Section: Environmental protection

Evaluation of fugitive emissions of hydrocarbons from a refinery during a significant pollution episode

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Abstract

Hydrocarbons and other Volatile Organic Compounds (VOC) a central role in the formation of ground level ozone, photochemical oxidants. High levels of photochemical smog and the related smog episodes are harmful to the ecosystem. Although allowed concentration levels are higher, there are also public health concerns about exposure to hydrocarbon vapors themselves. The main anthropogenic VOC sources are road traffic, the production and use of solvents and oil refineries.

On August 2000 several pollution episodes occurred nearby Ancona. Data acquired at monitoring stations showed very high levels of Hydrocarbons that were almost certainly due to fugitive emissions from an oil refinery located at short distance. Such emissions are always difficult to quantify. However, the simplest inventory methodology combines the crude oil throughput of refinery with a single emission factor, for fugitive process-emissions.

The aim of this study was to quantify "a posteriori" the fugitive emissions of hydrocarbons from the oil refinery during the significant pollution episodes. We applied a regulatory air dispersion model, namely AERMOD, to simulate the concentrations of Non Methane Hydrocarbons during August 2000 and to assign reliable fugitive emissions at API refinery. Dispersion models are deterministic models, based upon physical theories, that use source emission data, meteorology, and topography to create maps of pollutant concentrations. Such maps can be used to predict source-specific exposures. For this study, we focused on the oil refinery and its power plant, both located in Falconara Marittima (nearby Ancona, Central Italy) but we also considered all the main roads as line sources, while both combustion and other emissions sources were introduced as area sources.

The modeling system run about 30 times using different emission values. The results showed that fugitive emissions of VOCs in the refinery might have been, on August 2000, several times higher than those estimated by the refinery Company. Besides the obvious issues deriving from every emission underestimate, the VOC miscalculation in Falconara refinery may have fouled models so to misjudge ozone dynamics nearby.

Keywords: Volatile Organic Compounds; ozone; AERMOD; oil refinery.

1. Introduction

Volatile Organic Compounds (VOCs) constitute an important group of airborne pollutants to monitor and study as they contribute to some of the most serious environmental problems. Several VOCs, such as benzene and toluene, exert direct adverse effects on human health.

VOCs play a significant role both in particle and in ozone formation. Tropospheric ozone is produced by photochemical oxidation of carbon monoxide (CO), methane (CH_4) and Non-Methane Hydrocarbons (NMHC) in the presence of NO_X. The hydroxyl radical (OH) is the key reactive species in the chemistry of ozone formation, and it can react with CO, CH_4 and VOC. In general, increasing VOC concentrations means more ozone, increasing NO_X may lead to either more or less ozone depending on the prevailing VOC-to-NO_X ratio [5]. It is well know that modelling photochemical smog requires a precise knowledge of its precursor emissions especially on NMHC. Such knowledge should, if possible, include NMHC speciation. While attempting to model photochemical smog dynamics close to an oil refinery located nearby Ancona [1], we found that a well know model could not catch the exact chemistry of the observed phenomena. After several, in deep, studies and a complete sensitivity analysis, we found that the model could have had been fouled by a wrong amount of precursors given in input. In particular we found that a low amount of VOC was the prime suspect. Thus we decided to study the issue: in this paper we present the results of such study.

The determination of VOC emissions is remarkably arduous. Apart from natural sources of VOCs, which include forests, oceans, wetlands and volcanoes [2], volatile organic compounds are emitted by a wide array of human activities and products. Most of airborne VOCs are emitted as fugitive emissions that are strongly dependent on a plethora of conditions that include some parameters and circumstances very difficult to screen. For big petrochemical plants, between all, aging of apparatuses and their maintenance play a central role but quantifying such aspects is very difficult. On the other hand, monitoring diffuse emissions is almost impossible as environmental conditions associated with volatile organic compounds make accurate measurements challenging. In the end, in several cases, substance flows need to be estimated.

The major anthropogenic sources of VOC emissions are vehicles, paint industry, oil extraction and refining, organic solvents and solvent usage processes. Oil refineries plants are, in general, very large industrial installations. Their operation is associated with the emission of various organic compounds into the atmosphere, mainly originating from production processes and storage tanks [6].

In this study, we have used a regulatory air dispersion model, namely AERMOD, to simulate the concentrations of VOCs during August 2000 and, thus, to re-assign more consistent fugitive emission-rates to an oil refinery.

2. Ancona city and its district

The city of Ancona lies on the mid-Adriatic coast and it is a rather important junction for the distribution of goods and the transfer of passengers at European level. This happens due to the simultaneous presence of the port, a major railroad, a major highway, and a small airport also tailored for the movement of goods. The Ancona district is also dotted by several industries, mainly located along the Esino Valley. Most of the Ancona Province is a complex valley coastal area in central Italy comprising valleys, hills, highly populated areas and industrial districts. Certainly the most important source of concern for the environment has always been represented by the oil refinery founded in 1950 at Falconara Marittima [3].

