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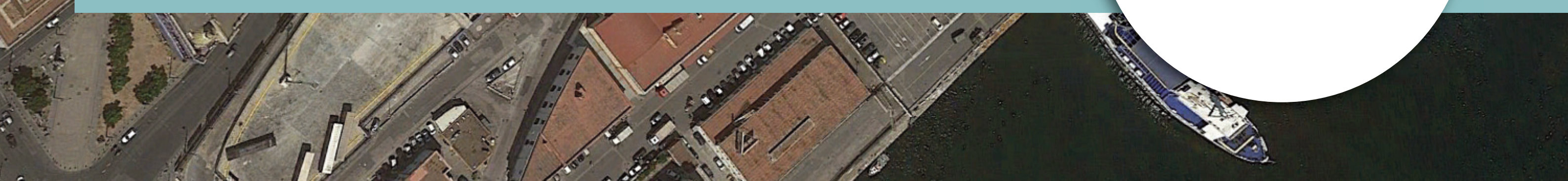

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Comparative Ozone Sensors Testing in an Anthropized Coastal Area

Test comparativo di sensori di ozono in un'area costiera antropizzata

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Cover Location of the test site (Waterfront of Naples Harbour, Naples, Italy) | *In copertina Il sito del test (Waterfront del Porto di Napoli, Napoli, Italia).*
Image from Google Earth

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Abstract

Air quality monitoring is traditionally performed using fixed monitoring stations in controlled environments. The instrumentation used in these stations, is often complex, bulky, very expensive, and it requires frequent maintenance works. Recently, the advancements in the field of digital technology and network communication made it possible to imagine a new paradigm of monitoring based on low-cost gas sensors. This latter is a very emerging technological area that offers considerable practical application.
In this work, the performance evaluation of a low-cost O_3 outdoor gas sensor was analysed by means of a comparative in-field test. At this scope, we collected data in a strongly urbanized coastal zone, using both a commercial O_3 monitoring station and a prototype station based on low-cost metal-oxide-semiconductors (MOX) gas sensors. Finally, the performance and reliability of the low-cost prototype sensor versus the commercial one was evaluated through direct comparison between the acquired data.

Riassunto

Il monitoraggio della qualità dell'aria è tradizionalmente eseguito utilizzando stazioni di monitoraggio fisse in ambienti controllati. La strumentazione utilizzata in queste unità è spesso complessa, ingombrante, molto costosa e richiede frequenti lavori di manutenzione. Recentemente, i progressi nel campo delle tecnologie digitali e delle comunicazioni hanno permesso di immaginare un nuovo paradigma di monitoraggio basato su reti di sensori di gas a basso costo. Quest'ultima è un'area tecnologica molto emergente che offre una notevole praticità applicativa.
In questo lavoro, la valutazione delle prestazioni di un sensore low-cost di O_3 atmosferico in ambiente outdoor è stata analizzata attraverso un test comparativo sul campo. A tal scopo, abbiamo raccolto i dati in una zona costiera fortemente urbanizzata, utilizzando sia una stazione di monitoraggio O_3 commerciale sia una stazione prototipale basata su sensori di gas a basso costo di ossidi metallici a semiconduttori (MOX). Infine, è stato valutato il livello di prestazioni e l'affidabilità del sensore prototipale a basso costo attraverso il confronto diretto tra i dati acquisiti dai due sistemi.

Introduction

Outdoor air pollution is one of the major challenges that policy makers and scientist have to face in the 21th century, as highlighted in 2014 by the World Health Organization (WHO) reporting that globally air pollution caused about 3.7 million of deaths. Moreover, air pollution seems to be responsible for global climate change [Ramanathan and Feng, 2009] and other intense effects on the whole Earth's environmental system.
The environmental dimension of air pollution is becoming more and more complicated by many issues that include new technologies development providing support to decision makers. In urban areas, the air quality can be considered as resulting from the overlapping of three different pollution components: regional background, urban background and hot-spot events [Ramanathan and Feng, 2009]. For these last, the pollutants quickly reach very high concentration peaks, but they decrease just as much. Therefore, the continuous monitoring of these components is of a critical importance [Ramanathan and Feng, 2009].
In this framework, the coastal urban areas are the most vulnerable Earth's habitats and they are significantly exposed to perceive the impacts coming from pollutant transfer between different environmental sub-systems. Many bio-geochemical processes, mostly interacting with processes

