

White Paper: Environmental Safety in Industrial Systems

Industrial Scientific



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1 Executive Summary

Air pollution is a result of industrialization and urbanization. The air pollution in urban areas, which was mainly the result of the exhaust gases from automobile tail pipes, became so alarming to the health of the people that states began passing legislation to reduce air pollution. It was later learned that the reaction of sunlight with automobile exhaust led to smog formation in urban areas. That discovery became the foundation for today's air pollution regulations.

The Clean Air Act legislations of 1970-1990 were enacted to protect the public from the releases of extremely hazardous substances. As a result, the Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) were required to set concentration limits for the presence of each pollutant in the workplace and environment and require the plant site implementation of the best available technologies for mitigating/reducing the pollutant source.

Since then, significant progress has been made in developing clear regulations and technologies that enable the realization of safer industrial systems in a compliant manner. However, there is limited literature that provides a comprehensive view of this space covering the following key questions:

- What are the relevant EPA Regulations related to industrial air pollution that every industrial plant should be aware of?
- What are the key air pollutants and why are they harmful to people and the environment?
- Which industries face these risks and issues?
- How can an industrial plant detect, monitor, and respond to the presence of these air pollutants?
- What technologies are available and have shown to be effective?
- What are the consequences, including fines, if these issues are left unaddressed?

This white paper presents a comprehensive set of answers to these key questions. The insights offered in this work reflect more than 30 years of research and development in the field, including the development of leading solutions used in practice today across the globe.

This document is written for industrial plant Environmental Health Safety (EHS) managers. It provides guidance for EHS managers to ensure that hazardous chemicals concentration levels within their plant and its surrounding environment are within EPA-acceptable levels, which meets the well-being of workers and surrounding communities. It also provides guidelines for selecting the best technology solution for their sensor procurement, deployment, and emergency planning and response to safeguards against the accidental release of chemicals into the environment.

2 EPA Regulations

The Clean Air Act (CAA) amendments of 1990 require, under the revisions to section 112, that the Agency evaluate and promulgate regulations requiring control of emissions of Hazardous Air Pollutants (HAP) from categories of major and area sources. Major source is defined in paragraph 112 (a) (1) to mean any stationary source or group of stationary sources located within a contiguous area and under common control that emits or has the potential to emit considering controls, in the aggregate, 10 tons per year (tpy) or more of any hazardous air pollutant or 25 tpy or more of any combination of hazardous air pollutants.

The CAA required that both OSHA and EPA develop regulations to prevent the accidental release of highly hazardous material. In February 1992, OSHA issued a chemical accident prevention regulation, its Process Safety Management (PSM) Standard. The PSM standard has twenty elements, of which the most relevant to our industry are process hazard analysis, measurement and metrics, and emergency response. The main goal of PSM is the protection of the plant personnel from hazardous chemicals by preventing/mitigating/minimizing hazardous chemical release to the ambient, by wearing the portable sensor and in-process placement of gas sensors for early detection for warning, evacuation, and shelter-in-place. In addition, the PSM requires plants to develop and implement an emergency response program.

The EPA, in June 1996, similarly issued a chemical accident prevention regulation, the Risk Management Program (RMP). RMP is very similar to PSM, and they have many overlaps. RMP is intended to protect the community and environment. It requires a hazard analysis to estimate the offsite impact due to worst-case and alternative releases. This analysis shall be updated every five years or within six months of a significant change and submitted to the EPA.

3 Environmental Pollutants of Concern

3.1 Urban Area Pollutants

3.1.1 Criteria Pollutants

The Clean Air Act requires the EPA to set National Ambient Air Quality Standards (NAAQS) for pollutants that are common in outdoor air, considered harmful to public health and the environment and come from numerous and diverse sources. These pollutants, referred to as criteria pollutants, are carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen dioxide (NO₂), ozone (O₃), lead (Pb), and particulate matters.

- **Carbon Monoxide (CO)**

Sources: Transportation fleet, fossil fuel burning, power generation, chemical processing, and refineries

Health and Environmental Effects: Reduces the amount of oxygen in the bloodstream affecting critical organs like the heart and brain causing dizziness, confusion, unconsciousness and death.

Pollutant	Primary/Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)	Primary	8 hours	9 ppm	Not to exceed more than once per year
		1 hour	35 ppm	

Table 3-1: National Ambient Air Quality Standard for CO

- **Sulfur Dioxide (SO₂)**

Sources: Transportation fleet, fossil fuel burning, power generation, chemical processing, and refineries

Health and Environmental Effects: Short-term exposures to SO₂ can harm the human respiratory system and make breathing difficult. People with asthma, particularly children, are sensitive to these effects of SO₂.

At high concentrations, gaseous SO₂ can harm trees and plants by damaging foliage and decreasing growth. In addition, SO₂ and other sulfur oxides can contribute to acid rain which can harm sensitive ecosystems.

Pollutant	Primary/Secondary	Averaging Time	Level	Form
Sulfur Dioxide (SO ₂)	Primary	1 hour	75 ppb	1-hr daily max conc. avg over 3 years
	Secondary	3 hours	0.5 pm	Not to exceed more than once per year

Table 3-2: National Ambient Air Quality Standard for SO₂

- **Nitrogen Dioxide (NO₂)**

Sources: Transportation fleet, fossil fuel burning, power generation, chemical processing, and refineries

Health and Environmental Effects: Breathing air with a high concentration of NO₂ can irritate airways in the human respiratory system. Exposures over short periods can aggravate respiratory diseases, particularly asthma, leading to respiratory symptoms (such as coughing, wheezing, or difficulty breathing). Longer exposures to elevated concentrations of NO₂ may contribute to the development of asthma and potentially increase susceptibility to

respiratory infections. NO₂ and other NO_x interact with water, oxygen, and other chemicals in the atmosphere to form acid rain. Acid rain harms sensitive ecosystems such as lakes and forests.

The nitrate particles resulting from NO_x make the air hazy and difficult to see through. This affects the view of many national parks for visitors.

Pollutant	Primary/Secondary	Averaging Time	Level	Form
Nitrogen Dioxide (NO ₂)	Primary	1 hour	100 ppb	1-hr daily max conc. avg over 3 years
	Primary and Secondary	1 year	53 ppb	Annual mean

Table 3-3: National Ambient Air Quality Standard for NO₂

- **Lead (Pb)**

Sources: Leaded gasoline burning fuel, Ore, and metal processing. Other sources are waste incinerators, utilities, lead-acid battery manufacturers, and lead smelters.

Health and Environmental Effects: Once taken into the body, lead distributes throughout the body in the blood and is accumulated in the bones. Depending on the level of exposure, lead can adversely affect the nervous system, kidney function, immune system, reproductive and developmental systems, and the cardiovascular system. Lead exposure also affects the oxygen-carrying capacity of the blood. The lead effects most likely to be encountered are neurological effects in children. Infants and young children are especially sensitive to lead exposures, which may contribute to behavioral problems, learning deficits, and lowered IQ. Furthermore, an elevated lead in the environment can result in decreased growth and reproduction in plants and animals.

Pollutant	Primary/Secondary	Averaging Time	Level	Form
Lead (Pb)	Primary and Secondary	Rolling 3-month average	0.15 $\frac{\mu\text{g}}{\text{m}^3}$	Not to be exceeded

Table 3-4: National Ambient Air Quality Standard for (Pb)

- **Particulate matter**

Sources: Construction sites, unpaved roads, smokestacks, coal processing units, industries, and automobiles. It is also created because of complex reactions of chemicals such as sulfur dioxide and nitrogen oxides, which are pollutants emitted from power plants, industries, and automobiles.

Health and Environmental Effect: Particulate matter contains microscopic solids or liquid droplets that are so small that they can be inhaled and cause serious health problems. Some particles less than 10 micrometers (μm) in diameter can get deep into your lungs, and some may even get into your bloodstream. Of these, particles less than 2.5 micrometers in diameter, also known as fine particles or PM_{2.5}, pose the greatest risk to health. Fine particles are also the main cause of reduced visibility (haze) in parts of the United States, including national parks and wilderness areas.

Pollutant		Primary/Secondary	Averaging Time	Level	Form
Particle Pollution (PM)	PM _{2.5}	Primary	1 year	12.0 $\frac{\mu\text{g}}{\text{m}^3}$	Annual mean, avg over 3 years
		Secondary	1 year	15.0 $\frac{\mu\text{g}}{\text{m}^3}$	Annual mean, avg over 3 years
		Primary and Secondary	24 hours	35.0 $\frac{\mu\text{g}}{\text{m}^3}$	Annual mean, avg over 3 years
	PM ₁₀	Primary and Secondary	24 hours	150 $\frac{\mu\text{g}}{\text{m}^3}$	Not to exceed once per year on avg over 3 years

Table 3-5: National Ambient Air Quality Standard for Particulate Matter

- **Ozone and Smog**

Ozone (O₃) is formed naturally in the upper atmosphere, which shields us from the sun’s harmful ultraviolet rays, and is formed at ground level through a complicated series of chemical reactions in the presence of sunlight of NO_x and volatile organic compounds or VOCs.

