AIR / SUPERFUND NATIONAL TECHNICAL GUIDANCE STUDY SERIES

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Emission Factors for Superfund Remediation Technologies

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INTRODUCTION

BACKGROUND

The U.S. Environmental Protection Agency (EPA) Air Program Office (Office of Air Quality Planning and Standards) and the Regional Air Offices have been given the responsibility to evaluate air impacts from Superfund sites and to advise Superfund Regional Offices on appropriate clean-up actions. The Air/Superfund Coordination Program, under the direction of the EPA Air Program Office, was begun to facilitate this effort. An important part of this program is the analysis of air impacts from various remedial options. These analyses are frequently required for planning purposes prior to actual remediation. They are, therefore, dependent on the ability to estimate emissions, rather than on field measurement approaches.

Work to estimate emissions from cleanup activities has already been done under the Air/Superfund Coordination Program, including a manual summarizing estimation techniques for emissions from remedial activities at abandoned hazardous waste sites - Volume III of the National Technical Guidance Series (NTGS). This manual (1) provides simple emission estimation procedures based on a mass balance approach and notes the general lack of predictive models for most remedial activities. Emissions of Volatile Organic Compounds (VOCs) from soils handling operations such as excavation and dumping have also been studied under the Air/Superfund Coordination program (2). Simple screening models to evaluate air impacts from many of the remediation technologies considered in this document are also under development (3).

The EPA recognizes the need to develop simple estimation techniques for air emissions from Superfund remediation activities. The work presented in this document attempts to address this need, by developing emission factors for six Superfund clean-up technologies.

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TECHNICAL OBJECTIVES AND APPROACH

The overall objective of this program was to develop an easy-to-use tool for decision makers to predict the air emissions associated with Superfund remediation actions. The specific objectives of this project were three-fold:

1) To develop process descriptions and process flow diagrams for common Superfund site treatment technologies;

2) To identify the emission points and types of pollutants associated with each technology; and

3) To summarize available air emissions data and develop emission factors.

As part of meeting these goals, six different remediation technologies were examined:

1) Thermal Treatment;
2) Air Stripping;
3) Soil Vapor Extraction;
4) Solidification and Stabilization;
5) Physical and Chemical Treatment Methods; and
6) Biotreatment and Land Treatment.

For each of the six technologies a literature review was conducted to develop a process flow diagram and identify emission points, as well as to analyze available air emissions data. For most of the technologies examined, emission factors were based on available data as well as assumed "typical" operating conditions for Superfund site remediation. Where possible, however, emission factors were based on actual operating data from site studies.

LIMITATIONS OF THE WORK

Developing air pollutant emission factors for any process is a challenging task. A limited data set must be used to generalize about a wide-spectrum of process conditions. Developing emission factors for the processes used to remediate Superfund sites is an even greater challenge. Many of the cleanup processes used at Superfund sites are emerging technologies and have short operating histories. For these technologies, data on which to base an emissions factor are very limited. Furthermore, each Superfund site possesses its own unique obstacles to cleanup. These obstacles, in turn, may force modifications to the cleanup hardware or operating conditions which could effect air emissions.

The development of air pollutant emission factors applicable to the maximum number of site conditions and site locations required assumptions regarding the rate and scope of the clean-up effort, the type of wastes being treated, the number and nature of emission release points, and so on. Assumptions were based on what is "typical" and "reasonable" for Superfund site remediations. Obviously, the diverse nature of sites on the National Priorities List (i.e. Superfund) results in the emission factors being more applicable to some sites than others.

ORGANIZATION OF TECHNICAL NOTE

The remainder of this technical note is divided into seven sections. Section 2 presents a summary of the emission factors developed in this study. Each of the other six sections are devoted to one of the six cleanup technologies examined (thermal destruction, air stripping, soil vapor extraction, solidification and stabilization, physical/chemical treatment, and biotreatment/land treatment). These sections are each divided into four parts: 1) a process description of the cleanup technology; 2) a review of air emission points and typical pollutants for the technology; 3) a summary of available emissions data and correlations; 4) a discussion of the emission factor

generated for that technology; and 5) where possible, a case study illustrating the development of the emission factor.

Example calculations are included as an appendix to this technical note.

SECTION 2
EMISSION FACTORS SUMMARY

EMISSION FACTORS

Table 2-1 shows air pollutant emission factors for the six Superfund cleanup technologies examined in this report. Emission factors are presented for total VOCs, criteria pollutants, total metals, and acid gases. For technologies where it is difficult to define "typical" operating conditions, emission factors are shown for a particular commercial process.

Many of the emission factors given in Table 2-1 are built upon several assumptions and may be more applicable to some sites or commercial processes than others.

ESTIMATED HOURLY EMISSIONS

Table 2-2 shows estimated hourly emission factors for the technologies discussed in this report. Hourly emission factors are based on "reasonable" operating conditions for Superfund remediation actions. These estimates may not be applicable to some clean-up programs.

TABLE 2-1. EMISSION FACTORS FOR SUPERFUND CLEANUP TECHNOLOGIES

Technology	Pollutant	Uncontrolled Emissions Factor	Controlled Emissions Factor
Thermal Treatment Rotary Kiln Incineration	VOC	0.1 g/kg VOC in waste feed	0.1 g/kg VOC in waste feed
	Metals	50.0 g/kg metal in waste feed	50.0 g/kg metal in waste feed
	HCl	1.03 g/kg Cl in waste feed	0.01 g/kg Cl in waste feed
	HF	1.05 g/kg F in waste feed	0.01 g/kg F in waste feed
	SO_2	2.00 g/kg S in waste feed	0.10 g/kg S in waste feed
	PM	11,750 mg/m^3 flue gas	72 mg/m^3 flue gas
	CO	50.0 ppmv flue gas	
	NO_x	100.0 ppmv flue gas	
Infrared Incineration	VOC	0.1 g/kg VOC in waste feed	0.1 g/kg VOC in waste feed
	Metals	50.0 g/kg metal in waste feed	50.0 g/kg metal in waste feed
	HCl	1.03 g/kg Cl in waste feed	0.01 g/kg Cl in waste feed
	HF	1.05 g/kg F in waste feed	0.01 g/kg F in waste feed
	SO_2	2.00 g/kg S in waste feed	0.10 g/kg S in waste feed
	PM	Not Available	180 mg/m^3 flue gas
	CO	25.0 ppmv flue gas	
	NO_x	100.0 ppmv flue gas	
Air Stripping	VOC	Emissions equal total mass VOC in Influent Water	0.1 g/g VOC in water
Soil Vapor Extraction	VOC	Emissions equal total mass VOC in Influent Water	0.05 g/g VOC Removed from Soil
Solidification and Stabilization	VOC	0.6 g/g/ VOC in soil	No Controls Typically Applied
Physical and Chemical Treatment Methods Ultrox Oxidation	VOC	0.2 g/g VOC in water	No Controls Typically Applied
Biotreatment and Land Treatment Flow Through Treatment w/Mechanical Aeration	VOC	.80 g/g VOC in water	No Controls Typically Applied
Quiescent Flow-Through Treatment	VOC	.10 g/g VOC in water	No Controls Typically Applied
Disposal Impoundment	VOC	.14 g/g VOC in water	No Controls Typically Applied
Land Farming (24-hour Total Emissions)	VOC	.36 g/g VOC in water	No Controls Typically Applied
Land Farming (20-day Total Emissions)	VOC	.90 g/g VOC in water	No Controls Typically Applied

TABLE 2-2. HOURLY EMISSION FACTORS FOR SUPERFUND CLEANUP TECHNOLOGIES

Technology	Pollutant	Estimated Controlled Hourly Emissions (g/hr)
Thermal Treatment		
Rotary Kiln Incineration	VOC	340
	Metals	170
	HCl	1.4
	HF	0.4
	SO_2	17
	PM	4,260
	CO	3,510
	NO_x	11,530
Infrared Incineration	VOC	10.0
	Metals	5.0
	HCl	0.04
	HF	0.01
	SO_2	0.5
	PM	16.2
	CO	2.7
	NO_x	16.0
Air Stripping		
Small-Size Unit	VOC	342
Medium-Size Unit	VOC	1,704
Large-Size Unit	VOC	3,420
Soil Vapor Extraction	VOC	1,250
Solidification and Stabilization	VOC	5,460
Physical and Chemical Treatment Methods		
Ultrox Oxidation	VOC	4.5
Biotreatment and Land Treatment		
Flow Through Treatment w/Mechanical Aeration	VOC	4,800
Quiescent Flow-Through Treatment	VOC	720
Disposal Impoundments	VOC	48.6
Land Farming (24-hour Average)	VOC	1,500
Land Farming (20-day Average)	VOC	188

SECTION 3
THERMAL TREATMENT TECHNOLOGIES

PROCESS DESCRIPTION

A broad range of technologies fall into the category of thermal treatment or incineration. The most common incineration technologies include liquid injection, rotary kiln, and multiple hearth (4,5). For Superfund site clean-ups any of these options may be used. Superfund site remediations by thermal treatment fall into two general categories: 1) on-site treatment using a transportable incinerator, or 2) off-site treatment where contaminated soils or solvents are shipped to a larger, permanent unit.

In general terms, thermal destruction of hazardous waste is an engineered process in which controlled combustion is used to reduce the volume of an organic waste material and render it environmentally safe. Thermal treatment is a flexible process capable of being used for many waste types including gases, liquids, solids, and sludges.

Figure 3-1 shows a generalized process flow diagram for thermal treatment systems. A typical system includes the waste feed system, primary and (in most cases) secondary combustion chambers, and exhaust gas conditioning system.

At the front-end of a hazardous waste incineration system is the waste feed process. The configuration of the waste feed system is determined by the physical characteristics of the waste. Solid wastes, normally packed in fiber drums, are introduced to the combustion chamber by means of a conveyor or pneumatic rams. Other solid wastes may require shredding or preheating before introduction to the incinerator. Liquids are injected into the incinerator by means of an atomization nozzle(s) which uses steam or compressed air as an atomization fluid. Liquids with entrained solids may require screening to prevent clogging of the atomizer nozzle.
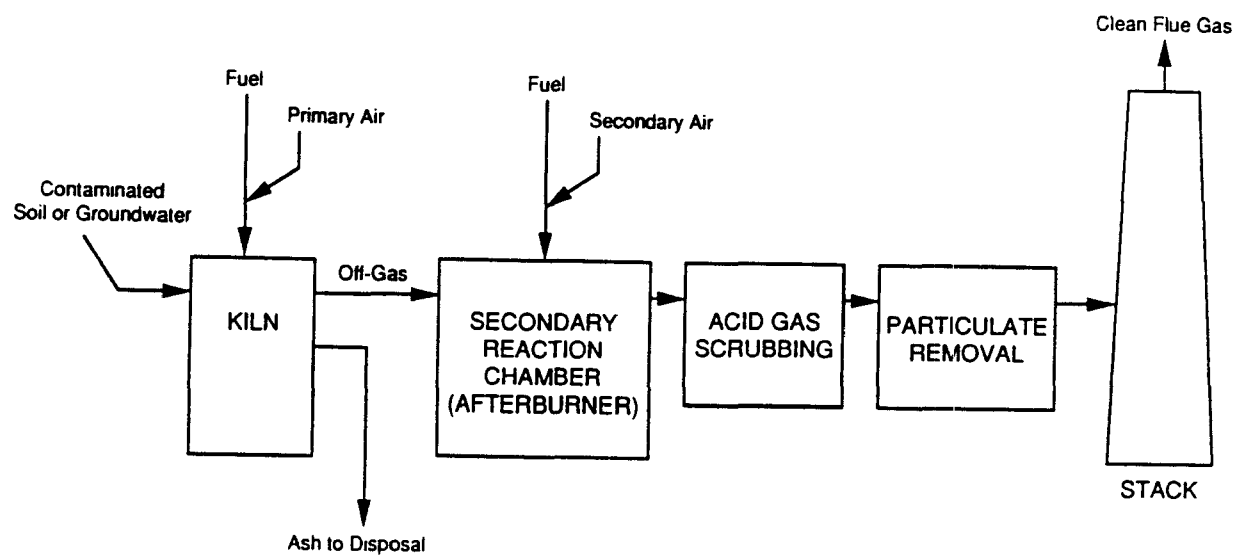
Figure 3-1. Generalized Process Flow Diagram for Thermal Treatment.

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Gases are usually fed to the incinerator through ductwork and a blower. If the waste stream contains oxygen, dilution air is frequently added to the gas stream so that the resulting mixture is below its explosion limit.

The largest part of the waste destruction usually takes place in the primary combustion chamber. As mentioned earlier, the chamber may be a rotating kiln, open hearth, or other design. Gases formed in the primary combustion chamber are then routed to a secondary combustion chamber, or afterburner, where any unburned hydrocarbons or products of incomplete combustion such as CO, can be fully oxidized.

After the combustion gases leave the incinerator, they may be routed through a variety of air pollution control devices including gas conditioning, particulate removal, and acid gas removal units. Gas conditioning is accomplished with equipment such as waste heat boilers or quench units. Typical particulate removal devices include venturi scrubbers, wet or dry electrostatic precipitators, ionizing wet scrubbers, and fabric filters. Acid gas removal units include packed, spray, or tray tower absorbers; ionizing wet scrubbers; and wet electrostatic precipitators.

IDENTIFICATION OF AIR EMISSION POINTS AND TYPICAL POLLUTANTS

The air emissions associated with full-scale thermal treatment are primarily stack emissions of combustion gas. However, there may be some additional evaporative emissions from equipment leaks and waste handling. Full-scale, off-site incineration units typically vent all emissions from waste handling and transfer activities to the combustion chamber as make-up air. The air emissions for on-site incinerators are similar to off-site units, except that waste handling activities have a greater likelihood of being uncontrolled. For off-site units, typical incinerator stacks will be 50-75 ft high. For transportable on-site units stack heights may be in the range 15-40 ft. The fugitive emissions sources associated with thermal treatment will likely be ground-level.

Emissions from both on-site and off-site incinerators include: undestroyed organics, products of incomplete combustion (PICs), metals, particulate matter, nitrogen oxides (NO_x), carbon monoxide (CO), and acid gases. The cause of each of these pollutants is discussed below.

Unburned Hydrocarbons

In general, incinerators treating wastes from Superfund sites must achieve a required destruction and removal efficiency (DRE) of at least 99.99% for RCRA wastes and 99.9999% for PCB- or dioxin wastes. The remaining 0.01% or 0.0001% of the can be assumed to through the system uncombusted (1).

Products of Incomplete Combustion

In the combustion process some reaction may produce a number of simpler organic compound, called PICs. PICs may include dioxin, formaldehyde, and benzo(a)pyrene and other polynuclear aromatic hydrocarbons. PIC formation is not restricted to the combustion chamber; the reactions which produce PICs may continue to occur in the combustion gases as they travel through the incineration system and out the exhaust gas (1,6).