depending on human activities, in fact complicate pollutant dynamics in coastal areas. In these areas, air pollution is often caused by traffic, industries and shipping emissions, impacting not only the level and the composition of gaseous pollutants but also the particulate fraction (e.g. enhancing new particle formation in urban areas). In the coastal zone, the monitoring activity could be a very interesting technological challenge, in order to distinguish natural sources of pollutant and anthropic sources especially in the so-called “hot-spot” areas.
Air quality monitoring is traditionally performed using analytical instruments, mainly spectrophotometers, to measure the concentrations of NO_2, SO_2, O_3, CO and C_6H_6 at fixed points for each target pollutant following the EU Regulation [European Parliament, 2009].
The advancements in the field of digital technology, network communication and gas sensors developments made it possible to imagine a new paradigm of monitoring [Hagler et al., 2013; Kumar et al., 2015]. As a matter of fact, the high-resolution and spatial-temporal datasets can be obtained by ubiquitous monitoring points based on low-cost sensors networks for monitoring real-time variation of air pollutant concentration. As discussed in [Rai et al., 2017], the low-cost gas sensing for air quality monitoring is an emerging technological area, providing a good data quality and feasibility.
One of the recent highlights of the available literature on this topic is that for achieving an effective low-cost sensor-based air quality management the crucial aspect is the “performance assessment” for monitoring different air pollutants [Rai et al., 2017; Castell et al., 2017; Jovašević-Stojanović et al., 2015; Judge and Wayland, 2014; Lewis and Edwards, 2016]. In this framework, the main aim of this paper is focused on the performance evaluation of a low-cost O_3 outdoor gas sensor by adding to the typical two stage calibration [Rai et al., 2017] a comparative in field test performed under final deployment conditions.
Aiming at this purpose, we collected data in a strongly urbanized coastal zone, using both a commercial O_3 monitoring station (Aeroqual AQM-65) and a prototype station based on low-cost metal-oxide-semiconductors (MOX) gas sensors [Carotta et al., 2001]. The main goal was to demonstrate also the whole low-cost prototypal station performance under final deployment conditions with respect to a larger and more expensive standardized monitoring station. To carry out the test we have chosen to deploy the two monitoring stations in a testing costal area located in the metropolitan city of Naples (Southern Italy). The test site is nearby the waterfront area where one can expect a daily significantly variation of O_3 concentration due to human-induced processes superimposed on the natural water-air exchanges.
The ozone behaviour in the costal zone is amplified by the presence of sea salt aerosol that is a source of halogens, in particular chlorine, inducing a reaction sequence starts first by dissolution of N_2O_5 in the sea salt aqueous particles and its subsequent reaction with chlorine [Chang and Allen, 2006].
This is most significant at night-time because N_2O_5 and its precursors are photolyzed by sunlight. $ClNO_2$, accumulated overnight, is rapidly photolyzed after sunrise, freeing the chlorine radicals to react with organics and eventually lead to a large change in ozone over a short period of time:

$N_2O_5 \rightarrow NO_2^+ + NO_3^-$	$ClNO_2 + hv \rightarrow Cl + NO_2$
$NO_2^+ + Cl^- \rightarrow ClNO_2$	$NO_2 + hv \rightarrow NO_2 + O$
$O + O_2 \rightarrow O_3$	

Evidence of the importance of this cycle comes from observed high concentrations of $ClNO_2$ in the subtropical marine boundary layer [Ostoff et al., 2008]. Indeed, in subsequent research, it has been shown that is an important part of chlorine cycling [Simon et al., 2010].
Therefore, research on the topic of sea salt aerosols and their interaction with a polluted environment, particularly ozone, is paramount to future decisions. For these reasons we decided to select the monitoring of O_3 concentration as parameter of our comparison.

The prototypal station herein presented and used for the test, is equipped also with NO_2 gas sensor module and this allowed us to evaluate the overall cross-sensitivity on the MOX O_3 sensor, that is a well known aspect discussed in literature [Bart et al., 2014; Lin et al., 2015].

1. Materials and Methods

1.1 Commercial Monitoring Station

The commercial monitoring unit is a compact air quality station model AQM 65 (Aeroqual) designed for precise measurement of ambient pollution and environmental conditions. The monitoring station consists of a custom made IP65 rated aluminium enclosure which houses a power module, thermal management system, embedded PC running Aeroqual Connect software and user analyser modules (Fig. 1).

