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TECHNICAL PAPER

Assessment of ambient air quality in the port of Naples

Maria Vittoria Prati, ¹ Maria Antonietta Costagliola, ¹ Franco Quaranta, ² and Fabio Murena ^{3,*}

Two experimental monitoring campaigns were carried out in 2012 to investigate the air quality in the port of Naples, the most important in southern Italy for traffic of passengers and one of the most important for goods. Therefore, it represents an important air pollution source located close to the city of Naples. The concentrations of sulfur dioxide (SO_2) , nitrogen dioxide (NO_2) , and BTEX (benzene, toluene, ethylbenzene, and xylenes) in the air were measured at 15 points inside the Naples port area through the use of passive samplers. In addition, a mobile laboratory was positioned in a fixed point inside the port area to measure continuous concentration of pollutants together with particulate matter, ambient parameters, and wind direction and intensity. The pollution levels monitored were compared with those observed in the urban area of Naples and in other Mediterranean ports. Even though the observation time was limited, measured concentrations were also compared with limit values established by European legislation. All the measured pollutants were below the limits with the exception of nitrogen dioxide: its average concentration during the exposition time exceeded the yearly limit value. A spatial analysis of data, according to the measured wind direction and intensity, provided information about the effects that ship emissions have on ambient air quality in the port area. The main evidence indicates that ship emissions influence sulfur dioxide concentration more than any other pollutants analyzed.

Implications: Two monitoring campaigns were carried out to measure BTEX, SO_2 , NO_2 , and PM_{10} (particulate matter with an aerodynamic diameter <10 μ m) air concentrations in the port of Naples. NO_2 hourly average and PM_{10} daily average comply with European legislative standards. Spatial variation of pollutants long the axis corresponding to the prevailing wind direction seems to indicate a certain influence of ship emissions for SO_2 . For NO_2 and PM_{10} , a correlation between concentrations in the harbor and those measured by the air quality monitoring stations sited in the urban area of Naples was observed, indicating a possible contribution of the near road traffic to the air pollution in the port of Naples.

Introduction

Ship emissions in port areas are dispersed in the atmosphere and in many cases transported to the nearby urban areas, affecting air quality and jeopardizing people's health and quality of life (Ault et al., 2009; Viana et al., 2014). Air pollution due to ship emissions mainly concerns sulfur dioxide (SO₂), nitrogen dioxide (NO₂), and particulate matter. Besides that the European Union (EU) legislation enforces the use of a cleaner fuel in terms of sulfur content during ship hotelling longer than 2 hr. Ships at berth are also still responsible for air pollution in the port areas, mainly because of the use of engines for supplying auxiliary devices (Adamo et al., 2014).

Several studies (modeling and experimental) dealing with air pollution from ports are reported in the literature. Monitoring campaigns were carried out in port areas and nearby urban areas (Marr et al., 2007). Schembari et al. (2012) demonstrated a strong relationship between sulfur content in the fuel and SO₂ air concentrations in four

Mediterranean ports. Recent studies show the contribution of ship emissions on fine and ultrafine particles (Healy et al., 2009; Donateo et al., 2014). Contini et al. (2011) stated that ships contribute directly to 10% of polycyclic aromatic hydrocarbon (PAH) concentration in the air of Venice and to almost 8% of PM_{2.5} (particulate matter with an aerodynamic diameter <2.5 μ m). Several studies recognized some metals as tracer of particulate produced by ships, such as vanadium and nickel, which are generally used as tracers of oil combustion emissions. In the case of ship emissions, correlation of V with ship fluxes was observed by Mueller et al. (2011), Zhao et al. (2013), and Cesari et al. (2014).

Air quality contribution by port activities was also assessed through the use of air dispersion models. Saxe and Larsen (2004) focused their study on three Danish ports, highlighting a considerable contribution to NO_2 and PM_{10} (PM with an aerodynamic diameter <10 μ m) air concentrations, posing health problems to people living or working near the harbors (Matthias et al., 2010). Gariazzo et al. (2007) applied a three-dimensional (3D)

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Lagrangian particle dispersion model to Taranto (Italy) port affected by multiple pollution sources (harbor, traffic, industrial). They conclude that about 9% of SO_2 and NO_2 originated from harbor activities. Assessment of port emissions can require the use of emission factors depending on the ship category, tonnage, and the specific activity: hotelling (operations while stationary at berth) and maneuvering (moving into or out of port) (European Commission [EC], 2002). Lucialli et al. (2007) used this classification to Ravenna port, showing a good correlation between NO_2 predicted and that measured by air quality monitoring stations.