Metals

The metals introduced to the incinerator via the waste feed stream are not destroyed. Depending on their boiling point, they can either be volatilized or remain as solids. Volatilized metals will exit the stack as a gas or they will condense or adsorb onto particles in the stack gas stream. Non-volatilized metals can be fluidized and swept up into the combustion gas or leave the incinerator in the bottom ash.

Particulate Matter

The waste feed, auxiliary fuel, and combustion air can all serve as sources for particulate emissions from an incineration system. Particulate emissions may result from inorganic salts and metals which either pass through the system as solids or vaporize in the combustion chamber and recondense as solid particles in the stack gas. High molecular weight hydrocarbons may also contribute to particulate emissions through several possible mechanisms. RCRA requirements for particulate emissions call for a limit of 0.08 grains/dscf corrected to 7% O_2.

Nitrogen Oxides

Achieving high levels of destruction of organic wastes is directly related to combustion chamber temperature: the higher the temperature, the greater the DRE of organics. Unfortunately, the fixation of nitrogen and oxygen to form NO_x also increases with combustion temperatures. NO_x emissions caused by this mechanism are referred to as thermal NO_x. Also if there are bound nitrogen atoms in the waste, e.g. amines. In such cases, two stage combustion or emissions controls may be needed.

Carbon Monoxide

Carbon monoxide emissions are generally low (<25 ppmv) in commercial incinerators due to the high operating temperatures and excess oxygen maintained in the process.

Acid Gases

Hazardous was incineration will also produce acid gases. These include oxides of sulfur (SO_x), and halogen acids (HCl, HF, and HBr). The sulfur, chlorine, fluorine, and bromine contents of the waste and fuel feed determine the emission levels of their respective acid gases. The concentrations of these elements range widely amongst different wastes; consequently, the resulting acid gas emissions will also show wide variability. Furthermore most incinerators will be equipped with some type of flue gas treatment system to control acid gas emissions. Control efficiencies will typically range from 85-99%. Units treating wastes from Superfund sites will generally be required to meet RCRA requirements governing HCl emissions. These requirements limit HCl emissions to 4 lbs/hr or mandate a control efficiency of 99%, whichever is less stringent.

SUMMARY OF AIR EMISSION DATA AND CORRELATIONS

The wide variety in design and operation of incinerators makes it difficult to identify a single emissions factor for each contaminant. Some general equations, however, can be developed from a mass balance approach to provide general guidelines for estimating emissions. Separate correlations for each pollutant of concern are presented.

Unburned Hydrocarbons

An emission rate for unburned hydrocarbons can be generated from a mass balance on the incinerator system:

$$ER_i = (1-(DRE_i/100))(C_i)(m_w)$$

where:
ER_i = emission rate for pollutant i (g/hr);
DRE_i = destruction efficiency (assume 99.99% if not known);
m_w = total mass flow rate of waste feed (kg/hr); and

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$$C_i \quad = \text{waste feed concentration for pollutant i (g/kg).}$$

Products of Incomplete Combustion

Emissions of PICs, both the amount and the type, will vary greatly from unit to unit depending on design and waste feed. Data is currently unavailable to generate a single emission factor.

Metals

Metals are not destroyed in the incineration process. They leave the system via either the bottom ash or the stack gas. There are currently no correlation available for determining the partitioning of metal emissions in incineration systems. An upper limit on emissions can be estimated by assuming all the metals present in the feed are emitted in the stack gas. If stack data is available for the incinerator in question, metals emissions rates can be estimated from:

$$ER_i = (C_i)(m_w)(\%ME_i/100)$$

where: ER_i = emission rate for metal i (g/hr);
             C_i = concentration of metal i in the feed (g/kg);
            m_w = mass flow rate of waste (kg/hr); and
      $\% ME_i$ = metal emitted to air expressed as a percentage of metal fed (See Reference #1).

Acid Gases

The production of acid gases (HCl, SO_2, and HF) is determined by the respective chlorine, sulfur, and fluorine contents in the waste and fuel feed streams. A conservative approach to calculating the air emissions of these acid gases is to assume complete conversion of Cl, S, and F into their respective acid gas products. These equations follow the form:

$$ER_i = (Cj)(R_{i/j})m_w(1-\%CE_i/100)$$

where
ER_i = emission rate for acid gas i (g/hr);
C_j = concentration of element (Cl, S, or F) in waste (g/kg);
$R_{i/j}$ = stoichiometric ratio of acid gas to element (kg/kg);
m_w = mass flow rate of waste (kg/hr); and
$\%CE_i$ = control efficiency of acid gas treatment system.

Nitrogen Oxides and Carbon Monoxide

In general, incinerator systems are not considered significant sources of NO_x emissions. NO_x is usually only a concern for wastes with high nitrogen content. Typical NO_x emissions for an incinerator may be on the order of 100-200 ppmv (dry basis), or expressed on a fuel basis, 0.12-0.33 lbs per MMBtu.

CO emissions from incinerators are also not considered a major problem. Most systems are designed to be fired with excess air (i.e. oxygen rich) to ensure complete combustion of organic material to carbon dioxide CO_2. Vendors typically guarantee CO emissions less than 100 ppmv (dry basis). Actual measured CO levels are often lower.

CASE STUDY: OFF-SITE INCINERATION

Process Description

A common method for Superfund site remediation is off-site incineration. This involves removing the contaminated soil or water from the site and transporting it to a commercial incinerator for disposal. The most common type of incinerator used in this application is the rotary kiln, based on the dependability and versatility of this design. Figure 3-2 shows a schematic of a typical rotary kiln incinerator with afterburner.
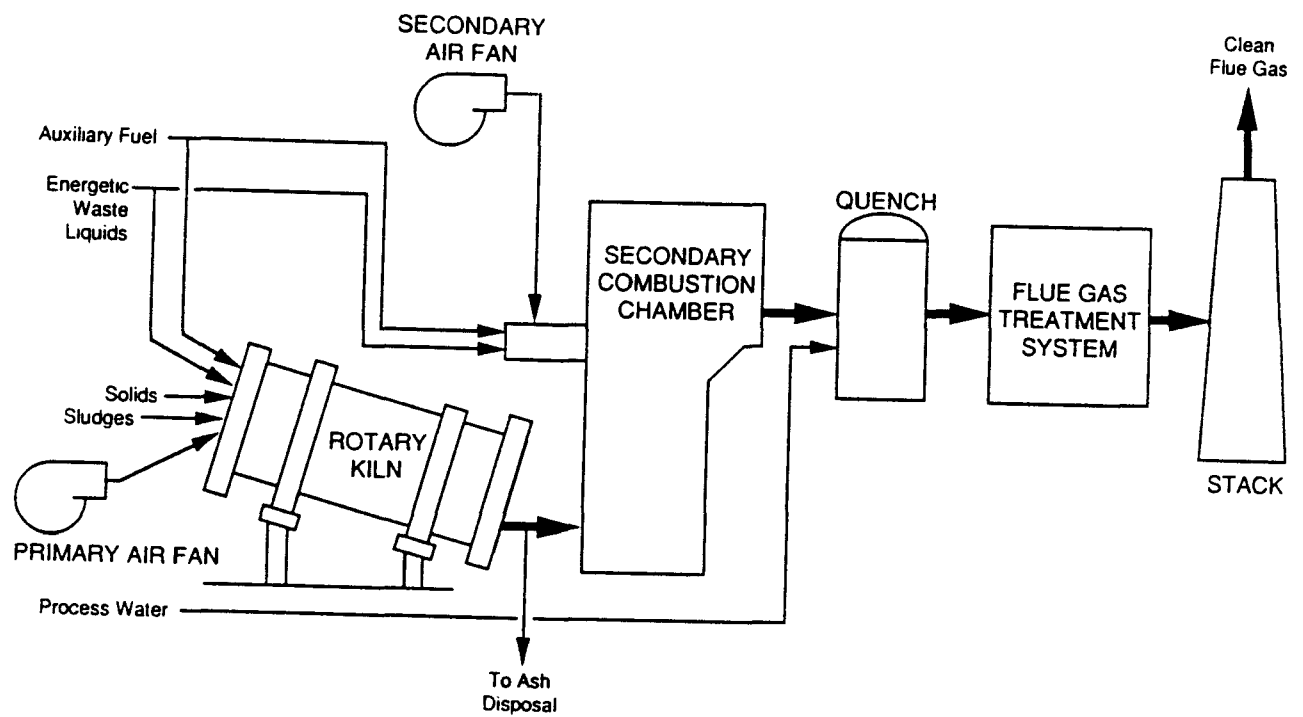
Figure 3-2. Process Flow Diagram for Commercial Rotary Kiln Incinerator.

Emission Factors

The correlations described in the preceding section were used to generate emissions factors for off-site incineration. These emission factors are only for stack emissions. In addition, emission estimates were generated for a typical incinerator assuming a heat duty of 63 MM Kilojoules/hours (60 MMBtu/hr) and a stack gas flowrate of 986 m³/min (35,000 SCFM). Based on a heating value of 18,590 kJ/kg (8,000 Btu/lb) for waste material, this corresponds to a feed rate of 3,400 kg/hr (7,500 lbs/hr). Table 3-1 shows the estimated emissions factors and emissions rates.

Other emissions associated with the handling and storage of contaminated soils should be estimated using published emission factors.

CASE STUDY: ON-SITE INCINERATION

Process Description

Superfund site remediation is occasionally accomplished using on-site incineration. This involves moving a transportable incinerator unit to the site. One type of incinerator demonstrated in this application is the Shirco Infrared Incineration System (7,9). Figure 3-3 shows a schematic of the Shirco, which uses infrared heating in the primary combustion chamber in place of fossil fuels.

Emission Factors

The correlations described earlier were used with field data to generate emission factors for the Shirco incineration system. These emission factors, along with estimated emissions, are shown in Table 3-2. Again, only stack emissions are considered.

TABLE 3-1. OFF-SITE INCINERATION STACK EMISSION FACTORS AND ESTIMATED EMISSIONS[a-c]

Pollutant	Uncontrolled Emission Factor and Units	Controlled Emission Factor and Units	Estimated Controlled Emissions (g/hr)
VOC	0.1 g/kg waste feed	NA	340
Metals	50.0 g/kg metal in waste feed	NA	170
HCl	1.028 g HCl/g Cl in waste feed	0.010 g HCl/g Cl in waste feed	1.4
HF	1.053 g HF/g F in waste feed	0.011 g HF/g F in waste feed	0.4
SO_2	2.000 g SO_2/g S in waste feed	0.100 g SO_2/g S in waste feed	17.0
Particulate Matter	11,750 mg/m^3	72 mg/m^3	4,260
CO[d]	50.0 ppmv flue gas	NA	3,510
NO_x[d]	100.0 ppmv flue gas	NA	11,530

[a]Basis for Emissions Estimates: Typical Incinerator
    Heat Load: 63 MM Kilojoules/hour
    Waste Feed: 3,400 g/hr
    Stack Gas Flow: 986 m^3/min

[b]Basis for Emissions Estimates: Waste Characterization
    Waste LHV: 18,590 KJ/kg
    Cl in Waste: 4.0%
    F in Waste: 1.0%
    S in Waste: 5.0%
    Metal in Waste: 0.1%

[c]Basis for Emissions Estimates: Acid Gas Scrubbing Efficiency
    HCl Removal Efficiency: 99%
    HF Removal Efficiency: 99%
    SO_2 Removal Efficiency: 95%

[d]Emission factors for CO and NO_x may also be expressed in kg/MMKJ or lb/MMBtu
    CO: 0.05 kg/MMKJ or 0.12 lb/MMBtu
    NO_x: 0.15 kg/MMKJ or 0.33 lb/MMBtu
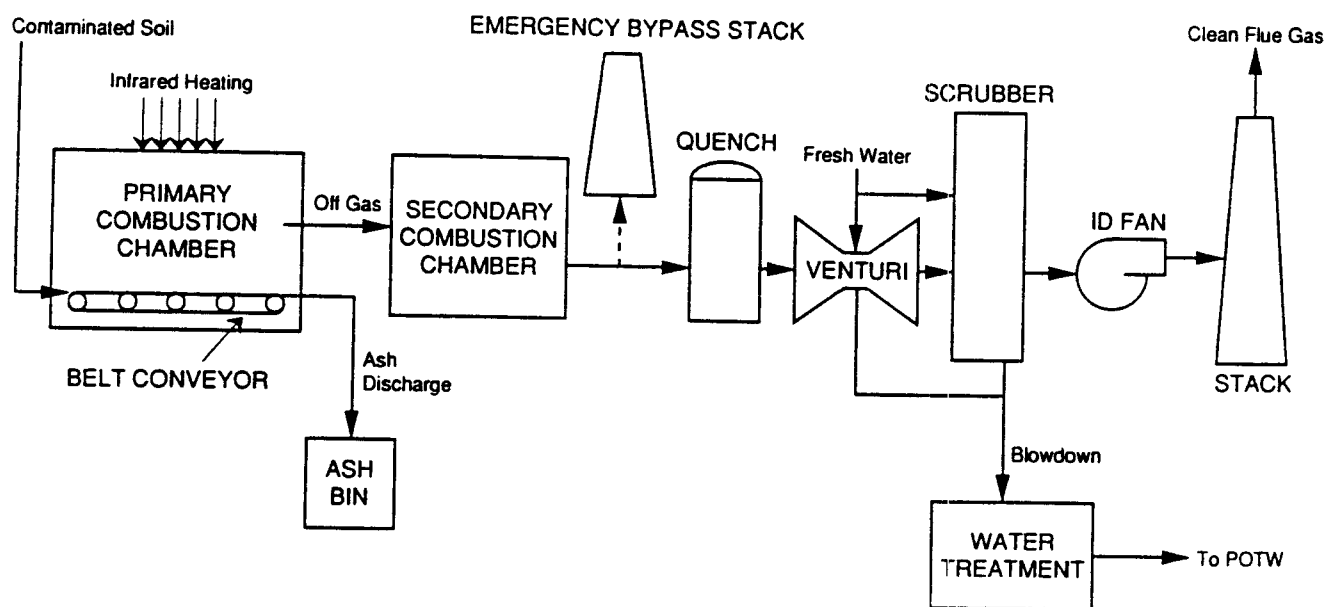
Figure 3-3. Process Flow Diagram for Shirco Incinerator.

TABLE 3-2. ON-SITE INCINERATION STACK EMISSION FACTORS AND
ESTIMATED EMISSIONS BASED ON DEMONSTRATION
TESTING OF SHIRCO INFRARED INCINERATOR

Pollutant	Uncontrolled Emission Factor and Units	Controlled Emission Factor and Units	Estimated Controlled Emissions (g/hr)
VOC	0.1 g/kg waste feed	NA	10.0
Metals	50.0 g/kg metal in waste feed	NA	5.0
HCl	1.028 g HCl/g Cl in waste feed	0.010 g HCl/g Cl in waste feed	0.041
HF	1.053 g HF/g F in waste feed	0.011 g HF/g F in waste feed	0.011
SO_2	2.000 g SO_2/g S in waste feed	0.100 g SO_2/g S in waste feed	0.500
Particulate Matter	NA	180 mg/m^3	16.2
CO	25.0 ppmv flue gas	NA	2.7
NO_x	100.0 ppmv flue gas	NA	16.0

[a]Basis for Emissions Estimates: Typical Incinerator
      Waste Feed: 100 g/hr
      Stack Gas Flow: 1.5 m^3/min

[b]Basis for Emissions Estimates: Waste Characterization
      Cl in Waste: 4.0%
      F in Waste: 1.0%
      S in Waste: 5.0%
      Metal in Waste: 0.1%

[c]Basis for Emissions Estiamtes: Acid Gas Scrubbing Efficiency
      HCl Removal Efficiency: 99%
      HF Removal Efficiency: 99%
      SO_2 Removal Efficiency: 95%

[d]Emission factors do not include the fuel requirements to produce the infrared radiation.