Figure 1 to 3 show the concentrations of ozone and its precursors monitored at "Falconara Scuola" Station (FSS) and at "Falconara Acquedotto" Station (FAS), in the summer of 2000. High peaks reached by VOC are easily noticeable. During that summer, VOC reached values higher than 3,000 μg/m^3 (15 times the highest recommended value) at FSS.
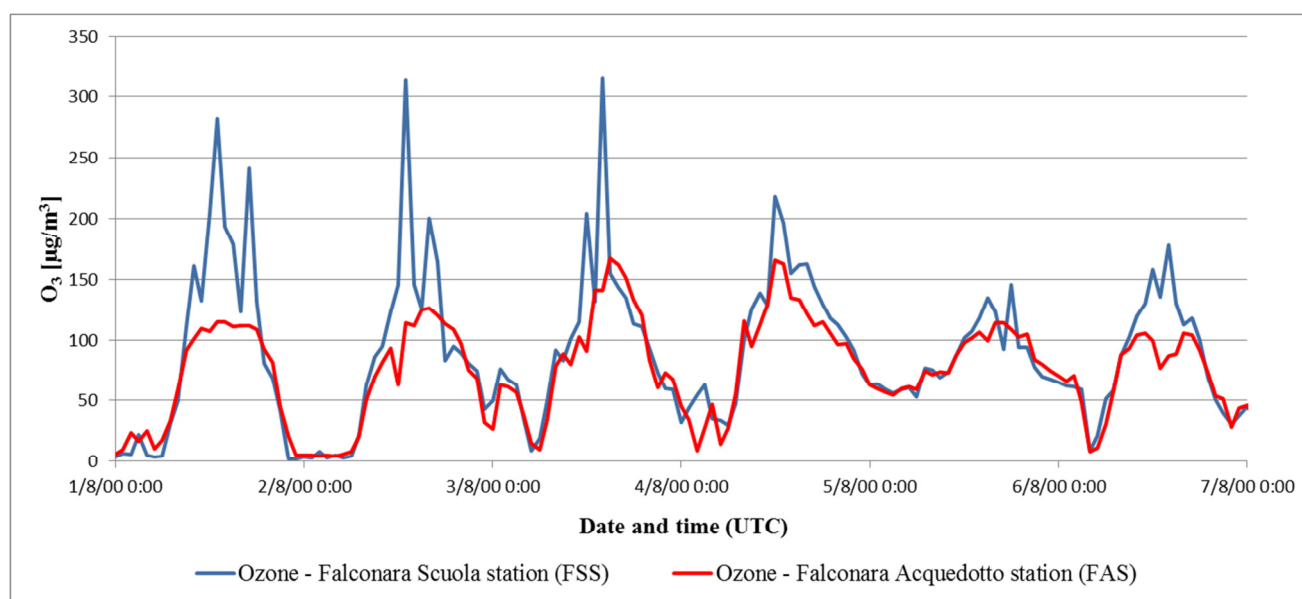

Fig. 1. Ozone concentration at Falconara Scuola (FSS) and Falconara Acquedotto (FAS) stations from August 1 to 7, 2000
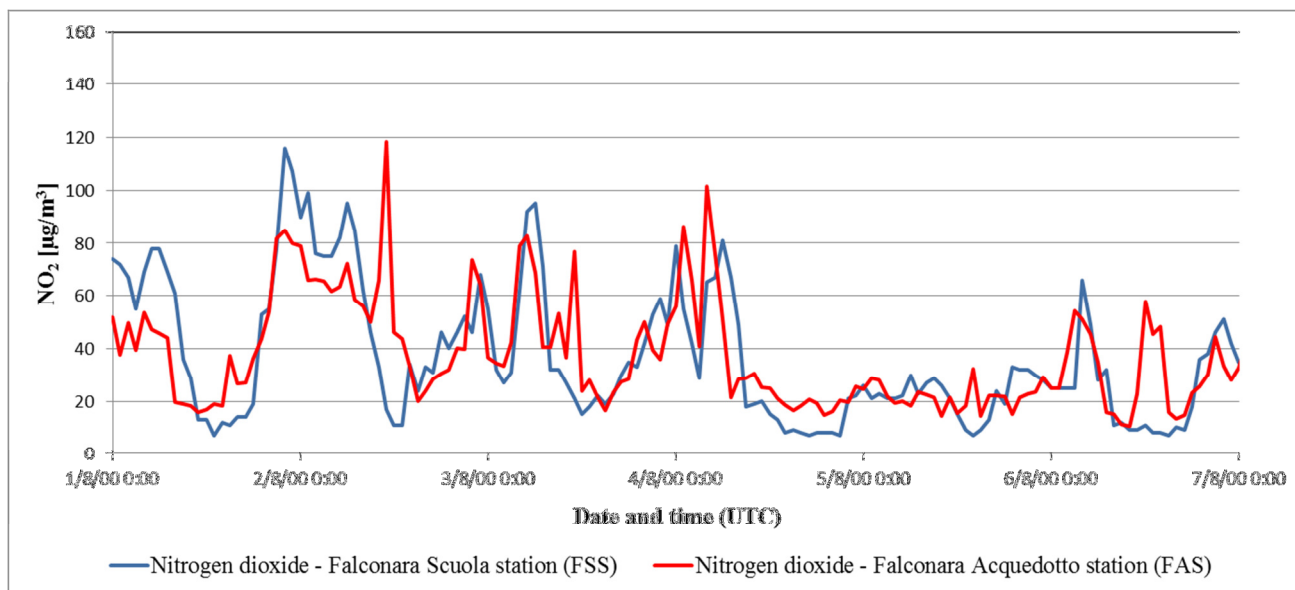
Fig. 2. Nitrogen dioxide concentration at Falconara Scuola (FSS) and Falconara Acquedotto (FAS) stations from August 1 to 7, 2000

The FSS is located in the Villanova of Falconara district, close to a primary school and is therefore situated in an urban environment. The FAS is located in the Fiumesino district, in a suburban setting. A distance of approximately 1.5 km separates the two monitoring stations. The FSS is only about 200 m away from the sea, whereas the FAS is about 1 km away from the coast. Both are close to the oil refinery (Fig. 4).

