A study on tropospheric ozone concentration near an oil refinery at Falconara, Italy

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Abstract

Data for ozone, nitrogen oxides, atmospheric stability and meteorological analyses by back-trajectories from two months of July and August 2001 were used to analyse the relative importance of local and mesoscale wind systems and vertical mixing at Falconara (Ancona, IT). The highest ozone concentrations coincided with elevated instability and occurred during the early afternoon when winds and turbulent mixing were at their maximum. Results show that the ozone season and the associated photochemical episodes in the Falconara area are not particularly important and comparable to other coastal areas on the Adriatic Sea. On the basis of this study the target air quality objectives for ozone are likely to be achieved in this area by the deadline set by the European Framework and Daughter Directives (i.e. 2010).

Keywords: tropospheric ozone, monitoring of ozone, back trajectory analysis.

1 Introduction

The operation of refineries is associated with the emission of various substances into the atmosphere, mainly originating from the production processes, the storage tanks, the transport pipelines and the waste area. Among the most important atmospheric pollutants emitted by refinery plants NO and NO2 (summed as NOx) and reactive volatile organic compounds (VOCs) are those of major concern which are involved in ozone formation in the downwind plume through a complicated series of photochemical reactions [1]. Possible health hazards from oil refineries have been a long-standing community concern particularly when such industrial activities are located near urban areas where housing, schools, shops and related public facilities are present [2, 3].
Ground-level ozone can cause serious human health problems and damage ecosystems, crops and materials. Since harmful ozone concentrations are observed throughout Europe [4, 5], the current European ozone directive 2003/3/EC [6] established ozone thresholds and required Member States to monitor and report exceedances. In Italy, pollution caused by ozone has become a major concern over the last few decades because the threshold for providing information to the public (hourly concentrations higher than 180 µg/m³) has been exceeded in many stations. In addition the warning threshold (hourly concentrations higher than 360 µg/m³) has also been exceeded in a few occasions [7]. The Directive has set a maximum acceptable ozone concentration of 120 µg/m³, for 8 h, to protect human health that has also been exceeded in many Italian stations [7].

The focus of the present work is the determination of air quality for ozone in the area surrounding the oil refinery located at Falconara (Italy) during the period July-August 2001. The local administration of Falconara operates a monitoring network that includes three monitoring stations for ozone [8]. In May 2001, in the wake of high ozone levels measured in one of the stations of the monitoring network during the previous year, two new stations for ozone, nitrogen oxides and a monitor for measuring the atmospheric stability were set up as an initiative by the refinery management. One of the stations (PON) was sited at the end of a pier whereas the other one (CAF) was located onshore approximately at a distance of 300 m from the refinery. The two new stations give a representative picture of the refinery area since they cover two opposite sections (NE and SW). When northeastern winds prevail (usually associated with the build-up of sea breeze) the two stations respectively are upwind and downwind of the refinery. The objectives of this study were: (1) to measure ozone and NOx concentrations in the two new locations near the refinery and to study the conditions that lead to ozone episodes; (2) to investigate the effect of meteorological parameters (wind speed, wind direction and atmospheric stability); (3) to describe the mixing properties of the lower boundary layer in the area of Falconara by monitoring the concentration of radon progeny. In particular, we were interested in determining whether the source of ozone was originated in Falconara or the result of a relatively “long range” regional air mass movement. Regarding this last point a study of back trajectories focussed on three particularly interesting ozone situations was also carried out.

2 Experimental

The town of Falconara has a population of about 30,000 inhabitants and is situated on the Adriatic coast 10 km northwest of Ancona (about 100,000 inhabitants) the administrative centre of Marche Region.

The inner-city area of Falconara has roads of varying traffic density bordered by low-rise blocks of houses. The API refinery is situated just outside the urban area on the northern edge of the town. The refinery (a 3.9-million-tonnes-a-year plant) includes also a power plant based on a gasification process of residual tar from refined heavy oil to generate 280 MW of electrical power. Two monitoring sites were chosen for the study. Figure 1 shows a map of the Falconara area.
The symbols indicate the two measurement sites (CAF and PON), which are downwind and upwind with respect to the refinery under conditions of sea breeze, respectively. The location of two other ozone monitoring stations belonging to the local network for air quality (ACQ and SCU, respectively) are also shown in the Figure 1.

Meteorological measurements (wind speed, wind direction) were made from a 10 m tower at site CAF over the measurement period. Air velocities were measured directly using a three-axis sonic anemometer (Model SWS-211/3CK, Applied Technologies, Inc.).

Ozone was measured with UV absorption technique using an ozone analyser (API, Mod. 400A, CA, USA). NOx was also measured using a chemiluminescence analyser (API, Mod. 400A, CA, USA). The ozone detector was calibrated by gas phase titration of a diluted NIST NO standard. The instrument used for stability measurements was a stability monitor (SM200, OPSIS AB, Furulund, Sweden) which was installed at the monitoring station CAF. The instrument consists of a particulate matter sampler equipped with a Geiger-Muller counter for determining the total beta activity of the short-lived radon progeny.

