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Guidance To Protect POTW Workers From Toxic And Reactive Gases And Vapors

DISCLAIMER:

This is a guidance document only. Compliance with these procedures cannot guarantee worker safety in all cases. Each POTW must assess whether measures more protective of worker health are necessary at each facility. Confined-space entry, worker right-to-know, and worker health and safety issues not directly related to toxic or reactive discharges to POTWs are beyond the scope of this guidance document and are not addressed.

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FOREWORD

In 1978, EPA promulgated the General Pretreatment Regulations [40 CFR Part 403] to control industrial discharges to POTWs that damage the collection system, interfere with treatment plant operations, limit sewage sludge disposal options, or pass through inadequately treated into receiving waters. On July 24, 1990, EPA amended the General Pretreatment Regulations to respond to the findings and recommendations of the *Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works* (the "Domestic Sewage Study"), which identified ways to strengthen the control of hazardous wastes discharged to POTWs. The amendments add two prohibitions addressing POTW worker health and safety to the specific discharge prohibitions that apply to all non-domestic dischargers to POTWs. At 40 CFR 403.5(b)(1) and 403.5(b)(7), respectively, the new regulations prohibit:

- pollutants which create a fire or explosion hazard in the POTW, including, but not limited to, wastestreams with a closed-cup flashpoint of less than 140° F or 60° C using the test methods specified in 40 CFR 261.21; and
- pollutants which result in toxic gases and vapors within the POTW in a quantity that may cause acute worker health and safety problems.

The *Guidance to Protect POTW Workers From Toxic and Reactive Gases and Vapors* fulfills EPA's commitment to issue guidance for POTWs on implementing the new specific prohibitions. The guidance document is designed to:

- help the POTWs understand reactive and gas/vapor-toxic hazards and how they happen,
- give the POTWs working knowledge of certain chemicals that cause reactive and gas/vapor-toxic conditions within the POTW and at industries during inspection, and
- recommend procedures to prevent or mitigate reactive and gas/vapor-toxic conditions.

The new specific prohibitions, together with this guidance should enable POTWs to improve protection of POTW workers from the serious health and safety problems that can occur from exposure to toxic and reactive substances in industrial discharges.

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Office of Wastewater Enforcement and Compliance

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1. INTRODUCTION

1.1 BACKGROUND

Publicly owned treatment works (POTWs) commonly transport and treat wastewaters from industrial users. As a result, POTW employees may incur safety or health risks from exposure to hazardous materials in these wastewaters. Such health effects include nausea, headaches, dizziness, skin irritation, respiratory distress, or even cancer or sudden death. (See Table 1-1.) Gases and vapors that form or accumulate in the collection system or volatilize in the treatment plant may pose a serious fire or explosion risk. (See Table 1-2.)

Recognizing that exposure of POTW workers to toxic and reactive chemicals is a serious health and safety problem, the U.S. Environmental Protection Agency (EPA) issued regulations to require POTWs to identify and control potential exposures to substances in industrial wastewaters that are reactive or that create toxic gases and vapors. In 1978, EPA promulgated the General Pretreatment Regulations [40 CFR Part 403] to control industrial discharges to POTWs that damage the collection system, interfere with treatment plant operations, limit sewage sludge disposal options, or pass through inadequately treated into receiving waters. On July 24, 1990, EPA amended the General Pretreatment Regulations to respond to the findings and recommendations of the *Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works* (the "Domestic Sewage Study"), which identified ways to strengthen the control of hazardous wastes discharged to POTWs. The amendments add two prohibitions addressing POTW worker health and safety to the specific discharge prohibitions that apply to all non-domestic dischargers to POTWs. At 40 CFR 403.5(b)(1) and 403.5(b)(7), respectively, the new regulations prohibit:

(1) pollutants which create a fire or explosion hazard in the POTW, including, but not limited to, wastestreams with a closed-cup flashpoint of less than 140° F or 60° C using the test methods specified in 40 CFR 261.21; and

(2) pollutants which result in toxic gases and vapors within the POTW in a quantity that may cause acute worker health and safety problems.

Materials that cause a fire,explosion, or intense chemical reaction are, for purposes of this manual, referred to as "reactive" materials. Materials that contain or generate toxic gases and vapors within the POTW are referred to as "gas/vapor-toxic" materials. Formal definitions of these terms are provided in Chapter 2.

TABLE 1-1. HEALTH INCIDENTS CAUSED BY INDUSTRIAL DISCHARGES TO POTW

Source(s)	Locality	State	Year	Industrial User Category	Pollutants	Symptoms
Kominsky, et al. 1980	Louisville	KY	77	Pesticide manufacturing	hexachlorocyclopentadiene& fuel oil	Skin & eye irritation, sore throat, cough
Elia, et al. 1983	Memphis	TN	78	Pesticide manufacturing	hexachlorocyclopentadiene,chlordane, hexachlorobicyclopentadiene	Eye, throat, nose, lung, & skin irritation
Salisbury, et al. 1982	Roswell	GA	79	Not Identified	1,1,1-trichloroethane, aliphatics	Headache, fatigue, nausea & eye irritation, cough
USEPA 1986 (DSS)	Baltimore	MD	80-85	Paint manufacturing	benzene, toluene, solvents	Nausea
USEPA 1986 (DSS)	Louisville	KY	80-85	Not Identified	hexane	Nausea
USEPA 1986 (DSS)	Mount Pleasant	TN	80-85	Hazardous waste treatment	organics, metals	Nausea
USEPA 1986 (DSS)	Passaic Valley	NJ	80-85	Leather tanning	volatile compounds, solvents	Shortness of breath, skin irritation
USEPA 1986 (DSS)	Pennsauken	NJ	80-85	Organic chemicals manufacturing	benzene, toluene, phenol, chloroform	Shortness of breath, watery eyes
USEPA 1986 (DSS)	St. Paul	MN	80-85	Electronics, metal finishing, printing	solvents	Headaches
USEPA 1986 (DSS)	South Essex	MA	80-85	Leather tanning	hexavalent chromium	Skin irritation
USEPA 1986 (DSS)	Tampa	FL	80-85	Not Identified	organic solvent	Nausea
USEPA 1986 (DSS)	Gloucester County	NJ	80-85	Not Identified	1,1,1-trichloroethane	Fatality by inhalation
McGlothlin and Cone 1981	Cincinnati	OH	81	Pigment manufacturing	1,1,1-trichloroethane, mineral spirits	Irritation of the eyes & nose, nausea, dizziness, vomiting, acute bronchitis
Lucas 1982	Cincinnati	OH	81	Not Identified	hexane, toluene, xylene, aliphatic naphtha, 1,1,1-trichloroethane, trichloroethylene, chlorobenzene, O-chlorotoluene, trichlorobenzene	Eye & nose irritation, difficulty in breathing
Pederson and Simonsen 1982	NA	NA	82	Not Identified	carbon dioxide	Unconsciousness & two resulting drownings
Carson and Lichty 1984	Omaha	NE	83	Not Identified	hydrogen sulfide	One death, nose & throat irritation, numbness, tingling of hands & feet, nausea, vomiting, & fatigue
Kraut, et al. 1988	New York City	NY	86	Not Identified	benzene, toluene, other organic solvents	Lightheadedness, fatigue, increased sleep, nausea, headaches
Tozzi 1990	Bergen County	NJ	88	Not Identified	organic solvents	Headaches, difficulty in breathing

NA = Not Available

TABLE 1-2. DISCHARGES TO POTWS CAUSING FIRES OR EXPLOSIONS*

State	Year	Pollutants	Origin of Discharge	Results
PA	66	methane, chlorine	Unknown.	Explosion occurred in sewage treatment plant. No injuries reported.
OH	69	crude oil	Oil pipeline ruptured sending an estimated 77,000 gallons into the sewer.	15 explosions occurred. No injuries reported.
TN	70	gasoline	Valve left open on bulk storage tank sending 46,000 gallons to sewer.	Sewage treatment plant damaged. Raw sewage released to river.
OH	70	gasoline	Gasoline entered sewer from leaking pump and flushing of a spill at another pump.	Slight damage to sewer. No injuries reported.
IL	71	xylol, benzene, toluene	Accidental discharge at chemical plant.	A series of explosions occurred. No injuries were reported.
OH	77	petroleum naphtha, acetone, isopropyl alcohol	Accidental discharge by rubber manufacturer.	Multiple explosions occurred, damaging water and gas mains, roads, playgrounds, and a church.
KY	81	liquid hexane	Accidentally spilled into sewer.	A series of explosions occurred in sewer, damaging sewers and ripping holes in streets.
PA	83	methane gas, chlorine, hydrogen sulfate gas	Unknown.	Explosion and fire occurred in sewage treatment plant. Two deaths and 13 injuries were reported.
NJ	86	gasoline	Gasoline was illegally dumped into a sink by workers at a manufacturing site.	Explosion occurred at lift station. One injury was reported.

* Adapted from the "National Fire Protection Association Summary of Incidents in Wastewater Treatment Plants." Casey C. Grant, memorandum to the Technical Committee on Wastewater Treatment Plants. February 22, 1991.

Many of the events listed in table 1-2 were caused by accidental slug discharges to sewers. For additional information on controlling slug discharges to POTWs, please see the EPA guidance manual *Control of Slug Loadings to POTWs* (1991).

1.2 PURPOSE AND ORGANIZATION OF THIS MANUAL

This manual is intended to help POTWs carry out EPA's July 24, 1990, regulations that prohibit reactive and gas/vapor-toxic discharges to POTWs. It also will help POTWs and their workers identify, prevent, and mitigate hazards associated with toxic gases, vapors, and chemically-reactive substances encountered in the POTW's collection system and treatment plant, as well as at industrial facilities during POTW inspections.

This manual has three specific purposes:

- to help POTW staff and management understand reactive and gas/vapor-toxic hazards and how they arise;
- to give POTW staff and management a working knowledge of certain chemicals that can cause reactive and gas/vapor-toxic conditions within the POTW and at industries during inspections; and
- to recommend procedures to prevent or mitigate reactive and gas/vapor-toxic conditions.

The manual is organized into the following chapters:

- Defining Reactive and Gas/Vapor-Toxic Hazards (Chapter 2) — Provides working definitions and characteristics of reactive and gas/vapor-toxic substances.
- Monitoring to Identify Reactive and Gas/Vapor-Toxic Hazards (Chapter 3) — Introduces a variety of field instruments and explores procedures for direct measurement of reactive and gas/vapor-toxic hazards.
- Screening Industrial Discharges (Chapter 4) — Presents screening procedures for determining whether a specific industrial discharge can cause gas/vapor-toxic conditions.
- Problem Identification Process (Chapter 5) — Presents specific inspection procedures that POTW personnel may use, incorporating the tools described in the preceding chapters, to identify actual or potential hazards from reactive and gas/vapor-toxic compounds.
- Control of Potential Hazards (Chapter 6) — Presents techniques for preventing and controlling reactive and gas/vapor-toxic hazards.

The appendices provide further background information and a glossary.

2. DEFINING REACTIVE AND GAS/VAPOR-TOXIC HAZARDS

This chapter will provide POTW personnel with a basic understanding of reactive and gas/vapor-toxic materials and their hazards. Section 2.1 defines and characterizes reactive materials, and Section 2.2 discusses gas/vapor-toxic materials. Table 2-1 documents chemical incompatibilities that include both reactive and gas/vapor-toxic hazards.

2.1 REACTIVITY

"Reactive" substances undergo rapid chemical transformations into other substances. These transformations may: (1) cause direct injury through chemical reactions; (2) generate intense heat, which can start fires or explosions or cause burn injuries; or (3) generate toxic gases or vapors.

EPA regulates reactive wastes as hazardous wastes under the Resource Conservation and Recovery Act (RCRA). Under EPA's hazardous waste regulations [40 CFR 261.23(a)], a solid waste exhibits the RCRA characteristic of reactivity if it:

- is normally unstable and readily undergoes violent change without detonating;
- reacts violently with water;
- forms potentially explosive mixtures with water;
- generates potentially harmful quantities of toxic gases or vapors when mixed with water;
- may detonate or explode if subjected to a strong initiating source or if heated under confinement;
- may detonate or explode at standard temperature and pressure; or
- is a forbidden Class A or Class B explosive pursuant to 49 CFR Part 173.

Reactive substances typically fall into one of the following three categories:

- <u>Water-reactive substances</u> — These substances may explode or release enough heat when in contact with water to cause fires or generate toxic gases or vapors. They include fluorine, which reacts with water to produce hydrofluoric acid mists; and phosphorus trichloride, which in water evolves gaseous hydrogen chloride.
- <u>Air-reactive substances</u> — These substances may cause fires or explosions, and may generate toxic gases, or vapors.
  - — <u>Flammable</u> air-reactives include hydrocarbon solvents (such as hexane, toluene, naphtha) and fuels (such as gasoline).
  - — <u>Explosive</u> air-reactives (such as nitroglycerine, dynamite, TNT, and lead azide) readily undergo rapid, violent combustion which may be triggered by impact, friction or heat.
  - — Other solvents, such as methylene chloride, generate toxic gases upon combustion.

TABLE 2-1. COMMON CHEMICAL INCOMPATIBILITIES

ALKALI METALS (such as calcium, potassium and sodium) with water, carbon dioxide, carbon tetrachloride, and other chlorinated hydrocarbons

ACETIC ACID with chromic acid, nitric acid, hydroxyl-containing compounds, ethylene glycol, perchloric acid, peroxides, and permanganates

ACETONE with concentrated sulfuric and nitric acid mixtures, aniline.

ACETYLENE with copper (tubing), fluorine, bromine, chlorine, iodine, silver, and mercury

AMMONIA (anhydrous) with mercury halogens, calcium hypochlorite, or hydrogen fluoride, chlorine, iodine

AMMONIUM NITRATE with acids, metal powders, flammable fluids, chlorates, nitrates, sulphur, and organic aerosols or other combustibles

ANILINE with acetone; or nitric acid, hydrogen peroxide, or other strong oxidizing agents

BROMINE with ammonia, acetylene, butadiene, butane, hydrogen, sodium carbide, turpentine, or powdered metals

CHLORATES with ammonium salts, acids, metal powders, sulfur, sugar, carbon, organic aerosols, or other combustibles

CHLORINE with ammonia, acetylene, butadiene, benzene and other petroleum fractions, hydrogen, sodium carbides, turpentine, and powdered metals

CHROMIC ACID with acetic acid, naphthalene, camphor, alcohol, glycerine, turpentine, and other flammable liquids

CYANIDES with acids

HYDROCARBONS (generally) with fluorine, chlorine, bromine, chromic acid, or sodium peroxide

HYDROGEN PEROXIDE with copper, chromium, iron, most metals or their respective salts, flammable fluids and other combustible materials, aniline, and nitro-methane

HYDROGEN SULFIDE with nitric acid, oxidizing gases, metal oxides, copper, or hydrated iron oxide (wet rust)

IODINE with acetylene, ammonia, or aluminum

MERCURY with acetylene, fulminic acid, or hydrogen

NITRIC ACID with acetic, chromic and hydrocyanic acids, aniline, carbon, hydrogen sulfide, hydrazine, flammable fluids or gases, and substances that readily become nitrated

OXYGEN with hydrogen, flammable liquids, solids, and gases

OXALIC ACID with silver, mercury, permangenates, or peroxide.

PERCHLORIC ACID with acetic anhydride, hydrazine bismuth and its alloys, alcohol, paper, wood, and other organic materials

PHOSPHORUS PENTOXIDE with water

POTASSIUM PERMANGANATE with glycerine, ethylene glycol, benzaldehyde, or sulfuric acid

SODIUM PEROXIDE with any oxidizable substances, such as methanol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerine, ethylene glycol, ethyl acetate, and furfural

SULFURIC ACID with chlorates, perchlorates, permanganates, oxilates, formates, chlorides, florides, and water

Source: Adapted from "Safety and Health in Wastewater Systems," Water Pollution Control Federation, 1983. (The Water Pollution Control Federation is now the Water Environment Federation.)

- Organic-reactive substances (corrosives) — May react directly with organic tissues or generate sufficient heat upon reaction to cause burns. Also react violently with hydrocarbon solvents. Consist of the following categories:

  — Strong acids include sulfuric acid, nitric acid, hydrochloric acid, and perchloric acid.

  — Strong bases include caustic soda, lye, and lime.

  — Oxidizing agents include potassium dichromate, potassium permanganate, hydrogen peroxide, fluorine, nitrous oxide, and chlorine.

  — Reducing agents include sodium borohydride, lithium aluminum hydride, phosphorus, lithium, potassium, and metallic sodium.

  — Heavy metal chloride and sulfate salts include alum, ferric chloride, ferric sulfate, and aluminum chloride, which produce strong acids in water.

  — Sodium, calcium, and potassium salts of strong bases include sodium, calcium, and potassium oxide, carbonate, hypochlorite, sulfide, and silicate, which produce strong bases in water.

2.2 GAS/VAPOR TOXICITY

This manual designates substances as "gas/vapor toxic" if they generate gases or vapors injurious to human health. Gas/vapor-toxic effects can either be acute (causing systemic poisoning, asphyxiation, or irritation of the eyes, skin, respiratory passages) or chronic (causing cancer).

This manual classifies gas/vapor-toxic substances according to how they generate toxic gases or vapors:

- Reactive gas/vapor-toxic substances — These substances are generated as a direct result of either an acid-base reaction or an oxidation-reduction reaction.

  — Acid-base reactions — When a volatile weak acid, or a salt of a volatile weak acid, is introduced to a strongly acidic wastewater, fumes of the volatile acid are emitted. Similarly, when a volatile weak base, or a salt of a volatile weak base, is introduced to a strongly basic wastewater, fumes of the volatile base are emitted. For example:

    - Hydrogen cyanide gas is evolved when a strong acid (such as sulfuric, nitric, or hydrochloric acid) is introduced to a wastestream bearing sodium or potassium cyanide.

    - Hydrogen sulfide gas is evolved when a strong acid is introduced to a sulfide-bearing wastestream.

    - Ammonia gas is evolved when a strong base (such as lye, caustic soda, or lime) is added to a wastestream bearing ammonium hydroxide (dissolved ammonia).

  — Oxidation-reduction reactions — An oxidation-reduction reaction is a chemical transformation in which electrons are transferred from one chemical (the reducing agent) to another chemical (the oxidizing agent). In oxidation-reduction reactions involving transfer of oxygen from one molecule to another, the molecule losing the oxygen is the oxidizing agent and the molecule gaining the oxygen is the reducing agent.

- Volatile gas/vapor-toxic substances — Generated through volatilization, either from aqueous solution or from liquid or solid, rather than through chemical reaction. Hydrocarbon solvents such as benzene, toluene, and naphtha are examples of volatile gas/vapor-toxic substances. Many volatile gas/vapor-toxic chemicals, such as hydrocarbon solvents, are also flammable.

- Asphyxiant gas/vapor-toxic substances — Generate oxygen-deficient atmospheres by displacing oxygen. Include methane, hydrogen sulfide, and nitrogen. Some asphyxiant gas/vapor-toxic substances, such as methane and hydrogen sulfide, are also flammable or explosive; some (such as hydrogen sulfide) are also highly toxic apart from their asphyxiant properties.

The most recent versions of the following documents provide information on identifying reactive and gas/vapor-toxic chemicals and associated hazards:

- *NFPA 49—Hazardous Chemicals Data*, National Fire Protection Association, Quincy, MA.
- *Condensed Chemical Dictionary*, Gessner Hawley (editor), Van Nostrand Reinhold, New York, NY.
- *Safety and Health in Wastewater Systems*, Manual of Practice 1, Water Pollution Control Federation, Alexandria, VA.
- *Dangerous Properties of Industrial Materials*, N. Irving Sax, Van Nostrand Reinhold, New York, NY.
- *Pocket Guide to Chemical Hazards* (NIOSH 90-117), National Institute for Occupational Safety and Health, U.S. Government Printing Office, Washington, DC.

3. MONITORING TO IDENTIFY REACTIVE AND GAS/VAPOR-TOXIC HAZARDS

As a basic safety procedure, POTW personnel with proper training and knowledge of the use of air monitoring equipment should periodically monitor their surroundings, including manholes, wet wells, and sewer lines, to determine whether reactive or gas/vapor-toxic conditions exist. They should also be familiar with the history and process areas of any industries being inspected or sampled, the potential hazards present, and the type of monitoring that might be required at those industries.

Because most hazards to POTW workers occur through direct contact with wastewaters or exposure to toxic gases or vapors, this chapter deals with wastewater and air monitoring equipment, particularly direct-reading equipment. POTW personnel should monitor to ascertain the safety of the work area, to institute appropriate protective measures (such as personal protective equipment or evacuation), and to identify the need for further monitoring.