The two monitoring stations have measured similar concentrations of NO_2 (Fig. 2). The peaks of ozone at FSS match the VOC concentrations: when the ozone concentrations exceed 200 μg/m^3, the VOC concentrations are always above 2,000 μg/m^3 and the nitrogen dioxide (NO_2) concentrations exceed 30 μg/m^3 for most of the day.

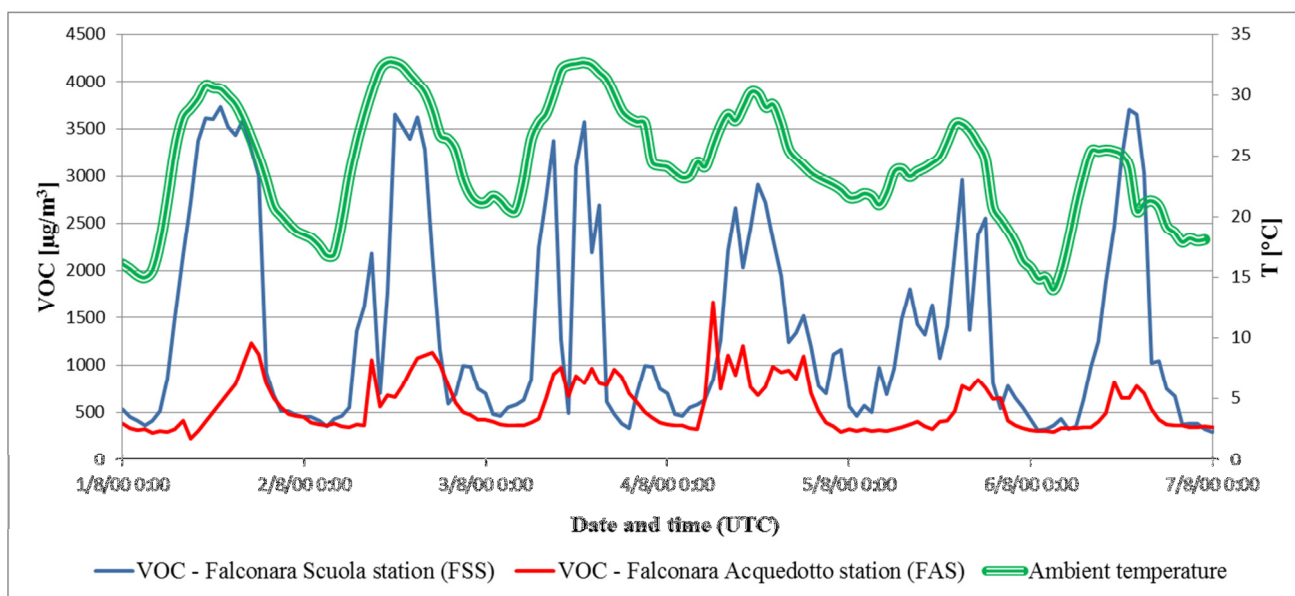

Fig. 3. Volatile organic compound concentration at Falconara Scuola (FSS) and Falconara Acquedotto (FAS)
stations and ambient temperature [°C] from August 1 to 7, 2000

Figure 3 also shows that the peak of VOC is connected to the behavior of ambient temperature. Conversely, the values are usually related to the daily temporal profiles of emissions for road transport and industrial activity.

In this case, the high concentrations seems to result from fugitive emissions, sources not associated with a specific process but scattered throughout the refinery. Fugitive process-emission sources are due to all valves, flanges, pumps and compressor seals, pressure relief valves, sampling connections and process drains. All these devices are used during the transport of crude oil, intermediates, wastes and refined products. Usually the valves are the major source type, due to their number and relatively high leak rate. Another main source of fugitive emissions in oil refineries is represented by storage tanks. Floating roof tanks (remarkably internal floating roof types) emit less airborne substances than fixed roof tanks that have nowadays almost disappeared in oil industry within developed countries.