Figure 1 a) Commercial monitoring station (mod. Aeroqual - AQM65); b) Installed sensor modules, cooling system (on the bottom), data transmission and embedded mini-pc.

Figura 1 *a) Stazione di monitoraggio commerciale (mod. Aeroqual - AQM 65); b) Moduli sensore istallati, sistema di raffreddamento (sotto in basso), trasmissione dati, mini-pc integrato.*

The AQM65 monitoring station is equipped by modules dedicated to ozone (O_3, see Tab. 1) measuring, particulate monitoring (PM1 PM2.5 and PM10; see Tab. 2) as well as meteorological parameters such as temperature, humidity, wind speed and direction.

Gas Module	Range (ppm)	Noise (ppm)	Lower detectable Limit (ppm)	Precision
Ozone (O_3)	0-0.5	<0.001	0.001	<0.002 ppm to 0.1 ppm (<2% of reading above 0.1 ppm

Table 1 Ozone Gas sensor specifications.
Tabella 1 *Specifiche del sensore di gas ozono.*

Sensor Name	Definition	Range	Units
PM1	Particle mass below 1 µm	200	ug/m^3
PM2.5	Particle mass below 2.5 µm	2000	ug/m^3
PM10	Particle mass below 10 µm	5000	ug/m^3

Table 2 Particulate matter sensors specifications.

Tabella 2 *Specifiche dei sensori di particolato.*

The Air temperature is measured in a range between -40° C to + 124° C with an accuracy of +/- 0.3° C and a resolution of 0.01° C, while relative humidity is detected in a range varying from 0 to 100 % RH with an accuracy of +/- 2 % RH and a resolution of 0.1 % RH.
The operability of O_3 gas sensor is guaranteed by a thermal management control system to maintain a stable internal temperature independently of ambient temperature variations.
Instrument and sensors module calibration is managed by means of a software interface hosted on the monitoring station local mini-PC. Evenly, data acquisition and management is made by means of the Aeroqual Connect software interface. This standard graphical interface allows the user to be connected directly to the AQM monitoring station permitting the management of sensors modules calibration, data visualization, management and export (e.g. csv format). It can be accessed via WiFi, Ethernet or a GSM modem.

1.2 Prototypal station

The prototypal monitoring unit (Figs. 2, 3) consists of a small aluminium box (25x35x20 cm) based on an array of metal oxide gas sensors (MOX) prepared via screen-printing technique. The technology of thick film gas sensors is an optimal candidate to be implemented in a portable, low-cost, small-sized and versatile equipment to monitor diffusely pollutant. Such a monitoring technique would constitute an advantageous solution for a wide range of situations, as for example along the roads of city centres or along heavy-traffic roads, or in historic centres where fixed monitoring stations cannot be used due to their large size.

Figure 2 Prototypal monitoring unit Aluminium case.

Figura 2 *Unità di monitoraggio prototipale in Alluminio.*

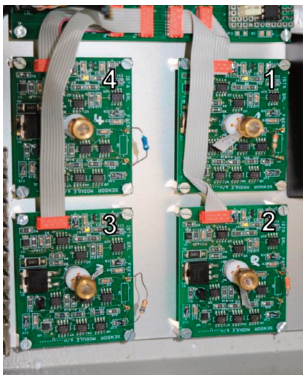

Figure 3 Sensor modules array for detection of carbon monoxide (1), nitrogen dioxide (2), ozone (3) and BTX (4).

Figura 3 *Insieme dei moduli sensore per il rilevamento di monossido di carbonio (1), biossido di azoto (2), ozono (3) e BTX (4).*

In order to monitor traces of gases in atmosphere, the sensors must exhibit sensitivity and selectivity comparable to those of the conventional devices, and also high stability, repeatability and reliability [Carotta et al., 2007; Fioravanti et al., 2016]. The semiconductors metal oxides have the capability to modify their electrical behaviour after environmental gas interaction.