Direct-reading instruments (providing real time measurements) were developed as early warning devices for industrial settings, where a leak or accident could release a high concentration of a known chemical. Because they are not designed for POTW use, direct-reading instruments have certain limitations:

- They detect or measure only specific classes of chemicals;
- They may fail to measure or detect airborne substances below certain concentrations (such as 1 part per million (ppm)); and
- They occasionally give false readings due to chemical or other interferences.

To understand advantages and limitations of direct-reading instruments read the manufacturer's instructions carefully, and, if necessary, raise questions with the vendor's technical representatives.

Table 3-1 lists the commonly-used wastewater and air monitoring instruments that will be discussed in this chapter, and their approximate costs.

TABLE 3-1 INSTRUMENTATION COSTS

Instrument	Approximate Cost (in 1991 Dollars)
WASTEWATER:	
pH meter	$269
Redox potential meter	
— hand held	$150
— laboratory	$1,000
Flashpoint tester (closed-cup)	$1,500
AIR:	
CGD/O_2 meter	$2,000
Photoionization detector	$4,500
— calibration kit	$150
Flame ionization detector	$6,000
— calibration kit	$150
Colorimetric tubes	$4 each
— bellows and pump	$330

3.1 WASTEWATER MONITORING EQUIPMENT

This section discusses methods for measuring corrosivity, oxidation-reduction, and flammability hazards in wastewater.

Corrosivity. pH is a measure of acidic intensity. Alkalinity, a measure of a wastewater's tendency to resist pH change upon acid addition, measures acid-neutralizing capability. A pH meter measures the acidic or alkaline strength of a wastestream. A wastestream of pH less than or equal to 2.0 is strongly acidic; greater than or equal to 10.0 is strongly basic.

Oxidation-reduction. An oxidation-reduction ("redox") meter identifies the presence of oxidizing or reducing agents, and is used in the field to measure a wastestream's tendency to carry out oxidation-reduction reactions (defined on p. 2-3). A large positive reading on the redox meter indicates the presence of a strong oxidizing agent; a large negative reading indicates the presence of a strong reducing agent. Either extreme indicates the potential for an oxidation-reduction reaction.

Flammability. Ignitable materials discharged to POTWs can cause fires and explosions in collection systems—particularly near the point of discharge to the sewer, where high temperatures promote evaporation of ignitable wastes into a relatively fixed volume of air and form vapors that are trapped within the collection system. These vapors can be ignited by electric sparks, friction, surfaces such as manhole covers heated by the sun, or heat generated by chemical reactions. Often POTW workers use metal tools that can accidentally strike against the street, concrete surface, or manhole cover, creating sparks.

The flammability of a wastewater sample can be detected in a laboratory with a flashpoint tester. Operation of a flashpoint tester is straightforward: a sample is collected at the point of discharge to the sewer, placed in the tester, heated slowly, and a flame is introduced periodically to the vapor space. The flashpoint is the lowest temperature at which vapor combustion spreads away from its source of ignition. Although two classes of flashpoint testers exist (open-cup and closed-cup), the specific prohibition against discharges that create a fire or explosion hazard in the POTW specifies a closed-cup flashpoint limit only. A substance's flammability, as derived using a closed-cup flashpoint tester, is characterized as the minimum ambient temperature at which a substance gives off sufficient vapor to create an ignitable mixture. EPA defines a flammable/explosive material as any wastestream with a closed-cup flashpoint less than 140° F or 60° C [40 CFR 403.5(b)].

3.2 AIR MONITORING EQUIPMENT

During normal work activities such as wet well inspections and inspections of industrial users, POTW workers should monitor the quality of the air before entering the area in which they work. The need for monitoring may be repeated or even continuous, depending on the likelihood of changing conditions. This section describes the equipment used for monitoring oxygen content, explosivity, and the concentration of toxic organic and inorganic gases or vapors.

Calibration methods for air monitoring equipment are not addressed in this section. The calibration and maintenance instructions in the operator's manual should be followed closely. Regular calibration and maintenance of air monitoring equipment is important and should be stressed in POTW management practices.

3.2.1 Monitoring for Oxygen Content

The normal oxygen content of the atmosphere at sea level is 20.8% by volume. Areas with oxygen levels lower than 19.5% are highly dangerous should not be entered without specialized training and equipment. Criteria developed by the National Institute of Occupational Safety and Health (NIOSH) require workers to use supplied-air respirators in areas in which atmospheric oxygen content is less than 19.5%. Oxygen levels at or above 25% constitute a severe fire hazard; when such levels are observed, workers should be evacuated and fire officials contacted.

Not only is lack of oxygen a respiratory hazard, but it also provides a warning that the oxygen may have been displaced by a potentially toxic, flammable, or explosive gas or vapor. Before work is initiated in an oxygen-deficient atmosphere, additional monitoring—and perhaps laboratory analysis—is necessary to pinpoint which gases and vapors are present.

Commonly, oxygen monitoring is performed with an oxygen meter, in which chemical reactions between atmospheric oxygen and an electrolytic solution across a semipermeable membrane produce a slight electrical current. The reaction and the resulting current increase with the amount of atmospheric oxygen present. Most oxygen meters provide a direct readout of the percentage of oxygen present; in so doing, they help determine whether oxygen levels are present at which air-reactive chemicals might explode or undergo rapid combustion. By identifying the percentage of oxygen present, an oxygen meter can help POTW personnel determine whether the ratio of oxidant to fuel mixture is sufficient for ignition. For ignition to occur, an electric spark or friction is necessary. Oxygen meters should be explosion proof, and equipped with audible and visible alarms.

An oxygen meter has two principal operating components: the oxygen sensor and the meter readout. In some units, an aspirator bulb or pump draws air into the detector and across the detector cell; in others, air is allowed to diffuse to the sensor. Some detectors are small hand-held units. Many have single-aspirating (hand squeeze) bulb pumps or battery-powered diaphragm pumps to draw the sample across the detector cell.

Most oxygen meters are operated by switching the power knob to "ON" with one hand and holding the oxygen sensor with the other. Once the unit is operating, oxygen molecules diffuse to the sensor, producing a minute electric current proportional to the oxygen content. The current passes through an electronic circuit, and the resulting signal is shown as a needle deflection on a meter or as a digital reading.

Despite the rapidity and ease with which oxygen meters can be used, they have limitations such as the following:

- Because the density of oxygen in the atmosphere depends upon elevation, the meter should be calibrated at approximately the same elevation at which it is to be used.
- Meters may give incorrect readings in atmospheres with oxygen levels below 19.5% or above 25%.
- The presence of carbon dioxide can shorten the life of the oxygen detector cell significantly.

3.2.2 Monitoring for Explosivity

Confined spaces, such as manholes or wet wells, are hazardous environments because they may let gases or vapors accumulate to explosive levels. For this reason, explosivity monitoring should be a routine part of all sewer line maintenance. This involves two parameters of concern: the lower explosive limit (LEL) and the upper explosive limit (UEL). The LEL is the minimum concentration in air at which a gas or vapor will flame with an ignition source. (Appendix A lists the LELs for some common chemicals.) The UEL is the concentration above which a gas or vapor concentration is too rich and not enough oxygen is present in the atmosphere to flame. Atmospheres with concentrations above the UEL may not be explosive, but they are extremely dangerous. Any sudden change in air flow (opening a door or manhole) can rapidly lower the concentration below the UEL into the explosive range. These areas should be evacuated, ventilated, and continuously monitored until the concentration is below the LEL.

Action levels are numeric limits at which actions must be taken to prevent adverse exposure to workplace hazards. Action levels for explosivity are expressed as a percentage of the LEL. OSHA has set explosivity action levels as follows:

Percent LEL	Action
< 10%	Continue operations with caution (respiratory protection if necessary).
10% - 25%	Continue operation with extreme caution. Attempt to identify specific combustible gases or vapors present.
> 25% (up to UEL)	Fire/explosion hazard exists. Leave immediately.

Explosivity is measured with a combustible gas detector (CGD), also called an explosimeter, which measures the concentration of combustible gases and vapors in the atmosphere across a hot filament of platinum. The CGD provides a direct readout of the presence of combustible gases or vapors, expressed as a percentage of the LEL. For example, a reading of 50% for a gas with a 5% LEL would indicate that the concentration of the gas is actually 2.5%.

Like oxygen meters, CGDs are portable and come with built-in pumps that draw samples from the immediate area or from confined spaces when used with an extension probe. CGDs and oxygen meters typically are combined in the same unit, so they can be used together (this is necessary since the CGD is not reliable at O_2 concentrations below 19% or above 25%). These units have separate calibration knobs and meter screens.

Like oxygen meters, CGDs screen rapidly but have drawbacks. The CGD must be used in conjunction with an oxygen meter, as mentioned above. It does not detect potentially explosive dusts or liquid explosives such as sprays of oil, nor does it work in the presence of silicon-based materials, leaded gasoline, or acids. Vapors and gases from leaded fuels, halogens, and sulfur compounds will harm the platinum filament contained in the apparatus, and silicone vapors or gases will destroy the filament altogether. Taking these limitations into account, the CGD is still a vital tool for ensuring the safety of field personnel, when used in conjunction with an oxygen meter.

3.2.3 Monitoring for Vapors and Gases

Vapors or gases may build up in sewer lines, at pump stations, or near the point of release around industrial processes. They may threaten worker health and safety if recommended exposure limits are exceeded and adequate worker protection is not provided. Workers should not enter high-risk areas unless absolutely necessary. To ensure that POTW personnel are adequately protected, determine which vapors or gases are present—and at what concentrations—in the work space and other areas.

Vapor and gas detectors provide a direct readout of either the total concentration of vapors and gases or of the specific types of contaminants present and their concentrations. The three basic types of vapor and gas detectors are as follows:

- Photoionization detectors (PIDs);
- Flame ionization detectors (FIDs); and
- Colorimetric indicator tubes.

3.2.3.1 Photoionization Detectors

A photoionization detector (PID) uses an ultraviolet light source to ionize a gas and measure its ionization potential. Ionization potential is the energy required to remove the outermost electron from a molecule. The ionization potential is specific for any compound or atomic species, and is measured in electron volts (eV). The presence of an organic vapor causes a positive ionization potential and a current field within the detection chamber. The detector measures this current and displays the corresponding gas concentration in parts per million.

Since a PID's ability to detect a chemical depends on its ability to ionize it, the ionization potential of the chemical to be detected must be compared to the energy generated by the instrument's ultraviolet lamp. Ultraviolet lamps are available in different energies (such as 8.3, 8.4, 9.5, 10.2, 10.6, 10.9, 11.4, 11.7, and 11.8 eV), and are selected to correspond to the chemical being analyzed and to eliminate the effects of other atmospheric gases (if the lamp is too energetic, for example, oxygen and nitrogen will ionize and interfere with the readings).

Consider for example, how a PID would be used to monitor a release of propane (with an ionization potential of 11.1 eV) and vinyl chloride (10.0 eV). To detect both, both would need to be ionized, and so a lamp with an 11.1-eV ionization potential would be used. To detect only the vinyl chloride, and prevent interference from the presence of propane, use a lamp 10.2- or 10.6-eV lamp, which would be strong enough to ionize vinyl chloride but not propane.

PIDs measure a variety of organic and inorganic gases and vapors, and differ in their analytical capabilities according to the manufacturer. POTW personnel should contact a scientific equipment supplier for a list of lamps it carries.

PIDs have several limitations:

- Dust can collect on the lamp and block the transmission of ultraviolet light, reducing the instrument reading. This problem can be detected during calibration and prevented through regular lamp cleaning.
- Humidity can cause condensation on the lamp and reduce the available light, lowering the validity of the reading.
- Radio-frequency interference from pulsed DC or AC power lines, transformers, generators, and radio wave transmission may produce an error in response.
- The validity of the readings will lower as the lamp ages.
- <u>PIDs cannot measure methane</u>.

Pollutant levels detected with the PID should be compared against their corresponding action levels, such as the threshold limit values (TLVs) discussed in Chapter 4. If a pollutant is detected at or near the TLV or other action level, the POTW inspector should evacuate the area and take appropriate action to identify the source. If it is necessary to enter the area, use the appropriate personnel protection equipment (e.g., respirator with appropriate filter).

3.2.3.2 Flame Ionization Detectors

Flame ionization detectors (FIDs) work on the principle of hydrogen flame ionization. A flame ionizes the organic vapors, resulting in a current that is measured and displayed on a readout in parts per million.

The organic vapor analyzer (OVA) is the most commonly used FID, particularly because it has a chemically-resistant sampling system and can be calibrated to almost all organic vapors, measuring gas concentrations accurately in the 0-to-10 ppm, 0-to-100 ppm, and 0-to-1000 ppm ranges. As with the PID, levels detected by the OVA should be compared to action levels such as TLVs. An alarm can be set to sound if the preset concentration level (usually one-half the TLV) is met or exceeded.

The OVA operates in either of two modes. In survey mode it monitors continuously for all detectable organic vapors. In gas chromatograph (GC) mode, air samples are drawn and injected into the system, and the user determines the identities and concentrations of specific organic vapors and gases relative to the methane response of the OVA. The OVA is most sensitive to hydrocarbons but its response varies for other chemicals. When specific compounds are to be tested, the OVA operator needs to know the capability of the OVA for the compounds. An inquiry of the manufacturer, a review of the literature, and a continuing calibration/verification program are necessary.

OVAs and other FIDs have some disadvantages:

- They do not detect inorganic gases and vapors, or some synthetics.
- They should not be used at temperatures below 4.5°C (40°F).
- Readings can only be reported relative to the calibration standard used.

3.2.3.3 Colorimetric Tubes

A colorimetric indicator tube measures the concentration of a specific gas by drawing an air stream of a known volume through a calibrated glass tube filled with an indicator chemical. If the gas of concern is present, it will react with the indicator chemical by staining or changing the color of the tube. The concentration of the gas or vapor is then read off the markings on the calibrated tube and compared to the appropriate TLV or other action level.

Colorimetric tubes have certain advantages:

- They are easy to use in the field.
- Detector tubes are available for gases that are not detected by the OVA.
- Tubes are available for gases which will "poison" the filament of an explosimeter and oxygen meter indicator, such as hydrogen sulfide, sulfur dioxide, sulfur trioxide, hydrogen chloride hydrogen cyanide, and chlorine.

Colorimetric tubes have certain disadvantages:

- They break easily.
- A different type of tube is needed for each specific gas or vapor, which could become costly.
- Interference with other chemicals can alter the accuracy of the tubes ±25%.

In addition, instructions vary for different tubes. For example, one chemical could require one pump to draw an air stream into the tube, while another chemical could require two. Also, the time required for color change varies with the manufacturer. POTW personnel must therefore closely follow the instructions for each tube.

4. SCREENING INDUSTRIAL DISCHARGES

Chapter 3 discussed instruments and tools that POTW personnel can use to detect the presence of reactive and gas/vapor-toxic substances. This chapter presents two methods for identifying wastewaters that may create gas/vapor-toxic conditions and require preventive controls. Section 4.1 describes how to use gas/vapor-toxicity criteria to calculate concentration-based screening levels. Section 4.2 discusses an alternative approach taken by the Cincinnati Metropolitan Sanitary District (CMSD).

4.1 DEVELOPING WASTEWATER SCREENING LEVELS BASED ON GAS/VAPOR TOXICITY

POTW personnel can determine whether a discharge may generate gas/vapor-toxic conditions by comparing gas/vapor toxicity criteria to pollutant concentrations in the industry's discharge. This involves three steps:

- Identifying the relevant gas/vapor toxicity criteria;
- Converting the gas/vapor toxicity criteria to wastewater screening levels; and
- Comparing the wastewater screening levels to current discharge levels.

4.1.1 Step 1: Identify Gas/Vapor Toxicity Criteria

This manual recommends gas/vapor-toxicity criteria based on occupational guidelines that have been developed by the American Conference of Governmental Industrial Hygienists (ACGIH) and used by the Occupational Health and Safety Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH). The guidelines establish air contaminant exposure limits above which the "average worker" should not be exposed, assuming that an "average worker":

- Is exposed to the substance throughout his/her entire occupational lifetime — between the ages of 18 and 65;
- Works a 40-hour work week;
- Weighs 70 kilograms (154.7 pounds);
- Is healthy with no prior physical or health deficiencies;
- Is not employed in a specific industry;
- Absorbs a certain percentage of the substance in his/her body and excretes or detoxifies the remainder;
- Has a normal respiration rate; and
- Varies in susceptibility according to physical condition (including pregnancy, stress, and lack of sleep) and lifestyle (such as alcohol or drug use, long work hours, or heavy exertion).

A threshold limit value (TLV) is the airborne concentration of a particular substance to which the average worker may be exposed without adverse effect. ACGIH publishes an annual list of TLVs for approximately 650 toxic substances. Its publication, "Threshold Limit Values and Biological Exposure Indices," is a convenient reference source for POTW personnel.[1] TLVs are based on the best available information from past industrial experiences, animal exposure studies, and documented worker reactions. ACGIH designates three categories of TLVs[2]:

- Threshold limit value/time-weighted average (TLV-TWA) is the average airborne concentration of a substance not to be exceeded in any 8-hour work shift of a 40-hour work week without causing any adverse health effects. The TLV-TWA is a chronic limit.
- Threshold limit value/short-term exposure limit (TLV-STEL) is the 15-minute time-weighted average exposure not to be exceeded during a work day without causing:
  - Irritation;
  - Permanent tissue damage; or
  - Narcosis (sleepiness) that may increase the chances of injury, lower the chances of self-rescue, or reduce work efficiency.

  Exposures at the TLV-STEL are limited to 4 times a day, with each exposure lasting less than 15 minutes and at least 1 hour between successive TLV-STEL exposures. The TLV-STEL is an acute limit, and is set at a value higher than the TLV-TWA to allow for excursions.
- Threshold limit value-ceiling (TLV-C) is the airborne concentration that may not be exceeded during any part of the work day. The TLV-C is an acute limit.

Table 4-1 lists current TLVs for some gas/vapor-toxic pollutants that are common in industrial wastewaters. TLVs can be used to set exposure levels for POTW workers and to identify the degree of protection needed when designing engineering controls for high-risk areas at the POTW. This manual uses chronic TLVs (TLV-TWA), which mostly are lower than acute TLVs (TLV-STEL). Using chronic TLVs to set screening levels will ensure that acute TLVs are also being addressed and acute health and safety problems avoided.

Exposure limits are developed for individual chemicals. For exposure to a mixture of two or more compounds, ACGIH has developed formulas to calculate adjusted TLVs for combined exposure effects. This approach, which assumes additive toxicity among the components of a mixture, is also used by OSHA. It is discussed in greater detail in Section 4.1.4.

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[1] "Threshold Limit Values and Biological Exposure Indices," American Conference of Governmental Industrial Hygienists, Cincinnati, OH. To order the published list, send requests to ACGIH, 6500 Glenway Ave., Bldg. D-7, Cincinnati, OH, 45211-4438.

[2] These definitions are paraphrased from ACGIH TLV booklets. The verbatim definitions can be found in the glossary in Appendix K.

TABLE 4-1. SOME GAS/VAPOR-TOXIC POLLUTANTS WITH THEIR RESPECTIVE THRESHOLD LIMIT VALUES (TLVs)

CHEMICAL COMPOUND	ACGIH TLV (1990-1991)			
Acrolein	0.1	ppm-TWA*	0.3	ppm-STEL**
Acrylonitrile	2	ppm-TWA		
Ammonia	25	ppm-TWA	35	ppm-STEL
Benzene	10	ppm-TWA		
Bromoform	0.5	ppm-TWA		
Carbon dioxide	5000	ppm-TWA	30000	ppm-STEL
Carbon tetrachloride	5	ppm-TWA		
Chlorobenzene	75	ppm-TWA		
Chloroform	10	ppm-TWA		
Chlorine	0.5	ppm-TWA	1	ppm-STEL
1,1-Dichloroethane	200	ppm-TWA	250	ppm-STEL
1,2-Dichloropropane	75	ppm-TWA	110	ppm-STEL
Ethyl benzene	100	ppm-TWA	125	ppm-STEL
Hydrogen sulfide	10	ppm-TWA	15	ppm-STEL
Methyl bromide	5	ppm-TWA		
Methyl chloride	50	ppm-TWA	100	ppm-STEL
Methylene chloride	50	ppm-TWA		
1,1,2,2-Tetrachloroethane	1	ppm-TWA		
Tetrachloroethylene	50	ppm-TWA	200	ppm-STEL
1,1,2-Trichloroethane	10	ppm-TWA		
1,1,1-Trichloroethane	350	ppm-TWA	450	ppm-STEL
Trichloroethylene	50	ppm-TWA	200	ppm-STEL
Vinyl chloride	5	ppm-TWA		
Toluene	100	ppm-TWA	150	ppm-STEL

Source: *Threshold Limit Values and Biological Exposure Indices for 1990-1991*, American Conference of Governmental Industrial Hygienists, 1990.

