Air Quality Impacts of Petroleum Refining and Petrochemical Industries

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Abstract: Though refineries and petrochemical industries meet society's energy demands and produce a range of useful chemicals, they can also affect air quality. The World Health Organization (WHO) has identified polluted air as the single largest environmental risk, and hence it is necessary to strive for and maintain good air quality. To manage potential health impacts, it is important to implement proper air quality management by understanding the link between specific pollutant sources and resulting population exposures. These industries release pollutants such as Volatile Organic Compounds, greenhouse gases and particulate matter, from various parts of their operations. Air quality should be monitored and controlled more meticulously in developing nations where increased energy demands, industrialization and overpopulation has led to more emissions and lower air quality. This paper presents a review of findings and highlights from various studies on air quality impacts of petroleum refining and petrochemical plants in many regions in the world.

Keywords: air pollution; Air Quality Index; air quality management; refinery; petrochemical; emissions; exposure; particulate matter; Volatile Organic Compounds; greenhouse gases; ozone; carcinogenic; toxicity; Persistent Organic Pollutants; polychlorinated biphenyls; heavy metals; cancer; Chronic Obstructive Pulmonary Disease; lung cancer; air sampling; atmospheric lifetime; heat integration; emission control

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1. Introduction

Air pollution and air quality impacts have been studied for many years now, and there are significant concerns around the world to varying degrees. This has led to the creation of Air Quality Indices (AQI), which are used to analyze the severity of air pollution and the level of risk to health, arising from particulate and gaseous air pollution. Though air quality management has been somewhat successful in developed nations, there is further room for improvement. In the case of developing nations, increased energy demands, industrialization and population growth call for better air quality management. Air Quality Indices communicate the exact condition of air quality to people, leading to both awareness of, and introspection about, necessary changes to regulations and actions. A variety of indices have been in use in various regions around the world. For instance, the Pollutant Standards Index (PSI) established by the United States Environmental Protection Agency (US EPA), the Common Air Quality Index in European countries, and the Air Quality Health Index in Canada, to name a few [1]. Many countries follow the AQI established by US EPA with an assigned value of 0 to 500, and it can be divided into the categories indicated in Table 1 [2].

Table 1. Categories of Air Quality Index (AQI).

AQI Values	Levels of Health Concern
0–50	Good
51–100	Moderate
101–150	Unhealthy for Sensitive Groups
151–200	Unhealthy
201–300	Very Unhealthy
301–500	Hazardous

The AQI can also signify the exposure of people to pollutants, which—although the pollutants are mainly outdoors—can also affect the indoor environment. Buildings only partially protect the people inside. Outdoor pollution is persistent enough to penetrate into the indoor environment and cause sustained, high exposures of occupants to some pollutants [3]. It is therefore crucial to understand the link between specific pollutant sources and the resulting population exposures in order to have proper air quality management [4]. Refineries and petrochemical industries are one of the contributing sources to the degradation of air quality, by releasing various pollutants like Volatile Organic Compounds (VOCs) into the surrounding environment. Though these industries meet the energy needs and growing demand for various products generated from them, they can also contribute to air quality concerns.

As an example, the sources of VOCs in air were analyzed at Wuhan, China [5]. Air was monitored at an urban site for 20 months spanning from February 2013 to October 2014. The contribution of vehicular exhausts, Liquefied Petroleum Gas (LPG) usage from households and catering applications, petrochemical industry, coal burning, and solvent use in cleaning/degreasing and coating, to the total VOCs at the site was analyzed. The concentrations of VOCs at the site and the source contributions have been tabulated in Table 2.

Table 2. Source contributions to VOCs (Volatile Organic Compounds) at Wuhan, China [5].

Source	Concentration ($\mu g/m^3$)	Contribution (%)
Petrochemical Industry	7.2 ± 0.5	14.4 ± 0.9
LPG Usage	9.9 ± 0.5	19.8 ± 0.9
Vehicular Exhausts	13.9 ± 0.5	27.8 ± 0.9
Coal burning	10.9 ± 0.4	21.8 ± 0.8
Degreasing/Dry cleaning	4.3 ± 0.3	8.5 ± 0.5
Coating/Painting	3.8 ± 0.2	7.7 ± 0.4

LPG: Liquefied Petroleum Gas.

From Table 2, one can see that the vehicular exhausts were believed to be the largest source of VOCs in Wuhan. LPG usage can be grouped with petrochemical industry for our consideration, as it is a petroleum product, and then we can conclude that the direct contribution of petroleum products (Petrochemical Industry and LPG usage) is $34.2 \pm 1.8\%$, thereby exceeding the contribution from vehicular exhausts.

Exposure to pollution causes many health impacts and has been identified as the world's largest single environmental health risk, contributing to numerous deaths [6] and therefore lowering air pollution levels can lead to a significant improvement in health outcomes. In the same analysis done by the World Health Organization (WHO), it was estimated that air pollution contributed to the death of 7 million people in 2012. Of these deaths, 40% related to outdoor pollution were due to ischaemic heart disease, 40% from stroke, 11% from Chronic Obstructive Pulmonary Disease (COPD), 6% from lung cancer, and 3% due to acute lower respiratory infection (in children). Similar effects were linked to indoor air pollution, with 34% of the deaths due to stroke, 26% from ischaemic heart disease, 22% from COPD, 12% from acute lower respiratory infection (in children), and 6% from lung cancer.