An interest in atmospheric port emissions was also demonstrated by several European researches and demonstration projects: PEARL project (www.pearl-project.eu), APICE project (www.apice-project.eu), CESAPO project (http://www.cesapo.upatras.gr), and CNSS project (www.cnss.no/project-description).

The aim of this paper is to characterize the air quality in the port area of Naples $(40^{\circ}51'19''N, 14^{\circ}15'36''E)$. The port of Naples has 75 berths, with a total length of 11 km, an annual traffic of about 22×10^6 t and 6×10^6 millions of passengers and of about 48,000 vessels (http://www.porto.napoli.it/). It is located very close to the urban area and to a commercial and industrial area of Naples (Figure 1). The National Institute of Environmental Protection and Research (ISPRA) in two emission inventories (ISPRA, 2012, 2014), both based on national data, shows that the effect on air quality caused by the emissions of maritime vessels had increased from 1990 to 2012. In particular, the percentage of SO_2 emissions coming from the port activities of Naples (ISPRA, 2012) is significant (about 40%).

In order to give an assessment of air quality in the port of Naples, two experimental monitoring campaigns were carried out to measure concentrations of BTEX (benzene, toluene, ethylbenzene, and xylenes), NO₂, SO₂, and PM₁₀ inside the port area. Air concentrations were compared with limit values established by European legislation concerning air quality and data from the monitoring stations located in the urban area of Naples. Furthermore, the data were correlated with wind intensity and direction in order to gain an understanding of what contribution ship emissions have on air quality in the monitored area.

Instruments and Methods

Two monitoring campaigns were performed in 2012, spring (April) and autumn (November): the first had a duration of 14 days, whereas the second had a duration of 19 days. Cylindrical passive samplers Radiello (Fondazione Salvatore Maugeri-IRCCS, Padova, Italy) were positioned in 15 sites of the port (Figure 1, right side) to analyze SO₂, NO₂, and BTEX (benzene, toluene, ethylbenzene, and xylenes). Sampling point F2 corresponds also to the location of a mobile laboratory equipped with continuous analyzers of SO₂, NO₂, NO, CO, and PM₁₀. Wind intensity and direction were also measured in F2.

At the end of each monitoring campaign, the passive samplers were collected and analyzed in a laboratory to obtain atmospheric average concentration in the period. Although 15 samplers for each species were exposed during both campaigns, numbers of valid samples are 12 and 6 for the first and second monitoring; some samplers were lost during the exposure time, however, probably due to acts of vandalism. For analyses of SO₂ and NO₂, the cartridges were extracted by using 5 mL of water and stirring vigorously for 1 min. Then, sulfite and sulfate ion concentrations were determined by ion chromatography analysis and nitrite ion concentration by absorbance measurement of samples at 537 nm (American Public Health Association [APHA], American Water Works Association [AWWA], and Water Environment Federation [WEF], 1998). Detection limits are 0.06 and 0.1 μ g/m³ for NO₂ and SO₂, respectively. BTEX were chemically desorbed by using 2 mL of carbon disulfide (CS₂) with an extraction time of 30 min. The extract was then analyzed by means of gas chromatography with flame ionization detection (GC-FID). 2-Fluorotoluene was used as an internal standard because its retention time does not interfere with other compounds in the chromatogram.

Analytical method: 100% dimethylpolysiloxane column, 50 m \times 0.2 mm \times 0.5 μ m (Agilent J&W HP-PONA); nitrogen flow: 0.63 mL/min; head pressure: 20 psi; split injection (25:1): 0.5 μ L; injector temperature: 240 °C; oven initial temperature: 35 °C for 5 min, 5 °C/min up to 90 °C, isotherm for 10 min, 10 °C/min up to 180 °C, final isotherm



Figure 1. Map of Naples and localization of passive samplers in the monitored area.

for 5 min. The detection limit of this method for each aromatic compound is $0.05 \mu g/m^3$.

The accuracy and consistency of results of passive samplers were checked by comparing the results of a pair of samplers located in two sites very close to each other (F1 and F2). It was on the average $\pm 20\%$. Concerning continuous gaseous analyzers of mobile laboratory (site F2), NO2 was measured with chemiluminescence detector (CLD), whereas SO₂ was measured using fluorescence detector. In addition, the mobile laboratory was also equipped with a PM₁₀ continuous analyzer based on orthogonal nephelometry (UniTec srl, LSPM10) and a weather station for ambient condition monitoring. Subsequently, all available data were analyzed in order to obtain hourly and daily average concentrations. Analyzers of the mobile laboratory used the same detection techniques for air quality to those of the monitoring stations of Naples. This homogeneity allowed us to make the comparison between the monitored species in the port with air concentrations in the urban area of Naples.