*TWA - Time Weighted Average
**STEL - Short Term Exposure Limit

4.1.2 Step 2: Convert Gas/Vapor Toxicity Criteria to Wastewater Screening Levels

POTW personnel may use an air monitoring device, such as those discussed in Chapter 3, to measure air concentrations directly and compare pollutant concentration to TLVs. More commonly, however, POTW personnel will have information on the concentration of pollutants in the wastewater and require some means of comparing the wastewater concentration to the air concentration TLVs. This section discusses how to use gas/vapor toxicity criteria for air contaminants to develop screening levels for pollutants in wastewater. Conversion of air criteria to water criteria requires an understanding of volatilization—the conversion to a gas or vapor of any substance that ordinarily is liquid or solid. Volatilization of a chemical from a water solution is driven by the chemical's vapor pressure and water solubility.

Vapor pressure. Vapor pressure is the pressure a gas exerts on the walls of a closed container. For example, if a liquid such as benzene partially fills a closed container, benzene molecules will evaporate from the liquid surface. Because the container is closed, some of the benzene molecules in the headspace above the liquid will return to the liquid by condensation. When the volatilization rate equals the condensation rate, vapor-liquid equilibrium is attained, and the benzene molecules in the headspace exert the vapor pressure of benzene on the walls of the container. The concentration of benzene in the headspace can be determined from this vapor pressure. Vapor pressure varies with temperature.

Water solubility. The water solubility of a chemical is the concentration of that chemical in water above which the chemical forms a separate liquid, solid, or gaseous phase. Water solubility is also a function of temperature.

With these definitions in mind, consider a volatile chemical discharged in wastewater to a sewer line. In the sewer line, some of the chemical molecules will volatilize and enter the headspace. Because the headspace is confined, some of the molecules in the headspace will, at the same time, condense and return to the wastewater. In this way the sewer line can be thought of as a confined space. Over a sufficient residence time, each wastewater constituent will volatilize to the extent determined by that constituent's vapor-liquid equilibrium relationship.

For many slightly- to moderately-soluble chemicals, this equilibrium is closely approximated by Henry's Law, a general thermodynamic relationship that can apply to sewer conditions. Henry's Law states that, in a closed system, the concentration of the constituent in the vapor phase and the corresponding equilibrium concentration in the liquid phase are related by a constant. This constant, the Henry's Law constant, is the ratio of the constituent's vapor pressure to its water solubility:

$$H = P_{vap}/S$$

where:

H = constituent's Henry's Law constant, in atm m^3/mol
P_{vap} = constituent's vapor pressure, in atm
S = constituent's water solubility, in mol/m^3

A chemical's Henry's Law constant determines how much it will volatilize. Every chemical has a unique Henry's Law constant.

This manual makes some simplifying assumptions about the applicability of Henry's Law constants to conditions in a sewer line:

- Temperature. Although the Henry's Law constant is affected by the temperature in the sewer line, this manual assumes that the wastewater and sewer headspace temperatures do not deviate significantly from 25°C. Where process discharges are known to contain pollutants of concern at higher temperatures, the POTW should not rely on the development of screening criteria, but require the industrial user to provide site-specific wastewater and headspace monitoring data.

- Other constituents. Although the Henry's Law constant is affected by the presence of other constituents in the wastewater, this manual assumes that other constituents have no effect.

- Air flow. The Henry's Law constant is affected by the rate of air flow through the sewer line. If the air flow rate is high enough, wastewater will be continuously exposed to fresh air and volatile constituents will be constantly carried off. Furthermore, equilibrium will not be reached and the concentrations of the constituents in the headspace and wastewater will remain low. Conversely, if the air flow rate is negligible, volatile constituents can accumulate in the sewer headspace and the resulting air and wastewater concentrations in the sewer line will be higher. The screening approach discussed here conservatively assumes that air flow is negligible.

- Rate of volatilization. Volatilization rate is affected by a number of complex and site-specific factors such as the temperature in the sewer line, the wastewater surface area, the air flow rate through the sewer line, the turbulence of wastewater mixing, and the wastewater residence time in the sewer line. This manual assumes instantaneous attainment of vapor-liquid equilibrium and does not consider volatilization rates.

With these simplifying assumptions, Henry's Law constants can be used to set wastewater screening levels and for evaluating the wastewater's potential to generate gas/vapor-toxic atmospheres. To convert an air criterion (the TLV-TWA) for a gas/vapor-toxic chemical into a corresponding wastewater screening level, the TLV is divided by the chemical's Henry's Law constant and then multiplied by appropriate conversion factors. Table 4-2 lists some wastewater screening levels for common gas/vapor-toxic chemicals. Appendix B summarizes the gas/vapor toxic screening procedure and lists additional screening levels. This procedure is also presented in detail in EPA's *Guidance Manual on the Development and Implementation of Local Discharge Limitations Under the Pretreatment Program* (December, 1987).

4.1.3 Step 3: Compare Wastewater Screening Levels to Current Discharge Levels

Once the POTW personnel set a wastewater screening level for a gas/vapor-toxic compound, the screening level should be compared to the concentration actually being discharged by the industrial user. A discharge that exceeds its screening level should be considered potentially gas/vapor-toxic.

4.1.4 Screening for Gas/Vapor-Toxic Mixtures

As mentioned earlier, TLVs are chemical-specific and do not readily account for the combined toxicity of a mixture of chemicals in air. One way to estimate the toxicity of a chemical mixture is to assume that its toxicity is equivalent to the sum of the individual toxicities of its components. Appendix B outlines a procedure in which a mixture's potential gas/vapor toxicity is determined in this manner. Unfortunately, for complex mixtures of chemicals, this procedure may be both cumbersome (screening levels must be obtained for all potentially gas/vapor-toxic constituents of the discharge) and inexact (it simplistically assumes additive toxicity).[3]

4.1.5 Screening for Reactivity

The reactivity prohibition [40 CFR 403.5(b)(1)] defined reactive pollutants to include wastestreams with a closed-cup flashpoint less than 140°F or 60°C. Unlike the prohibition of gas/vapor-toxic pollutants, compliance with the flashpoint condition can be directly measured in the industrial user's wastestream. Direct measurement is the easiest method for determining compliance with flashpoint condition of this mandatory prohibition. The approved test methods are specified in 40 CFR 261.21.

If further screening is needed, wastewaters which may create reactivity hazards can be identified by screening levels developed using the LEL as an indicator of reactivity. The screening level is calculated by dividing 10% of a chemical's LEL by its Henry's Law constant and multiplying by appropriate conversion factors. This procedure is described in Appendix C of this manual and in the *Guidance Manual on the Development and Implementation of Local Discharge Limitations Under the Pretreatment Program* (December, 1987). Table 4-2 presents screening levels for flammable or explosive priority pollutants for which criteria exist, as well as other industrial pollutants. The use of LEL-based screening levels should complement, rather than replace, field measurements of LEL, which are an important part of field safety procedures.

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[3] Many chemicals, in fact, show synergistic behavior, in which the presence of one chemical enhances the toxicity of another, or antagonistic behavior, in which the presence of one chemical detracts from the toxicity of another. Synergistic and antagonistic behavior are chemical-specific and, therefore, are not addressed by the generic screening procedure discussed here.

TABLE 4-2. DISCHARGE SCREENING LEVELS BASED ON GAS/VAPOR TOXICITY AND EXPLOSIVITY

Compound	Gas/Vapor Toxicity Screening Level (mg/l)	Explosivity Screening Level (mg/l) (Based on 10% of the LEL)
Acrylonitrile	1.19	1794
Benzene	0.13	20
Bromomethane	0.002	4.7
Carbon disulfide	0.06	6.3
Carbon tetrachloride	0.03	—*
Chlorobenzene	2.31	40
Chloroethane	5.73	1.6
Chloroform	0.41	—*
Chloromethane	0.29	1.1
1,2-Dichlorobenzene	3.75	165
1,4-Dichlorobenzene	3.55	104
Dichlorodifluoromethane	0.04	—*
1,1-Dichloroethane	4.58	128
trans-1,2-Dichloroethylene	0.28	14
1,2-Dichloropropane	3.62	164
1,3-Dichloropropene	0.08	435
Ethyl benzene	1.59	16
Ethylene dichloride	1.05	660
Formaldehyde	0.06	412
Heptachlor	0.003	—*
Hexachloro-1,3 butadiene	0.0002	—*
Hexachloroethane	0.93	—*
Methyl ethyl ketone	249	2486
Methylene chloride	2.06	494
Napthalene	—*	240
Nitrobenzene	—*	17046
Tetrachloroethylene	0.53	—*
Toluene	1.36	17
1,2,4-Trichlorobenzene	0.39	197
1,1,1-Trichloroethane	1.55	33
Trichloroethylene	0.71	114
Trichlorofluoromethane	1.23	—*
Vinyl chloride	0.004	2.2
Vinylidene chloride	0.003	3.3
Aroclor 1242	0.01	—*
Aroclor 1254	0.005	—*

* Criteria for these compounds have not yet been developed.

4.2 CINCINNATI METROPOLITAN SANITARY DISTRICT (CMSD) SCREENING PROCEDURE

In February 1981, six workers excavating a collapsed sewer at the Cincinnati Metropolitan Sanitary District (CMSD) reported experiencing eye and nose irritation, nausea, dizziness, and vomiting. NIOSH tested the sewer air spaces and identified 1,1,1-trichloroethane, naphtha, toluene, and other solvents — many of which were above the TLV-TWA values.[4] In another 1981 incident, CMSD requested a NIOSH investigation because organic vapors were detected near the bar screen area at one of the treatment plants and workers complained of breathing difficulties and eyes and nose irritation. Numerous organic compounds were detected near the headworks; one sewer airspace contained potentially explosive concentrations of hexane and at least two sewer airspaces contained levels of volatile compounds classified as immediately dangerous to life and health (IDLH)[5] for persons entering those areas. NIOSH found that routine activities could expose employees to a multitude of chemicals including toluene, xylene, aliphatic naphtha, 1,1,1-trichloroethane, trichloroethylene, chlorobenzene, o-chlorotoluene, and trichlorobenzene.

To address these problems, CMSD, in consultation with NIOSH, developed a generic discharge screening technique designed to identify the presence of explosive and gas/vapor-toxic compounds. The technique compares the discharge concentration of total volatile organics to a 300-ppm hexane equivalent limit. This limit was deemed to sufficient to protect the collection system from fires and explosions and to provide workers minimal protection from gas/vapor-toxic pollutants. Exceedances indicate a potentially gas/vapor-toxic or explosive discharge warranting additional investigation.

Under the CMSD monitoring procedure, the POTW staff:

- Collects an industrial user discharge sample in accordance with proper volatile organic sampling techniques (e.g., zero headspace);
- Withdraws 50% of the sample by volume, followed by injection of nitrogen gas to maintain one atmosphere total pressure;
- Equilibrates the sample (as explained in Appendix D);
- Analyzes the sample's headspace using gas chromatography/mass spectrometry (GC/MS);
- Expresses the headspace concentration of total volatile organics as an equivalent concentration of hexane; and
- Compares the headspace concentration of total volatile organics to the 300-ppm hexane limit.

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[4] Source: Health Hazard Evaluation Report, HETA 81-207-945 (1981) NIOSH.

[5] IDLH - Maximum level from which one could escape within 30 minutes without any escape-impairing symptoms or irreversible health effects.

The 300-ppm hexane equivalent limit was developed by CMSD to provide its POTW workers exposed to sewer atmospheres at least minimal protection from gas/vapor toxicity. CMSD concluded that below the 300-ppm limit, carbon filters will generally protect POTW workers adequately. The validity of this conclusion depends on which chemicals are of concern at a particular site. Wastewater and headspace analysis for specific volatile organic pollutants should be conducted before implementing the CMSD method. EPA's Technology Assessment Branch Wastewater Research Division, reviewed the NIOSH/CMSD documentation and noted that the limit is not chemical-specific and therefore does not ensure ACGIH or OSHA exposure limits will be met in the sewer or POTW atmosphere. EPA also concluded that CMSD's 300-ppm hexane equivalent limit does not apply to toxic vapors from spills, to generation of hydrogen sulfide or methane gas in sewers, or to vapor purging of oxygen from sewers, all of which represent significant health hazards.[6]

Initial screening by the CMSD approach can be used to identify discharges warranting detailed chemical-specific screening by the method discussed in Section 5.1 or, if the contributing source(s) of volatile organics are clear, to begin immediate mitigation.

Appendix D describes the CMSD screening methodology in more detail.

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[6] *Guidance Manual on the Development and Implementation of Local Discharge Limitations Under the Pretreatment Program* (December 1987), USEPA.

5. PROBLEM IDENTIFICATION PROCESS

Chapters 5 and 6 discuss a three-phase process by which the POTW, using the information and tools presented in Chapters 3 and 4, can identify and begin to mitigate reactive and gas/vapor-toxic hazards. As Figure 5-1 illustrates, the process consists of three phases:

- Phase 1: Collect Information
- Phase 2: Perform Hazards Analysis
- Phase 3: Select Mitigation Measures.

This chapter discusses the first two phases. Chapter 6 discusses Phase 3 and explores the preventive options available to the POTW.

Hazards facing POTW workers vary in complexity. This chapter focuses on the more complex problems to ensure that the subject matter receives adequate coverage. If a POTW faces problems that are more obvious or simple than those described here, it should follow the same principles—even if it actually performs procedures that are less rigorous.

5.1 PHASE 1: COLLECT INFORMATION

In this phase the POTW should review available data and conduct all necessary inspections of local industries, the collection system, and the treatment plant.

5.1.1 Identify Data Collection Needs

As the problem identification process begins, the POTW team first should define the overall objectives of the problem identification process. The POTW may wish to investigate how to reduce concentrations of specific chemicals in an industrial user's discharge because of potential gas/vapor toxicity problems, or investigate whether to require best management practices (BMPs) at an industrial user to protect POTW workers. (BMPs may include activities such as good housekeeping measures, waste segregation plans, and staff training.) All POTW employees who will collect and use data should be involved at the beginning of the process to ensure that their data collection goals are similar and that efforts will not be duplicated.

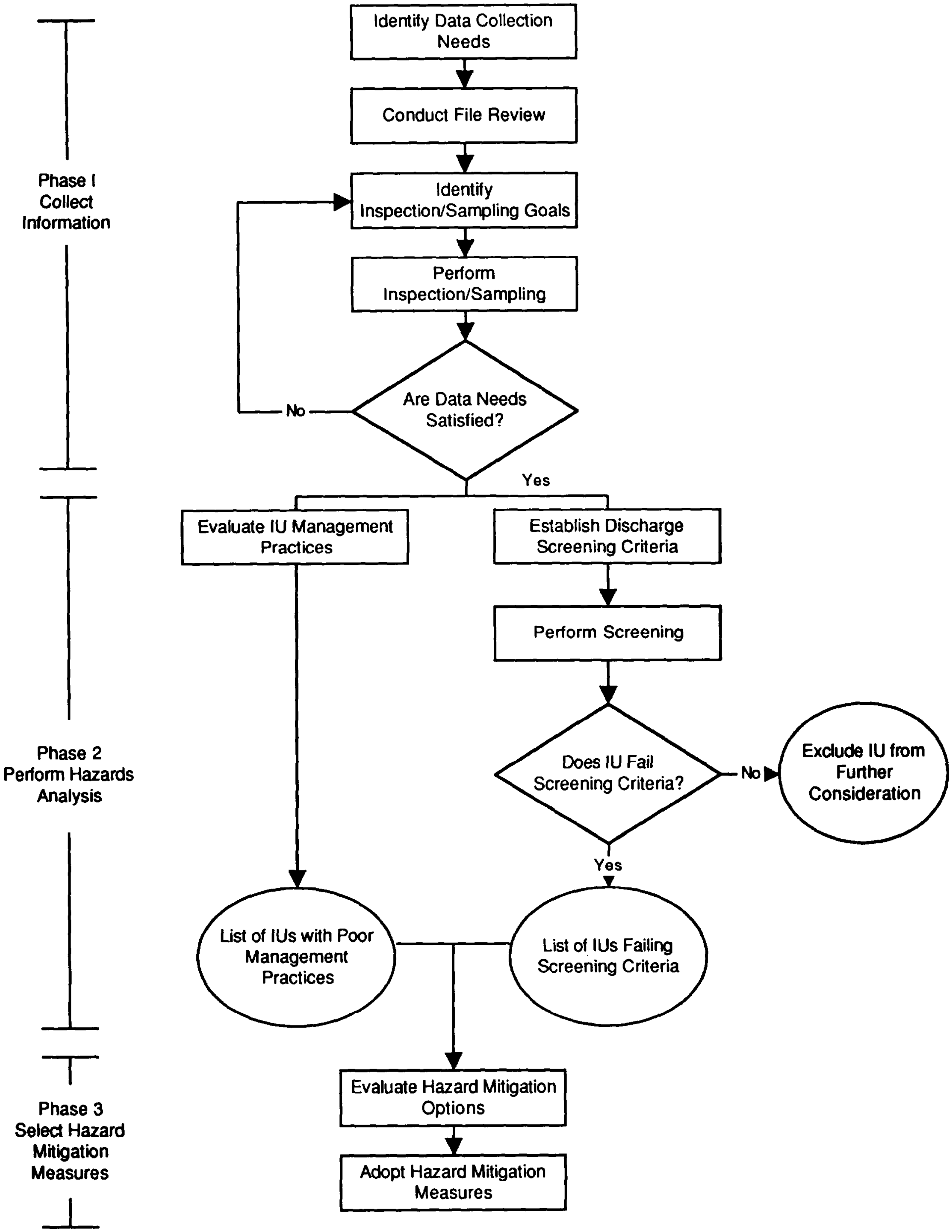

FIGURE 5-1. PROBLEM IDENTIFICATION PROCESS

Once the POTW team has identified the problem areas, it should identify the types of data necessary to support each decision-making process. For example, if the POTW team was investigating the need for BMPs to protect inspectors at a particular industrial user, it would seek the following types of data:

- Which chemicals are stored at the facility, and in what concentrations;
- How and where the chemicals are used and, correspondingly, how and where release or exposure might occur; and
- Which hazards are associated with exposure to the chemicals.

The POTW should develop criteria to ensure that these data are of sufficient quantity and quality. For the BMP example above, this would mean the following:

- Because the chemical inventory must be both complete and accurate in order to identify potential hazards, it should be reviewed by both POTW and industry personnel at the beginning of the inspection, updated as the inspector tours the facility, and checked again by industry officials at the end of the inspection.
- Pollutant concentration data must be representative because they are the basis for evaluating hazards. Where chemical concentrations fluctuate, the POTW must decide whether to collect a large body of data in order to account for slugs and other fluctuations.
- The manner and location of chemical handling (storage, transfer, use, treatment and disposal) must be based on recent information, since the POTW inspector cannot guarantee that results from an inspection conducted a year ago are accurate or up-to-date. The inspector should update chemical handling information regularly through discussions with industry personnel and a comprehensive plant tour.

The POTW should locate its industry files, reference documents, and contacts with the fire department and other knowledgeable municipal agencies, to facilitate this phase of the problem identification process.

5.1.2 Perform File Reviews

The POTW should review all in-house files on each industrial user of concern to obtain necessary background information before a site inspection. The POTW should review the following data sources on the industry:

- Discharge permit application and supporting files;
- Sewer connection application and supporting files;
- Inspection reports;
- Discharge sampling data;
- Building permit applications;
- Sewer maps;
- Sewer maintenance reports;
- Fire department records about chemical usage;
- Material safety data sheets (MSDSs);
- Citizen complaints;
- "Form R" reports submitted under the Emergency Planning and Community Right-to-Know Act (SARA Title III); and
- Notifications of hazardous waste discharges from the industrial user, as required under 40 CFR 403.12(p).

The POTW staff can also contact local OSHA offices to determine whether any complaints have been lodged against the industry, whether OSHA inspections have occurred, and the results of any such inspections.

The POTW should summarize the file review information on an Information Collection/Decision sheet. A blank copy of this form is provided in Appendix F; Figure 5-2 provides an example of a sheet that has been filled out.

1. STATE THE PURPOSE OF THE INFORMATION COLLECTION (e.g., response to worker health and safety concerns) This information collection activity is being undertaken in response to inspector concerns regarding noxious gases and vapors at XYZ Industries process line No. 3. The inspector has concerns that the discharge from the industry may affect the collection system maintenance crew. The data collected will determine the source of the gases and vapors, characterize the extent of hazard, and identify safety equipment and controls that may be appropriate.