3 Results and discussion

3.1 Monitoring of ozone

Many of the general features of ozone formation observed in the Falconara area during the entire study period are well illustrated by the data collected for the period 1-13 August.

Figure 2 (a and b) shows the ozone concentration measured at the two stations PON and CAF, (2a), and stability measured at station CAF for this period (2b).
Figure 2: a) ozone concentration measured at the two stations PON and CAF. b) beta radioactivity and ozone measured at station CAF for the period 1-13 Aug 2001 at Falconara (Italy).

The ozone concentrations measured at the two sites show a clear daily cycle with only two exceptions for the periods 4th to 5th and 10th to 12th August. The ozone maximum occurs in the early afternoon when solar radiation, temperature and photosynthetic activity are at their maximum. The difference in heat capacity between land and sea can produce a temperature differential between the land and adjacent water surfaces. This results in a localised atmospheric circulation usually described as a sea breeze in the daytime and a land breeze at night. This
land-sea circulation has been implicated as a controlling factor for air quality in coastal areas [9]. Land/sea breeze flow reversal occurs when high pressure dominates the area, resulting in light synoptic scale forcing. Land/sea breezes that are quite common in many coastal areas have been associated with ozone formation in these areas [10]. The light winds and subsidence allow high concentration of pollutants to accumulate during the night and morning rush hours. Although, in conditions of high pressure the winds are too weak to ventilate the urban area well, the land breeze carries the pollutants out into the Adriatic Sea. During the afternoon, the sea breeze carries the pollutants back into the Falconara area.

The substantially equivalent concentrations measured at the two sites during the day are clearly caused by a vertical transfer from upper layers due to turbulence. At night, when atmospheric stability is dominant, the loss of ozone due to dry deposition and/or reaction cannot be compensated by vertical transport from the air layer above. It is interesting to note that the lowest concentrations were measured at the CAF station. A scatter diagram of the two sites gives the following regression relationship: OZONE(CAF) = 0.89 OZONE(PON) with a $R^2 = 0.70$. The differences at the two sites can be analysed in terms of the loss mechanisms operating at these locations.

In fact, the CAF site can be affected by local NOx emissions from traffic and dry deposition over soil whereas at the PON site a lower dry deposition velocity over water surfaces is to be expected [11]. Since radon flux from ground is horizontally uniform and constant in time, the measurement of the time variation of natural radioactivity can be used to trace the mixing properties of the lower troposphere [12, 13, 14]. From figure 2b it is apparent that natural radioactivity shows a well-defined and modular temporal trend throughout the period except on 4-5 and 10-12 August. The trend shows minimum values during day-time that alternate to maximum values at night time following a pattern of convective mixing of the lower atmosphere and nocturnal atmospheric stability. From the figure, it can be seen that the highest levels of ozone are typical of periods characterised by minimum atmospheric stability (i.e. lowest radioactive counts). Typically, the mixing period starts rather early in the morning and lasts up till the late afternoon; therefore high levels of ozone (about 100 µg/m$^3$ rather close to the health level protection) were measured when convective mixing was high. On the 4th to 5th and 10th to 12th August advection and turbulence caused a prolonged instability; ozone was constantly high and in the range of 80 to 120 µg/m$^3$. Nocturnal increased levels of ozone in urban areas during unstable atmospheric weather conditions have been observed by several authors [e.g. 15] and can be attributed to vertical mixing of high ozone concentrations from higher levels or horizontal transportation from rural areas due to local and mesoscale wind systems.

From figure 3 it can be seen that the highest nitrogen oxides concentrations were always measured when east winds were blowing towards the oil refinery. The majority of NOx emissions originate from traffic. In fact, the CAF and PON measuring sites are very close to the Cities of Falconara and Ancona and therefore influence from this type of emissions is to be expected.
For a better assessment of the ozone air quality in the area surrounding the oil refinery, the number of exceedances of the information level as measured at the two monitoring stations operated by the local administration (Acquedotto and Scuola, ACQ and SCU in figure 1, respectively) was compared with that of two air pollution monitoring sites along the Adriatic coast about 80 Km away. These sites are located in urban areas which are similar to Falconara.

![Wind direction and concentration of nitrogen oxides measured at CAF monitoring station from 1 to 13 Aug 2001 at Falconara (Italy).](image)

Figure 3: Wind direction and concentration of nitrogen oxides measured at CAF monitoring station from 1 to 13 Aug 2001 at Falconara (Italy).

The number of the exceedances measured for the years 1998 to 2003 are presented in table 1. It is interesting to note that in the year 2000 an exceptionally high number of exceedances (117) were measured at Falconara Scuola compared to the exceedances measured in the same year at the Acquedotto Station (21) and in the two comparable stations of Marecchia (6) and Riccione (12).

Table 1: Number of exceedances of the information level measured at four stations on the Adriatic Riviera during the years 1998-2003.