This is why they are intensively studied and used as functional materials for pollutant gas sensing. The selection of the appropriate functional materials to detect the gases has been made on the basis of many laboratory characterizations and of previous in-field monitoring experiments. In particular, the sensing characteristics of tungsten trioxide (WO_3) suggested to test WO_3 based sensor as ozone sensor.
The array of MOX sensors (Fig. 3) used into the prototypal monitoring unit has been designed and realized to monitor the main atmospheric pollutants such as carbon monoxide, nitrogen dioxide, ozone and BTX (Benzene, Toluene, Xylene).
Each sensor module has its own electronic control containing the sensor signal measurement system and the control circuit of the sensor temperatures. It also contains an analogue/digital converter and a main unit, whose microprocessor manages all control operations, it acquires the values measured by analogue part, it stores the data and converts them in gas concentration and, in the end, it sends them via serial port to a GSM module which provides data transmission.
In order to measure the sensitive film resistance, a voltage generator supplies the bias voltage (5V) and an electrometric operational amplifier performs the conversion from current to voltage. The temperature is maintained steady as the external environmental conditions change, keeping stable the resistance value. To achieve this stability a Wheatstone bridge circuit was used. If the digital amplifier detects an unbalance voltage on the bridge nodes, then an adjustment element (MOSFET) changes the sensor supply current in order to bring the electrical current (that crosses the bridge) back into balance.
The prototypal unit has been realized to have low requirements in terms of power, consumables, maintenance and installation costs, including control electronics, firmware and interface software for the acquisition, processing and wireless transmission of the data, providing them in real time.
In order to manage the monitoring unit, a software in *LabVIEW* environment has been developed (Figs. 4, 5). In this way it is possible to remote control via GSM connection, to check and modify the operating temperature of the sensors and the baseline of the acquired electric signals. It is also possible to apply the algorithm for the conversion of the voltage level to gas concentration.

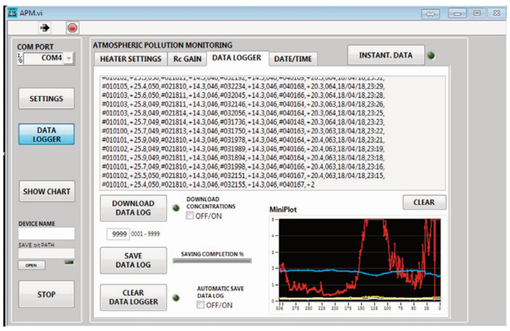

Figure 4 Graphical User Interface (LabVIEW Software): data logging and management of sensors parameters.

Figura 4 *Interfaccia Grafica Utente (Software LabVIEW): registrazione dati e gestione dei parametri dei sensori.*

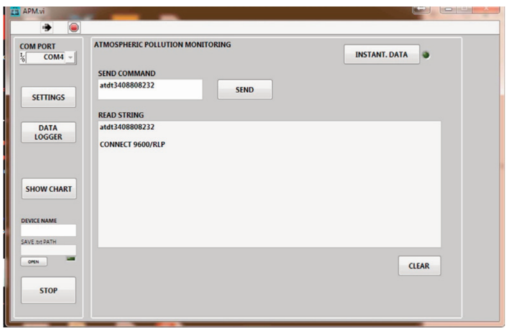

Figure 5 Graphical User Interface (LabVIEW Software): remote control by GSM connection.

Figura 5 *Interfaccia Grafica Utente (Software LabVIEW): controllo remoto attraverso connessione GSM.*

1.3 Field Test

The comparative performance in field test was conducted in a very suitable site both for the logistics and for the geographical location with respect to possible variation of ozone concentration in presence of multiples (anthropic and natural) sources. The test site is located in a strongly anthropized coastal area (Fig. 6a) in Naples (Southern Italy).
The test has been conducted coupling the two monitoring units by a back-to-back installation (Fig. 6b). In order to obtain a reliable measuring point we have chosen to install the monitoring stations on a standard Iso 20' container that is 2,59 metres height located in the front yard of the Institute for Coastal Marine Environment (IAMC) headquarters, National Research Council (CNR) (40°50'39.49"N, 14°15'35.69"E).

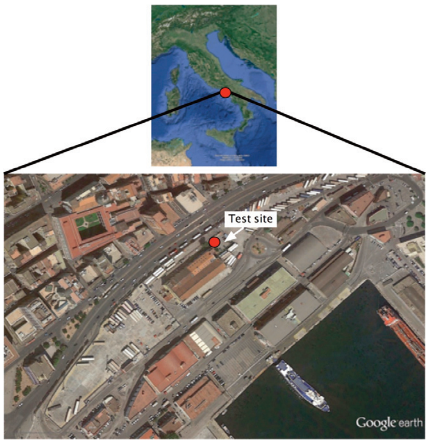

Figure 6a Location Map of the test site (Naples, Southern Italy).