SECTION 4
AIR STRIPPING

PROCESS DESCRIPTION

Air stripping is a mass transfer process in which volatile contaminants in water are evaporated (stripped) into air. The contaminated water is introduced at the top of a packed-tower through spray nozzles and allowed to slowly flow down through the column or tower. The packing media acts to retard the water flow and increase the effective surface area of the system. Air is introduced countercurrent to the direction of water flow. The saturated air containing the volatiles is emitted from the top of the column or routed to a control device.

Figure 4-1 shows a typical air stripping tower. The treatment system may also contain wells, separators, and vessels for treating inorganic contaminants (10,12).

IDENTIFICATION OF AIR EMISSION POINTS AND TYPICAL POLLUTANTS

The primary source of emissions from air stripping is the stripper exhaust, and VOCs are the major pollutants of concern. Depending on the concentration and nature of the VOCs present in the exhaust, some type of treatment such as carbon adsorption or catalytic oxidation may be required. For systems without control devices, the exhaust is vented through a short stack, typically a (3-6 ft) pipe, at the top of the column. For systems with control devices, the airflow from the column is usually vented down to the control device at ground level. A short stack (15-20 ft) is then used after the control device (10,12).

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To Atmosphere

Mist Eliminator ➔

Distribution Tray ➔

Packed
Column

Air

Blower

Pump

Well

Pump
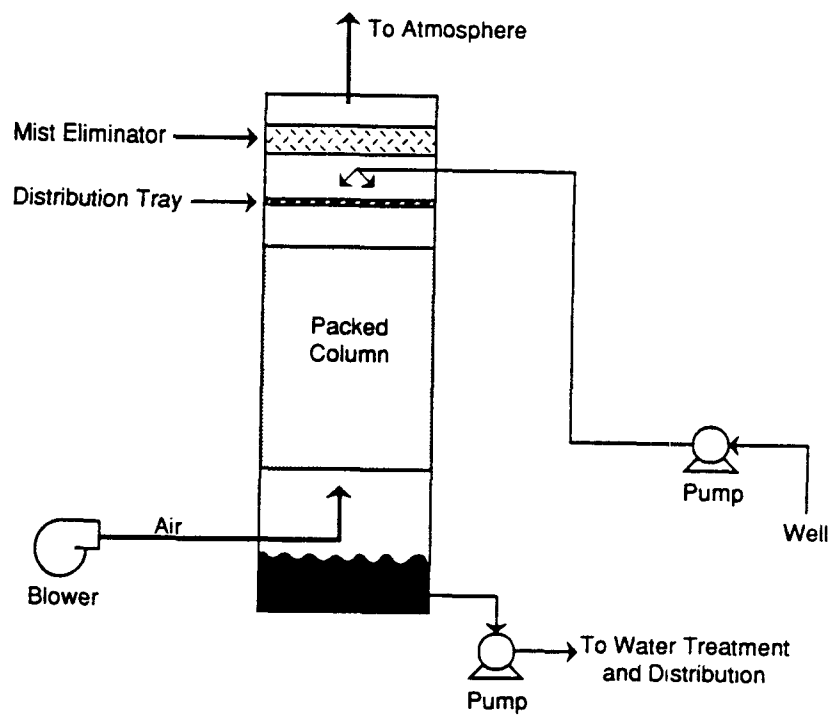
To Water Treatment
and Distribution

Figure 4-1. Process Flow Diagram for Air Stripper System.

The key design parameters effecting emissions from an air stripping unit include:

- Groundwater VOC concentration;
- Volatility (Henry's Law Constant) of the VOCs;
- Groundwater temperature;
- Air temperature;
- Air water contact time;
- Air/water contact ratio; and
- Use and efficiency of control device.

In addition to the exhaust stack, other emission sources may exist. Any place upstream of the air stripping tower where water is in direct contact with the atmosphere, such as separators, holding tanks, treatment tanks, or conduits, is an emission source. Fugitive losses from pumps, valves, and flanges are usually not significant due to the dilute nature of the water contamination.

SUMMARY OF AIR EMISSIONS DATA AND CORRELATIONS

The most accurate and precise way to estimate air emissions from an existing air stripper is to measure the air flowrate and exit gas contaminant concentrations under typical operating conditions. The most accurate and precise way to estimate air emissions from a planned air stripper is to use an air stripper design manual or software program that includes an air emissions prediction option (12). In many cases, however, actual measurements or detailed design simulations are not feasible. Therefore, an alternative approach is given below to allow estimation of emissions using a minimal number of input parameters.

As noted above, the important parameters affecting the emission rate for a given compound from an air stripping unit include: the concentration of the contaminant in the influent to the stripper, the influent flowrate, the stripping efficiency of the tower,

and the effectiveness of any control technologies that are in place. The stripping efficiency will depend on a number of factors including: the compound's Henry's Law constant, the type of packing material in the tower, and the gas to liquid contact ratio within the tower. Emissions for specific compounds from systems without any emission control devices can be estimated as follows:

$$ER_i = (C_i)(L_R)(SE_i/100)(0.06)$$

where ER_i =   emission rate for contaminant i (g/hr);
              C_i =   concentration of species i in influent water (mg/L or ppm);
              L_R =   influent liquid flowrate (L/min);
              SE_i =   stripping efficiency (%); and
              0.06   =   a constant (g-min/mg-hr).

For a well-designed unit, a stripping efficiency of 100% for volatile organic compounds is a reasonable, conservative assumption. Alternatively, the stripping efficiency of each contaminant can be determined from the ratio of gas to liquid (G/L ratio) in the tower and the log of the Henry's Law constant as shown in Figures 4-2 and 4-3 for low and high efficiency ranges (see Reference 3 for data for selected organic compounds). A conservative G/L ratio is 50 m^3 air/m^3 of water treated (12).

The use of a control device can reduce emissions by one to two orders of magnitude (i.e. 90-99% control). This can easily be incorporated into the equation for estimating emissions:

$$ER_i = (C_i)(L_R)(SE_i/100)(1-\%CE_i/100)(0.06)$$

where: ER_i =   emission rate for contaminant i (g/hr);
              C_i =   concentration of species i in influent water (mg/L or ppm);
              L_R =   influent liquid flowrate (L/min);
              SE_i =   stripping efficiency (%);
              $\%CE_i$ =   control efficiency of stripper exhaust treatment (%); and
              0.06   =   a constant (g-min/mg-hr).
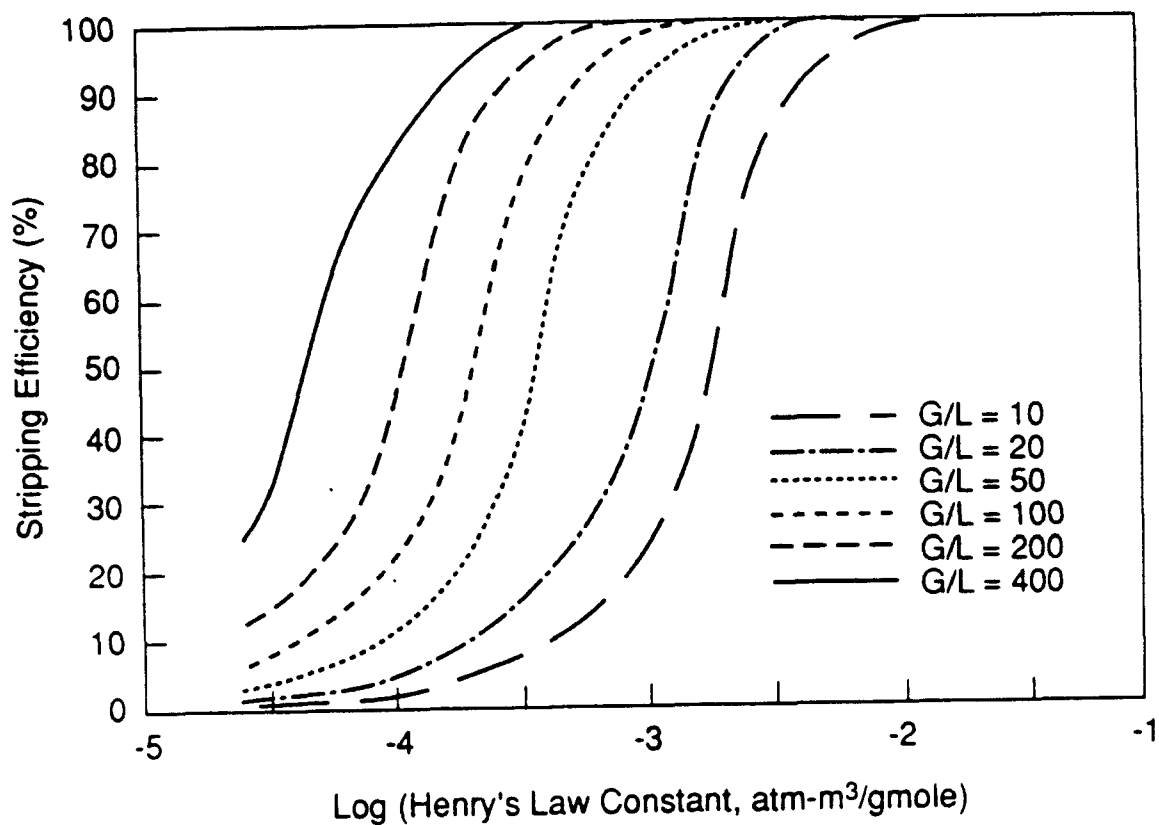
Figure 4-2. Stripper efficiency vs. Henry's Law constant, parameter = G/L (vol./vol.) low efficiency range.

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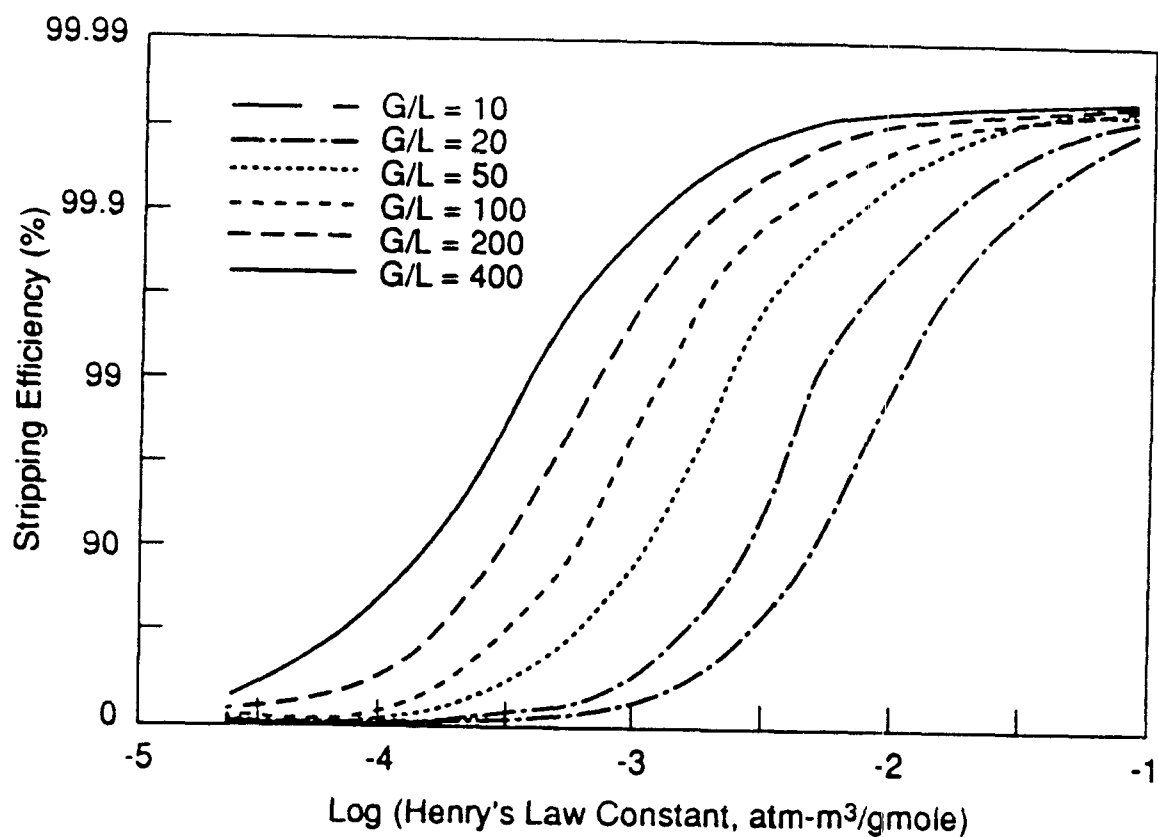
Figure 4-3. Stripper efficiency vs. Henry's Law constant, parameter = G/L (vol./vol.) high efficiency range.

EMISSION FACTORS

The correlations described in the preceding sections were used to generate a VOC emission factor for air stripping. Assuming a stripping efficiency of 100% and a control device efficiency of 90%, VOC emissions are 0.1 g VOC emitted/g VOC in the influent water. With a stripping efficiency of 100%, uncontrolled emissions are simply equal to the mass of VOC in the influent water.

Alternatively, the VOC emission factor can be converted to a g/hr basis for different air stripper designs. Table 4-1 shows three unit sizes typical for Superfund cleanup. Assuming a VOC influent concentration of 100 ppm (100 mg/L), uncontrolled emission factors are 57, 284, and 570 g/hr for the small, medium, and large units, respectively. Based on a 90% control efficiency, controlled emission factors are 5.7, 28.4, and 57.0 g/hr.

TABLE 4-1. ESTIMATED EMISSIONS FOR DIFFERENT SIZE SUPERFUND
SITE AIR STRIPPERS

Parameter	Units	Typical Superfund Unit Size		
		Small	Medium	Large
Total Influent Liquid Flowrate	L/min	570	2,840	5,700
Exhaust Gas Flowrate	m^3/min	29	140	285
Air/Liquid Ratio	--	50	50	50
Stripping Efficiency	%	99+	99+	99+
Uncontrolled Emissions[a]	g/hr	3,420	17,040	34,200
Controlled Emissions[b]	g/hr	342	1,704	3,420

[a]Based on influent pollutant concentration of 100 mg/L.
[b]Based on influent pollutant concentraiton of 100 mg/L and a control efficiency of 90%.