Results

Meteorological conditions and marine traffic during the monitoring campaigns

Temperatures monitored during the two campaigns are reported in Figure 2. Besides the temperature ranges that overlap (between 8 and 24 °C), the weather in the second campaign was characterized by warmer temperatures than those of the first one.

Wind-rose graphs of the two monitoring campaigns are reported in Figure 3. It was observed that during the first monitoring campaign, the wind was blowing predominantly from southwest (SW) sector, whereas in the second campaign the wind direction was more variable, with east-northeast (ENE) as prevailing sector and a not negligible south contribution from the SW. Results correspond to typical wind patterns observed in Naples during spring and autumn/winter, respectively. In fact, during spring, the prevailing wind direction is from south-southwest (SSW) and the second most frequent wind direction is from northeast (NE). In autumn/winter, these are still the prevailing wind directions, but the

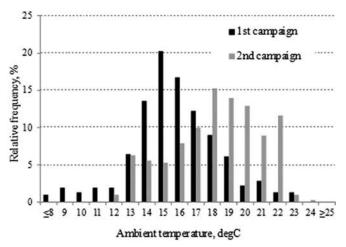


Figure 2. Relative frequency distribution of ambient temperatures in the port of Naples during the monitoring campaigns.

predominant wind is from north-northeast (NNE) and south-southeast (SSE) is the second most prevailing direction (Menna et al., 2007). As results from Figure 1 show, the urban area of Naples is mainly located at west, north, and east directions with respect to the port area. Therefore, wind flowing from south or southwest does not transport the pollutants from the urban area.

During the two campaigns, the number of daily arrivals and departures of passenger ships and crafts close to the studied area had been monitored. Fleet movements are summarized in Table 1. The daily schedule for the ferry/craft service remained unchanged between the two periods (see the average daily values in last rows of Table 1), whereas the number of cruise ships more than doubled in the second period (Battistelli et al., 2012).

Pollutant air concentrations in the port of Naples

Data of passive samplers and continuous analyzers were preliminarily filtered to eliminate the out-of-range values (outliers) based on a statistical analysis performed with Statgraphics (Centurion XVI). Outliers are identified as the points more than 3 interquartile ranges below the first quartile or above the third

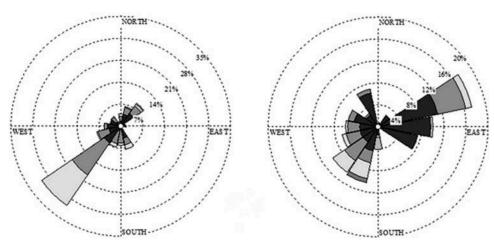


Figure 3. Wind-rose of first (left) and second (right) monitoring campaigns. Wind categories (m/sec) are 0.5–2.1; 2.1–3.6; 3.6–5.7; 5.7–8.8; 8.8–11.1; and >11.1.

Table 1. Number of arrivals and departures of passenger ships and crafts in the harbor area during the two campaigns

| Arrivals and Departures | Ships and Crafts | First Campaign | Second Campaign | | |
|---|-----------------------------------|----------------|-----------------|--|--|
| Total arrivals and departures during weekdays | Ferries, fast ferries, hydrofoils | 1551 | 1974 | | |
| | Cruise ships | 15 | 30 | | |
| Total arrivals and departures during weekends | Ferries, fast ferries, hydrofoils | 534 | 801 | | |
| | Cruise ships | 2 | 10 | | |
| Total arrivals and departures during campaign | Ferries, fast ferries, hydrofoils | 2085 | 2775 | | |
| | Cruise ships | 17 | 40 | | |
| Daily average arrivals and departure | Ferries, fast ferries, hydrofoils | 149 | 146 | | |
| · · · · · · | Cruise ships | 1.2 | 2.1 | | |

quartile. Then, average values of pollutant concentrations in the period and confidence intervals were evaluated. For passive samplers, average data correspond to the time-averaged concentration during the period (14 days in the first campaign and 19 days in the second one). Average, minimum, and maximum data of passive samplers relative to the first and second campaigns are reported in Table 2. The table also shows the 95% confidence intervals for passive samplers. For continuous analyzers, average values in the monitoring period are reported together with minimum and maximum of hourly average. The meaning of minimum and maximum values in Table 2 vary significantly to the data of passive samplers and continuous analyzers. For passive samplers, data correspond to the time-averaged concentrations during the observation period measured at different sampling points. Therefore, differences between average,

minimum, and maximum indicate the variability on a spatial scale. For the continuous analyzers, values are average, minimum, and maximum of hourly averages measured in the same place (at location F2). Therefore, the variability is, in this case, on a time scale.