Since industrial activities contribute to a decrease in air quality, it is important to address this issue, and identify new ways to improve the situation. As refineries and petrochemical industries release a number of pollutants into the surrounding air, we need to understand the sources of pollution in these industries and the nature of the pollutants, in order to develop effective control strategies. Knowing the global scenario and trends of release around various petrochemical sites in the world can give us a broad picture of the pollutants that are being identified in the ambient air surrounding these sources, and the way in which they can affect air quality.

Among the pollutants released by these sites, the main ones are Volatile Organic Compounds (VOCs), particulate matter and greenhouse gases. VOCs found in the ambient air near petrochemical sites are both of aromatic and aliphatic types [7]. Pollutants are released in various areas and sources in the petroleum refining and petrochemical industries, starting from process emissions to storage and handling emissions. It arises from the production process, pipelines, flanges, valves, storage tanks, and waste zones. Pollutants are released even during non-routine operations like maintenance and shutdown [8,9], and the release of pollutants can vary seasonally [10]. The following sections summarize the sources and nature of emissions in more detail.

2. Sources of Air Pollution from the Petroleum Industry

There are various sources of emissions in the petroleum refining and petrochemical industries, and the following are the major categories of emission sources [11].

2.1. Process Emissions

In petroleum refining and petrochemical industries, the typical processes that take place include separations, conversions, and treating processes like cracking, reforming, isomerization, to name a few. The emissions arising from these processes are termed as process emissions, and are typically released from process vents, sampling points, safety valve releases, and similar items.

2.2. Combustion Emissions

Combustion emissions are generated from the burning of fuels, which is done for production and transportation purposes. The nature and quantity of emissions depends upon the kind of fuel being used. Generally, combustion emissions are released from stationary fuel combustion sources like furnaces, heaters and steam boilers, but they can also be released from flares, which are used intermittently for controlled release of hazardous materials during process upsets.

2.3. Fugitive Emissions

Fugitive emissions include sudden leaks of vapors from equipment or pipelines, as well as continuous small leaks from seals on equipment. These emissions are not released from vents and flares, but may occur at any location within a facility. Sources of fugitive emissions are mostly valves, pump and compressor, and piping flanges. Fugitive emissions are a source of growing concern, as their effective control requires good process safety mechanisms for mitigation, as well as ongoing lead detection and repair (LDAR) programs. They can be minimized by proper design, and procedure alterations.

2.4. Storage and Handling Emissions

These emissions are released from the storing and handling natural gas, oil, and its derivatives. This is a potential problem in every petroleum refining and petrochemical industry, including any product distribution sites. Handling mainly includes loading and unloading operations for shipping products to customers. Though transport of many refinery products is through pipelines, some other means like marine vessels and trucks also exist. In these cases, there might be emissions during material transfer to these vehicles. These facilities have tanks for storage at the production sites and

terminals for transportation, and air pollution here arises from the boil off or evaporation losses. Breathing losses also contribute to the air emissions, as the air within the tanks expands and contracts with daily temperature changes. Likewise, when there is an increase in the liquid volume in a tank, there is a corresponding decrease in the vapor phase volume as VOC saturated air is pushed out.

2.5. Auxiliary Emissions

Auxiliary emissions originate from units like cooling towers, boilers, sulfur recovery units, and wastewater treatment units. Atmospheric emissions from cooling towers mainly include gases, which are stripped when the water phase comes into contact with air during the cooling process. In wastewater treatment units, emissions may arise by stripping of the VOCs from contaminated wastewater in the pond, pits, drains or aeration basins.

3. Pollutants of Concern and Global Scenario

3.1. Volatile Organic Compounds

Hydrocarbons, both aliphatic and aromatic, are the main VOCs (Volatile Organic Compounds) that are generated from the petroleum industry [7]. Regulated emissions and leaks both contribute to the VOCs concentration [12]. Aromatic VOCs are mainly comprised of Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) [13], and benzene is of particular concern since it is carcinogenic. VOCs are associated with a number of potential health effects. Short term exposure to VOCs may cause dizziness, fatigue, nausea and depression. Exposure to certain VOCs may even result in mutations and cancers [14], and others may cause damage to the central nervous system, kidneys and liver [15].

The detection of VOCs in air typically follows one of two strategies, active and passive sampling. In active sampling, a pump draws air from the sample location through an adsorbent substrate at a specific flow rate, or into a collection container, or to an in-situ continuous sensor [16], depending on the type of VOC and concentration to be measured. The benefits of using active samplers are the collection of greater sample volume, and independence from environmental factors, unlike passive sampling. On the other hand, passive sampling does not call for the usage of pumps to draw the air sample, but uses the principle of diffusion through a static air layer into a collection medium. For example, a badge containing a sorbent is contacted with air, for a specific amount of time. Since passive sampling does not involve the usage of pumps, it is less bulky and easier to use. It is cheaper than active sampling but dependent on uncontrolled environmental factors.

It is important to know the atmospheric lifetime of VOCs to gain an understanding of the distances they might travel in air. A higher atmospheric lifetime indicates that the VOC can travel a greater distance in the atmosphere, possibly leading to impacts much farther away from the emission source. Table 3 tabulates the atmospheric lifetime of several common VOCs [17].

