

1 Abstract

2 The Sea is often a fragile environment to be protected against possible pollutants. In this context, the  
3 present work contributes to its safeguard by proposing a new buoy equipped with advanced sensors for  
4 the detection of oil spills. In particular, the buoy is provided with various sensors for the evaluation of  
5 both meteorological and marine parameters (e.g. waves, wind, temperature), and chemical/physical data  
6 acquired by an electronic nose system specifically designed for the detection of hydrocarbons. The  
7 electronic nose is composed of a flow chamber, a chamber equipped with photo ionization sensors,  
8 pumps and valves for air inlet and outlet, and a low-cost electronic board. The designed system samples  
9 the air above the water and produces data that are processed through two artificial neural networks  
10 allowing for a classification of detected hydrocarbons and overall pollution level. Suitable network  
11 interfaces and a connector towards a Marine Information System (MIS) allow both for real-time data  
12 visualization and for long-term assessment of water quality.

13  
14 **Keywords:** Sensorized buoy; Marine pollution; Oil spills; Electronic noses; Hydrocarbons classification

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## 26 Introduction

27 The Mediterranean Sea represents a very fragile ecosystem, with the presence of highly polluted areas,  
28 heavy commercial and touristic traffic, as well as a particular position and shape, making its waters  
29 slowly renewable. In fact, the fast urban settlements expansions, along shorelines, as well as the high and  
30 increasing human pressure, made the Mediterranean Sea sensitive to pollutants, especially hydrocarbons,  
31 often produced by oil spills and ship transits (Er-Raioui et al., 1999; Ferraro et al., 2009). Therefore,  
32 massive global changes could affect this basin more rapidly and intensively than oceans, because of the  
33 persistent bio-accumulative chemical compounds that cause problems for the entire ecosystem (Zaghden  
34 et al., 2014).

35 Thus, in the Mediterranean as well as in other areas of Europe and worldwide, a number of safeguard  
36 methods has been adopted in last years in order to reduce the negative impact of pollution on the marine  
37 ecosystem. In particular, in the northern Tyrrhenian Sea and, specifically, in the area delimited by  
38 Corsica, Elba Island, Ligurian coast and Provence, which is considered one of the most important feeding  
39 and reproductive places for a number of cetaceans in the Mediterranean, the “*Pelagos Sanctuary*” was  
40 constituted. This measure was undertaken in order to preserve such animal species from the disruptive  
41 impact of environmental pollution (Azzellino et al., 2012).

42 Hence, the adoption of innovative strategies for environmental monitoring applied to marine areas has  
43 experienced a growing interest in last decades, thus involving state-of-the-art methods to accomplish  
44 successfully this aim.

45 Among the strategies adopted throughout the last years, the employment of electrochemical sensors,  
46 sometimes included in systems based on the Electronic Nose (E-Nose) – for air analysis – or Electronic  
47 Tongue (E-Tongue) (Czolkos et al., 2016) – for liquid analysis – technology, could represent a useful  
48 add-on to current methods, in order to increase their sensitivity and accuracy.

49 Thus, the aim of this work is to present a system, based on the technologies of E-Nose (Sobanski et al.,  
50 2006), integrated into moored buoys (Moroni et al., 2015) and capable of monitoring the presence of  
51 hydrocarbons, seen to be the highest-impact pollutants for the marine ecosystem (Clark, 1992), on the  
52 sea surface in a given area. This system, which samples the air above the water, could be complemented  
53 by similar approaches, for example, integrated into floating vehicles (e.g. AUV, ROV...), as already  
54 described in literature (Tonacci et al., 2015, 2016), for a complete monitoring – both from static and  
55 dynamic point of view – of an area of interest. The proposed system, based on a sensor-equipped moored  
56 buoy, is used as a node in a monitoring network – of different complexity depending on the size and  
57 traffic of the area to be monitored – to control areas of interest; to this end, the buoy is equipped with  
58 network interfaces allowing for external communication. A connector with a Marine Information System  
59 (MIS), offering storage functionalities as well as suitable interfaces for data fruition and processing (see  
60 e.g. Cortes et al., 2000; Jordi et al., 2006; Tampucci et al., 2013) is presented. Through the connector,  
61 the real-time access to the data acquired by the buoy and transmitted wirelessly to the MIS is possible,  
62 together with the request of particular procedures to be performed.

63 The paper is organized as follows. In Materials and Methods: the basic facts dealing with the buoy and  
64 its sensor payload are introduced; the E-Nose from a hardware perspective is presented, the onboard data  
65 processing functionalities are described and, finally, communication interfaces and connection to the  
66 MIS are reported. Results displays and discusses experimental results while final remarks are presented  
67 in the Conclusions section.