Figura 6a *Localizzazione del sito di test (Napoli, Italia Meridionale).*

Figure 6b Back-to-back installation of the conventional station (AQM-65) and of the prototypal station both mounted on an Iso 20' container.

Figura 6b *Istallazione della stazione convezionale (AQM-65) and e di quella prototipale montate entrambe su un container Iso 20'.*

2. Results and Discussion

Data acquisition was performed in November 2017 night and day hourly without interruptions. During this time period neither anomalous weather nor exceptional natural event occurred. In Fig. 7 the global dataset acquired is showed representing a first comparative analysis between the O_3 sensors. In order to perform a more detailed comparison between data, we plotted groups of hourly measurements with a time span of 6 days (from 06/11/2017 00:00:00 GMT to 23/11/2017 23:59:00 GMT) as showed in the followings (Figs. 8, 9). In Fig. 10 we report a close-up of two days where is evident the presence of the nocturne Ozone highlighted in dash boxes. Furthermore, when minimum values are detected a little difference in promptness between the two O_3 gas sensors is revealed (Figs. 8, 9).
We simply analysed the two datasets acquired just comparing values hour by hour, and

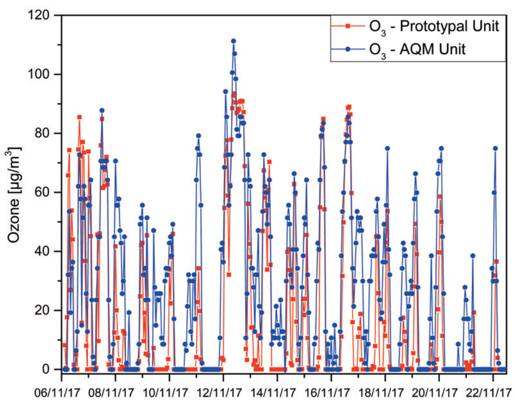

Figure 7 Entire data collection period (from 06/11/2017 00:00:00 GMT to 23/11/2017 23:59:00 GMT – hourly measurements).

Figura 7 *Intero periodo di raccolta dati (dal 06/11/2017 00:00:00 GMT al 23/11/2017 23:59:00 GMT – misure orarie).*

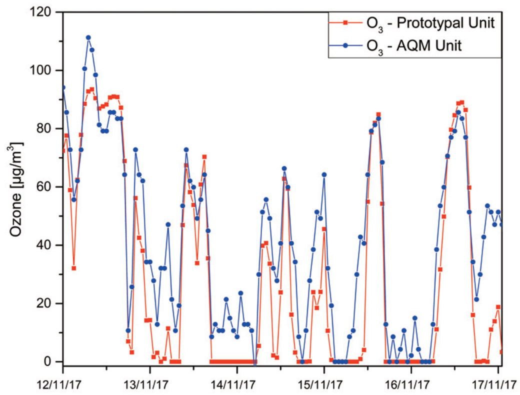

Figure 8 Close-up – period 12-17 November.

Figura 8 *Dettaglio – periodo 12-17 Novembre.*

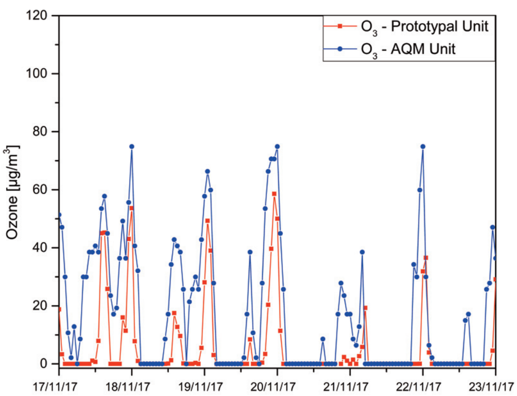

Figure 9 Close-up – period 17-23 November.