Table 3. Atmospheric Lifetime of some VOCs [17].

Compound	Atmospheric Lifetime
Benzene	9.4 days
Toluene	1.9 days
Ethylbenzene	1.6 days
o-Xylene	20.3 h
p-Xylene	19.4 h
m-Xylene	11.8 h
Methane	9.6 years
Ethane	60 days
Propane	10 days
Butane	5 days
Ethylene	4 days
Styrene	4.9 h

From Table 3 it is possible to infer that methane has the longest atmospheric lifetime among the listed VOCs and hence can travel a long distance from the source of release, when compared to styrene, which has an atmospheric lifetime of just 4.9 h. Among the common aromatics (BTEX), benzene has the maximum lifetime of 9.4 days, while the lifetime of m-xylene is only 11.8 h.

In urban areas close to refineries and petrochemical industries, the air quality is lowered by the combined effect of industrial emissions and traffic emissions. This was observed in Lithuania, which has a very large crude oil refinery. Benzene concentrations in air in the urban region exceeded the rural region by 0.63 ppb [13]. Air quality at rural regions near these industries was influenced only by the industrial emissions and traffic emissions played a minor role.

VOCs can also be aliphatic in nature. In a study performed in three sampling sites in Turkey, around large petroleum refining and petrochemical industries, it was observed that the aliphatic VOCs and their derivatives were predominant. Ethylene dichloride was the main pollutant, followed by ethyl alcohol and acetone [12]. It was stated that there is a high likelihood of finding ethylene dichloride near these petroleum refining and petrochemical industries as a result of its usage in these industries. In this case, ethylene dichloride is used as a lead scavenger for preventing deposition of lead oxide, in leaded gasoline blends. It is also formed as an intermediate compound in the petrochemical industries during production of vinyl chloride.

In a study of hydrocarbon source signatures at La Porte in Houston, Texas it was observed that in addition to BTEX, other major VOCs were ethene, propene, 1-butene, C2-C4 alkanes, hexane, cyclohexane, methylcyclohexane, isopropylbenzene, and styrene [18]. Some sites at which concentration measurements were taken were far away from major roads and highways such that traffic did not significantly affect the measurements. This is very important and we can infer that a non-urban region is the best indicator of the pollutant concentration from the industry, especially for VOCs. From a similar study around a major petroleum refinery in Greece, it was concluded that though aromatic hydrocarbons are a major source of VOCs, saturated hydrocarbons are also prevalent [7], which originated from the evaporation of oil products and organic solvents. In Tarragona region, Spain, which has many major petrochemical and chemical industries, ambient air concentrations of a group of 65 VOCs were measured [14]. It was assessed that average contributions to total VOCs made by BTEX, aromatic compounds, halogenated compounds, alkanes and alkenes ranged between 24% and 41%, 8% and 19%, 11% and 19%, 12% and 36%, and 15% and 33%, respectively.

Wind speed and direction are meteorological parameters that play a major role in the distribution of emissions and may vary from day to day. VOCs concentration decreases when wind speed is high, due to greater dilution. When the predominant wind direction is such that wind carries contaminants from the source to the sampling site, the concentration observed will be higher in this case, when compared to other wind directions.

Seasonal variations of VOCs have also been observed in various cases. In a study at Turkey, it was found that the VOC concentration was maximum in summer due to evaporation from fugitive sources, as a result of higher temperatures. The concentration was comparatively lower in the other seasons [12]. Diurnal variations in VOCs can also occur, and concentrations can be high at night. This can be attributed to the relatively calmer atmosphere at night than during the day, and the lack of photochemical activity, which acts to degrade VOCs in the atmosphere. During the day, the number of highly reactive species is lower compared to the low reactive VOC species, due to photochemical reactions. On the other hand, the low reactive VOC species are more abundant due to accumulation [19].

At a petrochemical industrial area in Yokohama Japan, 39 aliphatic and aromatic VOCs were measured in the ambient air, and aliphatic VOCs were the majority. n-Butane resulting from gasoline evaporative emissions and was found to be 3.5–6 ppb, while consumer products and petrochemical refining were the sources of isobutene in addition to gasoline evaporation. Propane was generated from the usage of LPG and natural gas processing [19]. Aromatic VOCs, mainly BTEX was also present in large amounts. Among BTEX, toluene was found to be most abundant (20.1 µg/m^3) followed by

ethyl benzene (12.6 μg/m^3), benzene (6.7 μg/m^3), and xylenes (m,p-Xylene: 9.1 μg/m^3, o-Xylene 2.9 μg/m^3). BTEX concentrations in some regions have been tabulated for comparison in Table 4.

Table 4. (**A**) Measured Benzene, Toluene, Ethylbenzene, Xylene(BTEX) and total VOC concentrations (ppbv) in urban regions; (**B**) Measured BTEX and total VOC concentrations (ppbv) in industrial regions; (**C**) Measured BTEX and total VOC concentrations (ppbv) in rural regions.