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## 69 Materials and Methods

### 70 Sensorized buoy sensors

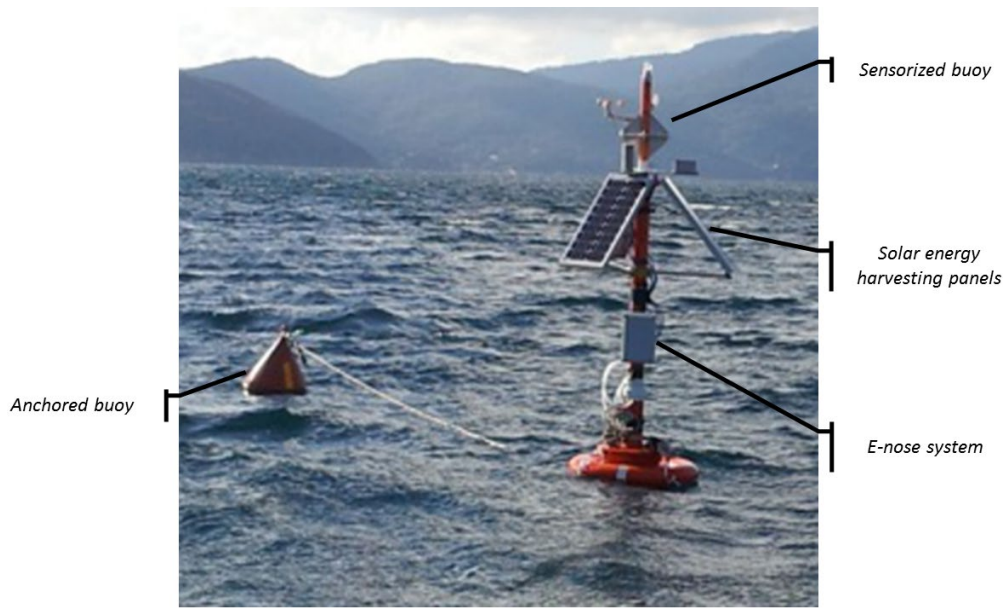
71 Two specific issues are on the basis of the proposed approach of using a network of moored buoys for  
72 the monitoring: first, the capability of a buoy to carry on sensors and allowing them to work just on the

73 surface of the sea, and secondly due to the geographical location considered for the monitoring. In fact,  
74 the “Pelagos sanctuary” is a part of the Mediterranean having many islands and a high density of ships  
75 navigating, which make it, at the same time exposed to environmental pollution, and a highly connected  
76 sea area in terms of communications coverage.

77 The proposed moored buoy (shown in Figure 1), is an autonomous system thanks to photovoltaic panels  
78 mounted. It is equipped with a configurable sensor payload. Its current equipment consists of: i) a  
79 complete weather station, ii) accelerometers for wave motion evaluation, iii) GPS sensor and GSM  
80 antenna, iv) batteries and v) the E-Nose which is housed in the immersed part of the buoy and described  
81 in detail in the following section.

82 The weather station is composed of a thermometer for measuring air and water temperature, a hygrometer  
83 for measuring humidity, an anemometer and a rain gauge for measuring the wind and liquid precipitation.

84 The sensors are connected to a main electronic board (specifically manufactured for the buoy), which  
85 performs the actual measurements. A 3-axis accelerometer fixed to the buoy is also connected to the  
86 electronic board and allows for wave motion estimation. Finally, a GPS is also available, providing time  
87 information as well as the exact location of the moored buoy. Communications are provided by means  
88 of a GSM modem mounted on board and connected to the electronic board; GSM coverage is assured in  
89 the area of interest since the buoys are installed not far away from coastlines. However, a satellite modem  
90 for communications can be installed without any specific issue or burden to the system.



91

92 *Figure 1 The developed moored buoy at sea, capable of sampling the air above the water through the*  
93 *E-Nose system.*

94 The E-Nose

95 A very important part of the overall monitoring system presented in this paper is the electronic nose. This  
96 important add-on, integrated within the moored buoy, aims to detect, in real time, the presence of  
97 pollutants on the sea surface. The E-Nose, a very reliable tool represents, together with other sensor  
98 systems included in this platform, an important addition, with respect to the majority of current marine  
99 monitoring systems.

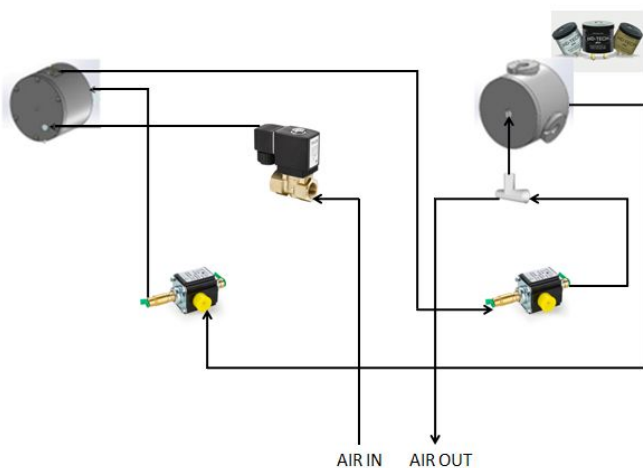
100 The E-Nose-based system is made of several components that ensure its correct functioning and its  
101 efficiency. Such elements include two pumps and an electrovalve for airflow inlet and outlet, a flow  
102 chamber for air sampling, a sensorized flow chamber and control electronics (composed of a low-cost  
103 electronic board, being the system based on the principles of open source and accessibility).