Sources: Emissions from industrial facilities, electric utilities, motor vehicles exhaust, and gasoline dispensers create ozone precursors of NO_x and VOC, which, by a complicated series of chemical reactions in the presence of sunlight, forms ozone at ground level. High ozone levels and particles in the air lead to “smog”, thus reducing visibility in the urban area. More efficient engines and cleaner-burning gasoline and diesel fuel have helped reduce smog in the urban environment.

Health and Environmental Effects: Ozone can cause the muscles in the airways to constrict, trapping air in the alveoli. This leads to wheezing, shortness of breath, inflammation, and damage to the airways. Children are at greatest risk from exposure to ozone. In addition, ozone damages vegetation by injuring leaves, reducing photosynthesis, impairing reproduction and growth, and decreasing crop yields. Ozone damage to plants may alter ecosystem structure, reduce biodiversity, and decrease plant uptake of CO₂. Ozone is also a greenhouse gas that contributes to the warming of the atmosphere.

Pollutant	Primary/Secondary	Averaging Time	Level	Form
Ozone (O ₃)	Primary and Secondary	8 hours	0.07 ppm	Annual fourth-highest daily maximum 8-hour concentration averaged over 3 years

Table 3-6: National Ambient Air Quality Standard for (O₃)

Criteria Pollutants Emissions from All Sources

EPA estimates nationwide emissions of ambient air pollutants based on actual monitored readings or engineering calculations of the amounts and types of pollutants emitted by vehicles, factories, and other sources. Emissions information is developed with input from state and local air agencies, tribes, and industry. The table below shows the criteria for pollutants emission in the year 2020 in the USA.

	CO	NOx	SO ₂	PM _{2.5}	PM ₁₀
	In 1000 of Tons				
Source Category	2020	2020	2020	2020	2020
Fuel Combustion, Electric Utility	588	809	818	107	132
Fuel Combustion, Industrial	811	1,032	377	185	246
Fuel Combustion, Other	2,671	494	44	364	370
Chemical & Allied Product Manufacturing	118	40	111	15	19
Metals Processing	468	66	85	35	51
Petroleum & Related Industries	652	623	94	23	27
Other Industrial Processes	448	322	146	297	767
Solvent Utilization	2	1	0	4	5
Storage & Transport	7	5	1	14	36
Source Category	2020	2020	2020	2020	2022
Waste Disposal & Recycling	1,301	81	25	203	227
Highway Vehicles	16,194	2,413	16	90	216
Off-Highway	11,334	1,931	27	114	122
Miscellaneous	28,676	409	218	4,189	14,777
Total	63,271	8,228	1,962	5,640	16,994

Table 3-7: Criteria for Pollutants Emissions in the USA (Year 2020)

Emissions of air pollutants continue to play an important role in several air quality issues. In 2020, about 96 million tons of pollution were emitted into the atmosphere in the United States. These emissions mostly contribute to the formation of ozone, particles, deposition of acids, and visibility impairment.

Urban Air Toxic Pollutants as a Subset of Industrial Hazardous Air Pollutants (HAP)

From the 187 industrial HAPs, EPA has identified 30 that pose the greatest potential health threat in urban areas because of their large population. These HAPs are referred to as the 30 urban air toxins.

List of 30 Urban Air Toxics		
Acetaldehyde	Dioxin	Mercury compounds
Acrolein	Propylene dichloride	Methylene chloride (dichloromethane)
Acrylonitrile	1,3-dichloropropene	Nickel compounds

List of 30 Urban Air Toxics		
Arsenic compounds	Ethylene dichloride (1,2-dichloroethane)	Polychlorinated biphenyls (PCBs)
Benzene	Ethylene oxide	Polycyclic organic matter (POM)
Beryllium compounds	Formaldehyde	Quinoline
1,3-butadiene	Hexachlorobenzene	1,1,2,2-tetrachloroethane
Cadmium compounds	Hydrazine	Tetrachloroethylene (perchloroethylene)
Chloroform	Lead compounds	Trichloroethylene
Chromium compounds	Manganese compounds	Vinyl chloride

Table 3-8: List of 30 Urban Air Toxics

EPA identified the following 68 area source categories responsible for contributing to urban air toxics to the environment:

List of 68 Area Sources of Urban Air Toxics	
Acrylic Fibers/Modacrylic Fibers Production	Iron and Steel Forging
Agricultural Chemicals and Pesticides Manufacturing	Iron Foundries
Aluminum Foundries	Lead Acid Battery Manufacturing
Asphalt Processing and Asphalt Roofing Manufacturing	Medical Waste Incinerators
Autobody Refinishing Paint Shops	Mercury Cell Chlor-Alkali Plants
Carbon Black Production	Miscellaneous Organic NESHAP
Chemical Manufacturing: Chromium Compounds	Municipal Landfills
Chemical Preparations	Municipal Waste Combustors (MWC)
Chromic Acid Anodizing	Nonferrous Foundries
Clay Products Manufacturing (Clay Ceramics Manufacturing)	Oil and Natural Gas Production
Commercial Sterilization Facilities	Paint Strippers
Copper Foundries	Paints and Allied Products Manufacturing
Cyclic Crude and Intermediate Production	Pharmaceutical Production
Decorative Chromium Electroplating	Plastic Materials and Resins Manufacturing

List of 68 Area Sources of Urban Air Toxics	
Dry Cleaning Facilities	Plastic Parts and Products (Surface Coating)
Electrical and Electronic Equipment – Finish Operations	Plating and Polishing
Fabricated Metal Products	Polyvinyl Chloride and Copolymers Production
Fabricated Plate Work	Portland Cement
Fabricated Structural Metal Manufacturing	Prepared Feeds Materials
Ferroalloys Production: Ferromanganese & Silicomanganese	Pressed and Blown Glass and Glassware Manufacturing
Flexible Polyurethane Foam Fabrication Operations	Primary Copper (Not Subject to Maximum Achievable Control Technology (MACT))
Flexible Polyurethane Foam Production	Primary Metal Products Manufacturing
Gas Distribution Stage 1	Primary Nonferrous Metals (Zinc (Zn), Cadmium (Cd), and Beryllium (Be))
Halogenated Solvent Cleaners	Public Owned Treatment Works
Hard Chromium Electroplating	Secondary Copper Smelting
Hazardous Waste Incineration	Secondary Lead Smelting
Heating Equipment, Except Electric	Secondary Nonferrous Metals
Hospital Sterilizers	Sewage Sludge Incineration
Industrial Boilers Fired by Coal, Wood, and Oil	Stainless and Non-Stainless-Steel Manufacturing Electric Arc Furnace
Industrial Inorganic Chemical Manufacturing	Stationary Internal Combustion Engines
Industrial Machinery and Equipment – Finish Operations	Steel Foundries
Industrial Organic Chemical Manufacturing	Synthetic Rubber Manufacturing
Inorganic Pigments Manufacturing	Valves and Pipe Fittings
Institutional/Commercial Boilers Fired by Coal, Wood, and Oil	Wood Preserving

Table 3-9: List of 68 Area Sources of Urban Air Toxics

3.2 Industrial Pollutants

3.2.1 Pollutants of Concern

HAPS, Volatile Organic Compounds (VOCs), Acid Rain Gases, Mercury, Criteria Pollutants, Greenhouse Gases

Hazardous air pollutants (HAPs), also known as toxic air pollutants or air toxics, are those pollutants known or suspected to cause cancer or other serious health effects, such as reproductive effects, birth defects, or adverse environmental effects. EPA is mandated to work with state, local, and tribal governments to reduce air emissions of 188 toxic air pollutants. The law directs EPA to establish "performance standards" or "maximum achievable control technology" (MACT), whichever the Agency deems most appropriate. Chemical processing Industries are required to implement MACT to Clean Air Act operating permits and to comply with all applicable emissions standards.

Examples of some of the HAP toxic air pollutants include.

- Benzene (C₆H₆), which is found in gasoline
- Perchloroethylene (C₂Cl₄), which is emitted from some dry-cleaning facilities
- Methylene chloride (CH₂Cl₂), which is used as a solvent and paint stripper by several industries

Other listed air toxics include dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds.

Volatile organic compounds are a subset of HAPS compounds with high vapor pressure and low water solubility. Many VOCs are human-made chemicals used and produced in manufacturing paints, pharmaceuticals, and refrigerants. VOCs typically are industrial solvents, such as trichloroethylene (C₂HCl₃); fuel oxygenates, such as methyl tert-butyl ether (C₅H₁₂O, MTBE); or by-products produced by chlorination in water treatment, such as chloroform (CHCl₃). VOCs are often components of petroleum fuels, hydraulic fluids, paint thinners, and dry-cleaning agents. VOCs are common ground-water contaminants. Exposure to high levels of VOCs may cause damage to the liver, central nervous system, vision, and memory problems. Some VOCs are carcinogens, e.g., benzene.

Acid rain results when sulfur dioxide (SO₂) and nitrogen oxides (NO_x) are emitted into the atmosphere and transported by wind and air currents. The SO₂ and NO_x react with water, humid air, or rain to form sulfuric and nitric acids before falling to the ground.

While a small portion of the SO₂ and NO_x that causes acid rain is from natural sources such as volcanoes, most of it comes from the burning of fossil fuels. The major sources of SO₂ and NO_x in the atmosphere are:

- Burning of fossil fuels to generate electricity. Two-thirds of SO₂ and one-fourth of NO_x in the atmosphere come from electric power generators.
- Vehicles and heavy equipment.
- Manufacturing, oil refineries, and other industries.