2. CHECK THE EVALUATIONS THAT MUST BE UNDERTAKEN

[✓] Chemical Inventory

a. Indicate the type of data needed: Inventory of all chemicals used or stored in the area north of process line No. 3.

b. What are the potential sources of data: XYZ permit application and file, past inspector notes. Reviewed both sources of information; information is 3 years old.

c. List specific needs relating to use of the data: Data needs to be current (within the last year.)

[✓] Determination of Chemical Characteristics at Process Lines

a. Indicate the type of data needed: Need a characterization of chemicals and chemical hazards relating to process line No. 1. (This is an open series of tanks and channels.)

b. What are the potential sources of data: 1. No information on process characteristics on file. Calls to XYZ have been unproductive. 2. Hazard evaluation can be accomplished using ACGIH reference manual, MSDSS, Dangerous Properties of Industrial Materials (Sax), and discharge permit application.

c. List specific needs relating to use of the data: Need to obtain detailed, current data (within the past year).

[✓] Identification of Chemical Release Points

a. Indicate the type of data needed: N/A

b. What are the potential sources of data: N/A

c. List specific needs relating to use of the data: N/A

FIGURE 5-2. SAMPLE INFORMATION COLLECTION/DECISION SHEET

[✓] Evaluation of Controls/Mitigative Measures

a. Indicate the type of data needed: Inspection reports indicate exhaust hoods above process line. Unclear whether the exhaust hoods work.

b. What are the potential sources of data: Contact plant foreman regarding operation and maintenance aspects.

c. List specific needs relating to use of the data: None.

[ ] Other, explain:

a. Indicate the type of data needed:

b. What are the potential sources of data:

c. List specific needs relating to use of the data:

[✓] Identification of Appropriate Safety Protocols for Future Inspections or Collection System Work
Delay on-site investigation pending receipt and analysis of data from XYZ on chemical characteristics and concentration.

Discuss health and safety concerns with XYZ staff in light of process chemical characterization data.

FIGURE 5-2. SAMPLE INFORMATION COLLECTION/DECISION SHEET (Continued)

3. IDENTIFY SPECIFIC DATA NEEDS TO BE MET BY FACILITY INSPECTION/SAMPLING AND DESIGN INFORMATION COLLECTION PROTOCOL

Need to verify that existing information on processes are up-to-date, that chemical usage is as permitted, and request data regarding the chemical composition of solutions in tanks P-3-1 and P-3-2. If data received are not adequate, request XYZ design a program of grab sampling to verify the constituents and concentrations present. Information obtained to date indicate that the characteristics of the wastewater are fairly constant and that grab samples will provide an adequate representation of the wastewaters.

Additional Comments:

Completed by: ______________________ Date: ______________________

FIGURE 5-2. SAMPLE INFORMATION COLLECTION/DECISION SHEET (Continued)

5.1.3 Conduct Inspections and Field Evaluations

After the file review, the POTW should know exactly what information it still needs to collect and how to collect it. An industry inspection will then be useful for evaluating (or verifying) the inventory of chemical management practices at the industry and identifying potential reactivity and gas/vapor toxicity hazards on site. The rest of this section discusses how to conduct a chemical management practices inspection and a field evaluation of reactivity and gas/vapor toxicity hazards. Although they are discussed separately here, the two inspections can be performed together.

5.1.3.1 Develop an Inventory of Chemical Management Practices

The POTW should conduct an on-site assessment of an industry's chemical management practices for two reasons: (1) to ensure that the information collected during the file review is complete and accurate; and (2) to identify and evaluate first-hand any hazards to which a POTW inspector might be exposed.

Preparing for the chemical management practices inspection

Before the inspection, the inspector should obtain or draw a map showing areas in the facility that should be examined during the inspection. These areas would include all chemical management locations, such as:

- Chemical storage areas;
- Chemical transfer areas;
- In-process chemical usage areas;
- Waste generation areas; and
- Treatment and storage areas for wastes and wastewaters.

The inspector should make lists of all chemicals expected to be found in each of these areas, including notes on chemicals posing reactivity (e.g., because of incompatibility), gas/vapor toxicity, or other hazards. (A list of the volatile organic priority pollutants is in Appendix E.) Figure 5-3, a facility hazard summary sheet, can be used to summarize this information. A copy of this sheet should be kept in the industry files and updated during subsequent inspections.

THE FOLLOWING NOTES ARE KEYED TO DESIGNATED AREAS ON THE FACILITY MAP [ATTACHED]. **Inspectors should update this sheet and the attached map after each visit to the industry. This sheet should be reviewed prior to each inspection and the safety equipment used should reflect the potential hazards listed on this sheet.**

FACILITY AREA	CHEMICAL HAZARD				PHYSICAL HAZARD					
	[O]	[C]	[F]	[E]	[S]	[C]	[H]	[O]	[A]	[N]
1 ____________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
2 ____________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
3 ____________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
4 ____________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
5 ____________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
6 ____________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

Chemical hazards

[O] = Strong oxidant
[C] = Corrosive
[F] = Fume toxic
[E] = Explosive

Physical Hazards

[S] = Splash and spill hazards
[C] = Construction area
[H] = Heavy machinery area
[O] = Open tanks and/or channels
[A] = Aerosols/fumes
[N] = High noise area

NOTES:

INSPECTION LOG

DATE	NAME	DATE	NAME

FIGURE 5-3. SAMPLE FACILITY HAZARD SUMMARY SHEET

Conducting the chemical management practices inspection

Before touring the industrial facility, the inspector should verify the completeness and accuracy of the map and the chemical list with facility personnel. The inspector should make any corrections necessary, but should not delete information from the list without first-hand confirmation (for example, if a change in plant processes has resulted in the use of different feed stocks, the inspector should not assume that all of the previously-used chemicals have been removed from the site). Facility staff should be asked to identify all known plant hazards, to evaluate potential hazards identified by the inspector, and to describe the safety equipment used and precautions followed at the facility.

After ensuring that he or she is carrying the correct monitoring instruments and using necessary safety equipment and clothing, the inspector should tour each chemical management area, giving particular attention to:

- Storage, use, or generation of potentially gas/vapor-toxic chemicals, potential accumulation of vapors or gases within the storage area, work area, and sampling locations, and the presence of adequate ventilation (important when considering the need for protective equipment and industry BMPs).
- Storage, use, or generation of reactive or incompatible chemicals.
- Discovery of chemicals not previously identified.
- Identifying, and gathering complete information on the existence of chemical management areas not previously identified.
- Proximity of incompatible pollutants to each other.
- Potential for direct contact with chemicals or wastes during an inspection (which may suggest a need for protective equipment).
- Physical condition and manner of operation of chemical storage/reaction/treatment vessels, and the potential for spills or catastrophic failure (which may suggest a need for BMPs).
- Visual evidence of reactive, particularly corrosive, chemicals. In extreme cases, the presence of salt deposits will reveal corrosive activity (strong bases react with carbon dioxide in air to form salts, for example).
- Proximity of floor drains to chemical management areas (for later use in evaluating the need for BMPs).

The inspector should take detailed notes on each of these points to best assess the potential hazards and make an informed selection of a industrial user hazard management plan (discussed in Chapter 6). The facility hazard summary sheet should be updated after the inspection.

5.1.3.2 Field Evaluation of Reactivity and Gas/Vapor Toxicity Information

A field evaluation of potential reactivity and gas/vapor toxicity hazards will enable the POTW to:

- Identify open wastewater conveyances and mixing areas within the industrial facility (as opposed to process and product areas identified through the inspection process described above). These areas are likely release points for volatile pollutants.
- Understand the variability of the effluent data used in screening exercises. This is important since the POTW may wish to protect against the highest concentrations of a pollutant detected, rather than the average or "representative" concentrations.

The POTW staff can accomplish these goals in a single inspection, since both require evaluation of the sources and flow of wastewaters and the variations in pollutant concentrations.

Preparing for the Field Evaluation of Reactivity and Gas/Vapor Toxicity Information

The inspector should obtain a detailed sewer map and flow diagrams for all industrial processes that contribute to the total wastewater flow. The flow diagrams should show all wastewater sources (including process blowdown and overflows, where applicable), sumps, floor drains, open tanks, treatment processes, and connections to both sanitary and storm sewers.

To ensure that all sources are accounted for, the inspector should perform a water balance for both peak operating periods and production down-times. The inspector should characterize each wastewater source as completely as possible—including the pollutants present and their concentrations—and highlight wastewaters with incompatible characteristics or the potential to cause gas/vapor toxicity problems. The inspector's review of the flow diagram and water balance should focus on:

- Specific wastestreams within the plant that should be kept separate to prevent the generation of toxic vapors and gases (such as wastestreams containing hydrogen cyanide or sulfide or with $pH < 2$ or > 12);
- Combined wastestreams with pollutant concentrations that might contribute to a gas/vapor toxicity or reactivity problem, and possible release pathways; and
- The adequacy of wastewater source information, as reflected by the water balances.

At this time the inspector also should obtain any additional flow information necessary to complete the water balance. The water balance should appear reasonable (including consideration of evaporation losses); the inspector should ask facility engineers for an explanation of discrepancies greater than 10%. The inspector should also ask for plant operating information that will show whether seasonal shut-downs, equipment failures, or emergency conditions might result in the re-routing of wastewaters (for example, tank overflows might be directed to emergency storage sumps in the event of a pump failure).

FOR EACH OUTFALL TO THE SEWER, PROVIDE THE FOLLOWING INFORMATION:

A. FACILITY: ____________________
OUTFALL NO: ____________________
OUTFALL LOCATION: ____________________

B. WATER SOURCE: [Include method of estimation (e.g., water meter)]

City Water: ________________ gpd
Private wells: ________________ gpd
Other: ________________ gpd

Total: ________________ gpd

C. WATER USAGE (Identify water usage and indicate flow):

Process waters:

1. ____________ flow: ____________ gpd
2. ____________ flow: ____________ gpd
3. ____________ flow: ____________ gpd
4. ____________ flow: ____________ gpd

Noncontact cooling water:

1. ____________ flow: ____________ gpd
2. ____________ flow: ____________ gpd

Domestic uses:

1. ____________ flow: ____________ gpd
2. ____________ flow: ____________ gpd

Total usage: ____________ gpd

D. STORM WATER (Provide numbers if flows are directed to the sewer):

1. Roof Drains flow: ____________ gpd
2. Drainage/Runoff flow: ____________ gpd

Total flow: ____________ gpd

Compare totals from parts B and C above. These two values should agree to within 10% and be reasonable when compared to measured/observed flows from the facility.

FIGURE 5-4. SAMPLE WATER BALANCE WORKSHEET

Conducting the Field Evaluation of Reactivity and Gas/Vapor Toxicity Information

Before the field evaluation, the POTW inspector should review the facility maps and chemical lists with facility personnel and correct any inaccuracies. This will ensure the best possible characterization of in-plant wastestreams and points of potential exposure.

At this time the inspector also should obtain any additional flow information necessary to complete the water balance. The water balance should appear reasonable (including consideration of evaporation losses); the inspector should ask facility engineers for an explanation of discrepancies greater than 10%. The inspector should also ask for plant operating information that will show whether seasonal shut-downs, equipment failures, or emergency conditions might result in the re-routing of wastewaters (for example, tank overflows might be directed to emergency storage sumps in the event of a pump failure).

The field evaluation should consist primarily of a plant tour. During the plant tour the inspector should:

- Note characteristics of wastewaters mixing in sumps or tanks, the capacity of holding vessels, and the relative turbulence that occurs during peak flows.
- Locate open wastewater conveyances or mixing structures.
- Find visible evidence of reactive or gas/vapor-toxic conditions, such as high temperatures or turbulence in a tank, mist formation, or evidence of equipment corrosion. If necessary, use instrumentation (such as a pH meter or redox meter)to check the corrosivity of solutions in open tanks, and the concentration of vapors that might be released.
- Identify potential hazards to future inspectors.
- Visually confirm the reasonableness of flow estimates used in the water balance.

After the field evaluation, the inspector should have identified any incompatible internal wastestreams and any wastewaters (including combined wastestreams) or exposure locations in the facility that may cause gas/vapor toxicity problems. The facility hazard summary sheets should be updated accordingly.

5.2 PHASE 2: PERFORM HAZARDS ANALYSIS

The hazards analysis phase has three parts: (1) evaluation of hazards resulting from chemical management practices at the industry; (2) screening of industrial discharges for their potential to cause reactivity or gas/vapor toxicity problems; and (3) selection of hazard mitigation options (See Figure 5-1). This chapter discusses the first two parts; Chapter 6 discusses the third.

5.2.1 Evaluating Chemical Management Practices

During the plant tour, the POTW inspector should observe, and ask questions about, the chemical management practices on site. At that time the inspector should either discuss changes in management practices directly with company officials or develop enough background information to justify setting specific permit requirements. After the plant tour the inspector should clarify new information (such as the hazards of previously-unidentified substances) and organize that information to help identify mitigation options. The following examples illustrate how the evaluation can be conducted:

EXAMPLE 1: A FUTURE HAZARD REQUIRING PREVENTATIVE ACTION

During the inspection of a paper mill, the inspector inquires about future changes in wastewater treatment practices. The inspector learns that the mill's treatment plant operator is planning to treat the wastewater from the bleach plant with ferric sulfate in order to flocculate solids. The inspector measures the pH of the bleach plant wastewater and finds it near neutral, but the redox meter indicates a large positive (strongly oxidizing) reading. The inspector identifies, and mill engineers confirm, that the mill's bleaching agents are chlorine, chlorine dioxide, calcium hypochlorite, and sodium hydroxide.

If the plant operator adds ferric sulfate to the wastewater as planned, acid will be released, the wastewater pH will decrease, and chlorine and chlorine dioxide gas (which are corrosive and potentially explosive) will evolve. This is an immediate hazard to the POTW inspector and plant personnel, and requires prompt action.

The inspector should immediately inform plant personnel of the potential problem and require immediate action. The inspector might recommend an alternative approach such as wastewater dechlorination before solids removal. Sulfur dioxide addition will treat both hypochlorite and chlorous/chloric ions (from chlorine dioxide addition) in the wastewater.

EXAMPLE 2: POTENTIAL REACTIVITY HAZARDS

A battery manufacturer notifies the POTW staff that it has installed a mercury-zinc specialty battery production line and wishes to recover mercury from process line wastewater by sodium borohydride addition. The manufacturer provides treatment plant specifications to the POTW for review.

Technical references note that sodium borohydride is a powerful reducing agent, which reacts with water and water vapor to evolve hydrogen gas and sodium hydroxide. Hydrogen gas is a dangerous fire risk at the industrial user and possibly in the collection system, and will require adequate ventilation at the industry's treatment plant. The generation of sodium hydroxide (and hence a high pH) will require wastewater neutralization prior to discharge to the POTW.

During the facility inspection, the inspector carefully reviews the manufacturer's batch treatment system. Although plant engineers seem knowledgeable about the treatment process, and continuously operating spark-proof exhaust fans have been installed in the treatment area, the treatment operator seems to have minimal knowledge of potential hazards. The inspector notes that development of standard operating procedures, including safety, by industry personnel should be evaluated as a BMP for the facility.

5.2.2 Screening Industrial Discharges

Chapter 4 described the two screening techniques the POTW can use when performing Phase 2 — hazards analysis — of the problem identification process. This section presents an example of such a screening.

EXAMPLE 3: DISCHARGE SCREENING

PART A: SCREENING FOR GAS/VAPOR TOXICITY

An organic chemical manufacturing industry produces carbon tetrachloride from carbon disulfide. When POTW personnel inspect the facility, they notice a sulfide ("rotten egg") odor to the facility's discharge. Suspecting the presence of volatile contaminants at high concentrations, the inspector—using personal protective equipment—collects a zero headspace (VOA) sample of the discharge. The sample results are as follows:

Carbon disulfide	50 mg/l
Carbon tetrachloride	10 mg/l
Chloroform	1 mg/l

These levels vastly exceed the gas/vapor toxicity-based screening levels in Table 4-2, which are:

Carbon disulfide	0.06 mg/l
Carbon tetrachloride	0.03 mg/l
Chloroform	0.41 mg/l

The discharge may pose a gas/vapor toxicity hazard to industrial user personnel and the collection system crew. To find the reduction needed, the screening procedure for mixtures in Appendix B is applied. The calculated vapor phase concentrations (discharge concentration x Henry's Law Constant), ACGIH TLV-TWA criteria, and concentration criteria ratios are as follows:

Pollutant	Equilibrium Vapor Phase (mg/m^3)	TLV-TWA (mg/m^3)	Fraction of TLV-TWA
Carbon disulfide	24500	31	790.32
Carbon tetrachloride	9560	31	308.39
Chloroform	120	49	2.45
			1101.16

Assuming additive toxicity for all three compounds, the reduction required for all three compounds to alleviate the potentially gas/vapor-toxic condition is: [1 - (1/1101.16)] X 100 = 99.9% reduction.

This reduction is so large that the industry may decide to uses pollution prevention measures to eliminate the three compounds from the wastestream, rather than install new treatment technologies.

PART B: SCREENING FOR REACTIVITY

As previously discussed, the screening procedure can also be used to evaluate reactive hazards posed by a wastewater discharge—such as the flammability of carbon disulfide in the example above. Carbon disulfide is highly flammable; it has a flashpoint of -30°C (-22°F) and an LEL in air of 1.3%. Table 4- 2 shows that the screening level for carbon disulfide, based on flammability and explosivity, is 6.3 mg/l, which is well below the 50 mg/l current discharge level. The industry's discharge, then, may also pose a flammability hazard. If the industry took remedial measures to reduce carbon disulfide by 99.9%, the potential flammability hazard would be alleviated. As was the case above, the percent reduction is so large that significant pollution prevention measures are likely to be necessary.

This example illustrates how the POTW can use screening levels to identify potential gas/vapor toxicity and flammability/explosivity hazards posed by an industry's discharge. If the POTW staff were to start a program to identify all potential hazards, the basic screening methodology would remain the same but be repeated for each potential hazard identified.

5.3 SURVEYING THE POTW

The POTW can also use the approaches described above to identify potential reactivity and gas/vapor toxicity problems in its collection system and treatment plant.

5.3.1 Collection System Concerns

Although most industrial users with potentially gas/vapor-toxic discharges should have been identified by the screening processes described above, some may not have been identified because of changes in operating practices, treatment system failure, or other problems. The POTW should identify, on a sewer map, which industrial users have the highest potential to cause gas/vapor toxicity problems and the trunk lines and laterals with the greatest number of these industries. POTW staff should sample wastewaters at these locations (using appropriate protective equipment), and should use Appendix B to calculate combined gas/vapor-toxic effects for these lines. If pump stations are located on these lines, the POTW should consider installing early-warning devices such as organic vapor analyzer (OVA) meters and explosivity meters.

The POTW should be aware of new industrial facilities and facilities that are changing or adding process lines when reviewing discharge characteristics and the potential for reactivity problems. The POTW should also consider the potential for solids to have accumulated in the sewers or collection system from previous operations; such solids could be reactive with constituents in the new discharge.

The POTW may also wish to review sewer maps and grades to identify spots where the construction of the system or the surrounding topography may let vapors accumulate. Some POTWs may have already completed this evaluation. For example, the POTW may have already completed the evaluation when seeking a waiver from the sulfide standards required by the leather tanning categorical standards.

5.3.2 Treatment Plant Concerns

POTW staff should be aware of potential reactivity and gas/vapor toxicity problems within the treatment plant itself, even if such problems are not associated with normal discharges. Toxic gases or vapors are likely to be of greatest concern toward the beginning of the treatment train, such as at the headworks or in aerated tanks or grit chambers, but reactivity or gas/vapor toxicity problems may exist throughout the plant—even at sludge drying operations.

The use of chlorine at the POTW may pose a fire, explosion, or toxicity threat as well. Workers should know emergency procedures for dealing with chlorine leaks at the plant, and, in case of an emergency, the local fire department should know where chlorine storage tanks are located. As described in Section 5.2, the POTW should characterize the results of the industrial facility survey according to the nature of the hazard (is it immediate or potential?), the cause of the problem (is it the discharge itself or the configuration of the enclosure?), and appropriate remedial actions.

6. CONTROL OF POTENTIAL HAZARDS

Chapter 2 of this manual introduced the reader to working definitions of reactivity and gas/vapor toxicity, and Chapters 3 and 4 discussed how to characterize their potential hazards to the POTW and its workers. Chapter 5 described how to identify and analyze the potential health and safety hazards of reactive or gas/vapor-toxic industrial discharges. This chapter addresses how a POTW can regulate facilities that store or discharge reactive and gas/vapor-toxic chemicals, and how it can protect its own workers from the discharges from such facilities.