104 The flow chamber for air sampling was designed and realized in order to have a cylindrical shape, to  
105 comply with the sensorized chamber later described. This first chamber features an embedded sensor  
106 aiming at checking for the presence of humidity within the chamber, while the two pumps and the

107 electrovalve are interfaced to the electronic board for their activation. In this way, they made possible  
108 the correct functioning of the air aspiration/purge system. As already stated, control electronics has been  
109 chosen in order to keep its control and programming as simple as possible, as well as to grant its full  
110 adaptability to final users' needs, with the employment of open access protocols. Therefore, the low-cost  
111 electronic board Arduino Mega 2560 (Arduino Electronic Board,  
112 <https://www.arduino.cc/en/Main/ArduinoBoardMega2560>) was selected, and it demonstrated its  
113 effectiveness in the control of the E-Nose system, including pumps and the electrovalve, as well as  
114 sensors. The E-Nose control board is physically connected via RS232 to the main electronic board of the  
115 buoy.

116 The sensorized flow chamber is realized in polyether ether ketone (PEEK), a thermoplastic polymer  
117 owning a number of important characteristics for this purpose, including the low density ( $1320 \text{ kg/m}^3$ ),  
118 chemical inertia and good mechanical properties (Young's modulus: 3.6 GPa, tensile strength: 90-100  
119 MPa, 50% elongation at break). This flow chamber, essential to the correct functioning of the E-Nose  
120 system, can be equipped with up to six sensors (for the application described here, only three detectors  
121 are employed, while other slots are left free for further customization) placed radially in the chamber.  
122 The cylindrical shape, as well as the radial symmetry of the sensors, were chosen in order to provide all  
123 the detectors with the same amount of airflow. Therefore, the optimal architecture for the chamber could  
124 be with two, three or six detectors, respectively placed at  $180^\circ$ ,  $120^\circ$  and  $60^\circ$  one from another. In  
125 particular, within this work, three Photo-Ionization detectors (piDs, Yin et al., 2013) with different  
126 sensitivities to volatile molecules in terms of response amplitude and detection limits are chosen, in order  
127 to provide reliable responses even in presence of low concentration of Volatile Organic Compounds  
128 (VOCs). Such sensors are classified depending on their label and named as "Silver", "Bronze" and  
129 "Black" piD (from the most to the least sensitive one). Among the sensors commercially available, piDs  
130 are chosen for the reliability of the data acquired, their stability to experimental condition changes, a

131 nearly absence of drift, as well as their non-responsiveness to major air compounds, such as nitrogen and  
132 oxygen (Figure 2).



133

134 *Figure 2 Layout of the electronic nose system.*

135

136 The functioning principle of the piDs is quite simple: their driving force is the ultra violet (UV) high-  
137 energy radiation produced by a gas discharge lamp placed in the upper part of the sensor, within a  
138 sensitive window. The lamp radiation has a nominal photon energy of 8.3-11.7 eV, and in our work it  
139 produces an energy of 10.6 eV, being represented by a Krypton lamp, characterized by a good VOCs  
140 detection range as well as by a long lamp life. Other common lamps are based on Xenon or Argon gases,  
141 with an energy, respectively, of 9.6 eV and 11.7 eV. VOCs are exposed to the UV radiation that causes  
142 their ionization, in particular referring to those compounds having an ionization potential lower than the  
143 lamp energy. This process of ionization converts the molecules into positive ions and negative electrons  
144 and their concentration is therefore detected through the use of two electrodes placed in the ionization  
145 chamber. Among them, the polarizing electrode is linked to a DC power supply, while the signal  
146 electrode is connected to the amplifier input. The electrodes create therefore an electric field, making  
147 ions and electrons to migrate toward their electrodes, thus generating a small current, amplified by a  
148 specific chip and seen in output as analog or digital signal. The output signal produced is proportional to

149 the difference between the energy of the molecule detected and that of the UV lamp employed, as well  
150 as correlated with the concentration of the detected molecule.

151 As stated above, major air components are not detected by the sensors, due to their higher ionization  
152 potential when compared to the piDs lamp radiation energy.

153 The piDs are power supplied through the E-Nose control board by a 5V supply pin, thus allowing for a  
154 low power consumption (current draw being around 30 mA per sensor), not otherwise requiring a pre-  
155 acquisition warming time, as occurring in the case of many other kinds of detectors, like Metal Oxide  
156 Sensors (MOS).

157 The principle of operation of the E-Nose solution adopted in this work is as follows: cycles of air suction  
158 are defined and performed by activating the inlet duct through pumps and electrovalve movement; the  
159 air passed through the air sampling flow chamber where the humidity sensor, also supplied and managed  
160 by the electronic board, is placed. Here, the first check of humidity ratio is performed, and the data  
161 acquired are important for output post-processing. Specifically, data featuring a too high humidity ratio  
162 (typically above 70-75%) could carry on potentially false responses, therefore they have to be discarded  
163 or corrected to avoid misleading warnings.