Air stream moves SO₂ and NO_x over long distances and across borders making acid rain a problem for everyone and not just those who live close to these sources.

Mercury (Hg) is a neurotoxin. The largest sources of mercury are mining, stationary coal combustion, nonferrous metal production, cement production, and product waste. Mercury emitted into the air eventually settles into water or onto land, where it can be washed into water. Once deposited, certain microorganisms can change it into methylmercury, a highly toxic form that builds up in fish, shellfish, and animals that eat fish. Most human exposure to mercury is from eating fish and shellfish

contaminated with methylmercury. In-Utero exposure to methylmercury increases the risk of learning disability.

3.3 Greenhouse Gases Pollutants (Climatological Effect) CAA 40 CFR Part 98

Greenhouse gases (GHG) affect the balance between radiant energy from the sun and energy emitted back into space from the Earth. GHGs in the air absorb some of the outgoing energy from the Earth, trapping it and warming the lower atmosphere and the Earth's surface. Some GHGs, such as water vapor, carbon dioxide, methane, nitrous dioxide, and ozone, occur naturally in the atmosphere. Certain human activities, however, add to the levels of those gases, causing an increase in the amount of heat retained in the atmosphere, thus gradually warming the Earth beyond what otherwise would occur.

Currently, more than 500 companies have set targets based on guidance and resources provided by the Science Based Target initiative (SBTi). SBT initiative provides a clearly defined pathway for companies to reduce greenhouse gas (GHG) emissions, helping prevent the worst impacts of climate change, and driving future-proof business growth. SBTi considers targets as "science-based" if they are in line with limiting global warming to 1.5°C above pre-industrial levels to meet the goals of the Paris Agreement.

The GHG Protocol Corporate Standard classifies a company's GHG emissions into three "scopes".

Scope 1, GHG emissions occur from the sources owned or controlled by the company, i.e., boilers, furnaces, vehicles, etc.

Scope 2, Emissions from purchased electricity, heat, and steam for use in business operations.

Scope 3, indirect emissions that occur in the value chain of the reporting company, including both upstream and downstream emissions. Those criteria require emissions reductions of 2.5% per year for targets that cover scope 1 and 2 emissions and emissions reductions of 1.23% per year for targets that cover scope 1, 2, and 3 emissions.

GHGs have varying heat-trapping abilities and atmospheric lifetimes. Global warming potential (GWP) is a metric used to compare emissions among GHGs. The GWP of CO₂ is 1.0, and the GWP of other GHGs is expressed relative to CO₂. CH₄ has a GWP of 21. Each metric ton of CH₄ emissions would have 21 times as much impact on global warming (over a 100-year time horizon) as a metric ton of CO₂ emissions. Mass emissions x GWP provides CO₂ equivalent (CO₂e) in metric tons.

Warming Potential of Greenhouse Gases	
Carbon Dioxide (CO ₂)	1
Methane (CH ₄)	21
Nitrogen Oxide (N ₂ O)	310
Perfluorocarbons (PFCs)	6,500
Hydrofluorocarbons (HFCs)	11,700
Nitrogen Trifluoride (NF ₃)	17,200
Sulfur Hexafluoride (SF ₆)	23,900

Table 3-10: Warming Potential of Greenhouse Gases

Chemical	Carbon Dioxide (CO ₂)	Methane (CH ₄)	Nitrous Oxide (N ₂ O)	Fluorinated Gases (SF ₆ , HFC, PFC)
Sources	Fossil fuel, forestry, industrial processes	Agricultural and dairy farms	Agricultural and fossil fuel	Industrial processes, refrigeration
Percentage	79%	11%	7%	3%

Table 3-11: Sources of GHG (United States)

GHG Emissions in the US (year 2020)

The reported emissions are the sum of the contribution from coal, natural gas, petroleum product mostly fuel oil No. 1 and 2, process emissions. The “Others” heading in the table includes, coke oven gas, propane, and wood products.

Sector	Power Plants	Petroleum and Natural Gas Systems	Refineries	Chemicals	Other	Minerals	Waste	Metals	Pulp and Paper	Total Reported Emissions
Million Metric Tons CO ₂ e	1,495	316	161	184	118	109	105	78	35	2,602
# of Reporting Facilities	1,339	2,377	140	453	1,320	379	1,465	294	221	7,634

Table 3-12: GHG Emissions in the US (year 2020)

The CO₂ emission is obtained either by continuously monitoring stack-gas volumetric flow rate and its concentration or by monitoring annual fuel consumption and their heating values specified by EPA rules.

3.4 Industries of Most Concern for Environmental Pollution

3.4.1 Petroleum Plants

Hazardous Air Pollution (HAP) source categories

The petroleum refining industry is the nation’s second-highest industrial consumer of energy. Nearly all the energy consumed is fossil fuel for combustion; therefore, the petroleum refining industry is a significant source of HAP emissions. In addition to the combustion-related sources (e.g., process heaters and boilers), there are certain processes, such as fluid catalytic cracking units (FCCU), hydrogen production units, and sulfur recovery plants, which have significant process emissions of VOC, metal, and PM. Emissions from a typical petroleum refinery arise from process equipment leaks, crude oil storage tanks, asphalt blowing, delayed coking units, and blow-down systems. Asphalt blowing and flaring of waste gas also contribute to the overall CO₂ and CH₄ emissions at the refinery which are GHG gases. GHG emissions from petroleum refineries are estimated to be around 214 million metric tons of CO₂ equivalents (CO₂e).

Petroleum Refining has diverse categories of emissions sources. For each emission source, several emission measurements specific to that source are ranked in order of preference. EPA recommends refinery owners or operators to use the highest rank methods 1 or 2 for which data is available. The methodology ranks 1 & 2 generally relies on continuous emission measurements. Where rank 1, using continuous emission monitoring system (CEMS), measures the flow rate and concentration of

each species, and rank 2 measures the amount of fuel burned using the published F factor to calculate the quantity of each species released into the ambient.

The emission sources are identified as:

- Equipment Leaks
- Storage Tanks
- Stationary combustion sources
- Process Vents
- Flare
- Wastewater
- Cooling Towers

The table below is a process description and typical vent stream composition.

Process	Vent Stream
Equipment Leak	VOC- H ₂ S
Storage Tank	VOC
Stationary Combustion Sources	CO, NO ₂ , NO _x , SO ₂ , HCN, VOC, Lead, Hg, PM
Catalytic Cracker Unit	CO, NO ₂ , NO _x , SO ₂ , HCN, VOC, PM, Metal HAPs
Fluid Coking Unit	CO, NO ₂ , NO _x , SO ₂ , HCN, VOC, PM, Metal HAPs
Catalytic Reforming Unit	VOC, Dioxin, Cl ₂ ,
Sulfur Recovery Plant	NO ₂ , NO _x , SO ₂ , VOC, HCL, CS ₂
Flare	CO, NO ₂ , NO _x , SO ₂ , HCN, VOC, H ₂ S
Wastewater	VOC

Table 3-13: Process Description and Typical Vent Stream Composition

Equipment Leaks: The equipment leaks are small emissions from various equipment, valves stem, flanges, pumps seal, etc. Leaks are typically identified by using EPA method 21, which requires a portable instrument capable of measuring VOC (photoionization detector (PID) or flame ionization detector (FID)) or using an optical leak imaging technique. To calculate the total organic carbon emissions from equipment, a correlation equation that relates mass emission to measured leak concentration is provided. The screening value correlations in the following table are used for petroleum and Synthetic Organic Chemical Manufacturing Industry (SOCMI) equipment components. When concentration measurements (SV, ppm) are zero, the values under the Default Zero Emission Rate column are used.

Equipment Type	Default Zero Emission Rate (kg/hr/Source)	Pegged Emission Rates (kg/hr/Source)		Correlation Equation (kg/hr/Source)
		10,000 ppmv	100,000 ppmv	
Leak Rates for Petroleum Industry (Refinery, Marketing Terminals, and Oil and Gas Production)				
Valve	7.8E-06	0.064	0.14	$2.29E-06x(SV)^{0.746}$
Pump	2.4E-05	0.074	0.16	$5.03E-05x(SV)^{0.610}$
Connector	7.5E-06	0.028	0.03	$1.53E-06x(SV)^{0.735}$
Flange	3.1E-07	0.085	0.084	$4.61E-06x(SV)^{0.703}$
Open-ended Line	2.0E-06	0.030	0.079	$2.20E-06x(SV)^{0.704}$
Other	4.0E-06	0.073	0.11	$1.36E-05x(SV)^{0.589}$
Leak Rates for Synthetic Organic Chemical Manufacturing Industry (SOCMI)				
Gas Valve	6.6E-07	0.024	0.11	$1.87E-06x(SV)^{0.873}$
Light Liquid Valve	4.9E-07	0.036	0.15	$6.41E-06x(SV)^{0.797}$
Light Liquid Pump	7.5E-06	0.140	0.62	$1.90E-06x(SV)^{0.824}$
Connector	6.1E-07	0.044	0.22	$3.05E-06x(SV)^{0.885}$

Table 3-14: Equipment Leaks

Storage Tank: Storage tanks emit significant levels of VOC and HAP during typical operation, venting, and tank filling or dispensing. If the tank emission is not vented to a control device, EPA recommends using the TANKS v4.09D emission estimation software. If the tank emission is vented to a control device, the constituent concentration and flow rate are directly measured at the outlet of the control device using the direct measurement methods for stationary combustion sources or process vents in the following sections.