Region	BTEX (Benzene, Toluene, Ethylbenzene, Total Xylene)	Total VOCs	Number of Sampling Sites	Duration of Sampling	Type of Site	References
(A)						
Berlin	2.09, 3.84, 0.78,2.72	33.52	27	1 month	Urban	[17]
Bucharest	1.75, 3.83, 0.63, 2.03	30.53	15	1 month	Urban	[17]
Krakow	2.43, 2.76, 0.5, 1.71	26.35	15	1 month	Urban	[17]
London	0.8, 2.01, 0.4, 1.34	13.46	14	1 month	Urban	[17]
Lithuania	2.75, 3.1, 0.9, 2.77	9.52	4	4 weeks	Urban	[13]
Prague	2.46, 3.49, 0.67, 1.72	32.58	16	1 month	Urban	[17]
Rome	3.62, 9.28, 1.77, 7.39	40.24	59	1 month	Urban	[17]
Vienna	0.99, 1.17, 0.25, 0.97	11.26	14	1 month	Urban	[17]
Warsaw	0.75, 0.96, 0.19, 0.67	9.56	17	1 month	Urban	[17]
Paris	1.42, 3.28, 0.57, 2.22	20.19	48	1 month	Urban	[17]
Hong Kong	1.64, 4.45, 0.57, 1.26	14.47	32	1 month	Urban	[17]
Lanzhou	1.94, 1.01, 0.56, 2.08	23.25	1	2 months	Urban	[20]
Wuhan	1.7, 2.0, 0.5, 1.0	24.3	1	20 months	Urban	[5]
Guangzhou	2.4, 7.0, 1.2, 3.5	64.41	1	1 month	Urban	[21]
Houston	0.34, 0.41, 0.06, 0.38	11.35	1	4 weeks	Urban	[18]
(B)						
Lanzhou	4.48, 4.0, 3.0, 4.4	125	1	2 months	Industrial	[20]
Taiwan	1.85, 22, 3.65, 8.1	103.3	26	1 week	Industrial	[22]
Izmir, Turkey	-	135.9	3	1 year	Industrial	[12]
Shiohama, Japan	0.4, 1.6, 0.7, 1.3	89.6	1	17 months	Industrial	[19]
Aliaga, Turkey	1.47, 1.03, 0.23, 0.63	-	9	5 weeks	Industrial	[23]
Kocaeli, Turkey	5.61,14.48, 2.5, 9.65	47.17	28	2 months	Industrial	[24]
(C)						
Lithuania	1.96, 1.4, 0.45, 1.18	4.99	9	4 weeks	Rural	[13]
Xinken	1.42, 8.46, 1.62, 4.59	41.3	1	1 month	Rural	[21]
Aliaga, Turkey	0.71, 1.23, 0.18, 0.27	-	14	5 weeks	Rural	[23]
Navarre, Spain	2.27, 3.71, 0.273, 0.85	9.54	40	6 months	Rural	[25]

From the above Tables, it is possible to calculate the concentrations of BTEX in Asian and Non-Asian countries. For the Asian countries, the average concentrations are 2.14 ppbv Benzene, 6.11 ppbv Toluene, 1.33 ppbv Ethylbenzene, and 3.34 ppbv total Xylene. On the other hand, for non-Asian countries, the average concentrations are 1.82 ppbv Benzene, 3.01 ppbv Toluene, 0.57 ppbv Ethylbenzene, and 1.99 ppbv total Xylene. Based on this data it can be observed that the concentrations of all components of BTEX tend to be higher in Asia, when compared to other continents. This could be due to a variety of reasons including temperature differences. However, increasing energy demand and industrialization, and looser regulatory criteria may also be a contributing factor. When total VOCs are taken into consideration, the mean (arithmetic mean) of all VOCs for industrial areas is 100.19 ppbv. This is the highest among all regions. This is followed by urban areas, which have 24.33 ppbv of total VOCs. Total VOCs concentrations are least in rural areas, where the mean concentration of total VOCs is 18.61 ppbv. This could be attributed to the fact that industrial areas have the highest concentration of VOCs due to emission from industries, as well as traffic emissions. VOCs in urban areas mainly arise from vehicular emissions. On the contrary, rural areas are lower on emissions as they have very little traffic or industrial emissions.

Since a refinery site has a huge number of potential point sources of release, it is common to consider it as an area source. Once a pollutant concentration at a site is found, Inverse Dispersion Modeling (IDM) can calculate its emission rate. In a petroleum refinery in Northern China, this method has been used to find the emission rates [26] using a three-step approach. First, VOC concentrations and

meteorological conditions were measured. The next step involved the quantification of the relationship coefficient between the VOC emission rate of the source and the ambient VOC concentration, under the actual meteorological conditions measured. As a result, the monthly VOC emission rate was calculated [26].

VOC emission is an increasing problem, with similar scenarios in many major regions of the world. In addition to the VOCs patterns in the regions discussed so far, the trend is similar in Beijing (China) where field VOCs measurements were made for a petroleum refinery. VOCs were monitored for a period spanning from June to September 2011. A 61 ppbv rise in the ambient VOCs was observed in this time span [27].