164 Indeed, high humidity decreases the response in piD sensors by up to 30%, when compared to dry air,  
165 because water molecules can absorb UV light without becoming ionized, and thus quench the PID signal,  
166 even though they work still better than MOS and other sensors in such conditions. Therefore, a strict  
167 control of the surrounding environment is mandatory to achieve reliable results.

168 Then, the air enters the PEEK flow chamber equipped with the piD sensors that perform an analysis of  
169 the VOCs contained in the air sample, providing a corresponding output signal correlated with the total  
170 VOCs concentration, as stated above. From the sensorized flow chamber, the air is then purged off the  
171 buoy through an outlet pump and electrovalve switch.

172 Within the purpose here described, the acquisition of data from the piDs is performed at a frequency of

173 10 Hz, with cycles carried out periodically; each cycle consisted of one minute of air suction, analysis,  
174 and purge, followed by a variable and adaptive period of resting, typically set to five minutes, but  
175 customizable to fulfill the application requirements. This particular procedure is chosen to assure the  
176 acquisition of reliable data, possible thanks to the short resting time needed by the E-Nose to make the  
177 sensors clean after each acquisition. Moreover, a lag time between two consecutive acquisitions could  
178 allow for a noteworthy energy saving thanks to the lower battery consumption.

179 The E-Nose system is customizable according to the user's requirements and environmental needs and  
180 can accommodate other piDs or other sensors possibly relying on different principles of operation.

181

182 E-Nose on-board data processing

183 The data collected from the piDs are pre-processed directly on the E-Nose control electronics. In order  
184 to reduce bandwidth consumption and to improve data transfer rate, a compact representation of the  
185 collected data has been chosen to minimize their dimension. In particular, the most significant features,  
186 according to the preliminary bench tests and sea trials, are extracted from the raw data consisting of  
187 temporal sequences of samples from each piD.

188 In detail, the following features have been considered:

- 189 • Mean value obtained during the acquisition for each of the three piDs (following the order  
190 "Bronze", "Silver", "Black" piD) and for the humidity sensor
- 191 • Maximum value (peak) obtained during the acquisition for each of the three piDs (following  
192 the order "Bronze", "Silver", "Black" piD) and for the humidity sensor
- 193 • Peak time obtained during the acquisition for each of the three piDs (following the order  
194 "Bronze", "Silver", "Black" piD) and for the humidity sensor, defined as the sample in which  
195 each sensor has reached the maximum value

196

197 All the processing for this preliminary but fundamental feature extraction is carried out on the E-Nose  
198 control board and the results are then transmitted to the buoy main board.  
199 Notice that this pre-processing is extremely useful to reduce the computational load required for system  
200 management, therefore allowing an improvement of the performances of the overall system, with  
201 considerable energy saving. Without this step, the data collected would have accounted for a significantly  
202 higher computational load, with a negative impact on bandwidth consumption either from the E-Nose  
203 control board to the buoy main board and in turn to the MIS, with an increase in the system's power  
204 consumption.

205

#### 206 Artificial Neural Networks

207 To further process the overall data obtained by the E-Nose and transmitted to the MIS, two artificial  
208 neural networks (ANNs), of the type Kohonen Self-Organizing Map (KSOM) have been trained through  
209 Matlab R2011b (The Mathworks, Natick, MA, USA). The two ANNs aim, respectively, at: i) assessing  
210 the concentration of the compounds detected (Table 1) and, ii) identifying the correct hydrocarbon within  
211 the subset of the known stimuli above cited (Table 2).

212 The characteristics of the ANNs, indicated in Table 1 and Table 2, were chosen to maximize the benefit-  
213 cost ratio between the performance of the network and the computational cost required for the operation.

214 To this extent, each of the ANNs was composed of a different number of neurons (12x12 and 15x15),  
215 featuring a training on 1500 epochs with 8 and 20 cross validations, respectively. 85% of the data  
216 acquired from the laboratory bench test, as well as from sessions at sea held in *La Spezia* and *Capo Enfoia*  
217 (Italy), was used for the training of the first ANN (80% in case of the second ANN), whereas the  
218 remaining 15% (20% in the second network) was employed as test set.

219

#### 220 Communication

221 The buoy is connected with the MIS (see e.g. Tampucci et al., 2013; Moroni et al., 2016 for details about  
222 the MIS) which is in charge of receiving, managing and correlating the buoy data and managing the buoy  
223 itself.

224 In more detail, the MIS is able of acquiring, storing and managing heterogeneous data from different  
225 sources (Fedra and Winkelbauer, 2002). Aiming at increasing data reliability and at an enhanced  
226 understanding of the events occurring in the monitored zones, MIS also cross-correlates the collected  
227 data. The E-Nose and the buoy itself are main actors in this context, thanks to their capability of  
228 performing reliable in situ measurements.

229 To create and maintain the connection to the MIS, the buoy is equipped with networking functionalities  
230 that are deployed through a specifically designed connector to the MIS. As mentioned before, the  
231 communication is bidirectional and is used to send acquired data and to configure buoy functionalities.  
232 The configuration of buoy functionalities is focused on the optimization of buoy resource and on ensuring  
233 buoy operability (in terms of battery endurance and electronic damage avoidance).