SECTION 5
SOIL VAPOR EXTRACTION TECHNOLOGIES

PROCESS DESCRIPTION

One technology used for for the treatment of contaminated soil at National Priority List (Superfund) sites is soil vapor extraction (SVE). By nature, SVE is employed on-site and is often used in conjunction with other remedial measures such as the removal (pumping) of any liquid hydrocarbon layer that is present and air stripping of contaminated ground water. In general terms, soil vapor extraction removes volatile organic constituents from contaminated soil by creating sufficient subsurface air flow to strip contaminants from the vadose (unsaturated) zone by volatilization. Complete removal may not be possible unless the source of vapors (e.g. hydrocarbon lens on groundwater) is also removed. As the contaminant vapors are removed, they may be vented directly to the atmosphere or treated in a number of ways:

1) activated carbon adsorption;
2) catalytic oxidation; or
3) thermal incineration.

The first two treatment options are the most commonly used at Superfund sites.

The criteria for determining the usefulness of soil vapor extraction for a particular site are numerous (13-20). The contaminants generally must have vapor pressures greater than 1.0 mm Hg at 20°F to ensure effective removal. This technique may be used in a variety of soil types but clearly soil porosity, grain size, moisture content and stratification must be taken into consideration when planning this type of remediation. This method is generally less costly than treatment involving excavation and can usually be implemented without disrupting any concurrent normal business operations at the site. If a large amount of contaminants is present in the ground water, the contaminated

water should usually be treated first to remove this source of vapors, followed by soil vapor extraction to remediate the vadose zone.

A few potential problems may arise in implementation of soil vapor extraction, but effective solutions to most problems exist. When there is some concern that contaminant vapors from a nearby site may be drawn in by the vacuum, air inlet wells may be placed around the perimeter of the Superfund site to limit remediation to the site under treatment. To avoid channelized flow, butterfly valves may be placed on the extraction wells so that they may be shut down if necessary. If contaminated water is extracted in the process, a liquid phase treatment system is usually installed.

As the vapors are removed from the soil they are either discharged to the atmosphere or treated to reduce air emissions. If the hydrocarbon content is high enough, direct combustion is possible. However, because concentrations typically drop significantly during removal, natural gas or some other fuel may be needed to maintain combustion. In some cases, the wells may be shut down for a period of time to allow subsurface vapor pressures to re-equilibrate, thus yielding concentrations sufficient to sustain a flame. For lower levels of hydrocarbons, catalytic oxidation may be effective. Carbon adsorption systems are often used but they may be costly to implement and are generally not acceptable for high-humidity gas streams.

Evidence of unusually high carbon dioxide levels indicates that some sites may experience enhanced subsurface biodegradation that may be partially or wholly a result of soil vapor extraction (21). Subsurface air flow may promote growth of aerobic hydrocarbon degraders which feed on the organic contaminants by improving the level of available oxygen for the microbes. At one site, carbon dioxide concetrations in the soil gas were 8.5%; much higher than the 0.03% or 0.04% typically present in the atmosphere. Rough calculations indicated that up to 40% of the gasoline was destroyed by degradation. Other sources of organic material such as co-disposed municipal waste

were not considered and may have been partially responsible for the high carbon dioxide levels.

Figure 5-1 shows a generalized process flow diagram for the soil vapor extraction process. Typical systems include extraction wells, monitoring wells, air inlet wells, vacuum pumps, vapor treatment devices, vapor/liquid separators and liquid phase treatment devices.

IDENTIFICATION OF AIR EMISSION POINTS AND TYPICAL POLLUTANTS

The air emissions associated with soil vapor extraction systems come primarily from the stack and from the treatment of the contaminated water extracted. Stack heights are typically 12-30 feet and usually only one stack is used. Additional releases of volatile organics occur while sampling and installing the wells. Fugitive emissions are considered negligible due to the negative pressure throughout most of the system. Besides the stacks, the only area of positive pressure includes the liquid phase pump and liquid treatment system. Because the stream is in the liquid phase, minimal fugitive emissions are likely.

Emissions include untreated volatile organics from the extraction process as well as any products that may be associated with the vapor and liquid treatment systems. Vapor treatment systems are usually catalytic oxidation or activated carbon adsorption canisters. Liquid treatment systems are usually liquid phase carbon or air stripping. Due to the variety of technologies used, stack emissions may include products of incomplete combustion, nitrogen oxides, particulate matter, carbon monoxide, acid gases and any other possible products of these technologies. Of primary concern, however, are the volatile organics emitted from the point sources.
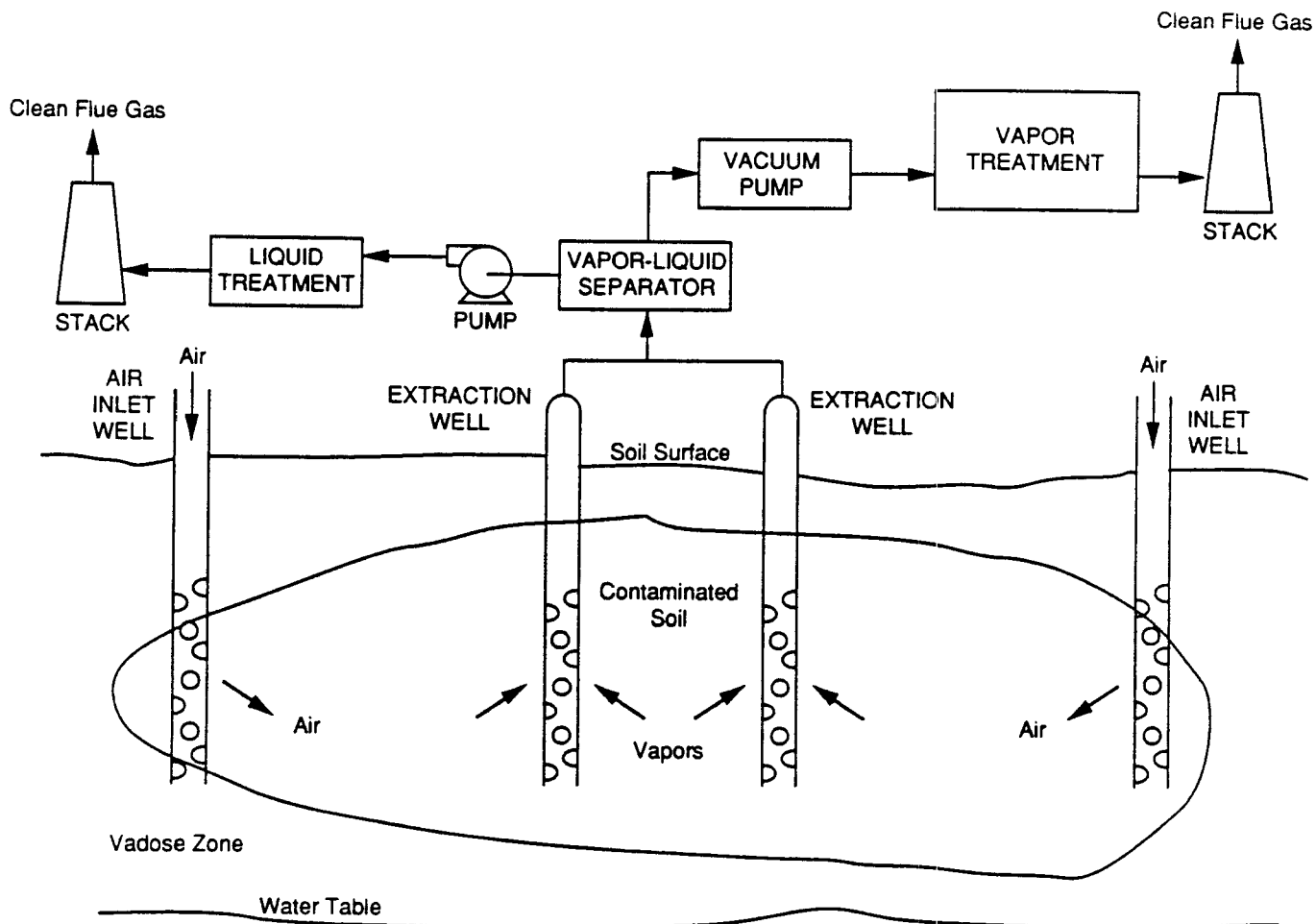
Figure 5-1. Generalized Process Flow Diagram for Soil Vapor Extraction.

SUMMARY OF AIR EMISSIONS DATA AND CORRELATIONS

Air emissions data for several SVE systems are summarized in Table 5-1. The data are from a variety of soil vapor extraction systems. Overall there is little detailed published information about SVE systems, making it difficult to assess the representativeness of this sample.

No practical theoretical models for predicting emissions or recovery rates for SVE systems exist at this time. Because of the complex nature of subsurface gas flow, pilot-scale demonstrations at every site are typically performed to evaluate the applicability and effectiveness of SVE as a treatment option. Some general equations can be developed from a mass balance approach to provide a simple method to estimate emissions from soil vapor extraction.

Air emissions can be estimated with the following equation for soil vapor extraction systems:

$$E_i = R_{l,i}(1 - (\%CE_{l,i}/100)) + R_{v,i}(1 - (\%CE_{v,i}/100))$$

where:

E_i = emission factor for soil contaminant "i" (g/hr);
$R_{l,i}$ = removal rate of contaminant "i" in liquid phase (g/hr);
$\%CE_{l,i}$ = % control efficiency of liquid treatment device;
$R_{v,i}$ = removal rate of contaminant "i" in vapor phase (g/hr); and
$\%CE_{v,i}$ = % control efficiency of vapor treatment device.

Removal rates can be 500-600 kg/day or higher and control efficiencies (when applicable) range from 60-99%. In one 1989 SVE assessment, only about half of the sites listed used any VOC control equipment. (15)

TABLE 5-1. SUMMARY OF EMISSIONS DATA FOR SVE SYSTEMS

Source	No. of Systems Surveyed	Parameter	Units	Range or Value	Approximate Average
Crow (1987)[a]	13	Flowrate per well	cfm	5.3 - 300	80
		Removal	lb/day	2 - 250	60
		Exhaust Gas Concentration	ppmv	20 - 350	100
Hutzler (1989)[b]	19	Total Flowrate	cfm	3 - 5,700	800
		Treatment:	# systems		
		- None		9	
		- Carbon		6	
		- Catalytic Incineration		1	
		- Combustion		1	
		Removal Rate	lb/day	4 - 430	100
PES (1989)[c]	17	Total Flowrate	cfm	25 - 11,300	2,200
		Pollutant Concentration	ppmv	150 - 38,000	4,000
		Control Efficiency	%	90 - 99	95

[a] Guidelines for Design, Installation, Operation, and Evaluation of Subsurface Ventilation Systems. Draft Report preapred by Radian Corporation for the American Petroleum Institute (API). July 23, 1987.

[b] Hutzler, N.J., B.E. Murphy, and J.S. Gierke. Review of Soil Vapor Extraction System Technology. In Proceedings of HazMat West 1989 Conference, Long Beach, CA, November 7-9, 1989. pp512-536.

[c] PES, Inc. Soil Vapor Extraction VOC Control Technology Assessment. EPA-450/4-89-017. U.S. EPA, Research Triangle Park, NC, September 1989.

EMISSION FACTORS

The correlations described above are useful for determining a VOC emission factor for soil vapor extraction. If 95% effective carbon adsorption systems were used to treat both vapor and liquid phases then VOC emissions would be 0.05 g VOC emitted/g VOC in contaminated soil. A default value for uncontrolled emissions from SVE systems can be assumed to be 250 kg/day of total VOCs. Based on 10-hours of operation on average per day ("pulsed" operation), uncontrolled emissions are 25,000 g/hr. Controlled emissions, assuming a control device efficiency of 95%, are 1,250 g/hr.

CASE STUDY: TERRA VAC IN SITU VACUUM EXTRACTION SYSTEM, GROVELAND, MASS.

Process Description

Terra Vac Incorporated has developed a vacuum extraction system designed to remove volatile organic contaminants from the vadose zone. At the Groveland, Massachusetts Superfund site, the contaminated air stream was treated with two sets of activated carbon canisters (17-19). Due to weather conditions, liquid water was extracted as well, so a vapor-liquid separator was included to remove contaminated water to a holding tank. The process design is shown in Figure 5-2.

Characterization of Air Emissions

Because no biodegradation was taking place in this case, the compounds released to the atmosphere were the same as those found in the soil. By far the most predominant contaminant removed was trichloroethylene, although 1,1,1-trichloroethane, trans-1,2-dichloroethylene, and tetrachloroethylene were also extracted.
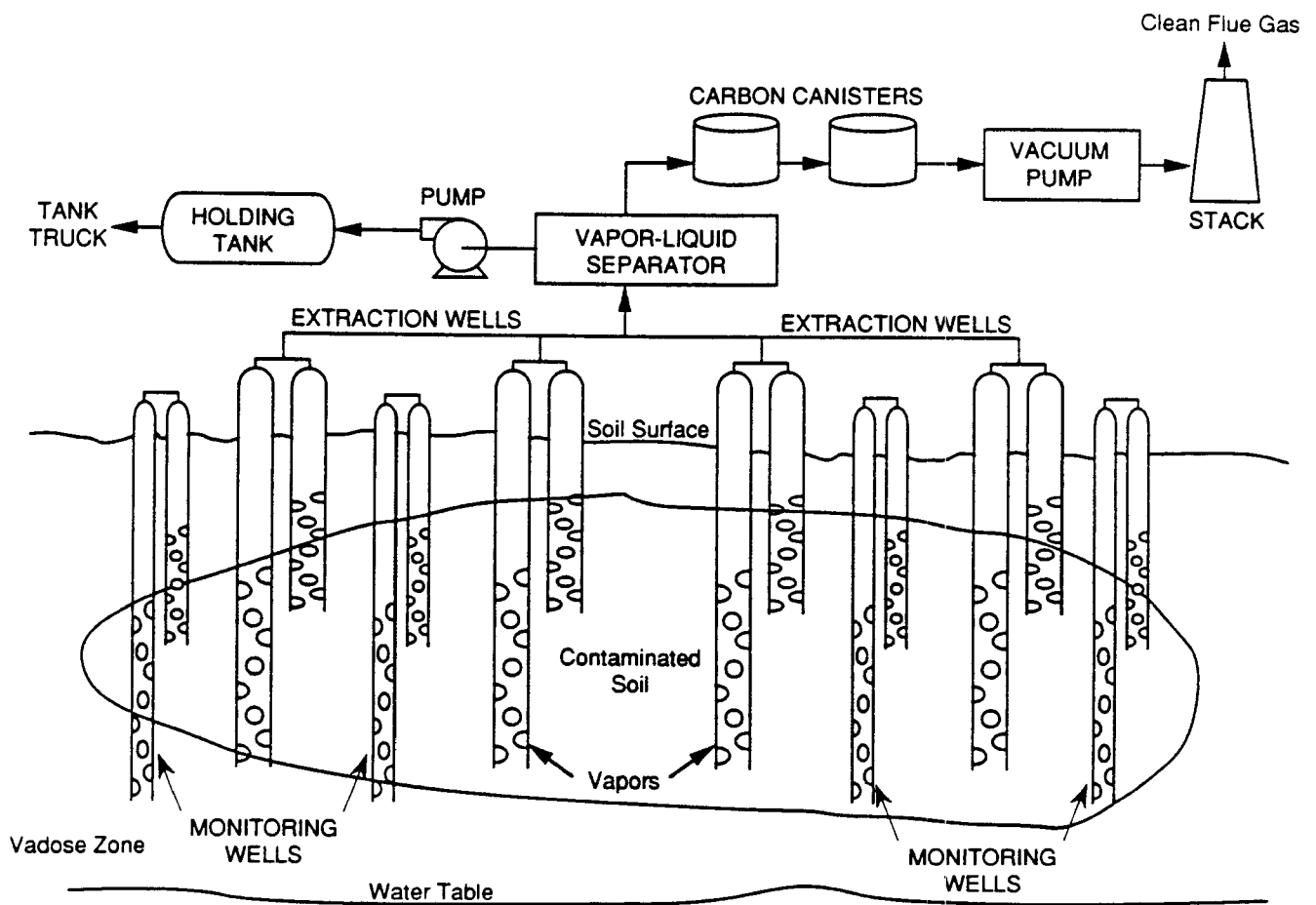
Figure 5-2. Process Flow Diagram for Terra Vac In Situ Vacuum Extraction System.