Atmospheric storage tanks (AST) store low-pressure fluids (0-0.5 psig) that do not pose any environmental hazard and are usually vented to the atmosphere. However, when storing certain fluids, such as when vapors of the stored liquid are flammable or when oxidation of liquid may form hazardous compounds, it is undesirable to have the tank vapor space vented to the atmosphere. In such cases, inert gas blanketing of the vapor space may be used or sent to a controlling device. Tanks designed to operate at pressures between 0.5 and 15 psig are termed as low-pressure tanks. Designs above 15 psig are treated as pressure vessels.

Summary of pollutants from storage tanks; benzene, 1,3-Butadiene, cumene, diethanolamine, ethylbenzene, n-hexane, methyl isobutyl ketone, styrene, toluene, triethylamine, xylene, Cresol, 2,2,4-trimethylpentane.

Stationary Combustion Source: Stationary combustion sources are the largest sources of VOC, criteria pollutants, metals, and GHG emissions at a petroleum refinery. Stationary combustion sources at a petroleum refinery include process heaters, boilers, combustion turbines, and similar devices. Typically, the largest process heaters at a petroleum refinery are associated with the crude oil atmospheric and vacuum distillation units and the catalytic reforming unit (if present at the refinery). In addition to direct process heat, many refinery processes also have steam and electricity requirements. Some refineries purchase steam to meet their process's steam requirements; others use dedicated on-site boilers to meet their steam needs. Similarly, some refineries purchase electricity from the grid to run their pumps and other electrical equipment; other refineries have co-generation facilities to meet their electricity needs and may produce excess electricity to sell.

The predominant fuel used at petroleum refineries is refinery fuel gas (RFG), which is also known as still gas. RFG is a mixture of light C1 to C4 hydrocarbons, hydrogen, hydrogen sulfide (H₂S), and other gases that exit the top (overhead) of the distillation column and remain uncondensed as they pass through the overhead condenser. RFG produced at different locations within the refinery is typically compressed, treated to remove H₂S (if necessary), and routed to a central location (i.e., mix drum) to supply fuel to the various process heaters at the refinery. This RFG collection and distribution system is referred to as the fuel gas system. A refinery may have several fuel gas systems, depending on the configuration of the refinery, supplying fuel to different process heaters and boilers.

A complete inventory for combustion sources will include emissions estimates for PM, SO₂, NO_x, VOC, and carbon monoxide (CO) and depending on the fuel combusted, hydrogen sulfide, metals like arsenic, chromium, mercury, lead, and selenium.

Many stationary combustion sources have a CEMS for NO_x and/or SO₂. CEMS is a comprehensive unit that continually determines gaseous or PM concentration or emission rates using pollutant analyzer measurements and a computer program to produce results in the desired units. There are two types of CEMS: in-situ and extractive. The extractive method is preferable due to the lower equipment cost, maintenance, and part replacement cost. The sample gas is extracted from the gas stream and transported to a gas analyzer for the measurement of the contaminant concentration. The gas is often conditioned to remove water vapor before analysis, so the concentration is commonly determined on a dry basis.

For cases where stationary combustion sources have CEMS which only measures pollutant concentration the published "F factor" can be used to calculate exhaust gas flow knowing the fuel gas composition and fuel flow measurements (EPA Method 19)

Flares: Flares are point sources used to destroy organic compounds in excess refinery fuel gas, purged products, or waste gases released during startup, shutdown, and malfunctions. Emission from flares consists of a fraction of hydrocarbons in the flare gas (e.g., CH₄, CO, VOC, and specific organic HAP) that are not combusted in the flares; SO₂ resulting from the oxidation of sulfur compound impurities, such as H₂S, in the gas stream; and CO₂ from the combustion process. If combustion conditions are not adequate, it may lead to the production of soot particles and NO_x. The EPA recommended methodology is continuous composition monitoring (or manual sampling at least once every 3 hours during a flaring event) and continuous flow rate monitoring of the gas sent to the flare.

Process Vents: Flares are commonly used in refineries as safety devices to receive gases during periods of process upsets, equipment malfunctions, and unit startup and shutdowns. There are a variety of processes and equipment at petroleum refineries that may release pollutants directly into the atmosphere through process vents. Those process vents may be controlled using flares, thermal incinerators, or other air pollution control techniques. At some facilities, the process gases may be routed to the refinery's fuel gas system rather than directly to a control device to the atmosphere, where it would be combusted with fuel gas in stationary combusted units or in a flare. Therefore, methods proposed for flare and stationary combustion sources can be applied to measure the gas composition and flow rate. This technique is applied to catalytic cracking units (CCU), coking units, catalytic reforming units (CRU), sulfur recovery plants, and hydrogen plants.

3.4.2 Pulp and Paper Plants

Pulp and paper technology convert wood into pulp for use in papermaking. This industry consumes a lot of water and energy and produces considerable wastewater, solids, and air pollutants. Pulping processes are generally categorized as chemical (Kraft pulping) and mechanical. The latter one has higher efficiency and produces less environmental pollutants but produces lower quality paper.

There are basically four stages involved in paper making: woodyard, pulp mill, recovery cycle, bleach plant, and paper machine.

The Kraft pulping receives wood chips from the woodyard, steams them, and adds it with white liquor into a digester. The white liquor consists of caustic (NaOH), sodium sulfide (Na₂S), and sodium carbonate (Na₂CO₃). Digester is a large heated pressurized vessel where lignin from woodchips is dissolved in the chemical. The content of the digester is sent to the washing process, where fiber is separated from lignin and organic compound in black liquor. The black liquor is sent to evaporators where the water is removed from the liquor to create high-density black liquor to burn in the recover boiler where the liquor is vaporized and burned, the organic in the liquor burn as fuel, while the chemicals fall to the bottom of the boiler and flow out as smelt. The smelt flows into a dissolving tank filled with weak wash liquor from the causticizing area. The liquor in the dissolved tank is called green liquor. The green liquor is pumped to the slaker where it is mixed with burnt lime and calcium oxide (CaO). The lime-green liquor mixture flows to two or three causticizers in a series to complete the reaction. The liquor is separated from the lime mud and becomes white liquor. The calcium carbonate precipitate is burned in the lime kiln to form calcium oxide for use in the causticizing area.

The pulp is processed in the bleach plant. Bleaching is the last step of the process, which aims to whiten and brighten the pulp. The production of white paper (pulp bleaching) includes five or six optional treatment steps with sequentially elemental chlorine, alkali, optional hypochlorite stage, chlorine dioxide, alkali, and chlorine dioxide. Air pollutants and gas emissions of concern for pulp and paper industries are given in the table below.

Source	Major Pollutants
Chemical Pulping Process	VOCs (terpenes, alcohols, phenols, methanol, chloroform, methyl ethyl ketone (MEK))
	Reduced sulfur compound
	Organo-chlorine compounds
Bleaching	VOCs (acetone, methylene chloride, chloroform, MEK, chloromethane, trichloroethane)
Wastewater Treatment Plant	VOCs (terpenes, alcohols, phenol, methyl acetone, chloroform, MEK)
Power Boiler	SO ₂ , NO _x , fly ash, coarse particulates
Evaporator	Evaporator non-condensable (sulfur compounds, VOC, alcohol, terpenes, and phenol)
Recovery Furnace	Fine particulates, sulfur compounds, SO ₂ , NO _x
Calcining (Lime Kiln)	Fine and coarse particulates

Table 3-15: Air Pollutant and Gas Emissions of Concern for Pulp and Paper Industries

Physico-chemical methods such as adsorption on activated carbon, filters, thermal oxidation, catalytic oxidation and condensation have been widely used to minimize these pollutants.

3.4.3 Electric Utility Plants

According to U.S. Energy Information Administration, in 2021, about 4.12 trillion Kilowatt-hours (kWh) of electricity were generated at utility-scale electricity generation facilities in the United States. About 61% of the electricity generation was from fossil fuels, coal, natural gas, petroleum, and other gases and 19% was from nuclear energy, and 20% was from renewable sources (wind, solar, etc.). Fossil fuel contribution breakdown for electricity generation is as follows: 36% from coal, 63% from natural gas, 0.4% from petroleum liquid, 0.3 from petroleum coke, and the rest from other gases. Fossil fuels consumption for 2021; coal 500,592,000 tons, natural gas 11,550,818x10⁶ cubic feet, petroleum liquid 20,678,000 barrels, and petroleum coke 2,940,000 tons. The total carbon dioxide emissions from power plants for all the fuels in 2021 was 4872x10⁶ metric tons.

There are differences in the hazardous chemicals in the flue gas release to the ambient from a power plant stack. It is recognized that various coals refuse like anthracite and bituminous produce different levels of hazardous chemicals than oil or gas-fired plants. The bituminous coals have higher sulfur and chlorine content than anthracite.