3.2. Greenhouse Gases

The petroleum industry consumes a significant amount of fossil fuels for operational purposes, and this contributes to greenhouse gas emissions. The greenhouse gases associated with the petroleum refining and petrochemical industries are mainly methane, carbon dioxide and nitrous oxide [28]. In 2006, it was noted that equipment leakage and venting of CH_4 and CO_2 from petroleum and natural gas industries contributed to 317 million metric tons of CO_2 equivalent (MMTCO$_2$e). Out of this, 261 MMTCO$_2$e of CH_4 and 28.50 MMTCO$_2$e of CO_2 were emitted from the natural gas industry, whereas 27.74 MMTCO$_2$e of CH_4 and 0.29 MMTCO$_2$e of CO_2 were emitted from the petroleum industry. Table 5 provides a clear comparison to understand the level of greenhouse gases emissions from each stage of the oil and gas industry.

Table 5. Comparison of process emissions from each segment of the natural gas and petroleum industries in the United States [28].

Segment Name	U.S. Greenhouse Gases Inventory Estimate for 2006 (MMTCO$_2$e)
Production	198.0
Processing	39.5
Transmission and Storage	52.6
Distribution	27.3

MMTCO$_2$e: Million Metric Tons of CO_2 equivalent.

Many processes involved are very energy intensive, like alkylation, isomerization and so on. In recent years, increasing stringent fuel specifications pose a greater challenge for the oil and gas industry. To meet these requirements, the industry is using more energy in order to remove contaminants such as sulfur. Heat and power are persistent needs with the former being required at higher levels, often indirectly in the form of steam. Many refineries meet their heat and electricity needs by producing it themselves from gas, Fluid Catalytic Cracking coke and fuel oil. In this case, the fuel requirement, and hence the greenhouse gases emissions, are higher than they are for the refineries which procure these utilities from elsewhere.

Sometimes, though a few processes may be less energy intensive, the volume of input material processed might be high [29]. The greenhouse gas emissions are also linked to the complexity of the refineries, where in general the more-complex refineries emit more such gases. Even during the production stage, greenhouse gas emissions are significant. In 2013, the carbon dioxide emissions during oil production and processing were estimated to be 130 kg CO_2 per Ton of Oil Equivalent (TOE) [30,31]. For each ton of hydrocarbon production, there would be release of 1 kg of methane, and 0.4 kg of nitrogen oxides [30].

The count of wells and the production rate from each well have an important effect on the green house gases emissions. During the well completion phase it is crucial for the methane released to be flared or recovered. Intensity of emissions mainly depends on the ultimate recovery from the well [32]. Table 6 gives a detailed picture of the type of greenhouse gases emitted from various sources in the processing stage, and the sources and type of greenhouse gases emitted [33].

Table 6. Potential Greenhouse Gas Emission Sources in Processing [33].

Source Type	Greenhouse Gas		
	CO$_2$	N$_2$O	CH$_4$
Combustion Sources—Stationary Devices			
Boilers/steam generators	X	X	X
Dehydrator reboilers	X	X	X
Heaters/treaters	X	X	X
Fire pumps	X	X	X
Internal combustion (IC) engine generators	X	X	X
Reciprocating compressor drivers	X	X	X
Turbine electric generators	X	X	X
Turbine/centrifugal compressor drivers	X	X	X
Flares	X	X	X
Catalytic and thermal oxidizers	X		
Incinerators	X	X	X
Indirect Sources			
Electricity imports	X	X	X
Process heat/steam imports	X	X	X
Vented Sources—Process Vents			
Dehydration processes	X		X
Gas sweetening processes	X		X
Sulfur recovery units	X		
Vented Sources—Other Venting			
Storage tanks and drain vessels	X		X
Pneumatic devices	X		X
Chemical injection pumps	X		X
Vented Sources—Maintenance/Turnarounds			
Gas sampling and analysis	X		X
Compressor blowdowns	X		X
Compressor starts	X		X
Vessel blowdown	X		X
Vented Sources—Non-Routine Activities			
Emergency shutdown (ESD)/emergency safety blowdown (ESB)	X		X
Pressure relief valves (PRVs)	X		X
Fugitive Sources			
Equipment component leaks	X		X
Wastewater treatment	X		X

Throughout the operation of the petroleum industry, some gases are vented intermittently during equipment failures and maintenance activities [34]. Hence, blowdown and purge can also result in emissions of methane, where blowdown refers to the venting of gases contained in an equipment, pressure vessel, or pipeline, and purge refers to the process of replacing air in the equipment with other gases. This is done after maintenance, to restore an oxygen-free environment after the maintenance activity is over, for safety purposes. When this happens, some purge gas may be released as the air is displaced from the equipment [35]. The factors that affect the amount of methane released from maintenance and blowdown are the frequency of blowdown (times/year/equipment), volume of methane released per blowdown event (function of pressure, volume within the equipment and gas composition) and disposition of the blowdown gas.

There are some solutions for minimizing the energy consumption in processes and thereby the magnitude of greenhouse gases emitted. Two main approaches are heat integration (heat management) and waste heat recovery, where the existence of large temperature differences between different streams provides an opportunity to recover heat and reduce overall energy use [29]. Pinch analysis is a very effective technique to achieve a high level of energy efficiency [36]. It is a rigorous approach that can

lead to significant improvements in process and utilities, which in turn has many benefits like reducing operating costs, debottlenecking processes, and improving efficiency. It enables the identification of streams that have the maximum potential for economical heat recovery.