Results of passive samplers measured at site F' (average value of F1 and F2), close to the site of the mobile laboratory, were compared with those of continuous analyzers for SO_2 and NO_2 . Comparison can be performed only for time-averaged values in the period. The time-averaged value of SO_2 by passive samplers is $6.6 \ \mu g/m^3$, whereas by continuous analyzer it is $6.8 \ \mu g/m^3$. For NO_2 , the values are respectively 43.0 and 40.0 $\mu g/m^3$. Therefore, results obtained by passive samplers can be compared with those obtained by continuous analyzers.

Table 2. Concentration averages for the total measuring period (passive sampler) and 1-hr average concentrations (continuous analyzers)

| Campaign | Analyzer | Pollutants | Average $(\mu g/m^3)$ | Min (μg/m³) | Max $(\mu g/m^3)$ | 95% Confidence Interval (µg/m³) |
|----------|------------------|--------------|-----------------------|-------------|-------------------|---------------------------------|
| First | Passive samplers | BTEX | 13.1 | 9.4 | 17.7 | 11.3–15.6 |
| | 1 | Benzene | 1.4 | 0.8 | 1.7 | 1.2–1.7 |
| | | Toluene | 5.7 | 2.7 | 9.6 | 4.3-7.1 |
| | | Ethylbenzene | 1.2 | 0.9 | 1.4 | 1.1–1.3 |
| | | m+p-xylene | 3.8 | 2.3 | 5.9 | 3.1-5.5 |
| | | o-xylene | 1.2 | 0.8 | 1.5 | 1.0-1.4 |
| | | NO_2 | 44.1 | 24.7 | 74.3 | 31.7–56.6 |
| | | SO_2 | 5.7 | 0.5 | 16.9 | 3.2-8.3 |
| | Continuous | PM_{10} | 27.1 | 0.6 | 95.5 | |
| | analyzers | NO_2 | 48.4 | 10.5 | 156.5 | |
| | • | SO_2 | 6.4 | 5.3 | 26.6 | |
| Second | Passive samplers | BTEX | 16.7 | 12.9 | 20.4 | 12.9–20.6 |
| | | Benzene | 0.5 | 0.5 | 0.6 | 0.5-0.6 |
| | | Toluene | 7.4 | 5.5 | 9.3 | 5.5-9.2 |
| | | Ethylbenzene | 1.8 | 1.5 | 2.2 | 1.5–2.2 |
| | | m+p-xylene | 5.1 | 4.0 | 6.2 | 3.9-6.3 |
| | | o-xylene | 1.8 | 1.4 | 2.2 | 1.3-2.3 |
| | | NO_2 | 38.8 | 31.1 | 52.6 | 32.8-44.9 |
| | | SO_2 | 10.6 | 5.6 | 27.6 | 3.8-17.3 |
| | Continuous | PM_{10} | 31.8 | 1.1 | 82.9 | |
| | analyzers | NO_2 | 32.1 | 1.5 | 84.2 | |
| | Ž | SO_2 | 7.1 | 5.0 | 40.5 | |

To assess the air quality in the port area, measured concentrations were compared with limit values established by European Commission (EC, 2008) in Table 3. Due to the limited number of days monitored during the two monitoring campaigns (on the whole 33 days in 1 yr), the comparison with limit values is only qualitative because the necessary minimum quantity of data was not collected. However, regulated pollutants (benzene, SO₂, NO₂, and PM₁₀) are all below the limit values. In particular, the hourly limit value of 200 μ g/m³ for NO₂ and daily limit value of 50 μ g/m³ for PM₁₀ were always respected. Only time period average of NO₂ (40.2 μ g/m³) exceeded slightly the limit value for the annual average (40 μ g/m³). It must be observed that this limit value is often exceeded in the urban area of Naples.