Figura 9 *Dettaglio – periodo 17-23 Novembre.*

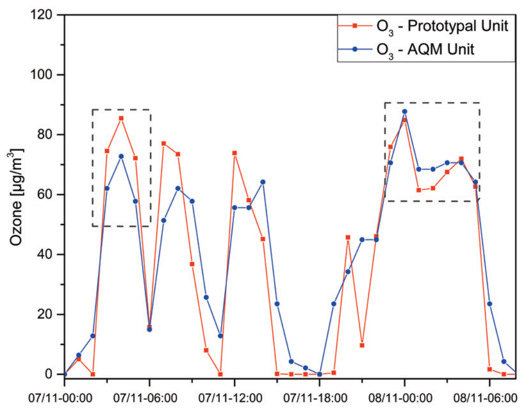

Figure 10 Nocturne Ozone data comparison in dash boxes (from 07/11/2017 00:00:00 GMT to 08/11/2017 07:00:00.

Figura 10 *Comparazione dei dati di Ozono notturno nelle aree tratteggiate (dal 07/11/2017 00:00:00 GMT all'08/11/2017 07:00:00.*

evidencing two magnification periods of five days each. Data comparison demonstrated that there is a good degree of similarity indicating a good performance and reliability of the prototypal station. Hourly data comparison revealed for the prototypal low-cost O_3 gas sensor a little difference in promptness when minimum values are detected.
Afterwards, we performed a statistical data analysis, synthetically expressed through a calculation of the correlation coefficient (Fig. 11). The value of the correlation index is 0.808, confirming a good level of performance achieved by the prototypal monitoring station versus the commercial one. The chart of Fig. 11 contains also an analysis of standardized residuals. It allows to prove that the residual distribution is normal. Indeed, only few points (red-brown in color) give rise to residuals greater than |1.96|. In Fig. 12 the maximum daily values detected by units are reported; also in this case it is possible to observe the good correlation of the collected data.

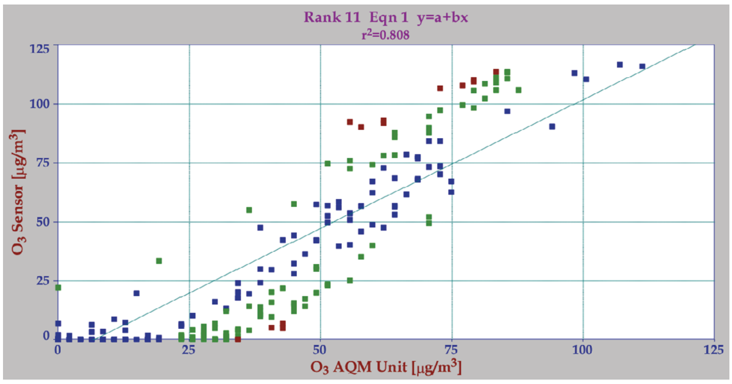

Figure 11 Data Correlation between O_3 data (prototypal sensor and AQM unit).

Figura 11 *Correlazione tra i dati di O_3 (sensore prototipale e unità AQM).*

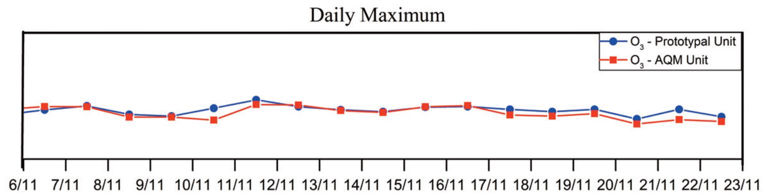

Figure 12 Maximum daily values for the testing period.

Figura 12 *Valori massimi giornalieri per il periodo di test.*

3. Conclusions

The overall aim of this work was to evaluate the performance level of a prototypal low-cost air quality monitoring unit versus a commercial one. The test was performed on O_3 gas sensor datasets acquired hourly during a time span of 16 days. The investigation was conducted installing the two monitoring station back-to-back at about 3 meters over the ground in a strongly anthropized coastal area that is a very suitable test case for O_3 monitoring. Globally, data analysis suggested a good level of performance of the prototypal low-cost O_3 gas sensor with respect to the commercial one.
The results obtained by the field test campaign widely confirmed the high performance of an O_3 gas sensors MOX-based suggesting its good reliability in field measurements conditions.
Furthermore, we selected the monitoring of O_3 concentration as parameter of performance comparison because sea salt aerosols and their interaction with a polluted environment, particularly ozone, is paramount to future decisions for air quality management in anthropized costal areas. Moreover, the prototypal monitoring box is characterized by extremely low-cost sensing modules and by the reduced dimensions of the external case. This aspect makes it very suitable and portable for on the field measures and particularly to design a monitoring network constituted by several measuring points. In this framework, a possible improvement of the prototypal unit could be the use of the LTE connection for a more effective data logging and remote control. Globally, the results obtained in this study suggest that the low-cost gas sensing for air quality monitoring is an emerging technological area, providing a good data quality and feasibility for achieving an effective low-cost sensor-based air quality management.