6.1 CONTROLLING HAZARDS AT INDUSTRIAL USERS

Historically, POTWs have used controls that respond to, rather than anticipate or prevent, industrial discharges of reactive or gas/vapor-toxic constituents. Such "after-the-fact" measures include narrative sewer use ordinance provisions that require notification after a spill has occurred. As discussed in Chapter 1, in 1990 EPA issued regulations which were developed to prevent discharges of reactive or gas/vapor-toxic compounds that may interfere with POTW operations, pass through the treatment works with inadequate treatment, or jeopardize POTW worker health and safety. This section discusses the legal authorities that must be in place and the specific provisions of industrial user permits (or other control mechanisms) that can be used to prevent or control the discharge of reactive or volatile pollutants to the POTW and that require the industrial user to provide a safe working environment for POTW employees on site. (Note: This section refers to permits, although POTWs may use other individual control mechanisms. See 40 CFR 403.8(f)(1)(iii).)

6.1.1 Legal Authority

A POTW's legal authority to control the use of its sewers and treatment systems typically derives from its local sewer use ordinance. The ordinance should describe the local pretreatment program in a manner that provides both control and flexibility: it must clearly define the minimum responsibilities of all industrial users while giving the POTW the flexibility to develop additional industry-specific controls as necessary. Additional industry-specific controls are usually enforced through industrial user permits (or other control mechanisms), and may be facility-specific where adverse health effects are apparent or suspected (see Section 6.1.2).

To ensure it can control the discharge of reactive and gas/vapor-toxic constituents to its collection system, the POTW should ascertain which authorities currently exist in its sewer use ordinance and seek authority to impose additional constraints where necessary. Section 1.1 discussed how the new specific discharge prohibitions in EPA's general pretreatment regulations [40 CFR 403.5(b)] control the discharge of reactive and gas/vapor-toxic compounds. Each municipality must adopt, in its local ordinance, or other source of authority, measures at least as stringent as the following prohibitions:

- No discharge to the POTW shall result in toxic gases or vapors within the POTW in a quantity that may cause acute worker health and safety problems; and
- No discharge to the POTW shall contain pollutants which create a fire or explosion hazard in the POTW, including, but not limited to, wastestreams with a closed-cup flashpoint less than 140° F (60° C).

In addition to adopting the new Federal prohibitions, the municipality should ensure that other provisions of the ordinance allow it the discretion to impose and enforce specific controls on its industrial users where site specific information exists. The following is an abbreviated list of the ordinance provisions which allow the POTW to institute and enforce controls specifically addressing reactive pollutants:

- Permit application requirement — The POTW should have the authority to require the user to submit all information necessary to characterize the quantity and quality of the user's discharge.
- Right to deny or condition any discharge — The POTW must have the authority to deny or limit the discharge from any nondomestic user that may, in any way, cause interference or pass through at the POTW. The POTW must also have the authority to discontinue any discharge which appears to present an imminent endangerment to the health or welfare of persons.
- Right of entry — The POTW must have access to the entire industrial facility, including all process and storage areas. Entry should not be limited to only those processes that normally generate wastestreams.
- Right to develop and enforce permit conditions — The POTW needs the authority to develop any conditions it deems appropriate to ensure compliance with the ordinance and with State and Federal laws and regulations.

EPA's *Industrial User Permitting Manual* (1989), and *Guidance for Developing Control Authority Enforcement Response Plans* (1989) further discuss legal authority and sewer use ordinances.

6.1.2 Specific Industrial User Requirements

If a POTW has identified a specific industrial user as an actual or potential source of a discharge containing reactive or gas/vapor-toxic constituents, it should place requirements in the user's control mechanism to specifically address that discharge. The POTW should also impose specific permit conditions if an inspection reveals unsafe practices or conditions at the user's facility. Chapter 5 described how to identify users with the potential to create these hazardous discharges or conditions. This chapter describes how to write permit conditions that will address such users and how to incorporate these conditions into industrial user permits or other control mechanisms. The POTW should consider three types of preventive permit conditions — management practices, data collection/studies, and discharge limitations — as well as notification requirements in the event of an accidental discharge or other permit violation.

6.1.2.1 Management Practices

Industrial user management plans are a practical way to control industrial discharges of reactive or gas/vapor-toxic pollutants and to mitigate unsafe conditions at the industrial user's facility. Such plans, incorporated into permit requirements, are an effective way to address existing or potential problems and help the industrial user understand its responsibilities to control the release of reactive or gas/vapor-toxic volatile pollutants. Slug control management plans [40 CFR 403.8(f)(2)(v)] and Total Toxic Organics (TTO) certification [40 CFR 433.12(a)] are other management plans which may be in place at an industrial user.

There are at least two ways to incorporate industrial user management plans into permits: (1) by requiring the user to develop and use a written set of procedures (on either a comprehensive basis or to address a specific problem); or (2) by imposing site- or pollutant-specific requirements (such as the removal or sealing of floor drains or containment of stored chemicals). The permit writer should be cautioned to use clear and enforceable language to identify the specific activities which must occur and when these activities must be completed.

If the industrial user is required to develop a procedures manual, a POTW engineer should carefully evaluate it when submitted to the POTW. However, it is not generally necessary or advisable for the POTW to approve the plan required by the permit. Approval of the plan may be misconstrued as a POTW sanction, even though the plan, when implemented, may not be effective in controlling the hazard.

Industrial user management plans may be grouped into two general categories: baseline and advanced. Both baseline and advanced plans should include the following types of management practices:

- A material inventory system to identify all sources and quantities of toxic materials present at the industrial facility;
- Employee training programs to help personnel of all levels understand the hazards at the facility and the mitigative and safety procedures to be followed;
- Inspection and preventive maintenance procedures to routinely inspect plant equipment and operations for potential hazards (such as possible equipment failure, or deterioration of pipes, valves, or tanks), and to correct such conditions;
- Inspections of chemical compatibility in storage areas, and the compatibility of containers with their surroundings; and
- An incident reporting system to ensure that problems are reported to proper authorities and that records are maintained regarding remediation measures taken and procedures that must be revised to prevent recurrences of problems.

Baseline management practices typically are used when information on a particular industrial site is limited but where potential problems have been identified. Baseline practices generally have the advantage of applying to all industries with similar manufacturing processes or chemical handling practices (such as industries that store or use significant amounts of organic solvents).

More advanced management plans are possible, and appropriate, when specific hazards need to be addressed:

- Prevention practices control the release of contaminants by covering, enclosing, or actually removing a hazardous substance from a site. These include construction of physical barriers to contain vapors or splashing, and the use of exhaust hoods to remove gases.
- Mitigation and detection practices are used when exposure to hazards is still possible despite prevention practices. These include use of protective clothing and direct-reading equipment by POTW staff, and the installation of hazard detectors by the industrial user.
- Response practices are adopted in case of accidental or otherwise uncontrolled releases. These include the identification of industry officials with first-line response authority, the identification of possible contaminant migration pathways, the stockpiling of sorbent/containment materials, and the placement of response and safety equipment.

The POTW may choose to require one or all of the management practices discussed above. Management practices should be individually tailored to each industrial user's own circumstances and should be incorporated into the "Special Conditions" section of the user's permit. Additional information on management practices to prevent accidental or uncontrolled discharges can be found in the EPA *Control of Slug Loadings to POTWs Guidance Manual* (1991).

6.1.2.2 Data Collection/Studies

The POTW may include monitoring and reporting requirements in its industrial users' permit beyond the routine compliance monitoring for discharge limits. Such special monitoring may be used to identify and set limits for pollutants known to be present, and can be used to evaluate whether a pollutant-specific management plan is necessary or whether facility-specific limits should be set based on the facility's ability to segregate or treat the wastestream in question.

The POTW may also require the industrial user to undertake special data collection activities in cases where problems such as worker health effects have been identified. In such a case the POTW might require special monitoring of both the industry's wastestream and the sewer air space at the point of connection to the sewer line to find any cause/effect relationship between the facility's discharge and the perceived health hazard. The industrial user may be required through its permit to conduct this study and to submit a report describing the conditions monitored and the actions to be taken to alleviate those conditions. In all cases, the permit writer must ensure that these monitoring and reporting requirements are incorporated into the permit as enforceable conditions. Likewise, where the industry proposes solutions to alleviate the hazardous situation, the POTW should incorporate the recommendations into an enforceable compliance schedule with fixed milestone dates and reporting requirements.

6.1.2.3 Facility Specific Discharge Limits

POTWs must apply the general and specific prohibitions to all industrial users [40 CFR 403.5(c)]. In order to ensure compliance with the prohibitions, the POTWs may find it necessary to set facility specific effluent limits for certain pollutants which have been identified as actual or potential hazards to the POTW or its employees.

If discharge monitoring data is available from a known event where an industrial discharge created a gas/vapor-toxic hazard, the POTW permit writer should use this monitoring data when establishing a discharge limit. If discharge monitoring data is not available, the permit writer may consider using the screening method discussed in Section 4.1 as a starting point for setting discharge limits. The permit writer should be aware of the limitations of the gas/vapor-toxicity screening method discussed in Section 4.1.2 and Appendix B. One of the most significant limitations of the screening method is that it does not take into account possible synergistic effects which could occur when the wastewater constituents combine. Section 4.2.3 of the *Guidance Manual on the Development and Implementation of Local Discharge Limitations Under the Pretreatment Program* (December 1987) discusses estimating the effects of mixed discharges.

The reactivity prohibition [40 CFR 403.5(b)(1)] defined reactive pollutants to include wastestreams with a closed-cup flashpoint less than 140°F or 60°C. Unlike the prohibition of gas/vapor-toxic pollutants, compliance with the flashpoint condition can be directly measured in the industrial user's wastestream. Direct measurement is the easiest method for determining compliance with flashpoint condition of this mandatory prohibition. The approved test methods are specified in 40 CFR 261.21.

6.1.3 OSHA Exposure Limits

The POTW may also consider using OSHA's Permissible Exposure Limits (PELs), to impose controls on gas/vapor toxicity. OSHA PELs were originally promulgated in 1971 based on 1968 ACGIH TLVs and other Federal and industry standards, and they continue to be revised and strengthened. OSHA has published PELs (at 29 CFR 1910.1000 - 1910.1101) for about 600 substances, including benzene, vinyl chloride, lead, acrylonitrile, asbestos, dibromochloropropane, and inorganic arsenic. OSHA standards also exist for 13 carcinogens for which zero inhalation exposure is allowed.

Since OSHA is a regulatory agency, its PELs are legally enforceable by OSHA or OSHA-approved State programs and apply to most private industries and all Federal agencies. Depending on State law, the PELs may also apply to State and local employees. Table 6-1 lists the 23 States and 2 Territories with OSHA-approved occupational safety and health programs. To determine whether PELs apply to its workers, the POTW should contact the appropriate State office listed in Appendix G.

OSHA PELs are based on both health effects and the economic and technical feasibility of achieving the exposure limits. Other exposure limits, such as the NIOSH Recommended Exposure Limits (RELs) and the ACGIH TLVs discussed in Chapter 4, are based solely on preventing adverse health effects. Therefore the more conservative exposure limit should be used as the controlling exposure limit whenever possible. Exposure limits can be used to develop industrial discharge screening levels using the procedures discussed in Chapter 4 and Appendix B.

TABLE 6-1. STATES AND TERRITORIES WITH OSHA-APPROVED WORKER HEALTH AND SAFETY PROGRAMS

Alaska
Arizona
California
Connecticut
Hawaii
Indiana
Iowa
Kentucky
Maryland
Michigan
Minnesota
Nevada
New Mexico
New York
North Carolina
Oregon
Puerto Rico
South Carolina
Tennessee
Utah
Vermont
Virgin Islands
Virginia
Washington
Wyoming

6.2 CONTROLLING HAZARDS AT THE POTW

Regardless of which controls are used to prevent reactive or gas/vapor-toxic discharges from its industrial users, the threat of an accidental spill into the sewer system cannot be overlooked. For this reason, the POTW's inspectors, maintenance personnel, and treatment plant operators should be aware of potential hazards and have protective equipment available to mitigate these hazards. The POTW also should develop a comprehensive health and safety program that identifies dangerous tasks and situations, provides training for field and POTW crews that might be exposed to these situations, and ensures that POTW staff have detection devices and protective equipment to safeguard them when hazardous situations occur. EPA's Office of Emergency and Remedial Response has published Standard Operating Safety Guides which provide detailed information on reducing employee exposure to chemical hazards. The EPA *Control of Slug Loadings to POTWs Guidance Manual (1991)* discusses management practices and other procedures to prevent, control, and respond to accidental and otherwise uncontrolled discharges to POTWs.

Reactive or gas/vapor-toxic chemicals may be present throughout the POTW — not only at the treatment plant, but also at pumping stations and points within the collection system. To prevent worker exposure to such chemicals, the POTW should develop a comprehensive worker health and safety program that identifies potentially hazardous conditions and sets strict protocols for workers under these conditions. The Water Environment Federation's *Manual of Practice on Safety and Health in Wastewater Systems* (1983) recommends that a written program consist of:

- Statement of policy, including major program objectives;
- List of work practice standards, rules, and regulations;
- List of assignments of responsibilities;
- Policy for enforcement of safety rules and disciplinary action;
- Means for detecting and correcting violations;
- Procedures for reporting and investigating accidents;
- Procedures for an emergency response system;
- Procedures for using new chemicals; and
- Procedures for documenting plant actions.

Each of the program elements above should include provisions to protect workers from gas/vapor toxicity and reactive chemicals.

6.2.1 Data Collection and Hazard Identification

The health and safety program should contain a hazard identification process that identifies potentially hazardous tasks and situations to which POTW workers could be exposed during daily work activities. Using the data collection and evaluation activities suggested in Section 5.1 of this manual, the hazard identification process should include every stage of wastewater generation, conveyance, and treatment—including the following:

- Detailed inspections of industrial facilities, including production and storage areas;
- Inspection and monitoring of industrial pretreatment processes;
- Inspection and monitoring within the industry's wastewater collection system;
- Inspection and monitoring within the POTW's collection system;
- Operation and maintenance of pump stations; and
- Operation and maintenance activities at the POTW treatment plant.

After identifying potential hazards, the POTW should outline them in a job safety analysis report which should be made available to all POTW employees working in the areas listed above. The job safety analysis outline should clearly which precautions and special equipment might be necessary when undertaking these tasks.

6.2.2 Worker Training

After identifying safe work procedures for POTW employees who might be exposed to reactive or gas/vapor-toxic industrial discharges, it is essential to train employees in these procedures. Central to any successful health and safety program is a clear mandate from the POTW administration that safety is a primary objective, that unsafe practices and conditions will not be tolerated, and that no employee should engage in any tasks without proper training to address the potential hazards of that task. This policy must be made clear to all POTW workers. The POTW should take follow-up actions, including disciplinary action, where violations of the policy occur.

An effective employee training program combines classroom discussions, on-the-job training, and practical exercises in emergency procedures. All employees, regardless of their work activities, should be trained in the following:

- The POTW's mandated health and safety policy;
- Basic requirements of the health and safety program;
- The employees' responsibility to report all unsafe working conditions to supervisors;
- Hazard identification;
- Accident reporting responsibilities;
- The operation and testing of safety equipment; and
- Emergency response procedures.

The POTW should provide additional, more specific, training to each worker who might be exposed to toxic gases and vapors, or reactive chemicals during inspection and monitoring duties. Each worker should be required to review the job safety analysis report for the industry to be visited, and be trained in use of detection equipment or protective gear that may be needed to perform the required tasks. Each employee who may be exposed to hazardous work conditions related to reactivity or gas/vapor toxicity should be trained in the following areas:

- Comprehensive knowledge of the POTW's health and safety program;
- Job safety analysis reports for each task or situation that might be encountered during normal duties;
- Use of vapor monitoring equipment, where applicable; and
- Use of protective clothing and equipment, where applicable.

6.2.3 Hazard Detection Equipment

POTW workers who inspect and monitor facilities where they may be exposed to toxic gases or vapors, should be outfitted with personal equipment designed to detect potential health hazards (which is readily available from safety and mining equipment manufacturers). This equipment should be able to detect all three types of hazardous atmospheres -- oxygen-deficient, combustible, and toxic. Ideally, such equipment would be capable of monitoring the atmosphere before a worker enters a potentially hazardous area (such as a chemical storage areas) as well as continuous monitoring while workers are in the work area. Of less general use, but still valuable to a health and safety program, are instruments designed to detect specific hazards, including oxygen meters, combustible gas detectors, hydrogen sulfide detectors, chlorine detectors, and sulfur dioxide detectors.

The POTW also may wish to use permanent gas detection equipment, installed at critical points within the collection system and the treatment plant, to provide early warning of potential problems and alert field personnel of potential hazards in or near these areas. Chapter 3 describes the capabilities and limitations of these instruments in more detail.

6.2.4 Personal Protective Equipment

Whenever source control, engineering controls, and safe work practices are either infeasible or insufficient to ensure worker protection, personal protective equipment (PPE) should be used to reduce exposure. PPE consists of respirators and protective clothing, and should be used with the air monitoring devices described in section 6.2.3.

POTW staff should be trained in the use of PPE, including the following:

- Capabilities and limitations of particular PPE ensembles;
- The consequences of not following instructions for checking, fitting, and using PPE;
- Cleaning, inspecting, maintaining, and repairing PPE; and
- Human factors affecting PPE performance.

6.2.4.1 Respirators

A respirator consists of a faceplate connected to either an air purifying device or a source of supplied air. The relative advantages of air-purifying and supplied-air respirators are outlined in Appendix H.

Air-purifying respirators are used in atmospheres containing known concentrations of specific chemicals. Canisters and cartridges in such respirators attach to the faceplate and remove specific airborne contaminants (particulates, organic vapors, acids, bases, gases, or fumes) by filtration, absorption, adsorption, or chemical reaction. Air purifying respirators may not be used in atmospheres with:

- Oxygen deficiencies;
- Immediately dangerous to life and health (IDLH) concentrations; or
- Contaminants having inadequate odor warning properties.

A supplied-air respirator (self-contained breathing apparatus, or SCBA) must be used if the above conditions exist. Generally, supplied-air respirators are more appropriate for POTW workers because of the large number of pollutants present and the limited availability of monitoring equipment that can identify specific contaminants.

The selection of a respirator depends on the hazards expected at the site and the nature and duration of the tasks to be performed. At a minimum, each POTW employee working in an area where toxic gases or vapors could occur should be equipped with an escape SCBA unit. All employees expected to use respirators should be fit-tested and trained in use and maintenance, with annual refresher training.

6.2.4.2 Protective Clothing

Protective clothing shields skin from injury caused by direct contact with chemical splashes or vapors. The extent of such protection varies according to the type of material used, since no material protects against all chemicals or combinations of chemicals. If possible, the POTW should choose the protective clothing ensemble that offers the highest protection possible against chemical hazards anticipated at the POTW or other areas where POTW workers might encounter hazards. When direct contact with known chemicals is anticipated, the clothing manufacturer should be contacted about the protective properties. Note that with all types of materials tears or penetration along seam lines, zippers, or imperfections may occur.

Appendix I lists the effectiveness of various protective materials against chemical degradation. For more information on the protectiveness of clothing types, the POTW should contact the manufacturer or consult ACGIH's 1985 *Guidelines for the Selection of Chemical Protective Clothing* (Second Edition). Other factors to consider when selecting protective material are:

- Durability;
- Flexibility;
- Temperature effects;
- Compatibility with other equipment; and
- Duration of use.

Appendix J describes various types of protective clothing, including head, foot, hand, eye, face, and ear protection. At a minimum, a POTW worker engaged in normal work activities (that is, without exposure to toxic gases, fumes, or vapors) requires the following:

- Tyvek or cotton overalls;
- Polyurethane or latex gloves;
- Safety glasses or goggles;
- Steel-toed shoes; and
- Safety helmet.

Protective clothing ensembles should be tailored to hazards known to exist at the POTW and should be reevaluated whenever hazardous conditions change.