Fig. 4. Location of Falconara Scuola (FSS) and Falconara Acquedotto (FAS) monitoring stations and oil refinery; each area of the plant is branded by a color: the oil storage area is branded in yellow, the process area is branded in red, and the refined-product storage area is branded in green [7]

3. Fugitive emissions estimate

We have already stressed that all fugitive process emissions are somewhat difficult to quantify. For petroleum industry, the simplest inventory methodology lets to evaluate the bulk of fugitive process emissions to the crude oil throughput of a plant (e.g. a refinery) by means of a single emission factor,. This approach, using single emission factors to estimate emissions from an entire refinery, is the easiest to apply if very limited information is available. Little account is taken of the true conditions of the petrochemical plants and of the blend of refined products and/or volatile products manufactured. For example, VOC emissions from a refinery, which reduces production of Diesel fuel and increases production of Gsoline, are expected to change (namely to increase at least for storage), even if the crude oil throughput remains the same.
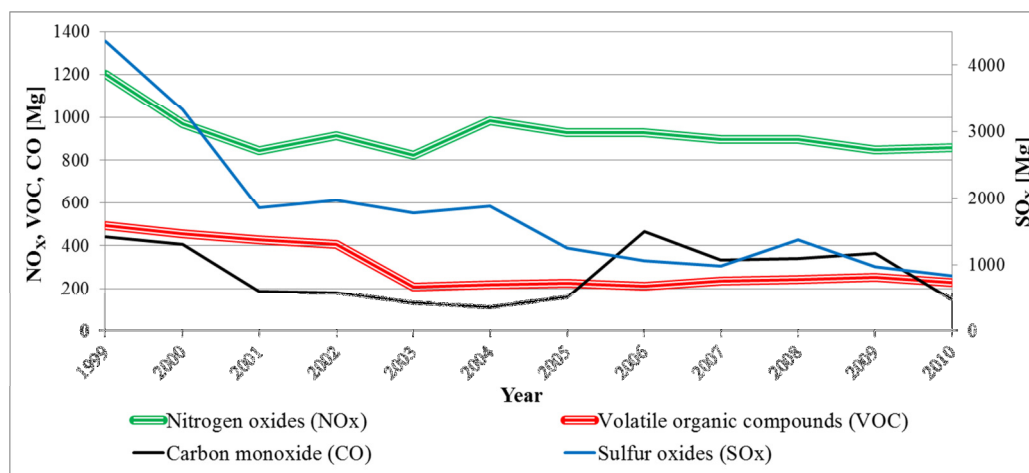

Fig. 5. Annual airborne emissions of Api oil refinery from 1999 to 2010; Api Annual Environmental Report [7]

The oil refinery we dealt with is located in Falconara Marittima, a municipality near the city of Ancona. All the Falconara Marittima territory and most of Ancona territory have been claimed "at risk of environmental crisis" also due to the presence of the petrochemical plant. For this reason, the oil refinery has been asked to consistently reduce airborne pollutant emissions. The company claimed that total fugitive emissions of volatile organic compounds have decreased from 456 tons in 2000 to 229 tons in 2010 (50% reduction). Over the same period (Fig. 5), nitrogen oxides remained nearly constant from 970 tons/year to 860 tons/year (11% reduction).

The VOC emissions asserted by oil refinery Company were evaluated by means of from two different methodologies. Up to 2002, the Company employed, as emission factors, values recommended by Unione Petrolifera, the Italian association of the major oil companies involved in refining and distribution of petroleum products. The total emission factor was about 0.11 VOC[kg]/ crude oil[Mg], and it depended on the type of processing plant and the amount of product handled and refined. Since 2003 the Company applied the methodology described in the EPA document 453/95 [8]. Such methodology,

led to an emission factor of 0.06 VOC[kg]/ crude oil[Mg] crude oil. The change of the main emission factor explains the abrupt VOC emission decrease of 2003 (Fig. 5) despite the same production capacity, and also the different distribution of emissions among the four refinery main sources as depicted in Figure 6.
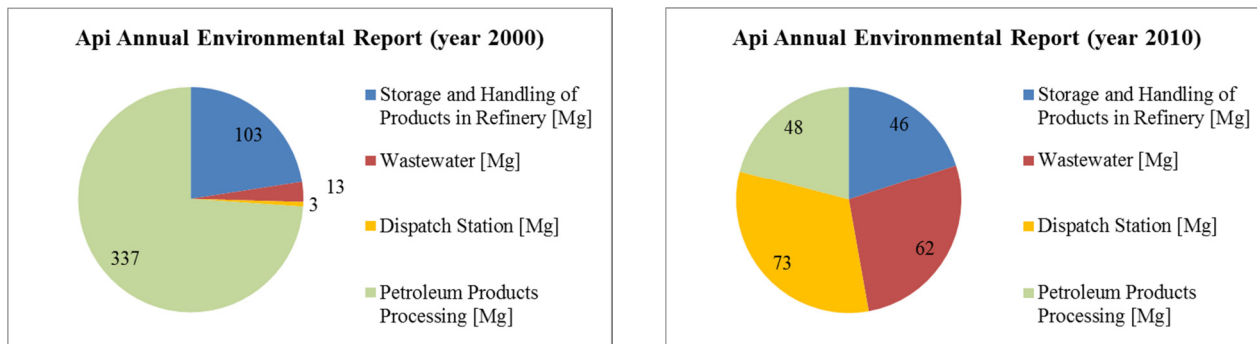

Fig. 6. Sources of VOC emissions from Api oil refinery (year 2000); Api Annual Environmental Report [7]

In fact, the EMEP/EEA Emission Inventory Guidebook [6] provide higher values foe emission factors compared to those declared by API. These factors, resulting from studies carried out in several countries around the world, do not take into account the specificity of the plant and the legislation of the country where it is located. The simpler methodology is based on aggregated average emission factors combined with information about crude oil and gasoline processed by Api refinery:

VOC Emission = (Average emission factor of Table 1) * (Total Gasoline or Crude oil handled)