The EPA promulgated the Mercury and Air Toxics Standards (MATS) and National Emission Standards for Hazardous Air Pollutant (NESHAP) for Coal- and Oil-Fired electric utility steam generation unit (EGU) on February 16, 2012. An EGU is a fossil fuel-fired combustion unit of more than 25 megawatts (MW) that serves as a generator that produces electricity for sale.

For coal-fired EGUs, the rule set standards to limit mercury emissions, acid gas HAP, non-mercury HAP metals (e.g., nickel, lead, chromium), and organic HAP (e.g., formaldehyde, dioxin/furan). Standards for hydrochloric acid (HCl) serve as a surrogate for the acid gas HAP, with an alternate standard for SO₂ that may be used as a surrogate for acid gas HAP for those coal-fired EGUs with flue gas desulfurization systems and SO₂ continuous emissions monitoring systems installed and operational. Standards for filterable PM serve as a surrogate for the non-mercury HAP metals, with standards for total non-mercury HAP metals and individual non-mercury HAP metals provided as alternative equivalent standards. For oil-fired EGUs, MATS includes standards to limit emissions of HCl and HF, total HAP metals (e.g., mercury, nickel, lead), and organic HAP (e.g., formaldehyde, dioxin/furan). Standards for filterable PM serve as a surrogate for total HAP metals, with standards for total HAP metals and individual HAP metals provided as alternative equivalent standards. Periodic combustion process tune-up work practice standards were established to limit the formation and emissions of organic HAP. For natural gas-fired EGU, the rule includes standards to limit NO_x and CO₂.

To meet MAT standards emissions, EPA requires the application of the maximum achievable control technologies, selective catalytic reduction, flue gas desulfurization, and electrostatic precipitator. The EPA requires the continuous monitoring of acid gas HAP and mercury, and selenium on a regular basis from stack.

3.4.4 Coke, Iron and Steel Plants

Emissions sources at coke-producing facilities are the coke oven charging, coke oven leaks, discharge, and quenching. In the charging oven, particulate matter (PM) and gas from the open oven containing benzene, polycyclic aromatic hydrocarbon (PAH), sulfur dioxide (SO₂), Hydrogen sulfide (H₂S), and Ammonia (NH₃) are captured and sent to gas recovery units for desulfurization, ammonia scrubber, and removal of particulate matter. The "cleaned" gas stream is then used as fuel in combustion stack emissions to generate heat for coke oven batteries. Burning of coke-oven gas results in typical combustion emissions, such as PM, NO_x, CO, and VOCs. It may also result in SO₂ emissions, even after going through desulfurization processes typically found at by-products facilities, as coke oven gas can potentially be a high-sulfur fuel depending on the coal that is being coked.

Emissions from the coke oven door leakages are the largest source of fugitive emissions from a coke oven battery and are a significant source of benzene and polycyclic aromatic hydrocarbon (PAH) emissions. Door emissions also may contain PM, CO, SO₂, H₂S, and NH₃.

The coke ovens are sealed to prevent air from entering the oven during the carbonization process. However, when pushing coke into the open rail car, a reaction with air produces many hazardous chemicals. The open rail car is transferred to the quenching tower. A huge amount of water is sprayed onto the rail car. The contact of coke with water produces huge amounts of steam, which is emitted into the atmosphere from the quenching tower. It basically contains PM and many hazardous chemicals like CO, H₂S, and benzene.

The coke, iron ore, and limestone are poured into an open-hearth blast furnace to produce molten iron, which is processed further to create steel. Waste gas coming from the top of the furnace is mostly carbon monoxide (CO) which is cleaned and used to create hot air for the blast furnace. (Oxygen and electric arc technology).

3.4.5 Wastewater Treatment Plants

Wastewater treatment plants are major sources of hazardous contaminants to the surrounding environments, air, soil, and water. The main stage of wastewater treatment is the primary treatment stage. Primary treatment removes scum, solid wastes, and suspended materials as sludge and the liquid is sent to second stage called biodegradation or digestion stage where microorganisms are used to decompose organic compounds, and oxidize phosphorous, and nitrogen compound from the wastewater. The effluent from the digester goes to secondary clarifier where the sludge is separated from the wastewater. The wastewater is sent to the disinfectant unit before routing it to the reclaimed water area. In sludge processing phase, thickening, and dewatering process, a lot of odorous gases are released to the atmosphere.

The processes of a wastewater treatment; aeration, digestion, mechanical thickening, and drying of sludge results in the release of a wide array of air pollutants for example, total organic compounds (VOC), carbon monoxide (CO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂), suspended particulate matter (PM), hydrogen sulfide (H₂S), and ammonia (NH₃), methane (CH₄) and Nitrogen Oxide (N₂O).

4 Monitoring Requirements

EPA regulatory for cleaner air requires companies in the chemical process industries to report quantities of certain pollutants released to the ambient. The source of pollutants may be from equipment leaks, storage tanks, stationary combustion sources, process vents, and flares.

4.1 Fenceline & Equipment Leak Monitoring (Fugitive Emissions)

In December 2015, the EPA issued under the National Emission Standards for Hazardous Pollutant (NESHAP), Maximum Achievable Control Technology (MACT) for refineries, rules to control hazardous air pollutants from petroleum refineries and provide important information about refinery emissions to the public and neighboring communities. This rule requires refineries to monitor benzene emissions at key emissions sources within their facilities and around their fenceline as well as the emissions of Volatile Organic Compound (VOC) from the processing equipment, valves, pumps, compressor, and flanges. The rule also applies to chemical processing industries where VOC are involved, e.g., the Synthetic Organic Chemical manufacturing industry (SOCMI)

The program has two parts:

- Manage Fugitive Emission for Entire Facility – **Fenceline Monitoring**
- Manage Equipment Leaks – **Leak Detection and Repair (LDAR)**

In the state of California, the Bay Area Air Quality Management District (BAAQMD) requires the refineries fenceline monitoring of benzene, toluene, ethylene, xylene (BTEX), H₂S, and if needed, alkane and ammonia in real-time.

4.1.1 Fenceline Monitoring

The Office of Air Quality Planning and Standards (ORD/OAQPS) of EPA has put in place a program to manage the fugitive emissions from refineries. The goal is to reduce the amount of benzene, a carcinogenic chemical, released into the environment. The EPA has provided 325 A/B guidelines for refineries to follow to achieve that objective. Method 325 A/B provides guidelines on sorbent tube placement, frequency, and sampling duration. Refineries are required to place sorbent tubes at regular intervals on the fenceline and send the tubes every two weeks to one of the EPA-approved laboratories for data analysis. The 2-week average concentration should be below 3 ppb. Any value above that requires a corrective action plan to identify and reduce the source of fugitive emission. According to EPA, the 3-ppb cap for benzene concentration will reduce 50,000 tons of VOC into the environment.

Although EPA proposed a sorbent tube for fenceline monitoring, it does not rule out other methods of benzene monitoring if it meets EPA objectives. Currently, the only commercially available monitoring devices capable of measuring benzene in ppb range are ultra violet-differential optical absorption spectroscopy (UV-DOAS) open path sensors, Infrared open path, and gas chromatography (GC). Open path sensors provide the real-time measurement of benzene concentration averaged over the light path. EPA does not support this technology for fenceline monitoring yet. EPA's goal is to capture maximum concentration with sorbent tube while open path sensors provide a concentration average over a path.

4.1.2 Leak Detection and Repair (LDAR)

Equipment leaks are emissions that occur throughout the process area from various equipment components and connections. The leak detection and repair (LDAR) programs are standardized regulatory work practices that are designed to reduce fugitive emissions of air pollutants from the industry by identifying equipment for repair. Leaks are typically identified using EPA method 21 using an organic vapor analyzer, e.g., PID or FID, or using an optical leak imaging technique. The

direct measurement method provides the most accurate means of quantifying equipment leak emissions. LDAR requires inspection or monitoring of equipment on a monthly, quarterly, or yearly basis, depending on the history of site compliance. This process is very time-consuming and labor-intensive. To help industries, EPA has provided a table where mass emissions for several types of equipment can be estimated using correlation equations that relate mass emissions to leak concentrations that are obtained from gas analyzers. LDAR trigger concentration refers to the concentration level defined for each equipment, e.g., pump and valves 10,000 ppmv.

Currently, sites are using the optical leak imaging technique, which uses passive infrared spectral imaging to produce a real-time video image of the emission plume. This technique can quickly and easily identify the presence of leaks, particularly large leaks, but is not able to quantify emissions. Therefore, it must be combined with gas analyzer sensors.

Plant sites are proposing to have fenceline monitoring for LDAR to help them capture the medium to large leaks in real-time and start the repair to prevent further emissions to the ambient. The following figure compares a real-time measurement advantage over the traditional Method 21.