APPENDIX A

LOWER EXPLOSIVE LIMITS

APPENDIX A

LOWER EXPLOSIVE LIMITS

Explosive Compound	Lower Explosive Limit (% by volume)	Explosive Compound	Lower Explosive Limit (% by volume)
Paraffin hydrocarbons		Alcohols	
Methane	5.0	Methyl alcohol	6.7
Ethane	3.0	Ethyl alcohol	3.3
Propane	2.1	Allyl alcohol	2.5
Butane	1.8	n-Propyl alcohol	2.2
Isobutane	1.8	Isopropyl alcohol	2.2
Pentane	1.4	n-Butyl alcohol	1.7
Isopentane	1.4	n-Amyl alcohol	1.4
2,2-Dimethylpropane	1.4	Isoamyl alcohol	1.4
Hexane	1.2		
Heptane	1.0	Aldehydes	
2,3-Dimethylpentane	1.1	Acetaldehyde	4.0
Octane	0.95	Crotonaldehyde	2.1
Nonane	0.85	Paraldehyde	1.3
Decane	0.75	Propionaldehyde	2.9
Olefins		Ethers	
Ethylene	2.7	Methyl ethyl ether	2.2
Propylene	2.4	Diethyl ether	1.9
Butene-1	1.6	Divinyl ether	1.7
Butene-2	1.7	Tetrahydrofuran	2.0
Amylene	1.4		
		Ketones	
Aromatics		Acetone	2.6
Benzene	1.3	Acetophenone	1.1
Ethylbenzene	1.0	Methyl ethyl ketone	1.9
Cumene	0.9	Methyl propyl ketone	1.6
Toluene	1.2	Methyl butyl ketone	1.2
Xylene (o.m.p)	1.1		
		Acids	
Cyclic Hydrocarbons		Acetic acid	5.4
Cyclopropane	2.4	Adipic acid	1.6
Cyclohexane	1.3	Hydrogen cyanide	5.6
Methylcyclohexane	1.1	Hydrogen sulfide	4.0
		Esters	
		Methyl formate	5.0
		Ethyl formate	2.8
		Methyl acetate	3.2

Source: Adapted from "Hazards Evaluation and Risk Control Services Data Guide Bulletin HE-109A," Hercules Corp., 1982

Explosive Compound	Lower Explosive Limit (% by volume)	Explosive Compound	Lower Explosive Limit (% by volume)
Esters (Continued)		Chlorides	
Ethyl acetate	2.2	Methyl chloride	7.0
Propyl acetate	1.8	Ethyl chloride	3.8
Isopropyl acetate	1.7	Propyl chloride	2.4
Butyl acetate	1.4	Butyl chloride	1.8
Amyl acetate	1.0	Allyl chloride	2.9
		Amyl chloride	1.6
Hydrogen		Vinyl chloride	3.6
Hydrogen	4.0	Propylene dichloride	3.1
		Chlorobenzene	1.4
Nitrogen Compounds			
Ammonia	15.0	Bromides	
Aniline	1.2	Methyl bromide	10.0
Cyanogen	6.6	Allyl bromide	2.7
Pyridine	1.8		
Ethyl nitrate	4.0	Amines	
Ethyl nitrite	3.0	Methyl amine	4.2
		Ethyl amine	3.5
Oxides		Dimethyl amine	2.8
Carbon monoxide	12.5	Propyl amine	2.0
Ethylene oxide	3.6	Diethyl amine	1.8
Propylene oxide	2.8	Trimethyl amine	2.0
Dioxan	2.0	Triethyl amine	1.2
Sulfides		Fuels	
Carbon disulfide	1.3	Gasoline	1.2
Dimethyl sulfide	2.2	Jet fuel JP-4	1.3
Hydrogen sulfide	4.0	Hydrazine	4.7
Ethyl mercaptan	2.8		
		Solvents	
		Butyl cellosolve	1.1
		Methyl cellosolve	2.5
		Methyl cellosolve acetate	1.7
		N,N-Dimethyl formamide	1.8
		Turpentine	0.7

Source: Adapted from "Hazards Evaluation and Risk Control Services Data Guide Bulletin HE-109A," Hercules Corp., 1982

APPENDIX B

SCREENING TECHNIQUE TO IDENTIFY GAS/VAPOR TOXIC DISCHARGES

APPENDIX B

SCREENING TECHNIQUE TO IDENTIFY GAS/VAPOR TOXIC DISCHARGES

To identify industrial user (IU) discharges which could potentially generate gas/vapor toxic conditions in sewer atmospheres, an IU discharge screening procedure should be established. This screening procedure would identify gas/vapor toxic pollutant discharges warranting control through the imposition of local limits and/or other IU requirements.

The screening technique discussed in this appendix entails: (1) identifying gas/vapor toxicity criteria; (2) conversion of gas/vapor toxicity criteria into corresponding IU discharge screening levels; and (3) comparison of these screening levels with actual IU discharge levels. Discharges above the specified screening level may warrant further investigation by the POTW.

The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value-time weighted averages (TLV-TWAs) serve as a reference for gas/vapor toxicity from which IU discharge screening levels can be calculated. The ACGIH TLV-TWA gas/vapor toxicity levels are the vapor phase concentrations of volatile organic compounds to which nearly all workers may be repeatedly exposed, over an 8-hour workday and a 40-hour work week, without adverse effect. In general, POTW workers are not exposed for an extended period of time to sewer atmospheres contaminated with volatile compounds, so the use of TLV-TWA concentrations as a basis for developing IU discharge screening levels can be considered a conservative practice.

The calculation of screening levels that are based on gas/vapor toxicity involves the following four steps:

1. Identify the ACGIH TLV-TWA concentration of the pollutant of concern. ACGIH TLV-TWA concentrations (mg/m^3) for several representative organic pollutants are presented in the second column of Table B-1.
2. Identify the Henry's Law Constant for the pollutant of concern. Table B-2 presents the Henry's Law Constants for several volatile organics.

3. Convert the Henry's Law Constant to the appropriate units. In order to calculate screening levels based on ACGIH TLV-TWA concentrations, the Henry's Law Constant must be expressed in terms of $(\text{mg/m}^3)/(\text{mg/l})$. The following equation should be used to convert the Henry's Law Constant expressed in units of atm m^3/mol to the equivalent constant expressed in $(\text{mg/m}^3)/(\text{mg/l})$:

   $$H_C = H_A \times \frac{1 \times 10^6}{(R)(T)}$$

   where: H_C = Henry's Law Constant, $(\text{mg/m}^3)/(\text{mg/l})$

   H_A = Henry's Law Constant, (atm m^3/mol)

   R = Ideal gas constant, 0.08206 (atm l/mol K)

   T = Temperature corresponding to vapor pressure* used to derive H_A (See Table B-2), K

   Henry's Law Constants expressed in $(\text{mg/m}^3)/(\text{mg/l})$ are presented for several volatile organics in the third column of Table B-1.

4. Calculate the IU discharge screening level from the Henry's Law expression:

   $$C_{LVL} = \frac{C_{VAP}}{H}$$

   where

   C_{LVL} = Discharge screening level, mg/l

   C_{VAP} = ACGIH TLV-TWA, mg/m^3

   H = Henry's Law Constant, $(\text{mg/m}^3)/(\text{mg/l})$

   Screening levels derived by this equation should be compared with actual IU discharge levels measured at the IU's sewer connection. This method for deriving screening levels assumes instantaneous volatilization of pollutant to the sewer atmosphere (i.e., instantaneous attainment of equilibrium) and does not take into account dilution of IU wastewater within the collection system. Screening levels should be used to identify gas/vapor toxic pollutants for control.

Screening levels calculated from ACGIH TLV-TWA data address only the toxicities of individual compounds. The screening levels presented in Table B-1 do not address the generation of toxic concentrations of gases that are produced from the <u>mixture</u> of chemicals in the wastestream. The following procedure allows the POTW to predict the potential vapor toxicity associated with the discharge of a mixture of volatile organic compounds:

1. Analyze the industrial user's wastewater discharge for volatile organics. The following are hypothetical monitoring data:

Pollutant	Discharge Level, mg/l
Benzene	0.1
Toluene	0.9
Chlorobenzene	2.2

Pollutant	Discharge Level, mg/L
1,2-Dichlorobenzene	3.57
1,4-Dichlorobenzene	3.39

Although these discharge levels are all below the corresponding screening levels presented in Table B-1, the POTW should determine whether the simultaneous discharge of the five pollutants could result in a gas/vapor toxic mixture within the sewer.

2. Use Henry's Law,

$$C_{VAPOR} = H \times C_{DISCHARGE}$$

where

C_{VAPOR} = Vapor phase concentration, mg/m^3

H = Henry's Law Constant, (mg/m^3)/(mg/l)

$C_{DISCHARGE}$ = Discharge level, mg/l,

to calculate the equilibrium vapor phase concentration of each pollutant:

Pollutant	Discharge Level, mg/l	Henry's Law Constant (mg/m^3)/(mg/l)	Equilibrium Vapor Phase Concentration, mg/m^3
Benzene	0.1	225	22.5
Toluene	0.9	277	249.3
Chlorobenzene	2.2	149	327.8
1,2-Dichlorobenzene	3.57	80.2	286.3
1,4-Dichlorobenzene	3.39	127	430.5

3. Express the equilibrium vapor phase concentrations (above) as fractions of the corresponding TLV-TWA's:

Pollutant	Equilibrium Vapor Phase Concentration, mg/m^3	TLV-TWA mg/m^3	Fraction of TLV-TWA
Benzene	22.5	32	0.70
Toluene	249.3	377	0.66
Chlorobenzene	327.8	345	0.95
1,2-Dichlorobenzene	286.3	301	0.95
1,4-Dichlorobenzene	430.5	451	0.96
			4.22

*Assume T = 298.15K if data not available.

4. Sum the fractions of the TLV-TWAs. In the example above, the sum of the TLV-TWA fractions equals 4.22.

   If the compounds in question are assumed to possess additive gas/vapor toxicities when mixed, then if the sum of the TLV-TWA fractions is greater than 1.00, a potentially gas/vapor toxic condition exists.

5. If the sum of the TLV-TWA fractions is greater than 1.00, calculate the percentage by which the concentrations of the compounds need to be reduced in order to avoid a potentially gas/vapor toxic condition. Using the example values:

$1 - \frac{1}{4.22} \times 100 = 76\%$ reduction of the discharge of all five pollutants to alleviate the potentially gas/vapor toxic condition (assuming additive toxicities and the applicability of the Henry's Law Constants).

TABLE B-1. DISCHARGE SCREENING LEVELS BASED UPON GAS/VAPOR TOXICITY

Compound	ACGIH TLV-TWA mg/m^3	Henry's Law Constant* (mg/m^3)/(mg/l)	Screening Level mg/l
Acrylonitrile	4.3	3.62	1.19
Aldrin	0.25	0.65	0.38
Benzene	32.0	225	0.14
Bis(2-chloromethyl)ether	0.0044	8.58	0.0005
Bromoform	5.2	22.0	0.24
Bromomethane	20.0	8189	0.002
Carbon disulfide	31.0	490	0.06
Carbon tetrachloride	31.0	956	0.03
Chlordane	0.5	0.39	1.27
Chlorobenzene	345	149	2.31
Chloroethane	2600	6152	0.42
Chloroform	49.0	120	0.41
Chloromethane	103	15796	0.07
1,2-Dichlorobenzene	301	80.2	3.75
1,4-Dichlorobenzene	451	127	3.55
Dichlorodifluoromethane	4950	121801	0.04
1,1-Dichloroethane	810	177	4.58
trans-1,2-Dichloroethylene	793	2785	0.28
1,2-Dichloropropane	347	96.0	3.62
1,3-Dichloropropene	4.5	55.3	0.08
Dieldrin	0.25	0.02	13.0
Diethyl phthalate	5.0	0.05	107
4,6-Dinitro-o-cresol	0.2	0.06	10.78
Dinitrotoluene	1.5	0.21	7.21
Endrin	0.1	0.02	4.9
Ethyl benzene	434.0	274	1.59
Ethylene dichloride	40.0	38.0	1.05
Formaldehyde	1.2	20.8	0.06
Heptachlor	0.5	163	0.003
Hexachloro-1,3-butadiene	0.21	1064	0.0002
Hexachloroethane	9.7	104	0.093
Hexachlorocyclopentadiene	0.11	0.0008	658

TABLE B-1. DISCHARGE SCREENING LEVELS BASED UPON GAS/VAPOR TOXICITY

Compound	ACGIH TLV-TWA mg/m^3	Henry's Law Constant* (mg/m^3)/(mg/l)	Screening Level mg/l
Methyl chloride	103	1798	0.06
Methyl ethyl ketone	590.0	2.37	249
Methylene chloride	174.0	84.4	2.06
Naphthalene	52.0	19.62	2.65
Nitrobenzene	5.0	0.53	9.41
Pentachlorophenol	0.5	0.11	4.37
Phenol	19.0	0.02	1024
1,1,2,2-Tetrachloroethane	6.9	15.5	0.44
Tetrachloroethylene	339.0	636	0.53
Toluene	377.0	277	1.36
Toxaphene	0.5	200	0.003
1,2,4-Trichlorobenzene	37.0	94.0	0.39
1,1,1-Trichloroethane	1910.0	1226	1.55
1,1,2-Trichloroethane	55.0	48	1.15
Trichloroethylene	269.0	378	0.71
Trichlorofluoromethane	5620.0	4573	1.23
Vinyl chloride	13.0	4251	0.0003
Vinylidene chloride	20.0	7766	0.003
Aroclor 1242	1.0	80.9	0.01
Aroclor 1254	0.5	106	0.005

*Henry's Law Constant (mg/m^3)/(mg/l) taken from Table B-2.

TABLE B-2. HENRY'S LAW CONSTANTS EXPRESSED IN ALTERNATE UNITS

Compound	**Henry's Law Constant***			**Temperature (°C)**	
	(atm m^3)/mol	**(mol/m^3)(mg/l)**	**(mg/m^3)(mg/l)**	**Vapor Pressure**	**Solubility**
Acenaphthylene	1.45 x 10^{-3}	3.96 x 10^{-4}	60.3	20	25
Acrylonitrile	8.80 x 10^{-5}	6.83 x 10^{-5}	3.62	22.8	25
Aldrin	1.60 x 10^{-5}	1.79 x 10^{-6}	0.65	--	--
Anthracene	1.25 x 10^{-3}	2.87 x 10^{-4}	51.1	25	25
Benzene	5.50 x 10^{-3}	2.88 x 10^{-3}	225	25	25
Bis(2-Chloromethyl)Ether	2.1 x 10^{-4}	7.46 x 10^{-5}	8.58	--	--
Bromoform	5.32 x 10^{-4}	8.41 x 10^{-5}	22	--	--
Bromomethane	1.97 x 10^{-1}	8.62 x 10^{-2}	8189	20	20
Carbon disulfide	1.20 x 10^{-2}	6.44 x 10^{-3}*	490*	--	--
Carbon tetrachloride	2.30 x 10^{-2}	6.21 x 10^{-3}	956	20	20
Chlordane	9.63 x 10^{-6}	9.61 x 10^{-7}	0.39	--	--
Chlorobenzene	3.58 x 10^{-3}	1.32 x 10^{-3}	149	20	25
Chloroethane	1.48 x 10^{-1}	9.54 x 10^{-2}	6152	20	20
Chloroform	2.88 x 10^{-3}	1.00 x 10^{-3}	120	20	20
Chloromethane	3.80 x 10^{-1}	3.13 x 10^{-1}*	15796	20	20
1,2-Dichlorobenzene	1.93 x 10^{-3}	5.46 x 10^{-4}	80.2	20	20
1,3-Dichlorobenzene	3.61 x 10^{-3}	1.00 x 10^{-3}	148	25	25
1,4-Dichlorobenzene	3.10 x 10^{-3}	8.62 x 10^{-4}	127	25	25
Dichlorodifluoromethane	2.98 x 10^{0}	1.01 x 10^{0}	121801	25	25
1,1-Dichloroethane	4.26 x 10^{-3}	1.79 x 10^{-3}	177	20	20
1,2-Dichloroethylene	1.10 x 10^{-3}	4.64 x 10^{-4}	44.96	--	--
trans-1,2-Dichloroethylene	6.70 x 10^{-2}	2.87 x 10^{-2}	2785	20	20
1,2-Dichloropropane	2.31 x 10^{-3}	8.50 x 10^{-4}	96.0	20	20
1,3-Dichloropropene	1.33 x 10^{-3}	4.98 x 10^{-4}	55.3	20	25
Dieldrin	4.58 x 10^{-7}	4.91 x 10^{-8}	0.02	--	--
Diethyl Phthalate	1.14 x 10^{-6}	2.10 x 10^{-7}	0.05	--	--
4,6-Dinitro-o-Cresol	1.4 x 10^{-6}	2.89 x 10^{-7}	0.06	--	--
Dinitrotoluene	5.09 x 10^{-6}	1.14 x 10^{-6}	0.21	--	--
Endrin	5.00 x 10^{-7}	5.37 x 10^{-8}	0.02	--	--
Ethyl benzene	6.60 x 10^{-3}	2.58 x 10^{-3}	274	20	20
Ethylene dichloride	9.14 x 10^{-4}	3.84 x 10^{-4}	38.0	20	20

*A temperature of 25°C was assumed in Henry's Law calculations.

TABLE B-2. HENRY'S LAW CONSTANTS EXPRESSED IN ALTERNATE UNITS

Compound	Henry's Law Constant*			Temperature (°C)	
	(atm m^3)/mol	(mol/m^3)(mg/l)	(mg/m^3)(mg/l)	Vapor Pressure	Solubility
Formaldehyde	5.1×10^{-4}	6.94×10^{-4}	20.8	--	--
Heptachlor	4.00×10^{-3}	4.38×10^{-4}	163	25	25
Hexachloro-1,3-butadiene	2.56×10^{-2}	4.08×10^{-3}	1064	20	20
Hexachlorocyclopentadiene	1.6×10^{-2}	2.40×10^{-3}	0.0008	--	--
Hexachloroethane	2.49×10^{-3}	4.37×10^{-4}	104	20	22
Methyl Chloride	4.4×10^{-2}	3.56×10^{-2}	1798	--	--
Methyl ethyl ketone	5.80×10^{-5}	3.29×10^{-5}*	2.37*	--	--
Methylene chloride	2.03×10^{-3}	9.93×10^{-4}	84.4	20	25
Naphthalene	4.80×10^{-4}	1.53×10^{-4}	19.62	--	--
Nitrobenzene	1.30×10^{-5}	4.32×10^{-6}	0.53	--	--
Pentachloroethane	2.17×10^{-3}	4.38×10^{-4}*	88.7*	--	--
Phenol	4.54×10^{-7}	1.97×10^{-7}	0.02	--	--
1,1,2,2-Tetrachloroethane	3.80×10^{-4}	9.25×10^{-5}	15.5	--	--
Tetrachloroethylene	1.53×10^{-2}	3.83×10^{-3}	636	20	20
Toluene	6.66×10^{-3}	3.01×10^{-3}	277	20	25
1,2,4-Trichlorobenzene	2.30×10^{-3}	5.18×10^{-4}	94.0	25	25
1,1,1-Trichloroethane	3.00×10^{-2}	9.19×10^{-3}	1226	25	25
1,1,2-Trichloroethane	1.17×10^{-3}	3.60×10^{-4}	48	--	--
Trichloroethylene	9.10×10^{-3}	2.88×10^{-3}	378	20	20
Trichlorofluoromethane	1.10×10^{-1}	3.33×10^{-2}	4573	20	20
Vinyl chloride	1.04×10^{-1}	6.80×10^{-2}	4251	25	25
Vinylidene chloride	1.90×10^{-1}	8.01×10^{-2}	7766	25	20

*A temperature of 25°C was assumed in Henry's Law calculations.

TABLE B-2. HENRY'S LAW CONSTANTS EXPRESSED IN ALTERNATE UNITS

Compound	**Henry's Law Constant***			**Temperature (°C)**	
	(atm m^3)/mol	**(mol/m^3)(mg/l)**	**(mg/m^3)(mg/l)**	**Vapor Pressure**	**Solubility**
Aroclor 1242	1.98 x 10^{-3}**	3.14 x 10^{-4}***	80.9	25	25
Aroclor 1248	3.60 x 10^{-3}**	5.04 x 10^{-4}***	147	25	25
Aroclor 1254	2.60 x 10^{-3}**	3.26 x 10^{-4}***	106	25	25
Aroclor 1260	7.40 x 10^{-1}**	8.38 x 10^{-2}***	30246	25	25

**Source: U.S. EPA "Aquatic Fate Process Data for Organic Priority Pollutants." EPA 440/4-81-014
***The molecular weights of the following compounds were used to represent the molecular weights of Aroclor mixtures in Henry's Law calculations:

Aroclor 1242	Trichlorobiphenyl
Aroclor 1248	Tetrachlorobiphenyl
Aroclor 1254	Pentachlorobiphenyl
Aroclor 1260	Hexachlorobiphenyl

APPENDIX C

SCREENING TECHNIQUE TO IDENTIFY FLAMMABLE/EXPLOSIVE DISCHARGES

APPENDIX C

SCREENING TECHNIQUE TO IDENTIFY FLAMMABLE/EXPLOSIVE DISCHARGES

This appendix describes a screening procedure that will help identify flammable/explosive pollutant discharges warranting control through the imposition of local limits and/or other IU requirements.