Emission Factors

Table 5-2 shows emissions factors for each of the four contaminants. The estimated total VOC peak emission factor is 9.57 g/hr. This includes 6.3 g/hr of stack emissions and 3.3 g/hr of evaporative emissions since the contaminated water was not treated on-site. Appendix A describes the mass transfer model used to estimate evaporative emissions.

TABLE 5-2. TERRA-VAC IN SITU VACUUM EXTRACTION SYSTEM ESTIMATED EMISSIONS

Pollutant	Molecular Weight g/mol	Peak Uncontrolled Stack Emissions g/hr[a]	Peak Controlled Stack Emissions g/hr[b]	Evaporative Emissions g/hr[c]	Total Emissions g/hr[d]
TCE	131.29	5,210.0	5.91	3.29	9.20
DCE	96.94	274.0	0.31	0.0	0.31
TRI	133.41	36.0	0.04	0.0	0.04
PCE	165.83	18.0	0.02	0.0	0.02
Totals		5,538.0	6.29	3.29	9.57

[a] Uncontrolled emissions equal removal rate of each contaminant.

[b] Based on a 99.75% overall control efficiency for two carbon adsorption canisters in series.

[c] Evaporative emissions from contaminated water storage.

[d] Total stack and evaporative emissions.

KEY:

    TCE - trichloroethylene
    DCE - trans-1,2-dichloroethylene
    TRI - 1,1,1-trichloroethane
    PCE - tetrachloroethylene

SECTION 6
STABILIZATION AND SOLIDIFICATION TECHNOLOGIES

PROCESS DESCRIPTION

Stabilization and solidification technologies are gaining increased use as Superfund site remediation methods. The goal of these processes is to immobilize the toxic and hazardous constituents in the waste, usually contaminated soil or sludge. This can be accomplished by several means:

1)   Changing the constituents into an immobile (insoluble) form;

2)   Binding them in an immobile, insoluble matrix; or

3)   Binding them in a matrix which minimizes the material surface exposed to solvents (groundwater) which could leach the hazardous constituents.

Several types of stabilization and solidification technologies exist as alternatives for remedial action. A few of these processes involve in-situ treatment, however, most generally require excavation and other soil handling activities. Nearly all the commercially available stabilization and solidification technologies are proprietary.

The basic steps in most solidification and stabilization processes are the same. Figure 6-1 shows a typical process. Solidification and stabilization processes are usually batch operations, but may be continuous. Wastes are first loaded into the mix bin (wastes are sometimes dried before addition to the bin), and other materials for the solidification or stabilization are added. The contents of the bin are then thoroughly mixed. After a sufficient residence time, the treated waste is removed from the bin (22-24). The material is usually formed into blocks and allowed to cure for up to several

Excavation of Contaminated
Soil or Sludge

Addition of Binding
or Stabilizing Agent

(Typical materials used
include Fly Ash, Portland
Cement, Cement Kiln Dust,
and Lime Kiln Dust)

MIXER

Treated Soil or Sludge

Waste Returned to Ground
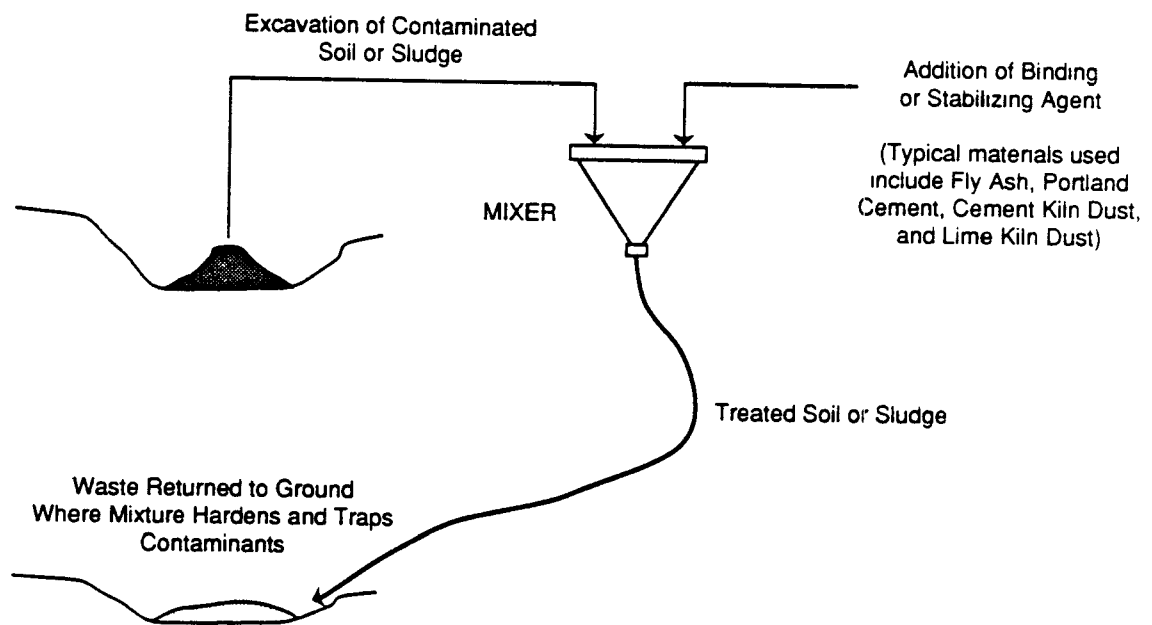Where Mixture Hardens and Traps
Contaminants

Figure 6-1. Process Flow Diagram for Stabilization and Solidification Technologies.

days. The blocks can then be placed in lined excavations on-site. It should be noted that this description does not apply to in-situ treatment methods, which use a variety of techniques (from applied high voltage to injection of stabilizing agents) to immobilize the contaminated waste in-place without excavation or soils handling (25,26).

Typical raw materials used in stabilization processes include fly ash, portland cement, cement kiln dust, lime kiln dust, or hydrated lime. Other additives that may be used to solidify or encapsulate wastes include asphalt, paraffin, polyethylene, or polypropylene.

IDENTIFICATION OF AIR EMISSION POINTS AND TYPICAL POLLUTANTS

The primary source of air emissions from stabilization and solidification processes is volatilization of organic contaminants in the waste. Volatilization can occur during waste handling activities such as soil excavation and transport or during the process of mixing the binding agents with the waste. Also, some evaporative emissions will occur from waste even after stabilization, especially during the curing period immediately after the blocks are formed. Lab studies, though, have shown that the largest fraction of volatile loss occurs during the mixing phase because heat may be required to assist mixing or generated by exothermic stabilization reactions (27).

In general, VOC emissions form stabilization and solidification processes will depend on the type and concentration of the VOCs in the waste, the duration and thoroughness of the mixing, the amount of heat generated in the process, and the average batch size processed. The longer or more energetic the mixing and processing, the greater likelihood that organic compounds will volatilize. The volatile losses will also increase as the temperature of the waste/binder mixture increases. Binding agents with high lime contents generally cause highly exothermic reactions. The batch size influences volatilization by affecting the mean distance a volatilized molecule has to travel to reach

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the air/solid interface at the surface of the stabilized waste. The larger the block of material, the lower the rate of volatilization.

In addition to volatile emissions, stabilization and solidification processes will generate fugitive dust emissions. Possible sources of fugitive dust emissions include storage of raw materials, preparation of the binding agents, transfer of wastes into the mixing bin, removal of the treated material from the mixing bin, and replacement of the material at the site after processing.

SUMMARY OF AIR EMISSIONS DATA AND CORRELATIONS

Little information exists about the fate of volatile contaminants in wastes treated by stabilization and solidification methods. A literature search found no available field data on air emissions at Superfund sites using this type of remediation technology. Laboratory studies, however, have estimated that 40-80% of the volatile contaminants in the treated waste eventually evaporate (27). Experiments also show that most of the loss occurs within 60 minutes of mixing the waste with binding agents.

Based on the laboratory tests, the simple expression given below can be used to estimate VOC emissions from stabilization and solidification processes:

$$ER_i = (C_i)(M)(\%V_i/100)$$

where: ER_i = emission rate for contaminant i (g/hr);
C_i = concentration of species i in contaminated soil (g contaminant/kg soil);
M = mass rate of soil treated (kg/hr); and
$\%V_i$ = percentage of contaminant i volatilized.

Particulate matter emissions for stabilization and solidification processes can be estimated using emission factors for soil handling. Typical ranges of emissions for handling of contaminated soil are shown in Table 6-1.

EMISSION FACTORS

The correlation given in the preceding section was used to generate a VOC emission factor for stabilization and solidification processes. Assuming 60% of the volatile contaminants evaporate, VOC emissions are 0.6 g VOC emitted/g VOC in the contaminated soil.

Alternatively, the VOC emission factor can be converted to a g/hr basis for a typical stabilization process. Assuming the stabilization equipment can treat 91,000 kg of soil per hour (100 tons/hr) and that the waste contains 0.1 g VOC/kg soil (100 ppm), the estimated emission factor is 5,460 g/hr.

TABLE 6-1. TYPICAL RANGES OF EMISSIONS FROM SOIL HANDLING ACTIVITIES

Activity	PM Emissions Factor[a,b]
Excavation	0.002-0.086 kg/metric ton
	0.015-0.220 kg/metric ton
Transport:	
Unpaved Roads	1.3 kg/VKT
Dry Industrial Paved Roads	0.022-0.15 kg/VKT
Heavily-loaded Roads	0.093-0.12 kg/VKT
Dumping	0.005-0.05 kg/metric ton
	0.015-0.03 kg/metric ton
	0.025-0.16 kg/metric ton

[a] Units are kilograms per metric ton of soil moved or kilograms of emissions per vehicle kilometer traveled (VKT).

[b] From Reference 1.

SECTION 7
CHEMICAL AND PHYSICAL TREATMENT TECHNOLOGIES

PROCESS DESCRIPTIONS

A broad range of technologies fall under the heading of physical and chemical waste treatment methods. Included in this category are emerging technologies such as ozone treatment of polluted groundwater, in-situ steam stripping of contaminated disposal sites, and solvent extraction of contaminated soil.

In general terms, a chemical treatment method is one in which a reactive compound (or compounds) is added to the contaminated groundwater or soil to react with pollutants and form less harmful products. As the name implies, the effectiveness of this type of treatment depends greatly on the chemical properties of the pollutants. An example of this type of method is ozone treatment of contaminated groundwater. In this process, contaminated groundwater or wastewater is mixed in a continuous reactor with ozone and other oxidizing agents. The oxidizers react with the organic contaminants to form CO_2 and water.

Physical treatment involves the addition of energy or another treatment agent to physically transfer the pollutants to another state in which they are easier to dispose of or treat. The path of physical transfer can be adsorption, absorption, dissolution, or a change of state such as evaporation. An example of this method is solvent extraction of contaminated soil. In this process a solvent is mixed with soil contaminated by organic pollutants to cause the organics to dissolve in the solvent phase. The solvent can then be recovered and reused, while the contaminant can be biologically treated, incinerated, or disposed of in another manner.

IDENTIFICATION OF AIR EMISSION POINTS

The air emissions associated with chemical and physical waste treatment techniques that may be used at Superfund sites have not been adequately characterized for most methods. A broad spectrum of technologies are included in this category, and the types and sources of air emissions may vary greatly. For most chemical and physical treatment methods, however, the emissions of primary concern are VOCs; with emissions of semi-volatile organic compounds and particulate matter also of potential concern. Emissions are usually from either ground level area sources or low-level point sources. Point sources are typically associated with the treatment method, while area sources are usually associated with the handling of contaminated soil or water.

In general, there are two types of process air emission sources that can be associated with chemical and physical treatment. First, transfer of the contaminants from the liquid- or solid-phase to the air may be an inherent consequence of the treatment method. For example, in-situ steam stripping volatilizes a significant fraction of the soil contaminants. In some cases, these air emissions are controlled by add-on control devices such as carbon adsorption units. Second, fugitive emissions can be generated as a by-product of the treatment method. For instance, in ozone treatment of contaminated water, trace emissions of unreacted organic contaminants and ozone may occur.

Additional fugitive emissions from physical and chemical treatment methods can result from leaking valves, pumps, and flanges in the unit, as well as from transfer or handling of the untreated contaminated material.

SUMMARY OF AIR EMISSION DATA AND CORRELATIONS

The wide variety of physical and chemical treatment methods and the lack of published information makes it difficult to summarize air emissions data or develop air emissions factors. Some general equations, though, can be developed from a mass

balance approach to provide a simple method to estimate emissions from these technologies.

Emissions of original groundwater or soil contaminants that are transferred to the air can be estimated by the following equation for physical and chemical treatment methods:

$$E_i = C_i(V)(R_{eff}/100)(T_{frac}/100)(1-\%CE_i/100)$$

where:
E_i = Air emissions of soil or water contaminant$_i$ (g/hr);
c_i = Concentration of contaminant$_i$ in soil or water (g/m^3);
V = Volume flowrate of soil or water being treated (m^3/hr);
R_{eff} = Overall removal efficiency of treatment technology (%);
T_{frac} = Fraction of removed contaminant transferred to air (%); and
$\%CE_i$ = Control efficiency of any add-on air emission control device (%).

Air emissions of byproducts from the treatment method can be estimated from a similar relationship:

$$E_i = C_i(V)(1-R_{eff}/100)$$

where:
E_i = Air emissions of soil or water contaminant$_i$ (g/hr);
c_i = Concentration of contaminant$_i$ in soil or water (g/m^3);
V = Volume flowrate of soil or water being treated (m^3/hr); and
R_{eff} = Overall removal efficiency of treatment technology (%).