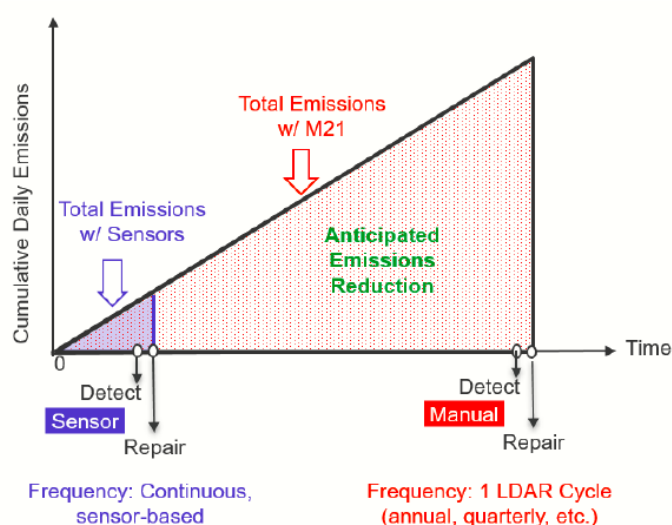


Figure 4-1: Advantage of Real-time Measurement vs. Long Cycle Measurement

For a plant site, LDAR is a cost-saving, environmental protection, and community safety program. Based on EPA estimates, petroleum refineries and chemical facilities can reduce VOC emissions from equipment leaks by 63% and 56%, respectively, by implementing effective LDAR programs. Assuming an average value of product loss due to equipment leak being \$1,370 per ton, a facility potentially can save \$730,000 per year.

4.2 Stationary Combustion Sources

Combustion equipment like boilers, turbines, and thermal oxidizers are widely used to destroy organic emissions that are produced during chemical, petrochemical and pharmaceutical manufacturing, and painting and packaging operations.

The most common stationary combustion sources are process heaters, boilers, and combustion turbines. These combustion sources are point sources for the release of pollutants to the ambient. Process heaters are used to preheat feedstock or process fluid for a given process. The boilers are used to generate steam for various operations and to raise the temperature of the process stream and feedstock. The primary fuel for process heaters and boilers is natural gas, fuel oil, and overhead organic compounds from process vents and coke. Combustion turbines are used for co-generation, and typically combust natural gas or refinery fuel gas.

There are two main technologies for monitoring these emissions on a continuous basis. The traditional one relies on sampling and analyzing exhaust gasses from a continuous emissions monitoring system (CEMS), and the newer one relies on software that uses mathematical algorithms and equations to predict emissions levels from existing control system data.

A CEMS consists of specific hardware installed on combustion equipment stacks that collect samples of exhaust gases and then analyses them to report the emission levels of regulated substances. Most CEM packages include an appropriate analyzer, data acquisition, software and generate the reports required by regulators.

CEMs are required to ensure that mandated reduction of SO₂ and NO_x are achieved under the Acid Rain Program of EPA. Boilers and fire heaters represent a major source of industrial NO_x emissions. CEMS measures SO₂ and NO_x concentration, volumetric flow rate, opacity, and diluent gas O₂ or CO₂. European Union directive also requires monitoring of HCl, dust, and heavy metals (i.e., mercury) in addition to SO₂ and NO_x.

Many stationary combustion sources have a CEMS for emission estimation of a complete inventory of combustion sources; NO_x, SO₂, CO, PM, and VOCs. A CEMS is a comprehensive unit that continually determines gaseous or PM concentration or emission rates using pollutant analyzer measurements and a computer program to produce results in a desired format. The CEMS or direct measurement measures both flow rate and gas composition. Another method is to use a gas analyzer to speciate the emission continuously and use the F factor to calculate the quantity of each species released to the environment.

There are two main types of CEMS: in-situ and extractive. An in-situ CEMS measures and analyzes the emission directly in the stack. In an extractive CEMS, the sample gas is extracted from the gas stream and transported to a gas analyzer for the measurement of the contaminant concentration.

To calculate emissions from a single boiler source, the EPA suggests the following equation.

$$E = A \times EF \times \left(1 - \frac{ER}{100}\right)$$

Where A is the total amount of fuel used over a defined period, ER is the emission reduction value for the control technology, and EF is the emission factor for the specific HAP in unit of mass per unit mass of consumed fuel. The emission factor published by EPA for a specific HAP depends on the combustion fuel, i.e., natural gas, crude oil, fuel oil, etc.

4.3 Process Vents

There are a variety of processes and equipment in a chemical processing facility that release pollutants directly into the atmosphere through process vents. The process vents may be controlled using a flare, thermal incinerator, or other air pollution control techniques. The process gases may be routed to a collecting system to be combusted with other fuel in a stationary combustion unit or routed directly to a control device to the atmosphere. Therefore, the emission from these gases is expected to be included in the emissions estimated for stationary combustion sources.

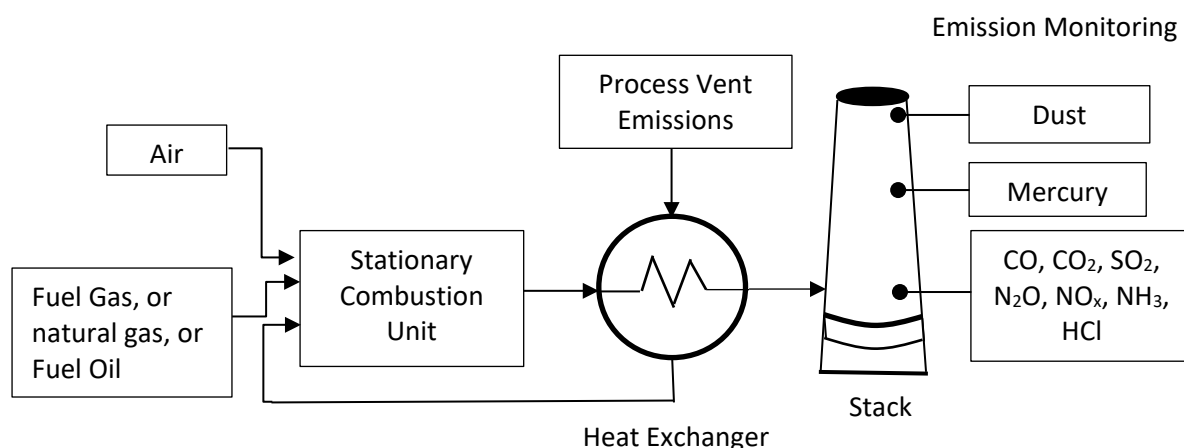


Figure 4-2: Thermal Oxidizer for Destruction of VOC.

In many cases, the flue gas is passed through other devices before venting to the stack. The most widely used post-combustion controls are selective catalytic or non-catalytic reduction. In this method, a reagent is injected into the flue gas stream to chemically reduce NO_x to N₂ and water. Another piece of equipment is an SO₂ scrubbing system to capture SO₂ and reduce the amount sent to the stack.

4.4 Flare

Most chemical plants and petroleum refineries have flare systems designed to relieve emergency process upsets that require the release of large volumes of gas. The vent stream enters the base of the flame, where it is heated by fuel and pilot burners at the flare tip, into the combustion zone for oxidation. Emissions from flares consist of a fraction of hydrocarbons in the vent stream (e.g., CH₄, CO, VOC, and specific organic HAP) that are not combusted in the flare; SO₂ resulting from the oxidation of sulfur compounds impurities, such as H₂S, in the gas stream; CO₂ from the combustion process. Soot particles and NO_x are also produced if combustion is not adequate. To address flare emissions, continuous monitoring of the gas stream prior to combustion in the flare is implemented, and the F factor methodology explained above is utilized.

4.5 Mercury

Since mercury occurs naturally in coal and other fossil fuels, burning these fuels for energy, the mercury becomes airborne and goes into the atmosphere. In the United States, power plants that burn coal to create electricity are the largest source of emissions; they account for about 44 percent of all manmade mercury emissions. Mercury exposure at high levels can harm the brain, heart, kidneys, lungs, and immune system of people of all ages. High levels of methylmercury in the bloodstream of babies developing in the womb and young children may harm their developing nervous systems, affecting their ability to think and learn.

The primary metals sector, which includes iron and steel manufacturers, accounts for 37% of the air emissions of mercury and mercury compounds reported to TRI for 2020. The electric utilities sector, which released the second-most mercury and mercury compounds into the air, accounted for 21% of these air emissions for 2020.

The EPA's final rule establishes power plant emission standards for mercury. It requires that the power plant combusts coal and oil to generate power to capture 90% of the mercury in the coal burned. This led to a reduction in U.S. mercury emissions from an estimated 48 tons/yr in 2003 to 15 tons/yr by 2020, for a total decrease of 69%. Power plants used adsorption to achieve that goal. The activated carbon and other adsorbents are being used to capture mercury from flue gas.

4.6 Odor Nuisance

Odor is a major community air pollution nuisance. Infrequent and short-duration odorous releases will not generate community outrage. However, frequent long-duration releases will create problems for the owner of the odor-generating facilities. The Clean Air Act published a list of hazardous air pollutants (HAP) and their health risk. Those health risks are inappropriate for odor. First, the relationship between odor and health risk is not well established. Second, our olfaction does not provide the margin of safety by allowing the detection of toxic chemicals that prompt avoidance of exposure. Third, their mechanism of affecting the body is different; odorant affects nasal olfactory epithelium, while toxicant affects various body organs. Fourth, Odorants need not be strong toxicants, and toxicants need not be odorous, so there is no rationale for making assumptions about risk based solely on odor perception.