A variety of screening procedures to identify flammable/explosive pollutant discharges have been developed. This section describes one approach, which entails:

1. Conversion of lower explosive limit (LEL) data into corresponding IU discharge screening levels, and
2. Comparison of these screening levels with actual IU discharge levels. Discharges that exceed screening levels may warrant further investigation by the POTW (e.g., monitoring and sampling to determine source).

The calculation of LEL-based screening levels is a five-step process:

1. Determine the LEL of the pollutant of concern. LELs are typically expressed as percent (volume/volume)-in-air concentrations. LELs for several volatile organics are presented in the second column of Table C-1.
2. Convert 10% of the compound's LEL concentration to a vapor phase concentration (C_{VAP}) expressed in mol/m^3 (third column of Table C-1):

$$C_{VAP} = (0.10 \text{ X LEL}) \frac{P}{(R)(T)} \text{ x } 10$$

where

C_{VAP} =LEL expressed as a vapor phase concentration, mol/m^3
LEL =Lower explosive limit, percent (volume/volume)
P =Total pressure, 1 atmosphere (atm) (assumed)
R =Ideal gas constant, 0.08206 atm L/mol K
T =Temperature, 298.15 K (assumed).

3. Determine the Henry's Law Constant for the pollutant of concern. Since the screening level is to be expressed as a concentration in water and the LEL is a vapor phase concentration, a partitioning constant is needed to convert LEL values to corresponding water phase discharge levels. The Henry's Law Constant serves this function for pollutants present in low concentration, as are normally encountered in IU discharges. Table C-2 presents Henry's Law Constants (in various units) for several organics.
4. Convert the Henry's Law Constant to the appropriate units. The Henry's Law Constants presented in Table B-2 are expressed in terms of three different units:

- (atm m^3)/mol
- (mol/m^3)/(mg/l)
- (mg/m^3)/(mg/l).

In the literature, Henry's Law Constants are most commonly expressed in terms of pressure [(atm m^3)/(mol)]. To derive LEL-based screening levels, however, the Henry's Law Constant must be expressed in terms of (mol/m^3)(mg/l). The following equation should be used to convert the Henry's Law Constant expressed in units of (atm m^3)/(mol) to the equivalent constant expressed in (mol/m^3)/(mg/l):

$$H_B = H_A \times \frac{1 \times 10^3}{(MW)(R)(T)}$$

where:

H_B = Henry's Law Constant, (mol/m^3)/(mg/l)

H_A = Henry's Law Constant, (atm m^3)/mol)

MW = Molecular weight, g/mol

R = Ideal gas constant, 0.08206 (atm l/mol K)

T = Temperature corresponding to vapor pressure* used to derive H_A (see Table C-1), K

Henry's Law Constants expressed as (mol/m^3)(mg/L) are presented for several volatile organics in the fourth column of Table C-1.

5. Calculate the IU discharge screening level using the Henry's Law expression (fifth column of Table C-1):

$$C_{LVL} = \frac{C_{VAP}}{H}$$

where

C_{LVL} = Discharge screening level, mg/l

C_{VAP} = LEL expressed as a vapor phase concentration, mol/m^3

H = Henry's Law Constant (mol/m^3)/(mg/l)

Screening levels derived by this equation should be compared with actual IU discharge levels measured at the IU's sewer connection. This method for deriving screening levels assumes instantaneous volatilization of the pollutant to the sewer atmosphere (i.e., instantaneous attainment of equilibrium) and does not take into account dilution of IU wastewater within the collection system.

Table C-1 presents LEL-based screening levels, calculated using the method described above, for several organics. The screening levels should be used to identify flammable/explosive pollutants for control.

---

*Assume T = 298.15 K if data not available.

TABLE C-1. DISCHARGE SCREENING LEVELS BASED ON EXPLOSIVITY

Compound	LEL %	C_{VAP}(mol/m^3)*	H(mol/m^3)/(mg/L)**	C_{LVL}(mg/L)***
Acrylonitrile	3.0	0.123	6.84×10^{-5}	1794
Benzene	1.4	0.057	2.88×10^{-3}	20
Bromoethane	10.0	0.409	8.62×10^{-2}	4.7
Carbon disulfide	1.0	0.041	6.44×10^{-3}	6.3
Chlorobenzene	1.3	0.053	1.32×10^{-3}	40
Chloroethane	3.8	0.155	4.54×10^{-2}	1.6
Chloromethane	8.1	0.331	3.13×10^{-1}	1.1
1,2-Dichlorobenzene	2.2	0.090	5.46×10^{-4}	165
1,3-Dichlorobenzene	2.2	0.090	1.00×10^{-3}	90
1,4-Dichlorobenzene	2.2	0.090	8.62×10^{-4}	104
1,1-Dichloroethane	5.6	0.229	1.79×10^{-3}	128
1,2-Dichoroethylene	9.7	0.396	4.64×10^{-3}	85
trans-1, 2-Dichloroethylene	9.7	0.397	2.87×10^{-2}	14
1,2-Dichloropropane	3.4	0.139	8.50×10^{-4}	164
1,3-Dichloropropene	5.3	0.217	4.98×10^{-4}	435
Ethyl benzene	1.0	0.041	2.58×10^{-3}	16
Ethylene dichloride	6.2	0.253	3.84×10^{-4}	660
Formaldehyde	7.0	0.286	6.94×10^{-4}	412
Methylene chloride	12.0	0.490	9.93×10^{-4}	494
Methyl ethyl ketone	2.0	0.082	3.29×10^{-5}	2486
Naphthalene	0.9	0.037	1.53×10^{-4}	240
Nitrobenzene	1.8	0.074	4.32×10^{-6}	17046
Phenol	1.7	0.069	1.97×10^{-7}	350253
Toluene	1.27	0.052	3.01×10^{-3}	17
1,2,4-Trichlorobenzene	2.5	0.102	5.18×10^{-4}	197
1,1,1-Trichloroethane	7.5	0.307	9.19×10^{-3}	33
Trichloroethylene	8.0	0.327	2.88×10^{-3}	114
Vinyl chloride	3.6	0.147	6.80×10^{-2}	2.2
Vinylidene chloride	6.5	0.266	8.01×10^{-2}	3.3

*Vapor phase concentration calculated from LEL, assuming temperature = 25°C.
**Henry's Law Constants (mol/m^3)/(mg/l) taken from Table B-2
***Screening level based on 10 percent of the LEL.

APPENDIX D

SAMPLE HEADSPACE MONITORING ANALYTICAL PROCEDURE (CINCINNATI APPROACH)

APPENDIX D

SAMPLE HEADSPACE MONITORING ANALYTICAL PROCEDURE (CINCINNATI APPROACH)

CMSD ANALYTICAL METHOD
VAPOR SPACE ORGANICS
January 28, 1984
July 11, 1986
REVISED September 27, 1990
Page 1 of 5

ANALYTICAL PROCEDURE

A vapor standard is prepared by injecting 1.6 μl (microliter) of hexane into a one (1) liter flask or bottle fitted with a septum stopper. The hexane is vaporized by heating the flask to 100°C for eight (8) minutes. The Flask is allowed to cool to room temperature. A one thousand (1000) μl aliquot of the vapor is removed with a gas-tight syringe. The vapor is injected into the gas chromatograph (GC). The area under the curve is integrated electronically.

The GC is equipped with a packed column and a flame ionization detector. (If a capillary column is used, the sensitivity will increase and the run time will decrease). Good separation will be achieved by using a 2 mm ID glass or stainless steel column 8 feet long, packed with 1% SP-1000 on Carbopak-B 60/80 mesh. The GC oven temperature is programmed as follows: 50°C for 3 minutes, 8°C/minute to 220°C for 18 minutes.

I. SAMPLING PROCEDURE

All samples will be grab samples.

A. Sample Vial Preparation

Use 40 ml vials (as described in 44 FR 69468, 12/3/79; Pierce No. 13075) equipped with open top screw cap and Teflon-coated silicon septum (Pierce No. 12722). Vials must be washed with detergent, rinsed with tap water followed by distilled water and then dried at 105°C for one (1) hour. Ten (10) mg $Na_2S_2O_3$ should be added to vials if the sample is suspected of containing an oxidant.

B. Sampling

1. A clean vial is immersed in the wastewater and is filled until the liquid forms a convex surface with respect to the top of the bottle. The bottle is capped and then inverted to check for an air bubble. If a bubble is present, repeat the process until no bubbles are present when the bottle is inverted after being filled and capped. Store the sample at 4°C (ice) and transport to the laboratory.

2. If it is not possible to fill the 40 ml vial directly from the wastestream, the following procedure may be employed: Using a 1 liter glass jar that has been washed as in section IA, fill the jar with the wastewater. Transfer a portion of the water to the 40 ml vial and proceed as described above. This method is useful when the wastestream is not readily accessible for sampling. For example, the 1 liter jar may be attached to a pole and the sample obtained by immersing the bottle below the surface of the wastestream.

C. Storage

The samples will be stored in a refrigerator at 4°C, all samples will be analyzed in less than 14 days from the time of collection. Vials will be stored inverted.

II. SUPPLIES AND EQUIPMENT

A. Equipment

1. Gas Chromatograph: Hewlett Packard Model 5880 with Flame Ionization Detector and level for integrator, or equivalent.
2. Microsyringe: Hewlett Packard 10 μL (PN 9301-0246) or equivalent.
3. Injector Septum: Hewlett Packard Blue (PN 5180-4184), or equivalent. (One for each six (6) injections.)
4. One liter Amber Boston Round (Fisher #03-320-1E) Modified to accept a septum, or equivalent.
5. Gas Tight Syringe: one (1) ml (Supleco #2-0739M), or equivalent.
6. Column: 8 ft. x 2 mm. ID stainless steel 1% SP-1000 on Carbopack B (Supleco #1-2548), or equivalent.
7. Sample vials: Clear glass 40 ml with hole in top cap and Teflon faced septum (supelco #2-3285M), or equivalent.
8. Assorted tubing, regulators, and purifying equipment for gas lines.

B. Supplies

1. Hexane GC/MS Grade (Fisher #H303-4)
2. Ultrapure Helium
3. Ultrapure Air
4. Ultrapure Hydrogen

III. INSTRUMENT SETTINGS

A. Temperature Profile: 50°C for 3 minutes, 8°C/minute to 220°C, 220°C for 18 minutes. Stop run.

B. Detector Temperature: 250°C

C. Injector Temperature: 220°C

D. Carrier: Helium, with the flow set to give hexane's main peak a retention time of 18-20 minutes (about 30 ml/minute).

IV. ANALYSIS

A 40 ml vial containing the sample is removed from the refrigerator and warmed to room temperature. Using a glass syringe (20 ml or larger) remove 20 ml of liquid by piercing the septum. It will be necessary to replace the liquid withdrawn with a gas. Nitrogen is preferred, to avoid contamination. The 20 ml of liquid removed can be discarded or injected into another 40 ml vial and used as a duplicate sample. It will be necessary to vent air from the second vial as it is filled.

The vial is equilibrated at 21 ± 3°C for a of minimum 1 hour, vigorously shaken 30 times and held quiescent at 21 ± 3°C for 10 minutes before analysis. Using a gas-tight syringe, withdraw a one thousand (1000) μL aliquot of the headspace gas and inject into the GC. The column and temperature programming should be as specific for the hexane standard. The carrier gas is helium at a flow rate that gives hexane a retention time of approximately 18-20 minutes (about 30 ml/minute).

The total peak area of the chromatogram will be used to calculate the ppm hexane to which the area is equivalent. The peak area of compounds eluting in less than 2 minutes will be considered as methane. The ppm equivalent to methane will be subtracted from the total ppm of hexane to yield the ppm of vapor space organics (VSOs). Samples with a VSO value equivalent to or greater than 300 ppm may be screened by GC/MS to identify whether major peaks represent substances classified as priority pollutants by the EPA.

V. QUALITY CONTROL

A. A field blank will be run daily and will be considered as a zero standard.

B. A 30 ppm standard will be run daily. The total peak area must be 9.0 to 11.0 percent of the 300 ppm standard.

C. A 300 ppm standard will be run daily.

D. Other standards may be run as necessary.

E. A same vial duplicate will be run for each 10 samples. The duplicate must have a margin of error less than 20 percent based on total hexane peak area.

VI. CALCULATIONS

The vapor concentration of the hexane standard is calculated as follows:

$$ppm = \frac{10^6 w/MW}{V/\bar{v}} \qquad \bar{V} = 24.47\ X\ \frac{(760)}{P}\frac{(t+273)}{298}$$

w = weight of hexane (density x volume (ml))
MW = molecular weight of hexane
$\bar{v}$ = gram molecule volume of mixture in liters
P = ambient pressure in mm
t = ambient temperature, °C
V = volume of flask or bottle in liters

The concentration of total organics in the head space is calculated as follows:

$$\text{ppm} = \frac{\text{(ppm hexane standard) (total peak area of sample)}}{\text{(total peak area of hexane standard)}}$$

The value is reported as hexane.

The concentration of the "methane" in the head space is calculated as follows:

$$\text{ppm} = \frac{\text{(ppm hexane standard) (total peak area of compounds with a retention time of less than 2.0 minutes)}}{\text{(total peak area of the hexane standard)}}$$

The concentration of VSOs in the head space is as follows:

ppm = (ppm total organics) - (ppm "methane")

CMSD technicians have found the following step-by-step sequence effective in preparing and running the hexane standard:

1. Record the date, lab temperature and barometric pressure. If using a new standard bottle, determine its volume by filling it with water, then measure the water volume in a graduated cylinder.

2. Purge the standard with house air for 30 seconds.

3. Rinse the standard about 6 times with hexane.

4. With the microsyringe needle in the hexane, pump the plunger several times to expel air from the needle. Then draw the plunger above the 2.5 μl mark.

5. Withdraw the microsyringe from the hexane, hold the syringe with the needle up, and tap to expel any air bubbles.

6. Gradually lower the plunger to the 1.5 to 1.6 μl mark. Pull the plunger back until all the hexane contents of the microsyringe are visible. There should be 2.7 to 2.8 μl of hexane in the microsyringe.

7. Inject the hexane into the standard bottle, being careful not to lose the septum.

8. After withdrawing the microsyringe from the septum, pull the plunger back to determine the amount of hexane left in the microsyringe. This should be about 1.1 μl.

9. Subtract the remaining amount of hexane in the microsyringe from the amount in step 6. This should yield approximately 1.5 - 1.7 μl of hexane. Record the value.

10. Heat the bottle in an 80°C oven for 30 minutes or an 103°C oven for 8 to 9 minutes. Cool thoroughly (about 30 minutes) before injecting standards.

11. Run a 30 and a 300 ppm standard each day. For the 30 ppm standard, a 100 μl aliquot of the vapor is removed from the standard bottle with a gas-tight syringe. The vapor is injected into the GC, being sure not to loosen the syringe needle. This procedure is repeated using a 1000 μl aliquot for the ppm standard.

APPENDIX E

VOLATILE ORGANIC PRIORITY POLLUTANTS

APPENDIX E

VOLATILE ORGANIC PRIORITY POLLUTANTS

1. Acrolein - used as feedstock for some types of plastics, plasticizers, acrylates, textile finishes and synthetic fibers.

2. Acrylonitrile - used in the manufacture of acrylic fibers, acrylostyrene plastics, nitrile rubbers, surface coatings and adhesives.

3. Benzene - used in the manufacture of detergents, dyes, linoleum, artificial leather, varnishes, lacquers, explosives, pharmaceuticals, and pesticides. Also used as a motor fuel constituent, as a solvent, and in the extraction of oils from seeds and nuts.

4. Bromoform - used in pharmaceutical and fire-resistant chemical manufacturing, and as a solvent.

5. Carbon tetrachloride - used as a solvent, and to chemically synthesize fluorocarbons; also used as dry cleaning agent, a fire extinguishing agent, and a fumigant.

6. Chlorobenzene - used as a solvent for degreasing and in paint and pesticide manufacturing.

7. Chlorodibromomethane (dibromochloromethane) - no uses.

8. Chloroethane - used in the manufacture of tetraethyl lead, dyes, drugs, and ethyl cellulose, as a solvent and a refrigerant. Has very low water solubility.

9. 2-chloroethyl vinyl ether - used in the manufacture of anesthetics, sedatives, and cellulose ethers.

10. Chloroform - widely used as a solvent, especially in the lacquer industry, is also used as a cleaning agent, and in the manufacture of pharmaceuticals, plastics, dyes, pesticides, floor polishes and fluorocarbons.

11. Dichlorobromomethane - used as a laboratory reagent.

12. 1,2-dichloroethane - converted to vinyl chloride and other chlorinated chemicals. Is also used as a solvent, degreaser, and a dry cleaning agent and in the manufacture of nylon, rayon, rubber, paint, varnish, and finish removers.

13. 1,1-Dichloroethane - is used as a solvent and cleaning agent in specialized processes.

14. 1,1-Dichloroethylene - used as an intermediate for the copolymerization with other monomers to produce "vinylidene polymer plastics."

15. 1,2-Dichloropropane - used as a degreaser and a dry cleaning agent and in the manufacture of plastics, rubber, and waxes.

16. 1,3-Dichloropropylene - used together with 1,2-dichloropropene as a soil fumigant.

17. Ethylbenzene - intermediate in the synthesis of styrene, and in the manufacture of cellulose acetate and synthetic rubber. Is used as a solvent for paints, varnishes, coatings, and enamels.

18. Methyl bromide - used as insect fumigant, a refrigerant, an herbicide, a fire extinguishing agent, for degreasing wool and extracting oils from nuts, flowers, and seeds.

19. Methyl chloride - used as an extractant in petroleum refineries, a solvent in the synthetic rubber industry, as a paint remover, or in solvent degreasing.

20. Methylene chloride - widely used as a solvent by many industries and for extraction in the food industry.

21. 1,1,2,2-Tetrachloroethane - used as a nonflammable solvent and as a dry cleaning agent and in the manufacture of chlorinated hydrocarbons, paint, varnish, lacquers, cement and rust removers.

22. Tetrachloroethylene - widely used solvent particularly as a dry cleaning agent and for metal degreasing.

23. Toluene - major raw material for organic chemical synthesis, is also used in paints, organic dyes, coatings, and inks and as a solvent.

24. Trans-1,2-Dichloroethylene - is used as a solvent in the extraction of rubber, as a refrigerant, and in pharmaceutical manufacturing.

25. 1,1,1-Trichloroethane - major use is as a metal cleaning solvent and degreaser.

26. 1,1,2-Trichloroethane - used as a solvent and as an intermediate in organic synthesis.

27. Trichloroethylene - used as metals degreasing agent and as an organic solvent; is in a wide variety of solvent cleaning products.

28. Vinyl Chloride - used primarily as a vinyl monomer in the manufacture of polyvinyl chloride plastic resin.

APPENDIX F

INFORMATION COLLECTION/DECISION SHEET

INSTRUCTIONS FOR THE INFORMATION COLLECTION/DECISION SHEET

PURPOSE:

The purpose of the information collection/decision sheet is to provide a convenient and organized structure for evaluating POTW information needs, and for determining the type, quantity and quality of additional data needed (if any) to support the POTW decision making process. The process includes (1) defining the purpose of the data collection, (2) evaluating the available data sources, and the adequacy of the data to support decision making, and (3) designing data collection efforts to address any identified information gaps.

INSTRUCTIONS:

1. STATE THE PURPOSE OF THE INFORMATION COLLECTION: Provide a concise statement on why the data are being collected, <u>and</u> how the data will ultimately be used. This second part of the question is important since it will dictate the quantity and quality of the data to be collected.

2. CHECK THE EVALUATIONS THAT MUST BE UNDERTAKEN: To achieve the purpose of the information collection, the chemical management practices may need to be characterized and evaluated. Six check-off areas ( ) are provided for this evaluation.

( ) Chemical inventory: This is applicable if the POTW wants more information about the types of materials being stored (and used) at a facility. For example, the POTW might need to review chemical inventories to verify that hazardous chemicals were no longer in use or to support efforts to characterize releases from process areas.

- **a. Indicate the types of data needed:** Provide the specific focus of information collection efforts.
- **b. List potential sources of the needed data:** List potential sources of information, indicating those already reviewed.
- **c. List specific needs related to the use of data:** Be as specific as possible about the exact nature of the data needed. For example, the data may need to have been collected within the last 2 months, or the data may need to be obtained during a POTW inspection (as opposed to industry-supplied information).

( ) Determination of chemical characteristics at the process line: Since inspectors will be walking between and breathing the air around chemical reaction tanks in the process areas, it is possible that health and safety concerns would require characterization of the open areas of the process train.