In 2000, 3,292,386 Mg of crude oil and 584.276 Mg of gasoline were processed in the refinery and these values are fairly constant over the next decade. Fugitive process emissions for the entire refinery are inventoried under Selected Nomenclature for sources of Air Pollution (SNAP) code 040101 (Petroleum Products Processing). Using crude oil throughput as the activity indicator and an emission factor of 0.09 kg/Mg crude for process unit (CORINAIR90), we obtained an emission of 296 Mg for the year 2000. Regarding SNAP code 040104 (Storage and Handling of Products in Refinery), we have used an emission factor of 0.25 kg/Mg crude oil obtaining 823 Mg. To calculate VOC emissions from activities 050501 (Refinery dispatch station) and 050502 (Transport and depots) we used the hydrocarbon emission factors for uncontrolled techniques: 0.31 and 0.74 kg/Mg of total gasoline handled, respectively. Refinery dispatch station category includes emissions from filling of transport equipment (e.g. truck tanks) taking place within the refinery area.

Table 1. Fugitive emissions of VOC from Api oil refinery (year 2000), using the emission factors of EMEP/EEA Emission Inventory Guidebook [6]

Category	Emission Factor (VOC)	Emissions (Mg VOC/year)	Emissions (g VOC/sec)
Petroleum Products Processing (SNAP 040101).	0.09 kg /Mg crude oil	296	9.4
Storage and Handling of Products in Refinery (SNAP 040104)	0.25 kg/Mg crude oil	823	26.1
Refinery Dispatch Station (SNAP 050501)	0.31 kg/Mg of total gasoline handled	181	5.7
Transport and Depots (SNAP 050502)	0.74 kg/Mg of total gasoline handled	432	13.7
TOTAL		1732	54.9

4. Aermod model

Dispersion models are deterministic models, based upon physical theories, that use source emission data, meteorology, and topography to create maps of pollutant concentrations. Such maps can be used to predict source-specific exposures. Receptor models can provide detailed concentration maps and precise source-to-destination ratio as cause-effect connections. Different types of deterministic receptor models, able to accomplish these objectives, exist but Gaussian models are more widely used for regulatory purposes.

The basic Gaussian plume-diffusion model is steady-state and hypothesizes that all meteorological, orographic and surface parameters are uniform and constant throughout the air layer into which the pollutants are discharged. The pollutants are released at a height above the ground that is given by the physical stack height and the rise of the plume due to its momentum and buoyancy. The degree of dilution is inversely proportional to the wind speed and pollutant material reaching the ground level is reflected back into the atmosphere. The pollutant field is conservative, thus, it does not undergo any chemical reactions, transformation or decay [4].

AERMOD is a steady-state plume dispersion model for the assessment of pollutant concentrations from point, volume, and area sources. The model employs hourly sequential preprocessed meteorological data to estimate concentrations by averaging times from one hour to one year. Sources may be located in rural or urban areas, and receptors may be located in simple or complex terrain. Complex terrain is defined as terrain in which ground elevations are above the stack tip or release height and the complex terrain capabilities of AERMOD are of particular interest. It employs continuous variables to characterize atmospheric conditions, rather than a fixed number of categories used by traditional Gaussian models [9]. The AERMOD modeling system consists of two preprocessors and a core dispersion model. AERMET is the meteorological preprocessor for the AERMOD [10] while AERMAP [11] is the terrain preprocessor that characterizes the terrain, generates receptor grids, and facilitates the generation of hill height scales. Input data can come from hourly cloud cover observations, surface meteorological observations, and upper air soundings and may include surface meteorological observations and parameters and vertical profiles of several atmospheric parameters. The model is very sensitive to land use parameters and complex coastal terrains.

AERMOD is recommended by the EPA as the preferred dispersion model for general industrial modeling scenarios. Its performance was evaluated against observed concentrations for impacts emitted from Falconara refinery. For our simulations, the required source data input includes source type, emission rate, location, stack height, stack gas exit velocity, stack inside diameter, stack gas temperature and elevation.

5. Simulation settings

The AERMOD model was applied to study the diffusion of volatile organic compounds from Falconara refinery and other sources in five days of year 2000 (namely August 3, 12, 17, 20, 30). Among the discrete receptors, we included the locations of air quality monitoring stations (FSS, FSA) to compare model output and measured values. This enables to compare the maximum values provided by the model with the maximum measurements of monitoring stations. These simulations could allow understanding cause-effect ratio related to refinery sources of VOC.

The sources of volatile organic compounds included are numerous. All the main roads of Ancona Province were added as line sources, while other emissions sources, such as combustion in the manufacturing industry, solvent and other product use, other mobile sources and machinery, waste treatment and disposal were inserted as area sources. Among the sources, we included the oil refinery and the Integrated Gasification and Combustion Cycle power plant, in Falconara Marittima.

About fugitive emissions, the most appropriate method of characterizing fugitive sources is to consider them as volume sources. We have included two volume sources: VOL1 to represent fugitive emissions declared by oil Refinery Company (456 tons of VOC, in 2000, see Fig. 1), never changed, and VOL2 to represent fugitive emissions estimated using emission factors as described in Table 1.

Assuming a constant emission rate throughout the year the VOL1 value added to AERMOD is 14.5 g/s. The modeling system run about 30 times using different emission values for VOL2 (30, 40, 50, 60 g/s).