What makes odor management so difficult is that continued exposure to odorous chemicals generally causes a decreased ability to smell these chemicals. A previously unexposed person may be warned by olfactory indicators from an episode of excessive chemical release, while a chronically exposed person might not as readily detect the release and thus be at greater risk. Therefore, our olfaction does not provide a margin of safety by allowing the detection of toxic chemicals that prompt avoidance of exposure.

Successful air quality monitoring and management requires identifying the sources of odor-causing gases at the plant and tackling them. Those sources are usually wastewater treatment plants, pulp and paper manufacturing, recycling, landfills, sewerage treatment facilities, refineries, etc.

Wastewater treatment plants emit CO₂, CH₄, and VOC from primary and secondary clarifiers, and the following odorous chemical from the sludge processing and dewatering systems.

Compound Name	Odor Description	Odor Threshold (ppb)
Hydrogen Sulfide	Rotten eggs	0.5
Indole	Fecal, Nauseating	0.1
Dimethyl Amine	Putrid, Fishy	340
Dimethyl Sulfide	Decayed Cabbage	1
Methyl Mercaptan	Rotten Cabbage	0.5
Acetic Acid	Sour	1000.0
Trimethyl Amine	Pungent, Fishy	0.4
Ammonia	Pungent, Irritating	47000
Phenyl Mercaptan	Putrid, Garlic	0.3

Table 4-1: Wastewater Stream with its Chemical/Odor Relationship

A list of 182 odorants with odor threshold values is published by American Industrial Hygiene Association.

Odor detection and management must be in place for facilities having the odor complaint to act quickly to reduce them for the comfort and the health of all employees and community residents.

This proactive approach provides clean air, reduction of complaints, and brings significant savings in operating costs, as well.

4.6.1 [Personal Protection Equipment](#)

Workplace regulations require workers to use personal protection equipment (PPE) designed to keep workers safe from hazardous chemicals. Wearing portable gas detectors plays an important role in the safety of workers in the plant environment. Potable gas monitors are small cost-effective single or multi-gas detectors that provide workers safe from atmospheric hazard by continuously monitoring the user's breathing zone. The alarm sounds and flashing light appears in critical safety scenarios. Basically, they have detectors to monitor oxygen level, existence of toxic or flammable atmosphere, and man down situation. Portable gas detection equipment is typically utilized when entering a confined space, performing hot work in potentially hazardous areas, or daily routine work at a plant site.

5 Emergency Response Requirements

The U.S. Occupational Safety and Health Administration (OSHA) rule for Process Safety Management (PSM) of highly hazardous chemicals (Title 29 CFR 1910.120 q) requires most chemical process industries to conduct emergency planning and response preparations. The law requires the development of a written Emergency Action Plan (EAP) for the entire facility per the directive of Title 29 CFR 1910.38 a. In addition, facilities should also follow the regulation set by EPA Emergency Planning and Community Right-To-Know Act (EPCRA). EPCRA's emergency planning provisions help communities prepare for potential chemical accidents. EPCRA's right-to-know provisions help public knowledge of and access to information on the presence, use, and release of chemicals at individual facilities. That information can be used by communities to improve chemical safety and protect public health and the environment.

Industrial facilities must conduct their business in a way that protects people, the environment and property, and continually seek ways to enhance that process. The public's expectations for the performance of chemical plants in their communities are becoming increasingly stringent and their tolerance for chemical release events, although minor, is low. Therefore, the implementation of a sophisticated emergency system to manage and respond to hazardous chemical spills is very serious. The system should have the ability to evaluate rapidly the possible consequences and risks of inadvertent releases of hazardous chemicals to the environment.

To help plant's emergency responder, National Oceanic and Atmospheric Administration (NOAA) and EPA jointly developed Areal Locations of Hazardous Atmospheres (ALOHA) dispersion modeling software which can be downloaded for free for emergency response application. It has a large database of chemicals, a set of sophisticated release estimation and dispersion modeling algorithms, a single weather station for weather data, and geographic information system (GIS) map for plume displays. However, it has many deficiencies which makes it more like a planning software than a real-time emergency tool.

ALOHA dispersion modeling cannot address the issues of plant sites in geographical areas with significant changes in elevations, hilly or mountainous regions, or complex wind patterns. It does not allow for wind shift, which is a crucial factor for accurately predicting plume trajectory for making decisions on evacuation, shelter-in-place, and closure of the businesses. ALOHA does not have any algorithm to quickly identify source location and the rate of chemical release, which is the Achilles hills of any emergency response system. The latter issues require the integration of gas sensors with dispersion modeling algorithms that do not exist in ALOHA. An effective and true emergency response package must address the gaps in ALOHA modeling capabilities.

6 Sensor Technologies for Effective Detection and Monitoring

The following sensor technologies can provide detection and monitoring for the requirements identified above.

6.1 Point Sensors

- **Electrochemical (EC)**
 - Substance-specific electrochemical sensors are available for a limited number of chemicals (less than 20). Ideally, they show little or no response to interferences. The sensors require little power, exhibit excellent linearity and repeatability, and generally have a long-life span. These sensors work best if they are operated below their maximum overload, which is chemical dependent, and have a good linear response. Exceeding the maximum overload gives erroneous readings and causes permanent damage to the sensor. Typically, most EC sensors offer 1 or 0.1 ppm resolution.

The table is a partial list of a few chemicals suitable for monitoring with electrochemical sensors.

Chemical	Sensor Technology
Carbon Monoxide (CO)	Electrochemical
Nitrogen Dioxide (NO ₂)	Electrochemical
Sulfur Dioxide (SO ₂)	Electrochemical
Ammonia (NH ₃)	Electrochemical
Chlorine (Cl ₂)	Electrochemical
Hydrogen Chloride (HCL)	Electrochemical
Hydrogen Sulfide (H ₂ S)	Electrochemical
Hydrogen Cyanide (HCN)	Electrochemical
Phosphine (PH ₃)	Electrochemical
Nitric Oxide (NO)	Electrochemical
Oxygen (O ₂)	Electrochemical
Hydrogen (H ₂)	Electrochemical

Table 6-1: Chemicals and the Sensor Technology for Measurement

- **Photoionization Detectors (PID)**
 - The most popular point sensor measurements for volatile organic carbon is PID. PID measures toxic volatile organic compounds (VOC) in concentrations ranging from low ppm to 10,000 ppm. PID is used to meet EPA method 21, which is a standard for monitoring equipment leaks, monitoring fugitive emissions, environmental soil contamination, and leaking of underground storage tanks. Although PID is excellent in identifying the presence of VOC but its weakness is its inability of speciating the

individual gases in a VOC gas mixture. There are about 32 VOC gases with an ionization potential of greater than 10.6 eV, which requires an ionization energy of 11.6 eV lamp. Unfortunately, those sensors are very hard to maintain due to frequent lamp burnout and replacement. PID cannot measure methane.

- **Catalytic Bead- Flames Ionization Detector (FID)**
 - FID measures toxic volatile organic compounds (VOC) in concentration up to 100,000 ppm. FID, like PID, is excellent in identifying the presence of VOC, but its weakness is the ability to speciate the individual gases in a VOC gas mixture. The performance of FID degrades with the reduction of oxygen in the ambient air. It is capable of measuring methane.
- **Infrared (IR)**
 - IR spectrometers contain a broad range (2.5 to 14.5 micro-meter) IR source and a variable pathlength gas cell. The longer the optical pathlength the more sensitive the response. The air sample is drawn into the sensing chamber, where it is exposed to infrared radiation. A thermophile detector measures absorbance. The absorbance data is compared to a library of absorbance spectra for a match to identify the composition of air pollutants in the sampled air.
 - Fourier transform infrared analyzers send light from an IR source to a reflector over a path in the atmosphere. The path can be 400 meters or more. This analyzer can measure in low ppm or ppb levels. It is ideal for assessing plumes and fugitive emissions. They are excellent detectors for speciating a mixture of volatile organic compounds. They cannot measure diatomic gas molecules, e.g., hydrogen, or chlorine gases.
- **Thermal Imaging**
 - Thermal imaging cameras detect radiation in the far infrared range of the electromagnetic spectrum. All objects with temperatures above absolute zero emit infrared radiation. The amount of radiation emitted by an object increases with temperature. Thermal imaging is promoted by EPA as an augment technology for the LDAR process. It is also the perfect technology for in-process leak detection and tank farm leak monitoring.
- **Sampling Tube (sorbent tube)**
 - Sorbent tubes are widely used for environmental and industrial hygiene studies. Air enters the tube by pump (active sampling) or through a diffusion process (passive sampling). The sample is absorbed by the sorbent, which is activated charcoal or silica gel. The chemicals are accumulated through the sampling period onto the sorbent material. The tubes are sent to laboratories to speciate and obtain the concentration of each chemical. Passive samplings are the recommended technique to monitor the fence line concentration of benzene in petroleum refineries.
- **Particulate Matter**
 - The basic operation of particulate matter concentration measurements is using light scattering of an optical source. The particulate matter (PM) is passed through a tube. In correspondence with a photodiode, particles in the airstream pass through a focused laser beam causing light scattering. The scattered light is then detected by the photodiode and converted to a mass concentration output. Providing appropriate filters can help to measure PM10 microns and PM2.5 microns.