<table>
<thead>
<tr>
<th>STATION</th>
<th>1998</th>
<th>1999</th>
<th>2000</th>
<th>2001</th>
<th>2002</th>
<th>2003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marecchia (Rimini)</td>
<td>12</td>
<td>4</td>
<td>6</td>
<td>11</td>
<td>13</td>
<td>6</td>
</tr>
<tr>
<td>Riccione</td>
<td>21</td>
<td>16</td>
<td>12</td>
<td>3</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Falconara Scuola</td>
<td>0</td>
<td>10</td>
<td>117</td>
<td>14</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Acquedotto</td>
<td>21</td>
<td>2</td>
<td>21</td>
<td>11</td>
<td>3</td>
<td>8</td>
</tr>
</tbody>
</table>

A search for a possible cause for this anomalous result led to the detection of a problem that had occurred in the procedure of validation of the results at the
station of Falconara Scuola. In this station, data which were clearly affected by an “hi-lo-hi-lo output” of the chemiluminescence analyser, were erroneously validated. The data validation should have included: first, a screening procedure based on comparison of measured values to upper and lower limits and, second, an assessment based on the rate of change of the ozone concentration.

3.2 Three meteorological case studies

We present three case studies: two of them (related to 5th and 12th August 2001) are characterised by high values of ozone during the night and we briefly analysed them by means of radon data and meteorological backward trajectories.

From the point of view of atmospheric stability, we can assess a very similar qualitative behaviour of radon concentrations at the ground in these two case studies: we find two plateaux characterised by low values of natural radioactivity at night. As is well known [14], this suggests the presence of turbulence and a mixing of the lowest atmospheric layers with the upper ones. This hypothesis is confirmed by local meteorological data and synoptic charts (not shown here) related to these days. From a more quantitative point of view, it can be seen that this mixing appears more efficient in the case study related to 12th August, when the values of natural radioactivity were lower.

In this situation, when at the ground one can recognise an entrainment of air coming from upper layers, endowed with background values of ozone (which strongly depend on the latitude), it is crucial to estimate the provenience of these air masses. For this reason, we built up two backward trajectories for the five days before 5 and 12 August, respectively. To do so, we adopted a simple Lagrangian model and used data by ECMWF analyses.

As shown in Figs. 4 and 5, the air advected on Falconara on 5 August came from the Iberian peninsula and the Mediterranean region, whereas on 12 August the air came from North-Western Europe (British islands) and then passed over the Northern Balcanic region. In the first case the background value of ozone in the air advected is typical of a latitude of 40°, while in the second case study we have to consider an ozone background concentration at a latitude of 50° or above.

Based on these evidences, even if our data of radon concentration suggest a more efficient vertical mixing on 12 August, this case study is characterised by a slightly lower value of ozone concentration, if compared with the night on 5 August. This is clearly due to the distinct background values of ozone advected from different latitudes.

As far as another case study (1 August) is concerned, we note that during the last days of July the meteorological situation was characterised by a strong anticyclone extending from the Azores islands to central Europe which became more and more intense day after day. As far as the horizontal transport was concerned, this led to trajectories coming from Eastern Europe and was characterised by an anti-cyclonic curvature (see Fig. 6). In this framework, at the synoptic scale averaged vertical descending motions (subsidence) favour the formation of weak thermal inversions at ground and allow the development of diurnal mixing layers characterised by a weak convection.
Figure 4: Trajectory arriving at Falconara on Aug 5\textsuperscript{th} 2001 at a height of 950 hPa (about 550 m).

Figure 5: Trajectory arriving at Falconara on Aug 12\textsuperscript{th} 2001 at a height of 950 hPa (about 550 m).

If we look at the behaviour of radon concentration at the surface, its relatively high values during the diurnal hours of 1st August suggest the formation of an inversion at a certain level above the ground that does not permit the creation of a fully developed diurnal convective layer.
Thus, in the meteorological situation described above, the high ozone peak in the afternoon can be considered as mainly due to effects of local formation and recycling, favoured by a high pressure situation and an inversion at a certain level above the ground, which do not permit the usual summer mixing with the layers of the free atmosphere in a fully developed convective layer.

4 Conclusions

The main conclusions of this study are as follows:

The emission pattern of the pollutants from the refinery is governed by southwesterly prevailing winds which tend to disperse the stack plume mainly in the northeast direction towards the Adriatic Sea. A first attempt at analysing specific situations in terms of a joint use of radon progeny measurements and a back-trajectory model was performed. In this framework the possibility of discriminating among long-range transport, entrainment from free troposphere and local formation has been shown.

A large part of pollutants comes from urban area sources rather than from point sources. Regional sources of NOx are coming from heavily travelled national roads in the area, from the highway and the outflow of pollution from the urban area of Ancona.

The ozone season and the associated photochemical episodes in the Falconara area is not particularly important and comparable to other areas along the Adriatic coast. On the basis of this study the target air quality objectives for ozone are likely to be achieved easily in this area by the deadlines prescribed by the Framework and Daughter Directives (i.e. 2010).
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References