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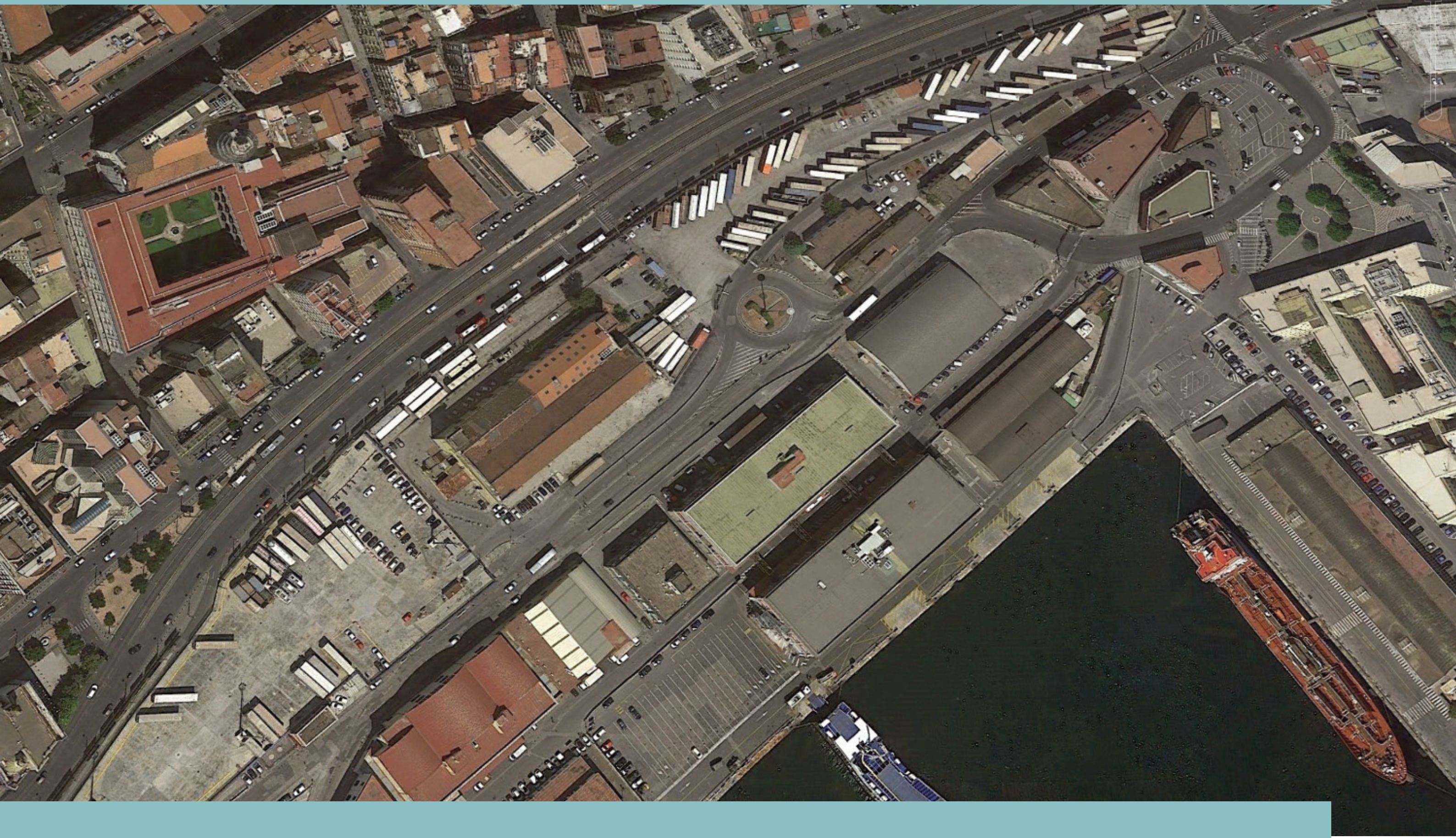

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