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Correlation of gaseous emissions to water stress in tomato and maize crops: From field to laboratory and back

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ABSTRACT

The application of Site Specific Crop Management consists in the knowledge of the soil variability. In particular, for a sustainable water management is fundamental to obtain differential responses in terms of selective irrigation, analyzing and evaluating the water content of the soil or the water requirement of the plants. The innovative contribution of this research lies in designing, developing and validating a technology platform consisting of a hardware for monitoring gaseous emissions, such as Volatile Organic Compounds (VOCs), from the soil-plant-atmosphere system of intensive crops, i.e., tomato and maize. In order to evaluate the water content of these systems, we analyzed experimental data acquired in-situ by portable sensing units based on Metal-OXide (MOX) gas sensors, thus comparing the results with meteo-sat data and farming operations (e.g. irrigations, rainfalls or pesticide-based treatments). The experimentation has proved a dependence of gaseous emissions on the hydric/metabolic status of the plants together with a correlation between sensor signals collected and significant events for the crops.

1. Introduction

Water plays a crucial role in the life of any plant. For each gram of organic matter produced by a plant, approximately 500 g of water are absorbed by the roots and transpired. Water typically makes up 80–95% of the plant tissue. Among the resources that plants need to grow and function, water is the most important and at the same time it is the most limiting for agricultural production [1].

Nowadays, technologies have gained a huge development to reach the expectations of precision farming. In particular, in the field of sustainable water management the effective irrigation scheduling has become an important tool that significantly influences growth development and production of crops, especially in regions characterized by long periods of drought and a strong interannual variability in rainfall amount and distribution, leading to a high year-to-year variability of agricultural development and production [2]. In this perspective, once the water availability is considered, the starting point for an investigation addressed to conscious water management is the assessment of soil-plant-atmosphere transfer processes that affect the crops water use, defined as EvapoTranspiration (ET) [3]. The crop coefficient-reference ET procedure is a robust method to estimate crop water requirements [4]. Despite this, the ET is difficult and expensive to measure, and it is even more difficult to separate transpiration, water released from leaves, and soil evaporation. With the aim of a better understanding of the relationship between crop growth and water content, a wide range of remote sensing systems that can support such computational methods are being developed [5]. Remote monitoring systems, even if underutilized until now, are more cost effective than standard sampling and lab-based analyses of the soil and plants, e.g., GC/MS, laser-induced fluorescence and VIS/NIR spectroscopy [6,7].

Although the technological science provides several tools and analysis techniques for the remote sensing, a well-structured system has not been widely documented for the parallel evaluation of the soil-atmosphere moisture status and the monitoring of emissions variability of the crops over a whole growing season. In fact, on one side the majority of studies on volatile gases profile in the soil atmosphere, i.e. gas fingerprints, are pointed towards the soil microbial metabolic activity [8,9]; on the other hand, the monitoring of Volatile Organic Compounds (VOCs) secreted by plants is mainly focused on the control of their health status, which can be affected by insects or diseases [10–14]. The emission of VOCs by plants, consisting for the 44% of isoprene, 11% of monoterpenes and 45% of the sum of the other compounds,

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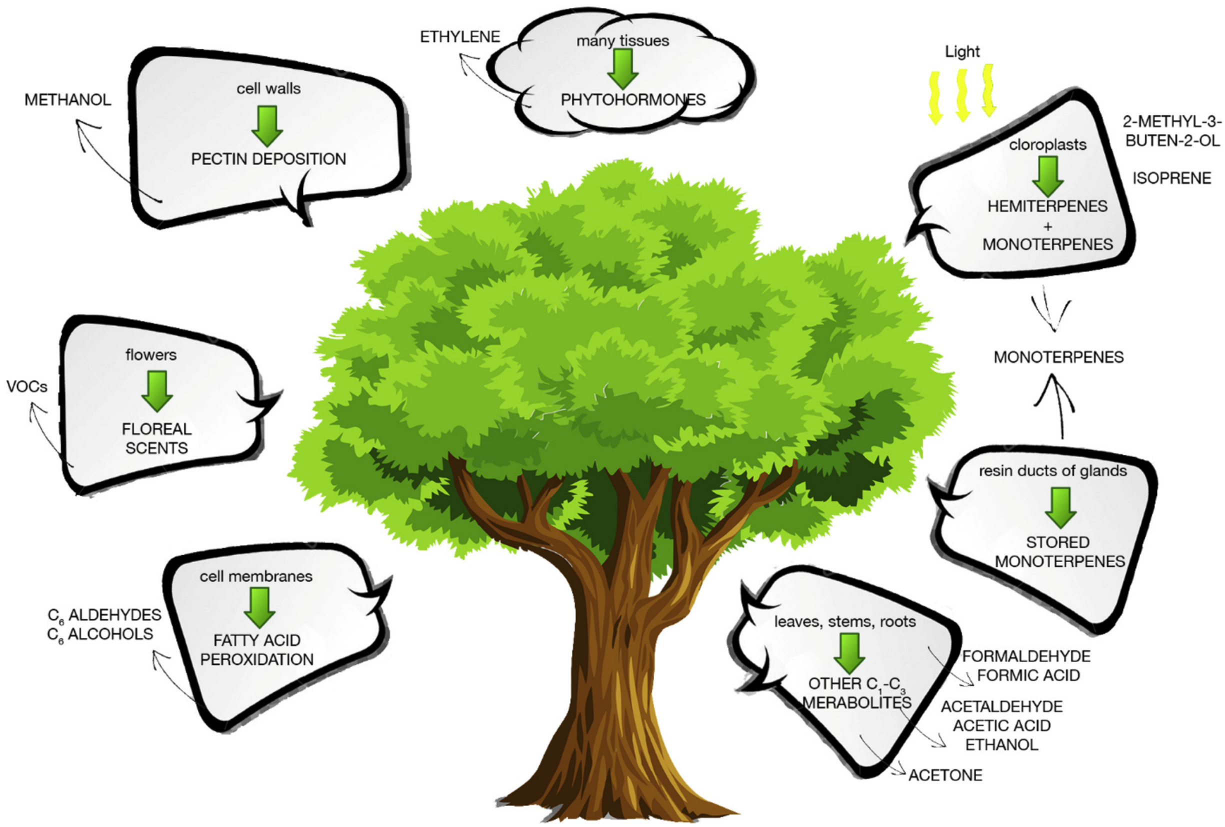