Figure 7 shows the relationship between wind direction and VOC concentration (average and maximum) on all days of August, in the two monitoring stations of Falconara Scuola and Falconara Acquedotto. The different ground elevation of monitoring stations can explain their distinct behavior. In fact, Falconara Scuola station is located on the top of a building and therefore it might be more influenced by emissions from storage tanks.
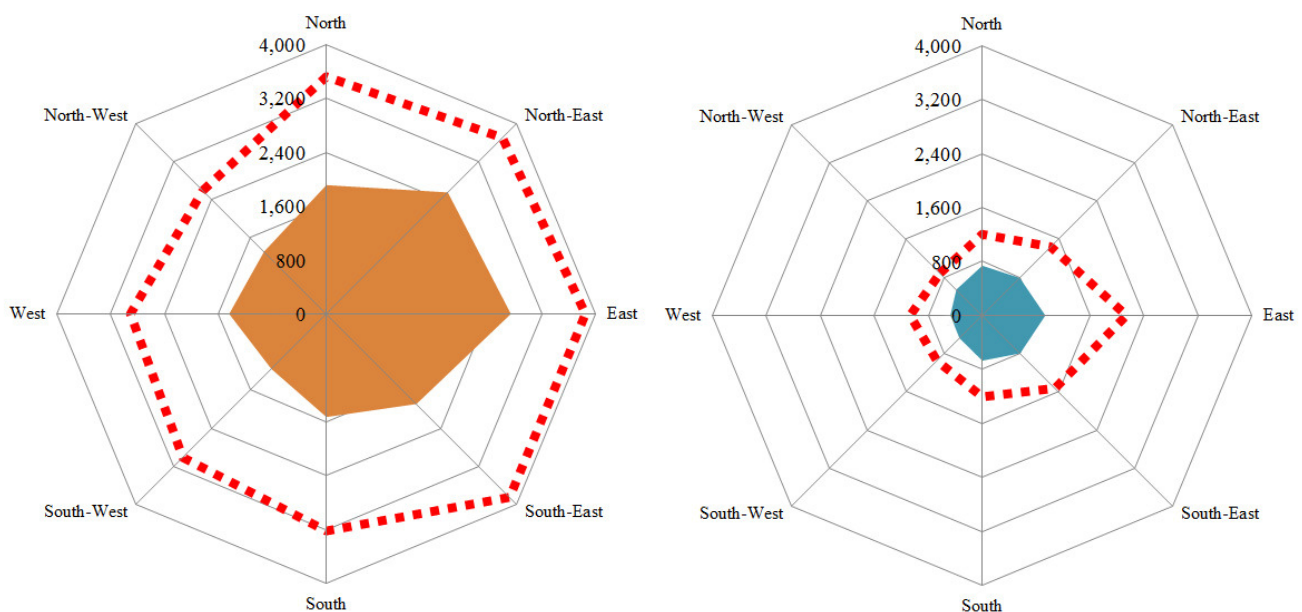

Fig. 7. Pollution roses at Falconara Scuola (left) and Falconara Acquedotto (right) on all days of August 2000; the red dashed line is the maximum concentration [$\mu g/m^3$] for each direction wind is blowing from, while the contour area is the average concentration for each direction wind is blowing from

In the five days we focused upon the wind fields were not uniform. As an example, Figure 8 shows the wind rose and the pollution rose of August the 20.
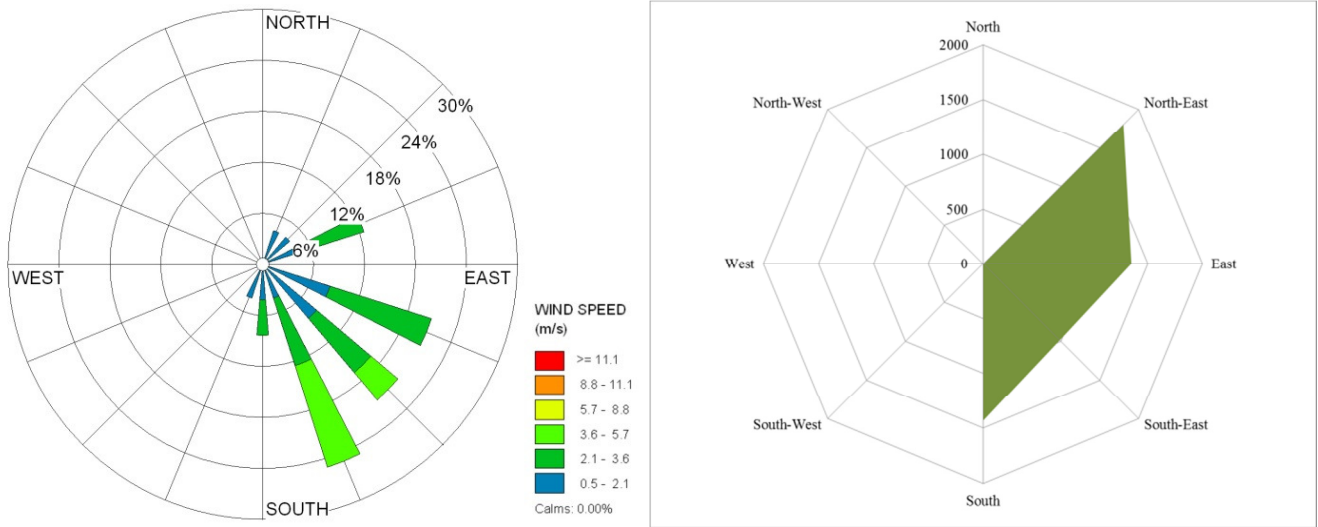