Air emissions from other fugitive sources can be estimated from predictive models and published emission factors, or can be measured directly (2,3,28).

CASE STUDY FOR SUPERFUND CHEMICAL WASTE TREATMENT: ULTROX INTERNATIONAL ULTRAVIOLET RADIATION/OXIDATION TECHNOLOGY

Process Description

Ultrox International has developed a technology that uses three oxidants: ozone, hydrogen peroxide, and UV radiation to destroy organic contaminants in water with low suspended solids levels. This technology is currently being tested at facilities across the country on groundwater contaminated with trichloroethylene, tetrachloroethylene, vinyl chloride, pentachlorophenol, phenol, and various other organics (28).

The Ultrox process can be described as a catalytic ozonation process where the oxidation of contaminants occurs either by direct reaction of the oxidants added or by reaction of the hydroxy radicals with the contaminants. Factors that affect the effectiveness of the Ultrox process include the type of waste treated, the hydraulic retention time, ozone dose, hydrogen peroxide dose, UV radiation intensity, and influent pH. Removal can also be dramatically affected by the presence of other species in the system which consume oxidants. These species include anions such as carbonates, bicarbonates, sulfides, nitrites, bromides, and cyanides, as well as trivalent metals. The process is enhanced by the presence of iron which catalyzes the hydrogen peroxide reactions. Also, the UV radiation is more effective for clear solutions.

From an equipment perspective, the Ultrox process is simple. It consists primarily of a reactor, ozone generator, and a catalytic ozone decomposer which decomposes any unreacted ozone back to oxygen. Figure 7-1 shows a typical equipment set-up, and Figure 7-2 provides a more detailed flow schematic.
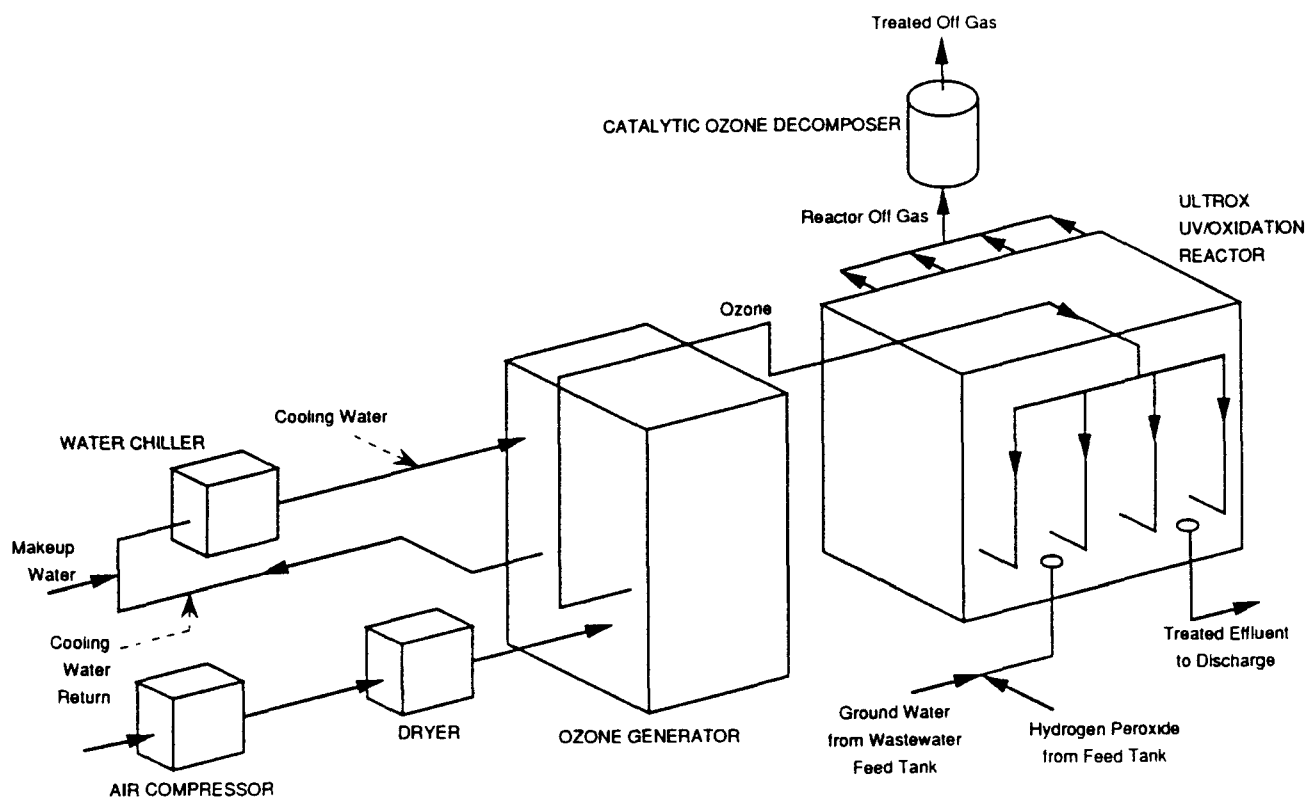
Figure 7-1. Typical Equipment Set-Up for Ultrox International Ultraviolet Radiation/Oxidation Technology.
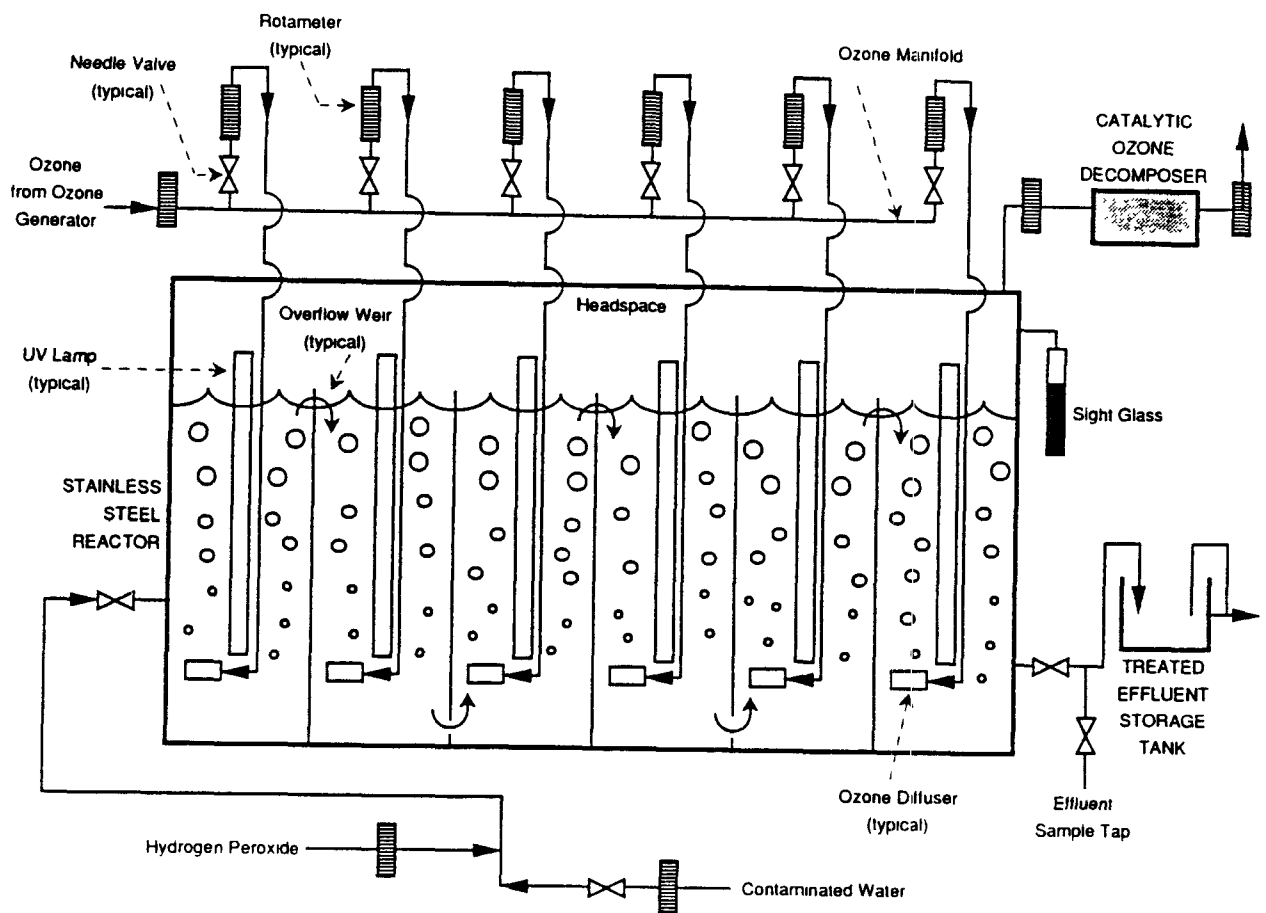
Figure 7-2. Detailed Flow Schematic of Ultrox International Ultraviolet Radiation/ Oxidation Technology.

Characterization of Air Emissions

Two types of process emissions are associated with the Ultrox process. First, there may be some unreacted ozone emitted through the decomposer. However, because of the high reactivity of ozone, these emissions are usually small. Concentrations below 0.1 ppmv in the off-gas were measured in field testing. When the decomposer failed, though, concentrations exceeding 10 ppmv were observed (28).

The largest emissions from the Ultrox process occur as a result of the ozone bubbling through the contaminated water and stripping VOC. The contribution of stripping to the total removal is a function of how difficult the compound is to oxidize. In field testing, stripping accounted for a significant fraction of the total removal of trichloroethane and dichloroethane. Conversely, the extent of stripping was low for vinyl chloride and tetrachloroethylene because these compounds contain double bonds between the carbon atoms and are easier to oxidize.

For the Ultrox process, the equation given before can be used to estimate the quantity of VOC emissions:

$$E_i = C_i(V)(R_{eff}/100)(T_{frac}/100)$$

Based on field testing, appropriate default values for highly oxidizable compounds, ones with carbon-carbon double bonds, are in the range R_{eff} is 90-95% and T_{frac} equals 1-10%. For less oxidizable compounds R_{eff} is in the range of 50-80% and T_{frac} varies from 10-90%.

Table 7-1 summarizes the removal efficiencies measured for different pollutants during field testing of the Ultrox process, as well as the estimated contribution of stripping to the overall removal. Tables 7-2 through 7-4 show estimated air emissions for the Ultrox process, generated using field data.

TABLE 7-1. SUMMARY OF MEASURED REMOVAL EFFICIENCIES AND STRIPPING CONTRIBUTION

Contaminant	Measured % Removal	Measured % Stripped
Trichloroethylene	76-99	2-26
1,1-Dichloroethane	30-69	4-37
1,1,1-Trichloroethane	37-85	12-99
Vinyl Chloride	N/A	0-13

TABLE 7-2. ESTIMATED AIR EMISSIONS ULTROX FIELD TESTING: TRICHLOROETHYLENE REMOVAL

Contaminant	Run	Average Influent Conc. (mg/m^3)	Ratio of Air to Water Flowrates	Measured % Removal	Measured % Stripped	Estimated Air Emissions (mg/hr)[a]	% Air Emissions (g/g-feed)
Trichloroethylene	1	86	2.1	95.0	2.0	37.1	1.9
	2	55	2.3	96.0	3.4	40.8	3.3
	3	64	2.1	94.0	2.7	36.9	2.5
	4	56	2.0	94.0	3.0	35.9	2.8
	5	50	2.1	88.0	3.5	35.0	3.1
	6	73	4.5	98.0	1.2	19.5	1.2
	7	70	1.0	76.0	1.2	14.5	0.9
	8	59	4.5	99.0	7.5	99.5	7.4
	9	65	4.5	98.0	6.6	95.5	6.5
	10	57	4.3	97.0	9.4	118.0	9.1
	11	57	4.6	98.0	24.0	304.5	23.5
	12	52	4.4	99.0	7.0	81.8	6.9
	13	49	4.3	99.0	26.0	286.5	25.7
AVERAGE		61	3.3	94.7	7.5	92.7	7.3

[a] Based on an estimated flowrate of 100 gpm contaminated water.

TABLE 7-3. ESTIMATED AIR EMISSIONS ULTROX FIELD TESTING: 1,1,-DICHLOROETHANE REMOVAL

Contaminant	Run	Average Influent Conc. (mg/m^3)	Ratio of Air to Water Flowrates	Measured % Removal	Measured % Stripped	Estimated Air Emissions (mg/hr)[a]	% Air Emissions (g/g feed)
1,1-Dichloroethane	1	11.5	2.1	46.0	7.4	8.9	3.4
	2	10	2.3	69.0	9.1	14.3	6.3
	3	10	2.1	35.0	9.9	7.9	3.5
	4	12	2.0	32.0	7.4	6.5	2.4
	5	10	2.1	36.0	17.0	13.9	6.1
	6	11	4.5	54.0	16.0	21.6	8.6
	7	13	1.0	30.0	4.9	4.3	1.5
	8	9.8	4.5	52.0	23.0	26.6	12.0
	9	11	4.5	54.0	16.0	21.6	8.6
	10	10	4.3	62.0	27.0	38.0	16.7
	11	11	4.6	50.0	44.0	55.0	22.0
	12	11	4.4	65.0	34.0	55.2	22.1
	13	10	4.3	60.0	37.0	50.4	22.2
AVERAGE		11	3.3	49.6	19.4	24.9	10.4

[a] Based on an estimated flowrate of 100 gpm contaminated water.

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TABLE 7-4. ESTIMATED AIR EMISSIONS ULTROX FIELD TESTING: 1,1,1-TRICHLOROETHANE REMOVAL

Contaminant	Run	Average Influent Conc. (mg/m^3)	Ratio of Air to Water Flowrates	Measured % Removal	Measured % Stripped	Estimated Air Emissions (mg/hr)[a]	% Air Emissions (g/g feed)
1,1,1-Trichloroethane	1	4.0	2.1	70.0	43.0	27.3	30.1
	2	3.7	2.3	83.0	34.0	23.7	28.2
	3	3.8	2.1	65.0	31.0	17.4	20.2
	4	3.9	2.0	53.0	29.0	13.6	15.4
	5	4.1	2.1	66.0	29.0	17.8	19.1
	6	3.9	4.5	73.0	65.0	42.0	47.5
	7	4.7	1.0	37.0	12.0	4.7	4.4
	8	3.5	4.5	80.0	85.0	54.1	68.0
	9	4.3	4.5	83.0	58.0	47.0	48.1
	10	3.4	4.3	82.0	73.0	46.2	59.9
	11	3.8	4.6	80.0	99.0	68.4	79.2
	12	3.3	4.4	87.0	76.0	49.6	66.1
	13	3.2	4.3	85.0	75.0	46.3	63.8
AVERAGE		4.0	3.3	72.6	54.5	35.2	42.3

[a] Based on an estimated flowrate of 100 gpm contaminated water.

Other air emissions from handling untreated waste must be estimated using other predictive models or emission factors (2,3,28).