Pinch analysis has achieved energy savings of 10–25% (expressed as a percentage of total purchased fuel) in oil refining areas, and 15–25% in the petrochemical industry [36]. It can also contribute to savings in water and hydrogen consumption. Another area of reduction in energy consumption is an increase in furnace efficiency, which refers to the ratio of the heat transferred to the material and heat supplied to the furnace. The heat losses in the furnace can include heat storage in the structure of the furnace, losses from the outer walls of the furnace, heat transported out through load conveyors, radiation losses, heat carried by the cold air infiltration into furnace, and heat carried by excess air in burners [37]. To increase the efficiency of the furnace and minimize heat loss, one could reduce the temperature of flue gas, lower the volume of flue gas by minimizing excess air, optimize the fuel air-ratio, and use combustion air that contains a higher amount of oxygen. Waste heat recovery is another way to improve furnace efficiency, where we can utilize the heat energy in the exit gases for the process. Recuperators and regenerators are a common option to consider for waste heat recovery.

3.3. Particulate Matter

Particulate matter (PM) is of increasing concern in recent years as studies have shown links with a variety of health impacts such as respiratory and cardiovascular morbidity, and even lung cancer [38]. According to the International Commission on Radiological Protection (ICRP) Publication 30, particulate matter that is larger in size (over 10 μm) is intercepted by the nasal, tracheal mucus and is concentrated mainly in the naso-pharyngeal region [39,40]. Particulate matter of very small diameter is considered to be the most problematic as it penetrates deep into the lungs, thereby depositing in the bronchioles and alveoli in the pulmonary parenchyma region. Therefore, in many regions the focus of measurement and regulation is on particulate matter with a size of less than 2.5 μm (PM2.5). According to World Health Organization (WHO) guidelines, the annual arithmetic mean concentration of PM2.5 should not exceed 10 μg/m^3, while the 24-h mean concentration of PM2.5 should be below 25 μg/m^3 [41]. Particulate matter in air is sampled using integrated sampling systems, typically for a period of 24 h. Filter substrates in the system capture PM, from which it is possible to measure the mass concentration using gravimetry. Captured PM can also then be analyzed for its chemical components where desired [16].

Based on the formation mechanism, particulate matter can be classified into two types, namely primary and secondary particulate matter. Primary particulate matter is directly emitted from the source to the atmosphere, and a major source from the petroleum refining industry is the Fluid Catalytic Cracking Unit (FCC) [8]. Secondary particulate matter is mainly formed in the atmosphere from precursor gases like SO_2, NO_x and VOCs, from photochemical reactions or liquid phase reactions in fog droplets or clouds. SO_2 and NO_x are oxidized to form sulfuric acid and nitric acid respectively, and SO_2 oxidation can follow two routes. In the first one, SO_2 is oxidized to sulfate through photochemical reactions during the day, and the presence of oxides of nitrogen and hydrocarbons accelerates the process of photochemical oxidation. Alternatively, SO_2 can be oxidized to sulfate in the droplets in clouds. When molecules of air pass through the clouds, the soluble SO_2 gas gets trapped by the water molecules, where it is then oxidized to sulfate. Secondary sulfates and secondary nitrates scatter light well, resulting in hazy conditions and reduced visibility. In rural areas, the ratio of PM2.5 to PM10 is higher since secondary aerosol sources contribute considerably to PM2.5 formation [42,43]. Secondary aerosol includes particulates formed as secondary organic aerosols (SOA) as a result of the atmospheric and photochemical oxidation of VOCs.

Hydrocarbon emissions from the petroleum refining and petrochemical industries increase the rate of the first mechanism (i.e., formation of secondary sulfates from photochemical oxidation). In a study at Edmonton Canada, the PM2.5 level was measured over a six-year span [44]. Secondary organic aerosols were the main contributor followed by secondary nitrate and secondary sulfate. Secondary nitrate

constituted 16.7% of the mass concentration of measured PM2.5. Correlations of nitrate were observed with NO_2, CO, VOCs such as BTEX and other aromatic hydrocarbons, and alkanes. Further evaluation revealed that the dominant wind directions for the local sources were from the petroleum refineries and petrochemical plants on one side and the local roads (vehicular exhaust) on the other side. Secondary sulfate was found to be the third major component, contributing 15.4% to the mass concentration of measured PM2.5. It was determined that the petroleum refining and petrochemical industry was the main source for the presence of secondary sulfates at the Edmonton sampling location. At Rio de Janeiro, a study was carried out to evaluate emissions of aerosol particulates [45]. It was observed that oil combustion and traffic were accountable for 52–75% of the fine aerosols emitted. Industrial emissions also increase the amount of sulfur present within PM2.5 emissions [46].

There is also the possibility of the presence of metals in the particulate matter due to the emissions from this industry. A study on the effect of oil refinery and vehicular emissions on airborne particulate matter in Gela, Italy, revealed that there were many metals and metalloids in the airborne particulate matter [47]. When assessed further, it was found that the presence of arsenic, molybdenum, nickel, sulfur, selenium, vanadium and zinc, was attributed to the petrochemical industry emissions. Vehicular emissions contributed to the presence of copper, lead, platinum, palladium, antimony and some portion of zinc. These metals are potentially toxic, and their association with the atmosphere aerosols can have adverse health impacts [47,48]. A similar experiment conducted at Houston, Texas showed the presence of metals in airborne particulate matter, resulting from emissions during non-routine operations like startup, shutdown, maintenance activities and equipment failures [8]. Scandium, vanadium, molybdenum and nickel are common due to combustion of crude oil and its fractions. Lighter lanthanoids are enriched in FCC catalysts and hence refining operations can also contribute to the presence of metals in PM10.