- **a. Indicate the type of data needed:** The information needed will vary depending on the particular pollutant of concern. For example, the POTW may want to request information about the corrosive nature of solutions and vapors or the chemical composition of solutions in process tanks.
- **b. List potential sources of data:** As addressed above, list potential sources of information. This should include all sources that might reasonably be surveyed; e.g., documentation from plant personnel, information from chemical manufacturers. To allow for proper evaluation of the data, list references that might be used to evaluate hazards.
- **c. List specific needs related to the use of data:** Qualify the data needs and indicate any data concerns. For example, if verbal information obtained during past conversations with industrial user representatives has not been reliable, it is appropriate to indicate that written information is required.

( ) **Identification of chemical release points:** Identify the locations where releases to the environment might occur. These release points will be the points of highest chemical concentration and possibly the focus of mitigation measures.

a. **Indicate the type of data needed:** Indicate whether formal drawings are needed, whether narrative descriptions are appropriate, and any other relevant details. Also indicate whether characterization or measurement of the actual releases is required.

b. **List potential sources of data:** List potential sources of information, indicating any that have already been reviewed.

c. **List specific needs related to the use of data:** This might include readings (using a specific type of instrument) and methodologies for collecting representative samples/measurements.

( ) **Evaluation of the controls/mitigation measures:** The POTW may be interested in evaluating the performance of existing or planned engineering controls to determine whether they are adequate to address hazards. Also the POTW may wish to review mitigative measures used to minimize the effect of releases after the fact.

a. **Indicate the type of data needed:** Include information on the design and actual performance of engineering controls, or information regarding equipment effectiveness for specific target chemicals. Evaluating the effectiveness of mitigation measures might include review of the monitoring data, and the effectiveness and types of mitigation employed.

b. **List potential sources of data:** Examples include manufacturer information, data from pilot-testing, and industry monitoring data.

c. **List specific needs related to the use of data:** For example, information regarding control equipment performance may need to be related to the particular contaminant matrix.

( ) **Other:** This section may be used as a catch-all for any other safety issues not addressed above.

APPENDIX F

INFORMATION COLLECTION/DECISION SHEET

1. STATE THE PURPOSE OF THE INFORMATION COLLECTION (e.g. response to worker health and safety concerns) ______

2. CHECK THE EVALUATIONS THAT MUST BE UNDERTAKEN

☐ Chemical Inventory

a. Indicate the type of data needed: ______

b. What are the potential sources of data: ______

c. List specific needs relating to use of the data: ______

☐ Determination of Chemical Concentrations at Process Line

a. Indicate the type of data needed: ______

b. What are the potential sources of data: ______

c. List specific needs relating to use of the data: ______

☐ Identification of Chemical Release Points

a. Indicate the type of data needed: ______

b. What are the potential sources of data: ______

c. List specific needs relating to use of the data: ______

☐ Evaluation of Controls/Mitigative Measures

a. Indicate the type of data needed:

b. What are the potential sources of data:

c. List specific needs relating to use of the data:

☐ Other, explain:

a. Indicate the type of data needed:

b. What are the potential sources of data:

c. List specific needs relating to use of the data:

☐ Identification of Appropriate Safety Protocols for Future Inspections or Collection System Work

3. IDENTIFY ADDITIONAL DATA

4. WILL THE COLLECTED DATA SUPPORT ALL EVALUATIONS

☐ Yes, stop here and perform necessary evaluations.

☐ No - Proceed to 5.

5. IDENTIFY SPECIFIC DATA NEEDS TO BE MET BY FACILITY INSPECTION **(e.g. verification of existing information)**

____

____

____

____

Additional Comments:

Completed by: ______________________________ Date: ____________

APPENDIX G

STATES WITH APPROVED OSHA PLANS

APPENDIX G

STATES WITH APPROVED OSHA PLANS
(AUGUST 1991)

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APPENDIX H

TYPES OF RESPIRATORS

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TYPES OF RESPIRATORS

Type of Respirator	Advantages	Disadvantages
Atmosphere Supplying		
Self-Contained Breathing Apparatus (SCBA)	Provides the highest available level of protection against airborne contaminants and oxygen deficiency. Provides the highest protection available under strenuous work conditions.	Bulky, heavy [up to 35 pounds (12.9 kg)]. Finite air supply limits work duration. May impair movement in confined spaces.
Positive-Pressure Supplied-Air Respirator (SAR) (also called air-line respirator)	Enables longer work periods than SCBA. Less bulky and heavy than a SCBA. SAR equipment weighs less than 5 pounds [or around 15 pounds (5.6 kg) if escape SCBA protection is included]. Protects against most airborne contaminants.	Not approved for use in atmospheres immediately dangerous to life or health (IDLH) or in oxygen-deficient atmospheres unless equipped with an emergency egress unit such as an escape only SCBA that can provide immediate emergency respiratory protection in case of air-line failure. Impairs mobility. MSHA/NIOSH certification limits have length to 300 feet (90 meters). As the length of the hose is increased, the minimum approved air flow may not be delivered at the facepiece. Worker must retrace steps to leave work area. Requires supervision/ monitoring of the air supply line.

Type of Respirator	Advantages	Disadvantages
Escape-only SCBA	Lightweight [10 pounds (4.5 kg) or less], low bulk, easy to carry. Available in pressure-demand and continuous-flow modes. Supplies clean air to the wearer from either an air cylinder or from an oxygen-generating chemical. Approved for escape purposes only. Enhanced mobility.	Provides only 5 to 15 minutes of respiratory protection, depending on the model and wearer breathing rate. Cannot be used for entry. Cannot be used in IDHL or oxygen-deficient atmosphere (less than 19.5 percent oxygen at sea level).
Air Purifying		
Air-Purifying Respirator (including powered air-purifying respirators [PAPRs])	Lighter in weight than SCBA. Generally weighs 2 pounds (91kg) or less (except for PAPRs)	High relative humidity may reduce protection. Limited duration of protection. May be hard to gauge safe operating time in field conditions. Only protects against specific chemicals and up to specific concentrations. Cannot be used when unknown contaminants are present. Must never be used for confined space entry where exposure conditions have not been characterized. Use requires monitoring of contaminant and oxygen levels. Can only be used (1) against gas and vapor contaminants with adequate warning properties, or (2) for specific gases or vapors provided that the service is known and a safety factor is applied or if the unit has an ESLI (end-of-service-life indicator).

Adapted from Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities, NIOSH, OSHA, USCG, and EPA, October 1985.

APPENDIX I

EFFECTIVENESS OF PROTECTIVE MATERIALS AGAINST CHEMICAL DEGRADATION

APPENDIX I

EFFECTIVENESS OF PROTECTIVE MATERIALS AGAINST CHEMICAL DEGRADATION (BY GENERIC CLASS)

Generic Class	Examples	Butyl Rubber	Polyvinyl Chloride	Neoprene	Natural Rubber
Alcohol	Methyl alcohol Ethyl alcohol	E	E	E	E
Aldehydes	Acetaldehyde Propionaldehyde	E-G	G-F	E-G	E-F
Amines	Methylamine Propylamine	E-G	G-F	E-G	G-F
Esters	Methyl formate Methyl acetate	G-F	P	G	F-P
Ethers	Ethyl ether Phenol ether	G-F	G	E-G	G-F
Fuels	Gasoline Jet fuel (JP-4)	F-P	G-P	E-G	F-P
Halogenated Hydrocarbons	Bromobenzene Chlorobenzene	G-P	G-P	G-F	F-P
Hydrocarbons	Hexane Ethane	F-P	F	G-F	F-P
Inorganic Acids	Hydrochloric acid	G-F	E	E-G	F-P
Inorganic Bases	Ammonia Ethylamine	E	E	E	E
Ketones	Acetone Methyl ethyl ketone	E	P	G-F	E-F
Organic Acids	Carbonic acid Carboxylic acid	E	E	E	E

Ratings are subject to variation depending on formulation, thickness, and whether the material is supported by fabric.

E = EXCELLENT G = GOOD F = FAIR P = POOR

Source: Adapted from Survey of Personal Protective Clothing and Respiratory Apparatus. DOT, USCG, Office of Research and Development (September 1974).

APPENDIX J

PROTECTIVE CLOTHING

APPENDIX J

PROTECTIVE CLOTHING

Body Part Protected	Type of Clothing or Accessory	Description	Type of Protection	Use Considerations
Full Body	Fully-encapsulating suit	One-piece garment. Boots and gloves may be integral, attached and replaceable, or separate.	Protects against splashes, dust, gases, and vapors.	Does not allow body heat to escape. May contribute to heat stress in wearer, particularly if worn in conjunction with a closed-circuit SCBA; a cooling garment may be needed. Impairs worker mobility, vision, and communication.
	Non-encapsulating suit	Jacket, hood, pants, or bib overalls, and one-piece coveralls.	Protects against splashes, dust, and other materials but not against gases and vapors. Does not protect parts of head or neck.	Do not use where gas-tight or pervasive splashing protection is required. May contribute to heat stress in wearer. Needs tape-seal connections between pant cuffs and boots and between gloves and sleeves.
	Aprons, leggings, and sleeve protectors	Fully sleeved and gloved apron. Separate coverings for arms and legs. Commonly worn over non-encapsulating suit.	Provides additional splash protection of chest, forearms, and legs.	Whenever possible, should be used over a non-encapsulating suit (instead of using a fully-encapsulating suit) to minimize potential for heat stress. Useful for sampling, labeling, and analysis operations. Should be used only when there is a low probability of total body contact with contaminants.

Adapted from Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities. October 1985. NIOSH/OSHA/USCG/EPA.

Body Part Protected	Type of Clothing or Accessory	Description	Type of Protection	Use Considerations
Head	Safety helmet (hard hat)	For example, a hard plastic or rubber helmet.	Protects the head from blows.	Helmet shall meet OSHA standard 29 CFR Part 1910.125
	Helmet liner	Commonly worn with a helmet.	Insulates against cold. Does not protect against chemical splashes.	
	Hood		Protects against chemical splashes, particulates, and rain.	
	Protective hair covering		Protects against chemical contamination of hair.	Particularly important for workers with long hair.
Eyes and Face	Face shield	Full-face coverage, eight-inch minimum.	Protects against chemical splashes. Does not protect adequately against projectiles.	Face shields and splash hoods must be suitably supported to prevent them from shifting and exposing portions of the face or obscuring vision. Provides limited eye protection.
	Splash hood		Protects against chemical splashes. Does not protect adequately against projectiles.	
	Goggles		Depending on their construction, goggles can protect against vaporized chemicals, splashes, large particles, and projectiles (if constructed with impact-resistant lenses).	
	Sweat bands		Prevents sweat-included eye irritation and vision impairment.	
Ears	Ear plugs and muffs		Protects against physiological damage and psychological disturbance.	Must comply with OSHA regulation 29 CFR Part 1910.95. Can interfere with communication.
	Headphones	Radio headset with throat microphone.	Provides some hearing protection while enabling communication.	Highly desirable, particularly if emergency conditions arise.

Adapted from Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities. October 1985. NIOSH/OSHA/USCG/EPA.

Body Part Protected	Type of Clothing or Accessory	Description	Type of Protection	Use Considerations
Hands and Arms	Gloves and sleeves	May be integral, attached, or separate from other protective clothing. Overgloves disposable gloves.	Protect hands and arms from chemical contact. Provides supplemental protection to the wearer. Should be used whenever possible to reduce decontamination needs.	Wear jacket cuffs over glove cuffs to prevent liquid from entering the glove. Tape-seal gloves to sleeves to provide additional protection.
Feet	Safety boots	Boots constructed of chemical-resistant material. Boots constructed with some steel materials (e.g., toes, shanks, insoles). Boots constructed from nonconductive, spark-resistant materials or coatings.	Protect feet from contact with chemicals. Protect feet from compression, rushing, or puncture by falling, moving, or sharp objects. Protect the wearer against electrical hazards and prevent ignition of combustible gases or vapors.	All boots must at least meet the specifications required under OSHA 29 CFR Part 1910.136 and should provide good traction.
	Disposable shoe or boot covers	Made of a variety of materials. Slip over the shoe or boot.	Protect safety boots from contamination. Protect feet from contact with chemicals.	Covers may be disposed of after use, facilitating decontamination.
General	Knife	Allows a person in fully-encapsulating suit to cut his or her way out of the suit in the event of an emergency or equipment failure.		Should be carried and used with caution to avoid puncturing the suit.
	Flashlight or Lantern		Enhances visibility in buildings, enclosed spaces, and the dark.	Must be intrinsically safe or explosion-proof for use in combustible atmospheres. Sealing the flashlight in a plastic bag facilitates decontamination.

Adapted from Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities. October 1985. NIOSH/OSHA/USCG/EPA.

Body Part Protected	Type of Clothing or Accessory	Description	Type of Protection	Use Considerations
General (Continued)	Personal locator beacon	Operated by sound, radio, or light.	Enables emergency personnel to locate victim.	Only electrical equipment approved as intrinsically safe, or approved for the class and group of hazard as defined in Article 500 of the National Electric Code, may be used.
	Two-way radio		Enables field workers to communicate with support personnel.	
	Safety Belts, harnesses, and lifelines		Enables personnel to work in elevated areas or enter confined areas and prevent falls. Belts may be used to carry tools and equipment.	Must be constructed of spark-free hardware and chemical-resistant materials to provide proper protection. Must meet OSHA standards in 29 CFR Part 1926.104.
	Orange vests or cones		Deflects vehicular traffic from POTW activities.	

Adapted from Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities. October 1985. NIOSH/OSHA/USCG/EPA.

APPENDIX K

ABBREVIATIONS AND GLOSSARY

APPENDIX K

ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
BMP	Best Management Practices
BPJ	Best Professional Judgment
CFR	Code of Federal Regulations
CGI	Combustible Gas Indicator
CMSD	Cincinnati Metropolitan Sanitary District
CMP	Chemical Management Practices
FID	Flame Ionization Detector
IU	Industrial Users
IDLH	Immediately Dangerous to Life and Health
LEL	Lower Explosive Limit
MSDS	Material Safety Data Sheet
NIOSH	National Institute for Occupational Safety and Health
NFPA	National Fire Prevention Association
OSHA	Occupational Safety and Health Administration
OVA	Organic Vapor Analyzer
PEL	Permissible Exposure Limits
PID	Photo Ionization Detector
POTW	Publicly Owned Treatment Works
PPE	Personal Protective Equipment
PPM	Parts Per Million
SARA	Superfund Amendments and Reauthorization Act
SCBA	Self-Contained Breathing Apparatus
TLV	Threshold Limit Values
TLV-C	Threshold Limit Value - Ceiling
TLV-STEL	Threshold Limit Value - Short Term Exposure Limit
TLV-TWA	Threshold Limit Value - Time Weighted Average
UEL	Upper Explosive Limit
WEF	Water Environment Federation (formerly the Water Pollution Control Federation (WPCF))

GLOSSARY

Action Level - A numerical limit of a chemical, biological, or radiological agent at which actions are taken to prevent or reduce exposure or contact.

Aeration - The addition of air in the form of bubbles to a liquid.

Air stripping - A physical treatment process used to remove volatile substances from wastestreams by the transfer of volatile pollutants from a high concentration in the wastestream into an air stream with a lower concentration of the pollutant.

Best Management Practices (BMP) - Schedules of activities, prohibitions or practices, maintenance procedures, and other management practices to prevent or reduce pollution discharges.

Best Professional Judgment (BPJ) - The highest quality technical opinion developed by a permit writer after consideration of all reasonable available and pertinent data or information which forms the basis for the terms and conditions of a permit.

Blowdown - The removal of accumulated solids in boilers to prevent plugging of boiler tubes and steam lines. In cooling towers, the blowdown is used to reduce the amount of dissolved salts in the recirculated cooling water.

Chlorine detector - Usually a mixed oxide semi-conductor (similar to an oxygen meter), which is calibrated to detect chlorine concentrations in the air.

Code of Federal Regulations (CFR) - A U.S. Government publication which contains finalized Federal regulations.

Combustible Gas Indicator - An instrument that measures the concentration of a flammable vapor or gas in air, indicating the results as a percentage of the lower explosive limit (LEL) of the calibration gas.

Condensation - A chemical reaction in which water or another simple substance is released by the combination of two or more molecules.

Equilibration - To maintain an equilibrium.

Flammable Liquid - A liquid with a flash point below 100°F and having a vapor pressure not exceeding 40 psig absolute at 100°F.

Flashpoint - The minimum temperature at which vapor combustion will spread away from its source of ignition.

Fume - The particulate, smoke-like emanation from the surface of heated metals. Also the vapors evolved from the concentrated acids (sulfuric, nitric); from evaporating solvents; or as the result of combustion or any other decomposition reaction.

Gas - A state of matter with a characterized by a very low density and viscosity (relative to liquids and solids); comparatively great expansion and contraction with changes in temperature and pressure; ability to diffuse readily into other gases; and ability to occupy with almost complete uniformity the whole of any container.

Gas/Vapor Toxicity - Indicates the likelihood of adverse health effects when the time weighted average threshold limit valve (TWA-TLV) is approached or exceeded.

Gas Chromatograph/Mass Spectrometer - Analytical instruments that determine presence and concentration of substances in a liquid.

Henry's Law - A thermodynamic relationship which states that in a closed system the concentration of a constituent in the vapor phase and the corresponding equilibrium concentration in the liquid phase are related by a constant. This Henry's Law Constant is the ratio of the constituent's vapor pressure to its water solubility:

$$H = P_{vap}/S$$

where: H = constituent's Henry's Law Constant, atm m^3/ml
P_{vap} = constituent's vapor pressure, atm
S = constituent's water solubility, ml/m^3

Hydrogen Sulfide Detector - An instrument similar to an oxygen meter except that it is adjusted to sound an alarm when a particular contaminant level is reached.

Lower Explosive Limit (LEL) - The point at which the concentration of a gas-in-air is sufficiently large to result in an explosion if an ignition source is present.

Material Safety Data Sheet (MSDS) - A document which provides pertinent health and safety information and a profile of a particularly hazardous substance or mixture.

Mitigation - Actions taken to prevent or reduce the severity of harm.

National Institute of Occupational Safety and Health (NIOSH) - A Federal agency that tests and approves safety equipment for particular applications, with a primary goal to eliminate on-the-job hazards to the health and safety of workers.

Occupational Safety and Health Act (OSHA) (1970) - A Federal law designed to protect the health and safety of industrial workers.

Organic Vapor Analyzer (OVA) - A portable instrument used to detect a variety of organic compounds in air, soil, and water.

Oxidation Reduction Reaction - A chemical transformation in which electrons are transferred from one chemical, the reducing agent, to another chemical, the oxidizing agent. In oxidation-reduction, reactions involving the transfer of oxygen from one molecule to another, the molecule losing the oxygen is the oxidizing agent and the molecule gaining the oxygen is the reducing agent.

Oxygen Meter - An instrument that measures the atmospheric oxygen (O_2) concentration directly by means of a galvanic cell.

Sublimation - A process by which solids will volatilize.

Sulfur Dioxide Detector - An instrument similar to a chlorine detector except that it is calibrated to detect sulfur dioxide concentrations in the air.

Teratogen - Any substance which tends to cause birth defects after conception.

Threshold Limit Value (TLV) - The average concentration of toxic gas or any other substance to which a normal person can be exposed without injury during an average work week.

Threshold Limit Value - Ceiling (TLV-C) - The concentration that should not be exceeded during any part of the working exposure. In conventional industrial hygiene practice, if instantaneous monitoring is not feasible, the TLV-C can be assessed by sampling over a 15-minute period, except for those substances that may cause immediate irritation when exposures are short.

Threshold Limit Value - Short-term Exposure Limit (TLV-STEL) - (1) Defined as a 15-minute TWA exposure which should not be exceeded at any time during a workday even if the 8-hour TWA is within the TLV-TWA. Exposures above the TLV-TWA up to the STEL should not be longer than 15 minutes and should not occur more than four times per day. There should be at least 60 minutes between successive exposures in this range. An averaging period other than 15 minutes may be recommended when s warranted by observed biological effects. (2) The concentration to which nearly all workers can be exposed continuously for a short period of time without suffering from irritation, chronic or irreversible tissue damage, or narcosis of a sufficient degree to increase the likelihood of accidental injury, impair self rescue or materially reduce work efficiency. It supplements the time-weighted average limit where there are recognized acute effects from a substance whose toxic effects have been reported from high short-term exposures in either humans or animals.

Threshold Limit Value - Time Weighted Average (TLV-TWA) - The time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek to which workers may be exposed, day after day, without adverse effects.

Vapor - An air dispersion of molecules of a substance that is liquid or solid in its normal state; i.e., at standard temperature and pressure. Examples are water vapor and benzene vapor. Vapors of organic liquids are also loosely called fumes.

Vapor pressure - The pressure exerted by a vapor in equilibrium with its solid or liquid phase.

Volatilization - The process of forming vapor.

Water solubility - The ability of a substance to dissolve in water.

APPENDIX L

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