Fig. 8. Wind rose (left) and pollution rose (right, VOC concentration in $\mu g/m^3$), at Falconara Scuola on August 3, 2000

6. Results

In Figures 9 to 11, we show the values of maximum concentrations measured at monitoring stations compared with data obtained through AERMOD simulations. They quite clearly show that increasing the value of "VOL2" emission makes the two data sets more comparable.
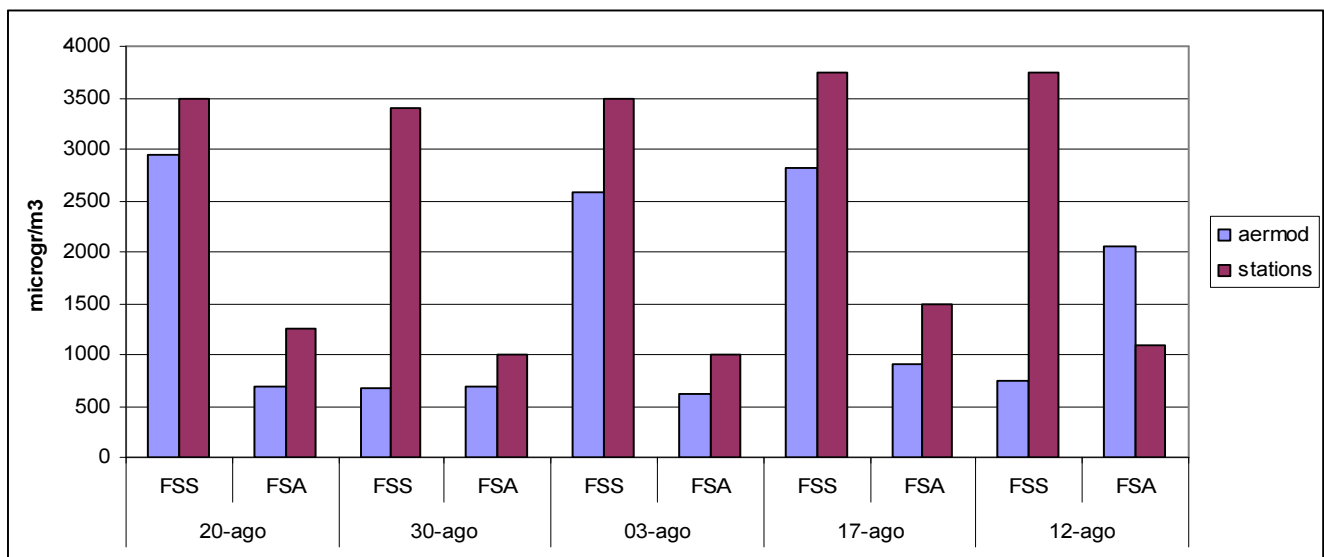

Fig. 9. VOC emissions of VOL2 = 30g/s. Comparison between maximum values provided by the model and maximum value from monitoring stations (FSS, FAS), in the five days of August 2000 (VOC concentration in $\mu g/m^3$)

VOC concentrations evaluated by AERMOD for August 12 and August 30 are unaffected by applying greater emission values in VOL2. We expected this behavior since the AERMOD model is based upon basic Gaussian diffusion equation. Thus, if the wind is not blowing from source to receptor, the concentrations at receptor site will not increase proportionally to emission increases.