234 From the hardware perspective, the buoy is equipped with a GSM modem. The installed SIM is enabled  
235 to send data packets. In brief, the buoy can be configured remotely by sending text messages (SMS) to  
236 the GSM modem, while the buoy can send acquired data to a configurable FTP server in binary format.

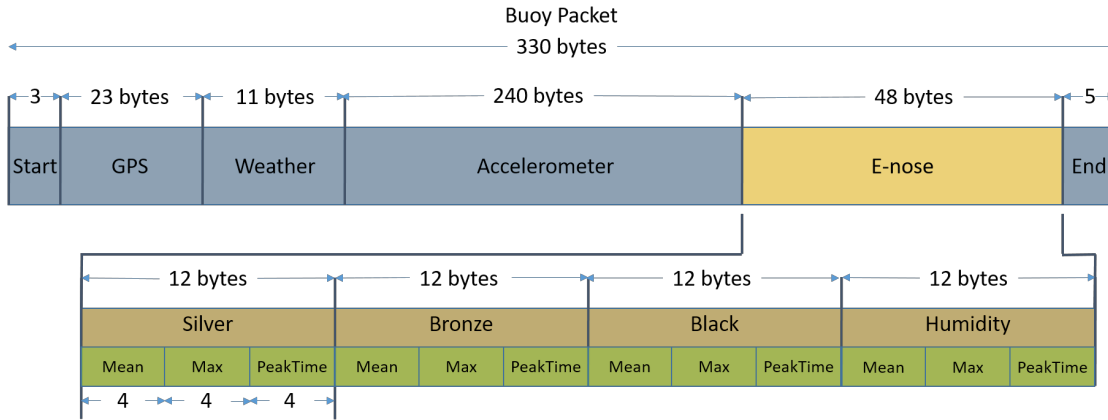
237

### 238 *From the Buoy to the MIS*

239 The buoy sends to the MIS two kinds of data: i) the actual observations made by the buoy and ii) an  
240 auxiliary file containing information and metadata about buoy configuration. The data are placed in a  
241 specific FTP folder of the MIS, exploiting a GPRS connection.

242 Sensors housed in the buoy have different measurement period. Thus, the data to be sent are not usually  
243 available together. Aiming at standardizing communication with the MIS and at having only one packet  
244 format, each packet contains the observations performed by all the sensors on the buoy. In case a

245 measurement is not available, the packet contains empty data for that sensor. Each packet has fixed length  
 246 equal to 314 bytes. The basic organization of the packet is shown in Figure 3.



247

248 *Figure 3 Buoy packet format.*

249

250 In details:

- 251 • The first three bytes and the five ending bytes are used for synchronizing packets and check  
 252 completeness.
- 253 • The following 23 bytes contain data from the GPS, including GPS time and quality of estimate  
 254 position.
- 255 • Weather bytes refer to meteorological measurements, including humidity, temperature, rain, wind  
 256 speed and direction. Battery status is also included in this block.
- 257 • After Weather bytes, the packet of 240 bytes refers to accelerometer data in three directions. These  
 258 data represent the wave motion.
- 259 • E-Nose bytes correspond to E-Nose measurement if performed. Otherwise, they are filled with  
 260 zeroes. Four sub-packets, each of 12 bytes, compose the E-Nose packet. The sub-packets specify  
 261 the silver sensor, the bronze sensor, the black sensor and the humidity values. Each sub-packet has  
 262 three blocks of four bytes that represent mean and max values and the peak time.

263

264 In addition, the buoy provides a text file containing information about its configuration, including its  
265 ID, GSM network configuration, FTP settings and other parameters for controlling acquisition and  
266 transmission frequencies.

267 Once data are received, the MIS parses and stores them into its inner database. Data are then analyzed in  
268 order to recognize the presence of oil spills and to check the correct functioning of the buoy.

269

### 270 *From the MIS to the Buoy*

271 The MIS is programmed to detect and manage hazardous situations, as well as to provide an optimal  
272 resource management. As mentioned before, once data arrive at the MIS, its proactive functionalities  
273 analyze them.

274 Based on the outcome of this analysis, in case of an alert state, functioning problems or merely for  
275 resource management, the MIS can change the buoy behavior.

276 The MIS communicates with the buoy through text messages (SMS). The buoy is equipped with a GSM  
277 modem used both for incoming and outgoing communication. While communication from the buoy to  
278 the MIS exploits FTP connection, communication to the buoy is achieved by sending formatted text  
279 messages. Indeed, since direct TCP/IP communication is not directly feasible because the buoy has a  
280 dynamic IP address, text messages are a convenient way to trigger promptly an update of buoy  
281 configuration and behavior.

282 The MIS is in charge also of controlling the power management of the buoy. Thanks to its internal logic,  
283 it defines the optimal acquisition rate in order to ensure the buoy operations. The optimal acquisition rate  
284 depends on battery status and on power supply obtained by the buoy solar cells. In case of low battery  
285 and/or low power supply (during the night or in cloudy days), the MIS can decide to slow down the  
286 acquisition rate; whereas, in case of high battery capacity and/or high power supply it can increase the

287 acquisition rate.