Furthermore, the air quality in the port of Naples is comparable to that of other Mediterranean ports, as shown in Table 3. The main difference is with respect to SO_2 levels. Average concentration measured in Naples is between 6.8 and 8.2 $\mu g/m^3$, whereas in Venice it is 3.7 $\mu g/m^3$ and in Marseilles it is 0.8 $\mu g/m^3$. The main reason, probably, lies in wind directions occurred during the monitoring campaigns in the three cities. In Marseilles, for example, Detournay et al. (2011) measured two prevailing wind directions (northwest and southeast) during experimental activity; port activities contribute to SO_2 pollution only when wind is from northeast.

Analysis of spatial distribution of atmospheric pollutants in the port area

Maps of spatial distribution of BTEX, SO₂, and NO₂ obtained by the analyses of passive samplers are reported in Figures 4 and 5 for the two monitoring campaigns. Sites in the second campaign were less numerous due to the loss of several samplers. In Figures 4 and 5, proportionally sized pie charts were used.

In the first campaign, a large homogeneity for BTEX can be observed, except for points E and B. The anomalous BTEX concentration observed at points E and B does not have a specific explanation due to their location. Point E is closer in respect to other points to the high-traffic road (via Cristoforo

Colombo), whereas point B is at the border of the monitored area in the north direction but with apparently no specific pollutant sources that could justify the observed BTEX percentage. These points, in the preliminary statistical analysis performed, were identified as possible outliers. This could be a motivation to overlook them in the discussion of BTEX concentration. The percentage of the single BTEX, numbers inside each pie, is relatively constant apart from at point Z. Toluene covers the maximum percentage (40-49%), followed by m+p-xylenes (22-33%) and benzene, ethylbenzene, and oxylene (all ranging between 8 and 15%). This distribution is typical in urban air where road transport is the main pollution source (Prestes de Castro et al., 2015). Point Z is, instead, characterized by the predominance of benzene (almost 54% of total BTEX). This observation should be explained by the different location of point Z: it is at the end of a berth and farther from road traffic. In other words, point Z is not directly influenced by road transport pollution and BTEX air concentration should be much more influenced by other parameters such as the reactivity of each compound in the atmosphere (toward OH and NO₃ radicals), local ambient temperature, and humidity. Benzene is the less reactive compound, and sampling rate by passive samplers increases with temperature and humidity (Roukos et al., 2011). All these aspects should be some explanations for the anomalous BTEX distribution in point Z.

In the case of NO_2 and SO_2 , a particular spatial variation is observed in the first campaign (Figure 4) where NO_2 and SO_2 seem to enhance moving from SW to NE. This finding is confirmed by correlations reported in Figure 6 and explained by the coefficient of determination R^2 . It is a measure of how well observed outcomes are replicated by a fitting curve or model and is calculated by eq 1:

$$R^2 = 1 - \frac{SS_r}{SS_t} \tag{1}$$

 SS_r and SS_t are the residual sum of squares and the total sum of squares, respectively, and are defined by eqs 2 and 3:

Table 3. Comparison of average values measured during the two monitoring campaigns with limit values (EC, 2008)

| | Passive Sampler | Continuous Analyzers | Limit Values | | Other Mediterranean Ports | | | | |
|--------------|---------------------|-------------------------|--|--------------------------------|------------------------------------|-------------------------------------|----------------------------|--|--|
| Pollutant | Period Avg. (μg/m³) | Period Avg. (μg/m³) | 1-hr or 24-hr Avg. (μg/m ³) | Year Avg. (μg/m ³) | Barcelona (Pérez and Pey, 2011) | Marseilles (Detournay et al., 2011) | Venice (ARPAV, 2012) | | |
| BTEX | 15.2 | _ | _ | | | | _ | | |
| Benzene | 0.9 | | | 5 | | | | | |
| Toluene | 6.7 | _ | _ | | | | | | |
| Ethylbenzene | 1.6 | _ | _ | | | | | | |
| m+p-Xylene | 4.6 | _ | _ | | | | | | |
| o-Xylene | 1.6 | _ | _ | | | | | | |
| NO_2 | 41.1 | 40.0 | 200 (1 hr) | 40 | 68 | 44 | 47 | | |
| SO_2 | 8.5 | 6.8 | 350 (1 hr) 125 (24 hr) | | | 0.8 | 3.7 | | |
| PM_{10} | _ | 29.8 | 50 (24 hr) | 40 | 32 | 37 | 42.5 | | |