Emission Factors

Based on the data presented above, an overall emission factor for the oxidative treatment of volatile compounds in contaminated water can be estimated as 0.2 g VOC emitted/g VOC present in influent water. This estimate is an average value based on field data for all three compounds studied.

Assuming an influent flowrate of 100 gpm and an initial contaminant concentration of 1.0 g/m^3, an overall emission can also be estimated as 4.5 g VOC emitted/hr of operation.

CASE STUDY FOR SUPERFUND PHYSICAL WASTE TREATMENT: CF SYSTEMS ORGANICS EXTRACTION SYSTEM

Process Description

The CF Systems Pit Cleanup Unit (PCU) uses a liquified propane/butane mixture to extract organic contaminants from soil or sludges (30). Figure 7-3 shows the process schematic. In the CF Systems process, the soil or sludge is diluted with water to make a pumpable slurry, and then fed to a first extractor where it is mixed with the liquified gas solvent. After the extractor, the mixture goes to a decanter where it is separated into two immiscible layers. The water and solids underflow then moves to the a second series of extractors, while the overflow is sent through a filter into the solvent recovery column. After the second decanter, the bottoms product passes to the treated sediment product tanks.
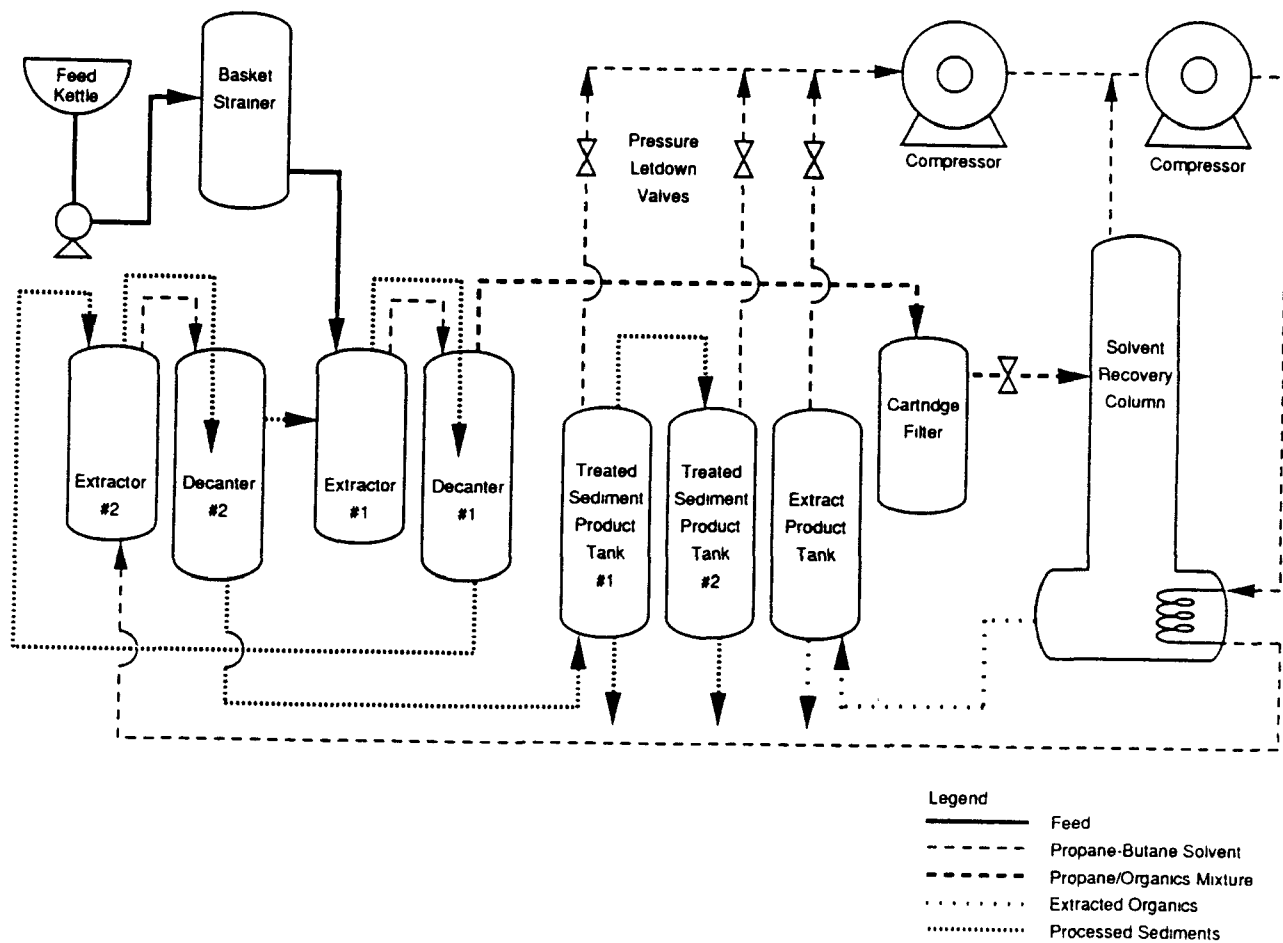
Figure 7-3. CF Systems Organics Extraction Process Schematic.

Factors that influence the effectiveness of the CF Systems process include: extractor pressure, extractor temperature, feed flowrate, solvent flowrate, feed-to-solvent ratio, and feed viscosity.

Characterization of Air Emissions

Two types of process emissions are associated the CF Systems PCU. First, fugitive emissions may occur from leaking valves, pumps, and flanges in the unit. Second, episodic or short term emissions may occur as a result of an overpressure of one of the vessels. To control these upsets, the unit is designed so that material is vented to a relief header which directs the stream to a blowdown tank where solids and liquids are removed. The gases from the blowdown tank then pass through an activated carbon filter to remove organic contaminants in the propane gas. The propane is then passed through a flame arrestor and vented to the atmosphere.

Emission Factors

The lack of published air emissions data makes it difficult to develop emission factors or correlations for the CF Systems PCU. However, fugitive losses from this unit may be estimated using published emission factors if an estimate of the number of components (pumps, valves, flanges) is available (28).

SECTION 8
BIOTREATMENT AND LAND TREATMENT TECHNOLOGIES

PROCESS DESCRIPTION

In biological treatment of hazardous waste, microorganisms are used to degrade or oxidize hazardous organic compounds in soil or water. When the growth of these microbes is enhanced both by the increased availability of oxygen and moisture, and the presence of hydrocarbons as feedstock, a significant amount of waste can be effectively oxidized. Treatment can be accomplished in-situ, such as in land treatment methods, or by pumping waste into a batch or continuous reactor.

Land treatment of a waste can be described as the application of waste onto land and/or incorporation into surface soil, sometimes with the addition of fertilizer or soil conditioner. The moisture content and waste loading are also controlled. Land treatment may include landfarming, land application, land cultivation, land irrigation, land spreading, soil farming, and soil incorporation. Wastes added to the soil environment are subject to decomposition, leaching, volatilization, and assimilation (31,32).

The main purpose of this in-situ treatment is to employ the microbiological activity of the upper layers of the soil to decompose organic waste constituents into carbon dioxide and water. Since the upper soil layer contains the largest microbial population, land treatment is generally confined to the soil plow-zone or zone of incorporation, i.e., the first six to eight inches of material. Waste oils and sludges are generally applied to soil by surface spreading or subsurface injection. Wastes can be effectively mixed into the zone of incorporation using a disk or rototiller (32).

The direct biotreatment of liquid or slurry waste differs greatly from land treatment (in-soil or in-situ) methods, and is a far more effective and common hazardous waste treatment method. In this approach, the liquid waste is pumped from the contaminated sump or pit into a bioreactor, where biological solids are mixed with waste. The types of reactors can vary greatly, from batch tanks to flow through impoundments. When high levels of biodegradation are desired the reactor is usually well aerated and the biological solids level maintained near 1%. Figure 8-1 shows a schematic of a flow-through system used for treating wastewater.

IDENTIFICATION OF AIR EMISSION POINTS AND TYPICAL POLLUTANTS

For land-farming operations, the primary air emissions are emissions from area sources such as the block of contaminated soil being treated. For surface impoundments, emissions also come from area sources. However, for batch bioreactors, the primary source of emissions is usually a process vent. In all cases, the emissions of concern are VOCs and PM when soil handling operations are required.

Air emissions from land treatment processes are influenced by waste characteristics such as biodegradability and volatility, as well as soil type, temperature, loading rate, mode of application, and tilling frequency. Other activities that are likely to occur in conjunction with land treatment processes that may generate air emissions included storage and handling operations.

For surface impoundments, the primary environmental factors, in addition to the biodegradability and volatility of the waste, which influence air emissions are temperature and wind speed. Emissions tend to increase with an increase in surface turbulence due to wind or mechanical agitation. Temperature effects emissions by promoting microbial growth. At temperatures outside the band for optimal microbial activity, volatilization will increase (33-36).

Air Emissions from Bioreactor
through Process Vent

BIOREACTOR   CLARIFIER

Contaminated   Treated
Water Influent   Water Effluent
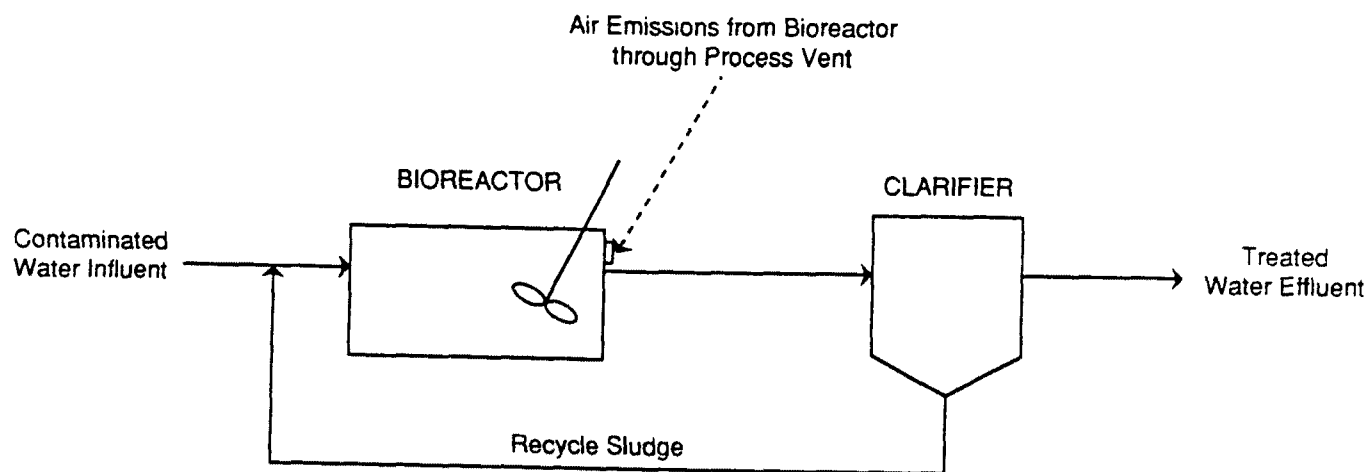
Recycle Sludge

Figure 8-1. Process Flow Diagram for Biotreatment.

Emissions from batch reactors are also in part determined by reactor design parameters such as the amount of air or oxygen used to aerate the waste. Higher gas flow will strip more volatiles out of solution and increase air emissions.

SUMMARY OF AIR EMISSIONS DATA AND CORRELATIONS

Estimating VOC emissions from biotreatment processes is a complicated task. Over the past fifteen years a wide array of models have been developed to estimate the relative contributions of biodegradation and volatilization to waste removal. Currently, several public-domain PC models, developed by the U.S. EPA, are available for estimating air emissions from a variety of biotreatment operations, principally surface impoundments. The two most commonly used models are ChemDat-7 and the Surface Impoundment Modeling System (SIMS).

Both ChemDat-7 and SIMS are based on mass transfer and biodegradation models developed by the U.S. EPA (36). The mass transfer model uses two-film resistance theory, along with the characteristics of the impoundment, to estimate overall mass transfer coefficients for each pollutant. The biodegradation model assumes Monod kinetics to estimate a biodegradation rate.

Both ChemDat-7 and SIMS have limitations and drawbacks. Both models perform all calculations for 25°C and rely on physical property and kinetic data that are not always readily available for the modeled compounds. Furthermore, SIMS is limited only to flow-through or disposal impoundments and is not applicable to estimating land-farming emissions.

Detailed models have not yet been developed for estimating emissions from batch bioreactors. These types of processes are, for the most part, developmental and difficult to generalize. As noted before, emissions from these system are usually through a process vent.

The simplest method for estimating emissions from all types of biotreatment processes is to use a mass balance approach. For continuous systems, such as flow-through impoundments treating contaminated water, the following correlation is applicable:

$$ER_i = (C_i/1,000)(V)(\%V_i/100)$$

where: ER_i = emission rate for contaminant i (g/hr);
              C_i = concentration of species i in contaminated water (mg/L);
              V = volume rate of water treated (L/hr); and
              V_i = percentage of contaminant i volatilized.

The percentage of each contaminant which is volatilized will vary greatly depending on the physical properties of the contaminant and the impoundment design and biological activity. Based on earlier research and modeling for benzene in a mechanically aerated impoundment (34), as much as 80% may be volatilized. In a quiescent impoundment, evaporative losses will likely be significantly lower since there is no stripping effect to increase volatilization. For benzene only 12% of the loading to a quiescent impoundment is estimated to be lost through volatilization (34).

For batch biotreatment systems, such as disposal impoundments, portable covered reactors, or landfarms, the relationship given below can be used to estimate air emissions:

$$ER_i = (C_i/100)(V)(\%V_i/100)/(t)$$

where: ER_i = emission rate for contaminant i (g/hr);
              C_i = concentration of species i in contaminated waste (mg/L);
              V = volume waste or wastewater treated (L);
              V_i = percentage of contaminant i volatilized; and
              t = residence time in treatment system.

Again, the percentage of each contaminant which is volatilized will depend on the physical properties of the contaminant and the design of the treatment system. based on earlier EPA research (34), the percentage of benzene volatilized from a disposal impoundment over a six-month period is estimated to be 14%. For land-farming, emissions will be significantly higher because of lower biological activity. The fraction volatilized in the first 24 hours after application is estimated to be as high as 36%. After 20 days evaporative losses are likely to have reached 90% of the total volatiles originally applied to the soil.

The estimates of the fraction volatilized for both continuous and batch biotreatment systems are based on mass transfer models developed by the EPA (34). The emission models for waste water treatment systems use Henry's Law and two-film diffusion theory to estimate volatilization. Monod Kinetics are to calculate the contribution of biodegradation to removal. For land-farming, emission models assume the presence of an oil film on the soil surface.

Emission Factors

The correlations given in the preceding section were used to generate VOC emission factors for biotreatment and land-treatment processes. For mechanically aerated flow-through impoundments, assuming 80% volatilization, VOC emissions are 0.80 g VOC emitted/g VOC in waste. For quiescent impoundments, volatilization will be on the order of 10%, so VOC emissions are expected to 0.10g VOC emitted/g VOC in the waste.