6.2 Open Path Sensors

Open Path Sensors yields path average concentration along a pathlength up to several hundred meters long, e.g., IR and UV spectroscopy. This technique provides real-time speciation of nearly all VOC and chemical mixtures at the part per billion level (ppb). Open path technology is finding wider.

Acceptance/adoption by chemical processing facilities due to its unique capabilities of gas speciation in low ppb level and real-time response. The EPA is considering allowing the application of open-path sensors for fence-line monitoring as a replacement for Sorbent tubes.

7 Technology and Solution Recommendations

We recommend the following technology and solution approach for industrial plant EHS managers to help realize environmental safety. This approach involves developing a plan, procuring and deploying technologies for detection, monitoring and response, and establishing a program to maintain safe outcomes.

7.1 Develop Site Plan

As a first step, a site team should review the requirements outlined in this document and develop a plan for this site. This plan should include relevant regulations, pollutants of concern, and detection and monitoring requirements aligned with a map of the site noting areas of risk and concern. The plan should also outline how data from monitored systems will be collected and managed. Further, the plan should include emergency response procedures as well as technology and preparedness that supports those procedures.

7.2 Deploy Detection Capabilities

To support the detection and monitoring requirements, key sensors must be procured and deployed. There are three types of sensing technologies utilized in environmental safety in industrial plant sites. Continuous emission monitoring system (CEMS) which is comprised of sensors, data acquisition, analyzers, and software to calculate the rate of emission of pollutants of interest over a designated period, and portable and fixed sensors.

Portable personal and handheld sensors are key for the well-being of workers. They are usually lightweight, compact, robust, and accommodate several detectors, i.e., O₂, H₂S, PID, CO, and SO₂. They must have the ability to send data wirelessly to a gateway device or directly to a cloud-based system. This allows for real-time assessment of hazardous chemical in the plant environment, inform workers if they enter a hazard zone, and dispatch rescue team to a man-down event. Portable sensors are extensively used for hot work and confined space entry.

Fixed and portable area sensors are mostly used for plant site perimeter monitoring or within plant process areas. They can usually accommodate up to five detectors and preferably use solar panels for power. They must be able to use a mesh network to communicate with each other and through a gateway device or directly upload the information to a cloud-based service.

Knowledge of the rate of emission of atmospheric pollutants is essential for the enforcement of air quality policies set by the EPA's emissions inventories. There are two methods to meet EPA requirements: direct and indirect. Both methods require a continuous emission monitoring system (CEMS) for pollutants. The direct method measures the concentration and the exhaust gas flow. The indirect method uses the "F-factor" method to calculate the chemical emissions flow rate using the measured concentration of each chemical and applying fuel-specific F factor published by EPA. The CEMS is a must-have technology for venting systems, e.g., flare and stack. CEMS output the rate of release for each EPA-designated hazardous chemical.

EPA regulations promulgated under title V require the plants to address fugitive emissions which are mainly due to equipment leakage and cannot pass through stack, flare, or plants' venting systems. Fugitive emissions are one of the important elements of EPA's environmental monitoring and mitigation program. The program has two elements: The Leak Detection and Repair (LDAR) program and fenceline monitoring.

Portable handheld sensors carrying multiple detectors utilizing PID, Infra-Red, and electrochemical technologies are suitable for LDAR programs. For fenceline monitoring, fixed and portable area sensors equipped with solar panels, capable of measuring VOC and able to speciate and measure benzene in low ppb level are essential.

7.3 Deploy Monitoring and Data Management

Sensing equipment connectivity is crucial to operate a network of disparate sensors dispersed over a wide area and need to communicate remotely. Reliable networking technologies, wired and wireless, must be utilized for the transmission of sensor data to the plant's in-house server or cloud server. Multiple, flexible modes of communication are recommended to allow for effective options across sites; this includes RF, Bluetooth, Wi-fi, Cellular, Ethernet, and Satellite communications.

Situational awareness is crucial for safety managers. Implementation of data management with an intuitive dashboard can empower them to have real-time visibility into workers' conditions and provide information to run a dispersion model and provide evacuation or shelter-in-place. So, they can quickly identify gas alarms, man-down events and panic alarms, and analyze historical data to detect patterns of repeated alarms at a single location or any unsafe conditions or behaviors that require attention.

7.4 Sensor Placement

There are three possible sensor placements for a fixed site:

- Site perimeter sensor siting (fenceline monitoring)
- In-Process sensor siting
- Sensor siting at the entrance of the air intake to the buildings
 - Fenceline Monitoring
To safeguard communities living around the plant site from exposure to hazardous chemicals and monitor the level of fugitive emissions, EPA and OSHA require a fenceline monitoring plan in place. For an effective plan, it is necessary to optimally position gas sensors on the site perimeter. Optimally positioned gas sensors on a plant boundary would sound a light alarm on the smallest chemical release, which might cross the plant's fenceline and affect the surrounding community.
 - In-Process sensor siting
A well-placed array of gas sensors within a plant process can provide an early warning of gas leaks, which allows operators to take the steps needed to reduce the likelihood of fire, explosion, and toxic load to plant personnel.
 - To design a gas-monitoring system for a plant process area, the layout of the process unit piping, the location of pumps, compressors, flanges, instruments, hose, and other flexible connections, as well as possible release locations and the relevant hazards is required. Then a dispersion software is utilized to visualize how the resulting hazardous plume will disperse and identify the zone of 20% LEL or Acute Exposure Guideline Level 2 (AEGl 2) for flammable or toxic gas respectively to pinpoint the best location to place a gas detector. In case of the proximity of many potential releases, the overlapping gas-dispersion pattern can lead to a single monitoring site which can cover release from all those potential failures. Since each plant layout is different, it is not possible to have generic software like fenceline monitoring described above to address the in-plant sensor siting.
 - Sensor siting at the entrance of the air intake to the buildings.
To protect plant personnel working inside the buildings from contaminant air, sensors should be placed at the building intake air stream. The sensor for the air intake to the building is designed such that if a sensor detects an unacceptable level of predetermined chemicals in the intake stream, it will sound a light alarm and closes the outdoor air dampers for the building until the concentration of the chemicals are below the safe level.

7.5 Deploy Emergency Response Systems

The plant sites must keep in mind that procurement of an effective chemical emergency management and response system needs to have a sophisticated dispersion modeling algorithm and a comprehensive data platform with a user-friendly interface for effective situational awareness (SA). The system should gather sensor gas concentrations along with meteorological data, provide sound and sight alarms when concentrations cross user-defined limits, and feed information to a sophisticated dispersion model with the ability to accommodate complex terrain, wind shift, and sensor-driven plume. SA provides the ability to identify, process, and comprehend critical information about an accident. A data management platform (typically a cloud-based IoT platform) also acts as a hub to track and connect workers in real-time and integrate various apps that can inform and drive action across all phases of emergency management.

Integration of the following capabilities through an Internet of Things (IoT) platform provides powerful situational awareness information for a real-time emergency response system.

- Developing an automated response system
 - Utilizing gas sensors data to locate the source and rate of chemical release into the environment.
 - Automatically activate the dispersion model
- Application programming interface
 - Allowing emergency response modules to be embedded in a third-party platform.
- Integrating with technologies that help customers to complete compliance and reporting for Toxics Release Inventory (TRI), Superfund Amendments and Reauthorization Act (SARA), Incident Command System (ICS), and National Emergency Management Agency (NEMA).
- Integrating with plants' intercom paging and alarm systems.
- Integrating with Reverse 911 emergency notification alert system.

8 Appendix B- Enforcements- EPA Environmental Settlement Cases

The following are examples of published cases relating to EPA settlements that highlight some of the consequences of inadequate focus on this problem. <https://www.epa.gov/enforcement>

Violation	Fine	Capital Investment For Upgrade	Date
Clean Air Act Settlement- Violation of NESHAP for Benzene Waste Operations and Volatile Organic Compound Emissions from Wastewater systems	\$40,000,000	\$197,000,000	May 17, 2023
Clean Air Act Settlement- Failure to Comply with Multiple Volatile Organic Compound Emission Control Requirements and Failure to Comply with Leak Detection and Repair (LDAR) Requirements	\$2,000,000	\$ 4,500,000	April 20, 2023
Clean Air Act Settlement- Violation of NEHSAP for Excess Emissions of Volatile Organic Compounds, Various Hazardous Air Pollutants and Climate Change-Causing Greenhouse Gases	\$3,400,000	\$118,000,000	March 9, 2022
Clean Air Act Settlement- Failure to Properly Operate and Monitor Flares at Their Sites causing Excess Emissions of Volatile Organic Compounds, Various Hazardous Air Pollutants and Climate Change-Causing Greenhouse Gases	\$3,400,000	\$50,000,000	October 15, 2021
Clean Air Act Settlement- Failure to Obtain Certificate OF Conformity for New Engines (Part of Mobile Source Program) And Unlawfully Generating Three Thousand Tons of Hydrocarbon and Nitrogen Oxides.	\$20,000,000	\$3,700,000	January 30, 2020
Clean Air Act Settlement- Failed to Obtain Pre-Construction Permits and Install and Operate the Appropriate Nitrogen Oxide and Sulfur Dioxide Control Technology which led to significant Release of Those Chemicals into Atmosphere	\$1,300,000	\$12,650,000	December 30, 2019