Apart from these pollutants, petrochemical industries also produce Persistent Organic Pollutants (POPs), which resist environmental degradation by many processes. Though the Stockholm Convention banned the usage of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and polychlorinated biphenyls (PCBs) in 2001, a study was performed at Tarragona County in Catalonia (Spain) in the year 2002 to determine the concentrations of POPs in the soil, from chemical and petrochemical industries [49]. This was used to assess the environmental exposure to PCDD/Fs, PCBs, polychlorinated naphthalenes (PCNs) and polycyclic aromatic hydrocarbons (PAHs). The results obtained for the exposure to pollutants in the case of petrochemical industries, has been tabulated in Table 7.

Table 7. Environmental exposure to PCDD/Fs (in ng WHO-TEQ/kg day), PCBs, PCNs (in ng/kg day) and PAHs (in μg/kg day) through different pathways for adults living in Tarragona [49].

Pollutant	Exposure Pathway	Exposure Amount
PCDD/Fs	Soil Ingestion	1.19×10^{-6}
	Dermal Absorption	4.23×10^{-6}
	Air Inhalation	1.73×10^{-6}
	Total	7.15×10^{-6}
PCBs	Soil Ingestion	7.23×10^{-4}
	Dermal Absorption	2.57×10^{-3}
	Air Inhalation	1.15×10^{-2}
	Total	1.48×10^{-2}
PCNs	Soil Ingestion	5.86×10^{-5}
	Dermal Absorption	2.08×10^{-4}
	Air Inhalation	3.10×10^{-3}
	Total	3.36×10^{-3}
PAHs	Soil Ingestion	3.65×10^{-4}
	Dermal Absorption	7.39×10^{-4}
	Air Inhalation	4.95×10^{-3}
	Total	6.06×10^{-3}

PCDD: polychlorinated dibenzo-p-dioxins; PCDFs: polychlorinated dibenzo dibenzofurans; PCBs: polychlorinated biphenyls; PCNs: polychlorinated naphthalenes; PAHs: polycyclic aromatic hydrocarbons.

The measured levels were on the higher side when compared to other chemical industries and unpolluted sites. The soil samples in the region also contained heavy metals like manganese, lead, chromium.

3.4. Ozone

Ozone is a secondary pollutant that is formed from the reaction between VOCs, oxides of nitrogen, and sunlight. Hence, ozone production depends on the amount of VOCs, NO_x, and also the ratio of VOC/NO_x. The petrochemical industry can be a significant source of hydrocarbons (VOCs) and NO_x [10,18], and hence it contributes to a favorable atmosphere for the formation of ozone. In the case of ozone resulting from coal-fired power plant emissions (which contain NO_x but very little VOCs), hydrocarbons have to be provided from the surrounding region, and the power plant location relative to sources of reactive hydrocarbons is important in determining the impact on ozone formation [10]. However, the petrochemical industry can release both ozone precursors and therefore can have a more direct impact on regional ozone formation. The effects can be worse in summer when temperatures and ozone production rates are higher [50]. Other factors such as vehicular emissions also increase ozone formation by contributing to high levels of ozone precursors. Hence the urban zones/ traffic prone regions near petrochemical sites are at high risk of ozone formation. The presence of ground level ozone and airborne particles is a characteristic of photochemical smog, which is characterized by haze and reduced visibility. Topography and meteorology such as inversions also influence smog retention by trapping the pollutants. Smog can cause respiratory problems, coughing, irritation, reduced lung function, asthma, lung inflammation and damage to the lung lining [51].

Surface ozone is abundant in urban areas due to the large number of emission sources, but can be more abundant in rural areas when nitrogen oxides and VOCs are transported in the downwind direction. The ozone formation in such cases, is more sensitive to the presence of NO_x as VOCs are already present in large amounts due to the abundance of Biogenic Volatile Organic Compounds (BVOCs) emitted by vegetation, and this trend was noted in a study in Korea [52]. High levels of ozone were observed in Chuncheon, in comparison to Seoul, which was located upwind, though the emissions were less in Chuncheon than Seoul. Ozone moving from Seoul to Chuncheon was more sensitive to NO_x. Chuncheon had abundant VOCs during day, hence NO_x emitted from Seoul played a major role in the ozone formation.

Other than the concentration level of pollutants (VOCs and NO_x), another important parameter to be considered is their photochemical reactivity, determined by the Relative Incremental Reactivity (RIR) analysis [5]. In a study on concentration of VOCs and its impact on ozone concentration at Wuhan, China, it was observed that ethane, ethene and toluene were the most abundant VOC species, with concentration levels 5.2 ± 0.2 ppbv, 3.3 ± 0.2 ppbv, and 2.0 ± 0.1 ppbv respectively [5]. However, from the RIR analysis it was found that ethene and toluene were the main species contributing to the formation of ozone although ethane was present at higher concentrations.