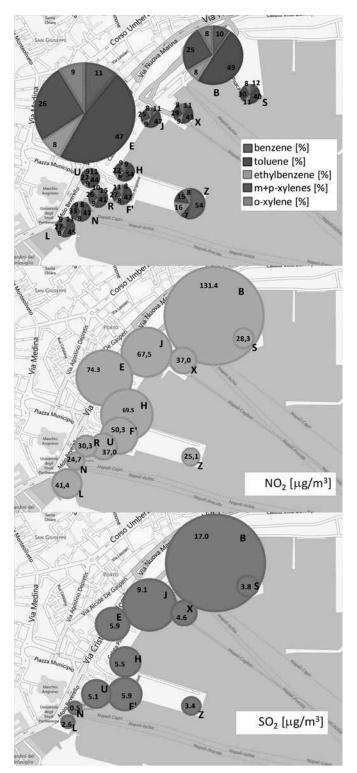


Figure 4. First monitoring campaign: spatial distribution of measured BTEX, NO₂, and SO₂ concentrations.



$$SS_{t} = \sum (y_{i} - Y) \tag{3}$$

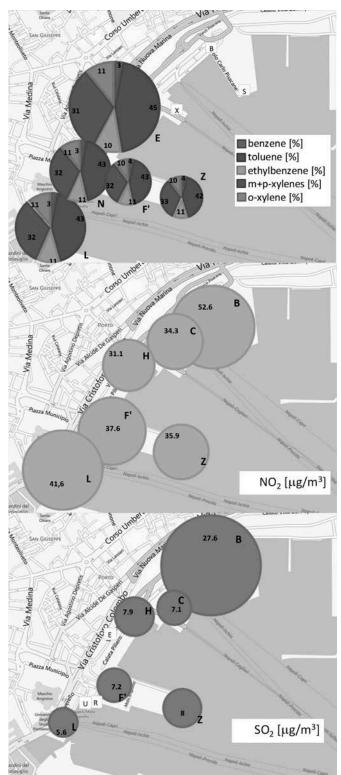


Figure 5. Second monitoring campaign: spatial distribution of measured BTEX, NO₂, and SO₂ concentrations.

where y_i is the single observation of a data set, Y is the average of sample, f_i is the predicted value. Plotting concentration versus distance in the SW-NE direction (x = 0 set in correspondence of most SW sampling point), namely, that of the

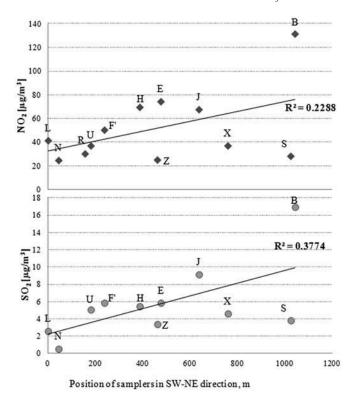


Figure 6. Correlation of NO₂ (up) and SO₂ (bottom) concentration measured by passive samplers with position in SW-NE direction (first monitoring campaign).

prevailing wind in the first monitoring campaign (Figure 3), a coefficient of determination $R^2 = 0.23$ is obtained for NO_2 and $R^2 = 0.42$ for SO_2 . A similar analysis cannot be realized in the second campaign because of a lack of prevailing wind direction. The higher coefficient of determination for SO_2 may indicate that concentration of this pollutant in the port area is subject to greater influence of ship emissions. In fact, when the prevailing wind is southwesterly, as during the first monitoring campaign, it blows from the sea, and not from the urban area of Naples (Figure 1). Moreover, the monitoring points located further north (H, E, J, X, S, and B) are downwind to berth areas of ferries, fast ferries, hydrofoils, and large cruise ships (Figure 1). Since SO_2 and NO_2 concentration levels moving from SW to NE increase, this could be evidence of the influence of ship emissions on the air quality in the port area.

Comparison between air quality in the port and in the urban area

Air pollutant concentrations measured inside the harbor of Naples were correlated with the air concentrations monitored by the urban air pollution network, operated by the Agency for Environmental Protection of the Region of Campania (ARPA Campania). The localization of air quality stations in the city of Naples is reported in Figure 1. This comparison is justified by the proximity of the port and the urban area in Naples. As suggested by the legislation on air quality assessment in urban areas, the monitoring stations are classified as suburban

background (SB; NA01), urban traffic (UT; NA02, NA03, NA04, NA05, NA06, NA07), and suburban traffic (ST; NA08, NA09).