288 The MIS can change the buoy behavior independently by the battery status and/or power supply  
289 depending on the data acquired by the E-Nose. In addition, the MIS can also change the acquisition rate  
290 in case of hydrocarbon detection. When a hydrocarbon is detected by the E-Nose, the MIS automatically  
291 increases the acquisition rate in order to follow the evolution of the possible oil slick. Finally, after the  
292 conclusion of an emergency status, the MIS will automatically slow down the acquisition rate returning  
293 it to its normal rate.

294 E-Nose acquisition rate can be also changed whenever some other MIS sources detect something  
295 anomalous. When an anomaly is detected, MIS proactive capabilities can decide to verify and ensure the  
296 detection requesting to perform additional measurements to the nearest buoy. If the hydrocarbon  
297 detection is confirmed, the MIS will act as mentioned before.

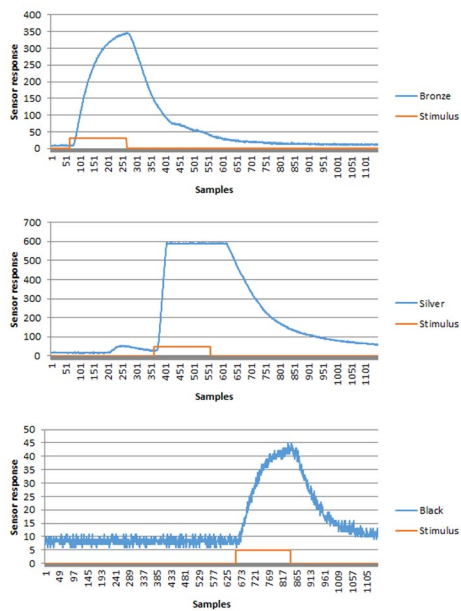
298 E-Nose data also include the measurement of the humidity in the air chambers. This is a crucial value  
299 because it determines the reliability of the E-Nose measure and, in case of high humidity values, is used  
300 by the MIS to decide to stop the E-Nose acquisitions. MIS stops the acquisition because high humidity  
301 values can indicate a chamber flooding that could result in damage to the E-Nose.

302

### 303 Results

304 The first step for the characterization of the E-Nose system has been the testing on the laboratory bench,  
305 in order to evaluate the responses produced by the piD sensors employed. Such trials have been necessary  
306 not only to evaluate the performances of the sensors employed, but also the feasibility of the approach  
307 chosen for our specific purpose. To accomplish these aims, the optimal air flow rate for increasing the  
308 reliability of the data acquired, thus maximizing the signal to noise ratio (SNR) produced in output by  
309 the piDs used, was searched. The result of this characterization revealed an optimal SNR obtained with  
310 an air flow rate of 2 l/min, later chosen to properly size the pumps, electrovalves and flow chambers for

311 the system overall. Therefore, the characteristics of the response to the different hydrocarbons were  
312 determined using an air flow rate of 2 l/min. Thus, the Minimum Detectable Concentration (MDC) of a  
313 set of compounds has been computed, including those hydrocarbons normally present on the sea surface  
314 after an oil spill or illicit ship transits through a marine protected area. Such substances on which the  
315 system was tested included diesel fuel, gasoline, kerosene and crude oil, of which the MDC parameter  
316 has been considered as the minimum concentration capable of producing a SNR of at least 3:1.  
317 The results obtained in this first assessment are consistent with the technical data provided by the piDs  
318 manufacturer, thus spanning from a -3 log v/v for the “Silver” piD (most sensitive) to a -2 log v/v for the  
319 other two piDs employed. Such results were similar to each other on all the compounds above described  
320 (Figure 4).



321  
322 *Figure 4 piD Sensor responses to diesel fuel stimuli at a concentration of -2 log v/v.*

323  
324 Another analysis performed in this first test session aimed to evaluate the “T90” parameter, determined  
325 as the time needed by a sensor, in presence of odorized air, to reach 90% of the maximum value in terms  
326 of output signal amplitude. In this analysis, all the three sensors displayed a fast response time (under

327 20s between the stimulus onset and the reaching of the 90% of the maximum output signal), in accordance  
328 with the characteristics reported in the datasheet provided by the manufacturer. Arising from the data  
329 described, the detection time calculated is adequate for early warning the authorities and organizing a  
330 prompt response to the pollution accident possibly occurring.

331 Afterward, the E-Nose system, comprised of its electronics, has been integrated with the overall  
332 electronics of the buoy and the communication mechanisms have been tested. In particular, data transfer  
333 to the MIS and setting of acquisition frequency have been validated.