Hydrocarbon release events with a frequency of several times in a year—which occur intermittently and unexpectedly—can cause ozone peaks. In the Houston and Galveston area, which has several petrochemical complexes, irregular emissions generated plumes that had rapid ozone formation [53]. In another event at Galveston Bay, 3000 kg of ethene was released over a time period of half an hour, and the ozone concentration measured within this event plume was 50 ppb higher than the concentration that was observed outside the plume, and 100 ppb higher than the regional background. In Houston, a discrete emission event releasing more than the allowable range of hydrocarbons occurs rarely at any single industrial facility, but if all industrial facilities are considered as a whole, then a large emission event releasing greater than 1000 kg of hydrocarbons occurred every week [54]. By modeling hundreds of such release events in Houston, it was found that approximately 1.5% of all the emission events that have occurred in that area produced over 10 ppb of additional ozone, 0.5% of emission events produced over 70 ppb of additional ozone, compared with the results with

no emission events [54]. Episodic events can have significant regional effects as they can cause ozone peaks in downwind regions.

4. Recommendations for Emissions Reduction

Petroleum refining and petrochemical industries produce emissions at many stages of the operations. These emissions can significantly lower the air quality and cause short-term and long-term health impacts for workers, and people living near the sites and in the same region. The only way the situation can be improved is to analyze the process and operations in detail and identify areas where control measures can be taken to reduce these emissions.

For example, proper venting and flaring technologies can reduce losses of natural gas, and this has been examined and quantified as shown in Table 8 [34].

Table 8. Potential nationwide reductions on onshore federal leases from increased use of venting and flaring reduction technologies [34].

Emission Source	Potential Reduction (Bcf)	Percentage of Total Volume EPA Estimated Vented and Flared
Gas well liquid unloading	7.2—Expand use of smart automated plungers	5.7
Well Completions	14.7—Expand use of reduced emission completions	11.7
Glycol dehydrators	5.7—Install vapor recovery devices	4.5
Pneumatic devices Oil and Condensate storage tanks	9.7—Use low-bleed devices 12.9—Install vapor recovery units	7.7 10.2
Total	50.2	39.8

Emissions from storage can be greatly reduced by employing measures such as vapor recovery systems, and using double seals in storage tanks. Leaks due to faults or seal failures in equipment are a common maintenance problem, and periodically checking or maintaining the equipment through a leak detection and repair program can minimize this. Likewise, fugitive emissions can be reduced through proper design, procedures, and good maintenance practices. In portions of the processes using combustion, lower NO_x burners are available, and SO_x emissions can be minimized by desulfurization of fuels, or by directing the sulfur-containing fuels to units that are equipped with SO_x emission control technologies [55]. Combustor and furnace efficiency should be improved, as it can also reduce emissions.

There are some Best Available Techniques (BATs) for the reduction of NO_x. They include the usage of low NO_x burners, gaseous fuel usage, selective catalytic reduction, and energy integration [56]. Usage of low NO_x burners lowers the flame temperature and reduces NO_x generation. A few burners employ recirculation of flue gas in order to reduce flame temperature. Replacing liquid fuels with almost N_2 free gaseous fuels, also tends to lower NO_x. Selective catalytic reduction is another way to achieve lower emissions, using V_2O_5/TiO_2 catalysts where oxides of nitrogen react to form nitrogen and water.

5. Conclusions

In common with various other industrial activities, refineries and petrochemical industries can affect air quality. They may release pollutants like VOCs (Volatile Organic Compounds), particulate matter, greenhouse gases and contribute to ozone formation, mainly from separation, conversion, treating, combustion, storage, sudden leakages from process equipment, or even from auxiliary sources like cooling towers, boilers, and sulfur recovery units. These emissions lower the quality of air—quantified by Air Quality Indices—and air quality management is critical to resolve this problem and minimize the impact. Although air quality management has been successful in many developed nations, it has more scope for improvement. In developing countries, factors like increased energy

demands and rapid industrialization have made it necessary to achieve better air quality management before the condition worsens further. Industrial areas have the highest concentration of VOCs when compared with urban and background areas. This could be attributed to emissions from industries and traffic emissions. In urban areas, vehicular emission is the main source of VOCs. Rural areas have the least amount of VOCs when compared to other industrial and urban regions. The level of exposure to polluted air is important in determining the potential effects on people, and as the World Health Organization has identified polluted air as the largest single environmental health risk, we need to ensure that air quality is well managed and improved.

Exposure to poor air quality appears to contribute to health conditions and deaths from COPD (Chronic Obstructive Pulmonary Disease), respiratory infection, lung cancer, and heart damage [6]. The direct contribution of refining and petrochemical emissions to health effects cannot be determined for certain, as many other factors such as population lifestyle and habits, and other emission sources also need to be considered before drawing any firm conclusions. This needs more research and extensive studies before we can infer more from any associations between specific emissions and health effects, but it is clear that any positive impacts on air quality can be beneficial. To maximize the benefits of new legislation and policies to improve air quality, it is desirable to carry out policy analysis using statistical modeling [57]. Such statistical modeling enables the analysis of the distributional consequence of different scenarios for emission reduction. This could thereby make it easier to conclude whether certain emission reduction policies could lead to minor or significant improvements.

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