During the other surveyed days, only when the VOL2 emission rate is around 50 g/s, the evaluated data are in good agreement with observations (Fig. 11). It is important to stress that the model simulates very well the distinct behavior of the maximum concentrations in the two sites, although they are very close each other.
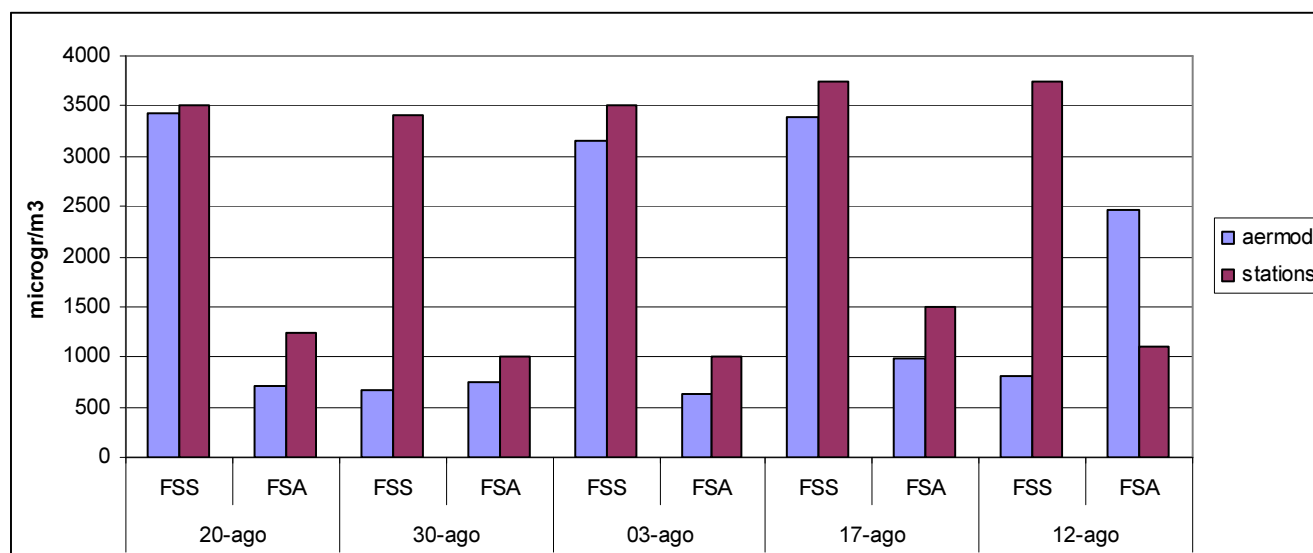
Fig. 10. VOC emissions of VOL2 = 40g/s. Comparison between maximum values provided by the model and
maximum value from monitoring stations (FSS, FAS), in the five days of August 2000 (VOC concentration in μg/m³)
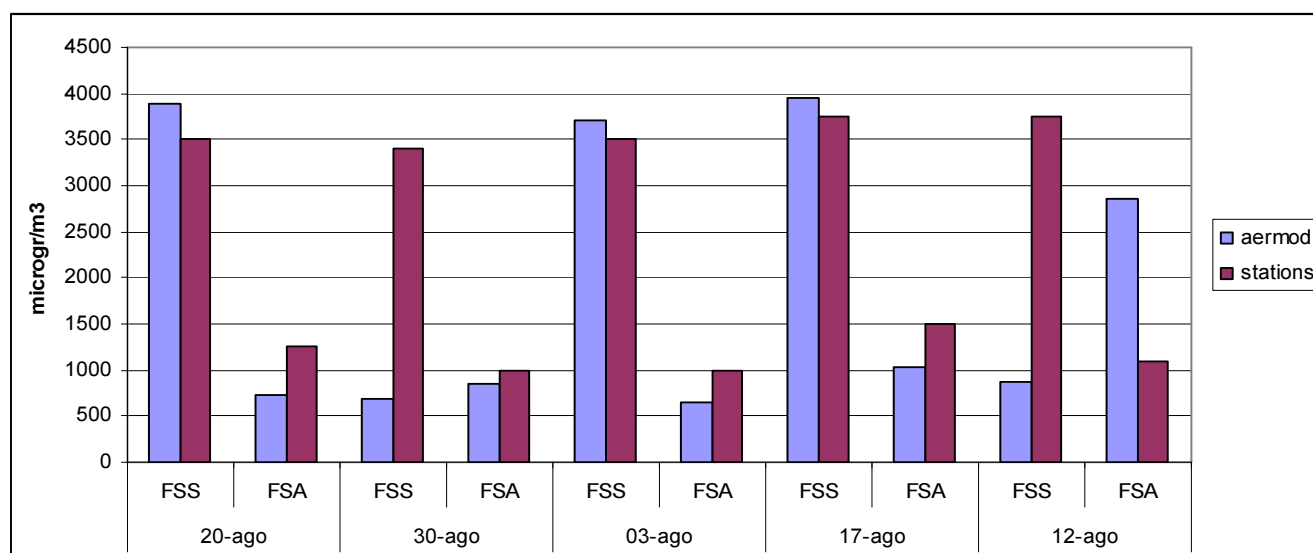

Fig. 11. VOC emissions of VOL2 = 50g/s. Comparison between maximum values provided by the model and
maximum value from monitoring stations (FSS, FAS), in the five days of August 2000 (VOC concentration in μg/m³)

7. Conclusions

The results with AERMOD indicate that evaluated levels of VOC concentrations are similar to the monitored concentration data only if we hypothesize that the refinery emits at least 5 tons per day of VOCs. This means three times circa the amount of VOCs evaluated by emission factors of Emission Inventory Guidebook as shown in Table 1. Therefore, the study indicates that fugitive emissions of VOC in the refinery were, on August 2000, roughly an order of magnitude higher than the emissions estimated by Oil refinery Company. Such emissions, by the way, makes easy to explain the ozone acute episodes that happened nearby refinery area on August 2000 [1].

Several questions need further explanations and further studies. However some points can be outlined.

The refinery, for sure, underestimated VOC emissions by applying emission estimates reductively, not including some of the sources. This might have happened unintentionally although scientists and stakeholders had advised about.

In 2000 the refinery was undergoing a major revamping that included the renovation of many tanks. At that time, some of them might have been leaking airborne pollutants due to their obsolescence.

The amount of VOC monitored at Falconara Scuola station and Falconara Acquedotto station steadily decreased from 2000 for several years and this probably means that refinery emissions decreased. Unfortunately, in 2007–2008 values increased again but never reached the peaks of 2000.

Besides the obvious issues deriving from every emission underestimate, the VOC miscalculation in Falconara refinery may have fouled researchers and stakeholders in trying to deal with the ozone episodes that occurred there especially in

2000 but also in subsequent years. In particular, the possibly false amount of NMHC emitted by the refinery may have fouled models so to misjudge ozone dynamics nearby the refinery.

Acknowledgements

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