334 Then, two tests for the overall system at sea have been performed. The first of them has been held in *La*  
335 *Spezia*, Italy, located in a highly polluted area, due to ship transits towards the nearby harbor, as well as  
336 to sewage from factories located in the suburban area of this maritime town. The second test has been  
337 otherwise carried on in *Capo Enfoia, Elba Island*, within the protected area of the Tuscan Archipelago,  
338 thus representing a completely different environment, without the presence of oil spills and ship transits,  
339 and with a well-preserved marine environment. The MIS has been able to receive and store all the data,  
340 with no appreciable delay. The data acquired during the two sessions have been visualized through the  
341 MIS web interface (Figure 5); they have been found as consistent with the two different environmental  
342 models typical of the two settings, with pollution detected in the first case and completely absent in the  
343 second test.

344 As stated in the Methods, two ANNs were implemented to classify the stimuli detected by the E-Nose  
345 system. The methodology employed provided a good outcome as both the ANNs showed satisfying  
346 performances. In particular, the first ANN demonstrated its reliability in classifying stimuli into three  
347 risk classes (high, moderate, low risk) in 88.45% of cases, with only an 11.55% of misclassification. On  
348 the other hand, the second ANN provided a correct feedback in 80.83% of cases, failing to recognize the  
349 correct hydrocarbon in just 19.17% of trials, a noteworthy result considering the similar chemical  
350 composition and properties of the hydrocarbons taken into account for characterizing the system.

351

352

TABLE 1. ANN FOR HYDROCARBON CONCENTRATION LEVELS ASSESSMENT

ANN size (neurons)	12x12
Training epochs	1500
Number of cross validations	8
Data normalization range (min-max)	0.1-0.9
%Training Set/Test Set	85%/15%
%Correct classification	88.45%
%Misclassification	11.55%

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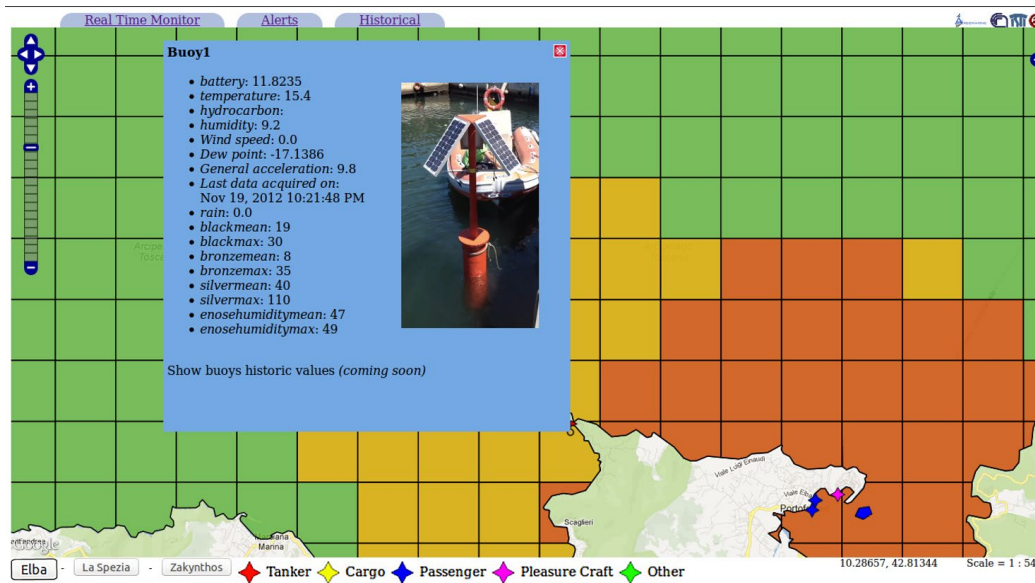
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TABLE 2. ANN FOR HYDROCARBON IDENTIFICATION

ANN size (neurons)	15x15
Training epochs	1500
Number of cross validations	20
Data normalization range (min-max)	0.1-0.9
%Training Set/Test Set	80%/20%
%Correct classification	80.83%

%Misclassification	19.17%
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356

357 *Figure 5 Buoy data including E-Nose visualized through the MIS web interface.*

358

359 **Conclusions**

360 In this paper, we have presented a novel system for the detection of environmental pollution caused by  
 361 hydrocarbon spills on the sea surface. In particular, an innovative moored buoy integrating an ad-hoc  
 362 designed E-Nose for pollutant detection has been described. The buoy, whose custom electronics and  
 363 mechanics have been discussed in the text, was also integrated into a more general framework for sea  
 364 monitoring thanks to a connector to the Marine Information System (MIS) presented in Tampucci et al.  
 365 (2013). Thanks to this integration, it is possible to analyze in real-time the data acquired by the buoy and  
 366 to explore historical data in order to understand seasonal trends. In addition, the data acquisition and  
 367 transmission frequency can be configured remotely, in order to adapt the buoy behavior to the level of  
 368 monitoring required at a particular time. The E-Nose itself, even as a standalone solution, is capable of  
 369 detecting hydrocarbons normally present in illicit discharges and oil spills. It has been shown to provide

370 reliable results in terms of repeatability and reproducibility of the signal acquired under similar  
371 conditions, thanks to the good stability of the sensors employed. Moreover, the response in terms of  
372 sensitivity (specifically, the minimum detectable quantity) has been largely forecasted before the test  
373 session, being characterized by the sensitivity of the different sensors employed and reported in the  
374 datasheet provided by the manufacturer. Additional processing methods have been included for  
375 discriminating several levels of hydrocarbons concentration and for their discrimination into classes.  
376 Such methods, based on a machine learning approach, have shown very promising results, also  
377 considering that hydrocarbons employed for this analysis were chemically similar, making their  
378 identification challenging.