The comparison of ambient air concentration measured in the port of Naples with that measured by the air quality monitoring stations in the urban area of Naples is reported in Figure 7 for NO₂, PM₁₀, and benzene. Unfortunately, data of SO₂ from the air quality network of Naples were not available in either period of the two campaigns. Plots report the average values measured by each monitoring station over the observation time of the experimental campaign in the port of Naples. Data of nine monitoring stations are grouped for the first and second monitoring campaigns. Vertical lines represent the concentration measured by passive samplers and continuous analyzers in the port area. Figure 7 shows that concentration levels measured in the port area are generally comparable to those measured in the urban area. This is particularly true for PM₁₀. For NO₂ in the first campaign, concentration measured in the port area was higher than that in the urban area. For benzene, data measured in the different stations in the urban area are highly scattered and a comparison is difficult. However, in the second campaign, benzene concentration in the port area was lower than in the urban area.

The significance of the comparison is strictly dependent on the duration of the two campaigns. The first one lasted 14 days in April and is representative of the spring season; the second one lasted 19 days in November and is representative of autumn. Since meteorological conditions observed were quite typical of the two seasons, the results obtained can be considered representative of the two seasons.

A time analysis was performed to verify the correlation of hourly average values measured in the port area with those measured at fixed stations in the urban area of Naples for NO_2 and PM_{10} . Results in terms of coefficient of determination R^2 are reported in Table 4.

High correlation between data measured in the port area with data measured in the urban area was observed mainly for traffic-oriented stations (i.e., 2, 5, 6, and 7). Lower correlation is registered with background station (station 1) and suburban stations (stations 8 and 9). High correlation is also observed among stations of the same typology (i.e., traffic stations). Further to this, low correlation is observed among the urban area stations of different typology (i.e., station 9 with other). This is an indication that the phenomena determining the concentration levels of NO₂ and PM₁₀ in the port area have a time dependence similar to that registered at traffic stations located in the urban area of Naples.

Conclusions

The results of the two monitoring campaigns conducted in the port of Naples in 2012, even though not exhaustive, due to (i) the relatively short observation time (only 33 days in two different seasons: spring and autumn); (ii) the loss of numerous passive samplers particularly in the second campaign; and (iii) the unavailability of SO_2 concentration from the Naples air quality network, supplied some useful indications.

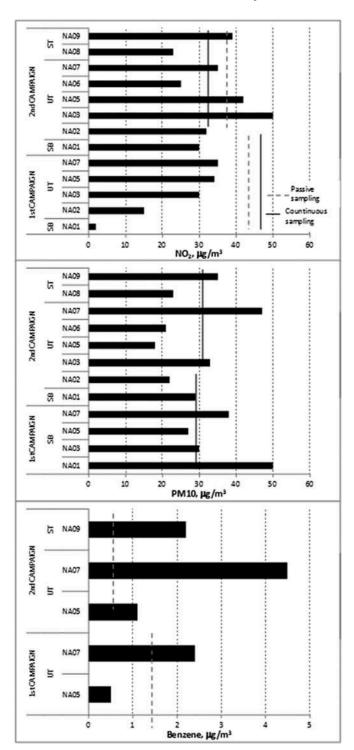


Figure 7. Comparison of NO_2 , PM_{10} , and benzene concentrations measured in the port area and in fixed stations in the urban area of Naples.

The main indications are as follows:

(1) About the air quality in the port of Naples, the results obtained have not indicated any particular problem. A proper comparison with limit values (LVs) established by European legislation would require a 1-yr observation period, a much longer time than the duration of our

monitoring campaigns. However, it can be observed that NO₂ hourly average (200 μg/m³) and PM₁₀ daily average (50 μg/m³) concentrations were always below the respective LV. Time-averaged concentrations in the period for PM_{10} (29.8 $\mu g/m^3$) and benzene (1.0 $\mu g/m^3$) were below the respective yearly average LVs (40 μg/m³ for PM₁₀ and 5 μg/m³ for benzene). Only NO₂ average concentration in the period measured by passive samplers (41.1 µg/ m³) exceeded slightly the year limit value (40 μg/m³). SO₂ concentration was well below the hourly and daily average LVs. For the reasons stated above, a definitive assessment on the air quality in the port of Naples cannot be inferred from our data. However, it must be highlighted that results, even though relative to a limited range of days, were obtained with meteorological conditions typical of the two seasons monitored. Therefore, their time significance can be higher than the actual observation time.

