear Regulatory Commission, Draft Environmental Impact Statement on 10 CFR Part 61 - Licensing Requirements for Land Disposal of Radioactive Waste, NUREG-0782, Volume 4, Appendix M (September 1981).

37. Lu, A. H. and J. M. Matuszek, "Transport Through a Trench Cover of Gaseous Tritiated Compounds from Buried Radioactive Wastes," in Behavior of Tritium in the Environment, IAEA-SM-232/60, IAEA, Vienna (1979).