379

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383

#### 384 CONTRIBUTORS

385 DM, GP AND MT DEVELOPED THE MIS, WERE IN CHARGE FOR COMMUNICATION PART BETWEEN BUOY AND  
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388 REVIEWED THE MANUSCRIPT; CD AND AT IMPLEMENTED THE E-NOSE SYSTEM, CONDUCTED THE TESTS,

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391

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393

#### 394 References

395 Azzellino, A., Panigada, S., Lanfredi, C., Zanardelli, M., Airoidi, S., Notarbartolo di Sciara, G., 2012.  
396 Predictive habitat models for managing marine areas: Spatial and temporal distribution of marine  
397 mammals within the Pelagos Sanctuary (Northwestern Mediterranean sea). *Ocean Coastal Manage.* 67,  
398 63-74.

399 Clark, R.B., 1992. *Marine pollution* third ed. Oxford University Press, New York.

400 Cortes, U., Sanchez-Marrè, M., Ceccaroni, L., Roda, I.R., Poch, M., 2000 Artificial intelligence and  
401 environmental decision support systems. *Appl Intell.* 12, 77–91.

402 Czolkos, I., Dock, E., Tønning, E., Christensen, J., Winther-Nielsen, M., Carlsson, C., Mojžíková, R.,  
403 Skládál, P., Wollenberger, U., Nørgaard, L., Ruzgas, T., Emnéus, J., 2016. Prediction of wastewater  
404 quality using amperometric bioelectronic tongues. *Biosens. Bioelectron.* 75, 375-382.

405 Er-Raioui, H., Bouzid, S., Marhraoui, M., Saliot, A., 1999. Hydrocarbon pollution of the Mediterranean  
406 coastline of Morocco. *Ocean Coastal Manage.* 52, 124-129.

407 Fedra, K., Winkelbauer, L., 2002. A hybrid expert system, GIS, and simulation modeling for  
408 environmental and technological risk management. *Comput. Aided Civil Infrastruct. Engineer.* 17, 131–  
409 146

410 Ferraro, G., Meyer-Roux, S., Muellenhoff, O., Pavliha, M., Svetak, J., Tarchi, D., Topouzelis, K., 2009.  
411 Long term monitoring of oil spills in European seas. *Int. J. Remote Sens.* 30(3), 627-645.

412 Jordi, A., Ferrer, M.I., Vizoso, G., Orfila, A., Basterretxea, G., Casas, B., Tintoré, J., 2006. Scientific  
413 management of Mediterranean coastal zone: a hybrid ocean forecasting system for oil spill and search  
414 and rescue operations. *Mar. Pollut. Bull.* 53(5), 361–368.

415 Moroni, D., Pieri, G., Salvetti, O., Tampucci, M., Domenici, C., Tonacci, A., 2015. Sensorized buoy for  
416 oil spill early detection, in: *IEEE Proceedings OCEANS 2015*, 2015.7271541.

417 Moroni, D., Pieri, G., Tampucci, M., Salvetti, O., 2016. A proactive system for maritime environment  
418 monitoring. *Mar. Pollut. Bull.* 102(2), 316-322.

419 Sobanski, T., Szczurek, A., Nitsch, K., Licznarski, B.W., Radwan, W., 2006. Electronic nose applied to  
420 automotive fuel qualification. *Sens. Actuator B-Chem.* 116, 207-212.

421 Tampucci, M., Martinelli, M., Moroni, D., Pieri, G., Salvetti, O., Villa, P., 2013. A proactive system for  
422 oil spills and marine environment monitoring. *Bollettino di Geofisica Teorica e Applicata*, 54, 222-223.

423 Tonacci, A., Corda, D., Tartarisco, G., Pioggia, G., Domenici, C., 2015. A smart sensor system for  
424 detecting hydrocarbon Volatile Organic Compounds in sea water. *Clean-Soil Air Water* 43(1), 147-152.

425 Tonacci, A., Lacava, G., Lippa, M.A., Lupi, L., Cocco, M., Domenici, C., 2015 Electronic Nose and  
426 AUV: A Novel Perspective in Marine Pollution Monitoring. *Mar. Technol. Soc. J.* 49(5), 18-24(7).

427 Yin, C., Liu, S.Q., Li, Y.Z., Chen, X.Y., 2013. Wireless Sensor for Oil Leakage Detection of Depots.  
428 *Applied Mechanics and Materials* 336-338, 244-247.

429 Zaghden, H., Kallel, M., Elleuch, B., Oudot, J., Saliot, A., Sayadi, S., 2014. Evaluation of hydrocarbon  
430 pollution in marine sediments of Sfax coastal areas from the Gabes Gulf of Tunisia, Mediterranean Sea.  
431 *Environ. Earth Sci.* 72, 1073-1082.

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