(2) Concentration levels of BTEX, NO₂, and PM₁₀ are comparable to those registered in the urban area of Naples. A time dependence analogous with urban traffic-oriented stations of the air quality network sited in Naples urban area was also observed. For SO₂, the comparison was not possible to operate because of the unavailability of data from the air quality network stations in the urban area of Naples.

Concentrations monitored are also comparable to those observed by other authors in other Mediterranean ports. Only SO₂ showed concentration levels higher than those observed in other ports. Regardless, absolute values of this pollutant are very low.

(3) A preliminary attempt to assess the impact of naval emissions on the ambient air concentration level in the port area based on the analysis of the spatial variation of concentration along the SW-NE direction has shown that SO₂ concentration in the port area may be affected by naval emissions more than other pollutants. For other pollutants (NO₂ and PM₁₀), a high correlation between concentrations measured in the port area and urban area was observed for urban traffic oriented stations. These findings, even though not definitive as highlighted at the beginning of this section, seem to indicate that ship emissions do not constitute the unique source of air pollution in the port of Naples, a considerable contribution coming from the nearby urban traffic roads. Moreover, it is not possible to conclude that ship emissions from the port area have a significant impact on air quality in the city.

Further studies are necessary in order to make a more precise assessment of the contribution of ship emissions to the air quality in the urban area of Naples. On the basis of the results of this study, the following activities would be necessary: (i) development of a bottom-up procedure for a reliable time dependent emission database of ship emissions due to maneuvering and hotelling at berths in the port of Naples; (ii) the use of models for the individuation of the fate of atmospheric pollutants emitted by ships on a local scale of few kilometers from the sources; (iii) the realization in 1 yr of at least four

Table 4. Coefficient of determination (R^2) for NO_2 and PM_{10} between data measured in the port area and in the urban area of Naples

| | | First Campaign | | | | | | | | |
|----------------------|-------|----------------|-------|-------|-------|-------|-------|-------|-------|-------|
| NO_2 | | Port | NA 01 | NA 02 | NA 03 | NA 05 | NA 06 | NA 07 | NA 08 | NA 09 |
| Second campaign | Port | | | 0.31 | _ | 0.28 | _ | 0.08 | _ | |
| | NA 01 | 0.25 | | | | | | | | |
| | NA 02 | 0.79 | 0.23 | | | 0.80 | _ | 0.22 | _ | |
| | NA 03 | | | | | | | | | |
| | NA 05 | 0.72 | 0.20 | 0.86 | _ | | | 0.24 | _ | |
| | NA 06 | 0.55 | 0.23 | 0.56 | _ | 0.60 | | | | |
| | NA 07 | 0.15 | 0.15 | 0.11 | _ | 0.20 | 0.26 | | | |
| | NA 08 | 0.28 | 0.15 | 0.39 | _ | 0.39 | 0.35 | 0.20 | | |
| | NA 09 | 0.41 | 0.38 | 0.34 | — | 0.35 | 0.39 | 0.16 | 0.14 | |
| $\overline{PM_{10}}$ | | Port | NA 01 | NA 02 | NA 03 | NA 05 | NA 06 | NA 07 | NA 08 | NA 09 |
| Second campaign | Port | | | | 0.30 | 0.60 | _ | 0.62 | _ | |
| | NA 01 | 0.34 | | | | | | | | |
| | NA 02 | 0.44 | 0.41 | | | | | | _ | |
| | NA 03 | | | | | 0.11 | | 0.27 | | |
| | NA 05 | 0.55 | 0.53 | 0.80 | _ | | | 0.70 | _ | |
| | NA 06 | 0.62 | 0.56 | 0.56 | | 0.69 | | | | _ |
| | NA 07 | 0.69 | 0.40 | 0.53 | _ | 0.65 | 0.63 | | | |
| | NA 08 | 0.41 | 0.32 | 0.49 | | 0.58 | 0.44 | 0.74 | | _ |
| | NA 09 | 0.01 | 0.04 | 0.07 | _ | 0.13 | 0.05 | 0.01 | 0.02 | |

monitoring campaigns each lasting 15 days in each of the four seasons. Passive samplers, necessary for the coverage of such a large area, would be associated with two or three mobile laboratories equipped with analyzers for PM₁₀, NO₂, SO₂, and BTEX. If SO₂ data were still unavailable from the "Regional Air Quality Network," it would be necessary to provide for the use of two to three analyzers located in the urban area of Naples.

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