For a batch disposal impoundment, VOC emissions are estimated to be 0.14 g VOC emitted/g VOC in the waste. For land-treatment, emissions over the first 24 hours are estimated to be 0.36 g VOC emitted/g VOC in the waste. After 20 days, though, land treatment emissions increase to 0.90g VOC emitted/g VOC in the waste.

Alternately, these emission factors can be converted to a g/hr basis for typical treatment processes. Table 8-1 shows these estimates and the bases used to generate them.

TABLE 8-1. ESTIMATED EMISSIONS FOR BIOTREATMENT AND LANDTREATMENT PROCESSES

Treatment Process	Basis	Residence Time	Estimated VOC Waste Concentration	Emissions Factor (g VOC emitted/ g VOC in waste)	Estimated Emission Rate (g/hr)
Flow through Impoundment w/Mechanical Aeration Quiescent	1.0 M3/min	NA	100.0	0.80	4,800.0
	1.0 M3/min	NA	100 0	0.12	720.0
Disposal Impoundment	15,000 M3	6 months	100.0	0.14	48.6
Land Farming	1,000 M3 waste	24 hours	100.0	0.36	1,500.0
	1,000 M3 waste	20 days	100.0	0.90	187.5[a]

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APPENDIX

SAMPLE CALCULATIONS

EMISSIONS FROM THERMAL DESTRUCTION
(Section 3)

Air Emissions from Off-Site Rotary-Kiln Incineration (Controlled)

Emission Factors:

0.1 g VOC / kg VOC in Waste
50 g Metals / kg Metal in Waste
0.01 g HCl / g Cl in Waste
0.01 g HF / g F in Waste
0.10 g SO_2 / g S in Waste

72 mg PM / m^3 flue gas
50 ppmv CO / m^3 flue gas
100 ppmv NO_x / m^3 flue gas

Assumptions:

- Incinerator

  - Stack Gas Flow   986 m^3/min
  - Waste Fed   3,400 kg/hr
  - Heat Load   63 MM KJ/hr

- Waste Characterization

  - Cl in waste   4.0%
  - F in waste   1.0%
  - S in waste   5.0%
  - Metal in waste   0.1%

Estimated Control Efficiencies for Acid Gas Scrubbing

HCl	99%
HF	99%
SO_2	95%

A-1

EMISSIONS FROM THERMAL DESTRUCTION
(Section 3)

<u>Hourly Emissions:</u>

$$\text{VOC: } \frac{3,400 \text{ kg}}{\text{hr}} \times \frac{.999 \text{ g Organic}}{\text{g waste}} \times \frac{.1 \text{ g VOC}}{\text{kg waste}} = 340 \text{ g VOC/hr}$$

$$\text{Metals: } \frac{3,400 \text{ kg}}{\text{hr}} \times \frac{.001 \text{ kg M}}{\text{kg Waste}} \times \frac{50 \text{ g emitted M}}{1 \text{ kg M in waste}} = 170 \text{ g Metal/hr}$$

$$\text{HCl: } \frac{3,400 \text{ kg waste}}{\text{hr}} \times \frac{.04 \text{ kgCl}}{\text{kg waste}} \times \frac{.011 \text{ g HF}}{\text{g F}} = 0.4 \text{ g HF/hr}$$

$$\text{HF: } \frac{3,400 \text{ kg waste}}{\text{hr}} \times \frac{.01 \text{ Kg F}}{\text{kg waste}} \times \frac{0.11 \text{ g HF}}{\text{g F}} = 0.4 \text{ g HF/hr}$$

$$\text{SO}_2\text{: } \frac{3,400 \text{ kg waste}}{\text{hr}} \times \frac{.05 \text{ kg S}}{\text{kg waste}} \times \frac{.10 \text{ g SO}_2}{\text{g S}} = 17.0 \text{ g SO}_2\text{/hr}$$

$$\text{PM: } \frac{72 \text{ mg PM}}{\text{m}^3} \times \frac{986 \text{ M}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{\text{g}}{1,000 \text{ mg}} = 4,260 \text{ g PM/hr}$$

$$\text{NO}_x\text{: } \frac{986 \text{ M}^3}{\text{min}} \times \frac{\text{gmole}}{.0236 \text{ M}^3} \times \frac{100 \text{ gmole NO}_x}{10^6 \text{ gmole Air}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{46 \text{ g}}{\text{gmole}} = 11,530 \text{ g NO}_x\text{/hr}$$

SAMPLE CALCULATIONS FOR AIR STRIPPING
(Section 4)

Air Stripping Emissions from Controlled Source

Emission Factor

$$\frac{0.1 \text{ g VOC Emitted}}{\text{g VOC in Contaminated Water}}$$

Hourly Emissions from Large Unit

- Assumptions:

  Liquid Flowrate   5,700 L/min
  VOC Conc.   100 mg/L

- Total VOC Treated/Stripped per hour:

$$\frac{5,700 \text{ L}}{\text{min}} \times \frac{100 \text{ mg}}{\text{L}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{\text{g}}{1,000 \text{ mg}} = 34,200 \text{ g/hr}$$

- Emissions:

$$\frac{0.1 \text{ g VOC Emitted}}{\text{g VOC in Water}} \times \frac{34,200 \text{ g VOC in Water}}{1 \text{ hr}} = \frac{3,420 \text{ g VOC Emitted}}{\text{hr}}$$

SAMPLE CALCULATIONS FOR SOIL VAPOR EXTRACTION
(Section 5)

Stack Emissions from Soil Vapor Extraction

Emission Factor

$$\frac{0.05 \text{ g VOC Emitted}}{\text{g VOC Removed From Soil}}$$

Hourly Emissions

- Assumptions:

  250 Kg VOC removed per 10 hr workday

- Emissions:

$$\frac{250 \text{ kg VOC}}{\text{day}} \times \frac{1 \text{ day}}{10 \text{ hr}} \times \frac{1,000 \text{ g}}{1 \text{ kg}} \times \frac{0.05 \text{ g VOC Emitted}}{\text{g VOC Removed}} = \frac{1,250 \text{ g VOC Emitted}}{\text{hr}}$$

SAMPLE CALCULATIONS FOR EVAPORATIVE EMISSIONS FROM SVE AT THE GROVELAND, MA SITE
(Section 5)

Estimated Evaporative Emissions from Semi-Closed Tank of Contaminated Water (100 ppm)

Apply Simple Mass Transfer Model (Two-Film Resistance Theory)[a]

$$Q = K_i \, C_i \, M_i$$

where: Q =   evaporative emissions flux $(g/m^{2.5})$;
         K_i =   overall mass transfer coefficient (m/s);
         C_i =   concentration of contaminant (mol/m^3); and
         M_i =   molecular weight of contaminant (g/mol).

In turn, the overall mass transfer coefficient is given by the equation:

$$\frac{1}{K_i} = \frac{1}{K_{il}} + \frac{RT}{K_{ig} \, H_i}$$

where: K_{il} =   liquid film mass transfer coefficient for contaminant i (m/s);
         K_{ig} =   gas film mass transfer coefficient for contaminant i (m/s); and
         H_i =   Henry's Law Constant for contaminant i $(atm\text{-}m^3/mol)$.

K_{il} calculated from the correlations of Mackay and Yuen[b].

K_{il} = $1.0 \times 10^{-6} + 144 + 10^{-4} \, U^* \, Sc_l^{-0.5}$
U^* =   friction velocity
     = $.01 \, (6.1 \times .63 \, U_{10})^{0.5}$
U_{10} =   wind speed at 10 m above water surface
     =   0 for semi-covered tank at Groveland
Sc_l =   Schmidt Number for Liquid Film
     = $\dfrac{M_{water}}{\rho_w D_{iw}}$
M_w =   viscosity of water
P_w =   density of water
D_{iw} =   diffusivity of contaminant i in water

K_{ig} calculated from correlation of Mackay and Yuen[b].

$$K_{ig} = 1.0 \times 10^{-3} + 46.2 \times 10^{-3} U* (Sc_g)^{-0.67}$$

Sc_g = Schmidt Number for gas film

$$= \frac{\mu_{air}}{\rho_{air} D_{air}}$$

μ = viscosity of air

ρ = density of air

D_{air} = diffusivity of contaminant i in air

Total Evaporative Emissions:

$$E_i = QA$$

E_i = emissions from contaminated water

Q_i = emissions flux (g/m$^2 \cdot$S)

A = surface area of water (m^2)

Estimated Stack Emissions:

Assume uncontrolled VOC emission rate is equal to recovery rate of VOCs:

Uncontrolled Emissions = Recovery Rate
= 5,538 g VOC/hr

SAMPLE CALCULATIONS FOR EVAPORATIVE EMISSIONS
FROM SVE AT THE GROVELAND, MA SITE
(Section 5)

Calculate controlled VOC emission rate using control efficiency for carbon canisters:

$$\text{Controlled Emissions} = \text{Recovery Rate} * \left[1 - \frac{\text{eff}}{100}\right]$$

$$= 5,538 * \left[1 - \frac{99.75}{100}\right]$$

$$= 6.29 \text{ g/hr}$$

Notes:

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SAMPLE CALCULATIONS FOR SOLIDIFICATION/STABILIZATION
(Section 6)

Emissions from Stabilization/Solidification Processes

Emission Factor

$$\frac{0.6 \text{ g VOC}}{\text{g VOC in Contaminated Soil}}$$

Hourly Emissions From Typical Process

- Assumptions: 100 tons soil processed/hr

$$\left(100 \text{ tons } \times \frac{2{,}000 \text{ lbs}}{\text{ton}} \times \frac{.4536 \text{ kg}}{\text{lb}} = 91{,}000 \text{ kg/hr}\right)$$

  0.1 g VOC/kg Soil (100 ppm)

- Total VOC in soil processed:

$$\frac{91{,}000 \text{ kg soil}}{\text{hr}} \times \frac{0.1 \text{ g VOC}}{\text{kg soil}} = \frac{9{,}100 \text{ g VOC}}{\text{hr}}$$

- Emissions

$$\frac{9{,}100 \text{ g VOC}}{\text{hr}} \times \frac{0.6 \text{ g VOC emitted}}{\text{g VOC intreated}} = \frac{5{,}460 \text{ g VOC emitted}}{\text{hr}}$$

EMISSIONS FROM CHEMICAL/PHYSICAL TREATMENT METHODS
(Section 7)

Emissions from Chemical/Physical Treatment Methods

Emission Factor

$$\frac{0.2 \text{ g VOC Emitted}}{\text{g VOC Treated}}$$

Hourly Emissions (From Ultrox Process Testing)

- Assumptions: influent flowrate 100 gpm

$$100 \text{ gpm } x \frac{1 \text{ M}}{264.17 \text{ gallons}} = \frac{.3785 \text{ M}^3}{\text{min}}$$

VOC influent conc. 1.0g/M^3 (1 ppm)

- Total VOC treated (g VOC/hr):

$$\frac{.3785 \text{ M}^3}{\text{min}} x \frac{60 \text{ min}}{\text{hr}} x \frac{1.0 \text{ g}}{\text{M}^3} = \frac{22.71 \text{ g VOC Treated}}{\text{hr}}$$

- Emissions:

$$\frac{22.71 \text{ g VOC Treated}}{\text{hr}} x \frac{0.2 \text{ g VOC Emitted}}{\text{g VOC Treated}} = \frac{4.5 \text{ g VOC Emitted}}{\text{hr}}$$

EMISSIONS FROM BIOTREATMENT SYSTEMS
(Section 8)

Flow-Through Impoundments with Mechanical Aeration

Emission Factor

$$\frac{0.8 \text{ g VOC Emitted}}{\text{g VOC in Waste}}$$

Hourly Emissions

- Assumptions

  Influent Flowrate $1 \text{ M}^3/\text{min}$
  VOC Influent Concentration 100 g/M^3 (100 ppm)

- Total VOC Treated (g VOC/hr)

$$1 \frac{\text{M}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{100 \text{ g}}{\text{M}^3} = \frac{6,000 \text{ g VOC Treated}}{\text{hr}}$$

- Emissions

$$\frac{6,000 \text{ g VOC Treated}}{\text{hr}} \times \frac{.8 \text{ g VOC Emitted}}{\text{g VOC in Waste}} = \frac{4,800 \text{ g VOC Emitted}}{\text{hr}}$$

Quiescent Impoundments

Emission Factor

$$\frac{0.12 \text{ g VOC Emitted}}{\text{g VOC in Waste}}$$

EMISSIONS FROM BIOTREATMENT SYSTEMS
(Section 8)

Hourly Emissions

•   Assumptions

Influent Flowrate	$1 \ M^3/min$
VOC Influent Concentration	$100 \ g/M^3$ (100 ppm)

•   Total VOC Treated (g VOC/hr)

$$1\frac{M^3}{min} \ \text{x} \ \frac{60 \ min}{hr} \ * \ \frac{100 \ g}{M^3} \ = \ \frac{6,000 \ g \ \text{VOC Treated}}{hr}$$

•   Emissions

$$6,000 \ g \ \frac{\text{VOC Treated}}{hr} \ \text{x} \ \frac{.12 \ g \ \text{VOC Emitted}}{g \ \text{VOC in Waste}} \ = \ \frac{720 \ g \ \text{VOC Emitted}}{hr}$$

Disposal Impoundment

Emissions

$$\frac{0.14 \ g \ \text{VOC Emitted}}{g \ \text{VOC in Waste}}$$

Hourly Emissions

•   Assumptions

Impoundment Size	$15,000 \ M^3$
VOC Influent	$100 \ g/M^3$
[1]Disposal Time	6 months

EMISSIONS FROM BIOTREATMENT SYSTEMS
(Section 8)

- Total VOC Treated (g VOC)

$$15{,}000 \text{ M}^3 \times \frac{100 \text{ g}}{\text{M}^3} = 1{,}500{,}000 \text{ g VOC}$$

- Emissions

$$1{,}500{,}000 \text{ g VOC} \times \frac{.14 \text{ g VOC Emitted}}{\text{g VOC in Waste}} \times \frac{1}{6 \text{ months}} \times \frac{1 \text{ month}}{30 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ hour}} = \frac{48.6 \text{ g VO}}{\text{h}}$$

Land Farming

Emission Factor

$$\frac{0.36 \text{ g VOC Emitted}[2]}{\text{g VOC in Waste}}$$

Hourly Emissions

- Assumptions

Volume of Waste	1,000 M^3
VOC Concentration	100 g/M^3
Treatment Time	24 hours

EMISSIONS FROM BIOTREATMENT SYSTEMS
(Section 8)

- Total VOC Treated (g VOC)

$$1,000 \ M^3 \ x \ \frac{100 \ g}{M^3} = 100,000 \ g \ VOC$$

- Emissions

$$100,000 \ g \ VOC \ x \ \frac{0.36 \ g \ VOC \ Emitted}{g \ VOC \ in \ Waste} \ x \ \frac{1}{24 \ hours} = \frac{1,500 \ g \ VOC \ Emitted}{hour}$$

[1]Time between impoundment turnovers.
[2]Based on 24-hour period.