Fig. 1. Representation of the possible various emissions from plants.

including alcohols, aldehydes, ketones and esters, exceeds by several orders of magnitude that of animals and, on a global scale, amounts to about 1–1.5 PgC per year (Fig. 1). Even if the total VOCs emission represents only 2–3% of the total carbon exchanged between the biosphere and the atmosphere, their presence and high reactivity can influence the chemical and physical properties of the atmosphere [15]. Besides, VOCs emissions are affected by internal (genetic and biochemical) and external (abiotic and biotic) factors, being in particular dependent on temperature and radiation. However, among the diverse causes for plant emissions, the role of water stress is not yet identified, probably because it affects them in different ways.

Indeed, while under drought conditions leaf emissions are reduced due to limited carbon acquisition; on the contrary, it has been demonstrated that heat and/or oxidation factors increase emissions from non-water-stressed plants [16,17]. Moreover, in plants there is a conflict between the need for water conservation and that for assimilation of carbon dioxide (CO_2). Indeed, despite being the source of the CO_2 necessary for the process of photosynthesis, the atmosphere is relatively dry compared to plant tissues and can easily dehydrate and wilt the plants. To make the limitation in water loss effective while maximizing the absorption of CO_2, plants have developed adaptations such as the capability to control water loss from the leaves, replacing at the same time that lost in the atmosphere. This problem is exacerbated by the large surface of the leaves, necessary to maximize the interception of solar radiation and to have a continuous possibility of absorption of carbon dioxide.

Therefore, it is necessary to clarify the relationship between the soil-atmosphere water availability and variability, and the potential water need of plants. For the estimation of VOCs emitted from soil and plants, equipment should be cheap and not bulky, whereas analysis techniques should be easy to perform and non-invasive. In this perspective, the electronic nose (eNose) is a potential and non-destructive technology, which may comply with these requirements. This monitoring system is composed of an array of gas sensors whose signals data processing is managed by means of a pattern recognition (PR) program. eNose allows real-time acquisitions, providing a fast response without a direct contact with soil or plants, and it is capable to recognize simple odors or mixture without the need to identify and quantify individual components [9,10,18,19].

Despite these potential advantages, eNose was not usable for the experimental study here proposed because if on one side the PR technique is a complex signals deconvolution system with respect to work purposes, on the other side this system requires dedicated electronics weighting down the power needed by the device and its dimensions.

In fact, the goal of the experimental study here presented was to provide a system that, after collecting and properly calibrating data from the field, returns directly to the technician or the agricultural operator an information on the crop status vs. water stress. Considering the times and methods of agriculture, the information obtained should be easy to access and use, so as to be indispensable to decision-support systems used by the agricultural producer.

In order to reach this objective, we developed a gaseous monitoring system composed of a hardware, characterized by limited dimensions and power consumption, a simple assembly and subsequent maintenance, and a very straightforward software to collect the gas sensors signals remotely processed.

The gas detection system that we propose in this work is a sort of simplified eNose. Indeed, it is a non-invasive technology and it is easier to use and more cost-effective than computational methods and lab-based analyses, therefore more usable and sustainable than a real eNose.

Starting from these considerations, we designed and prepared two simplified portable sensing units for an in-situ monitoring of gaseous emissions from the sowing to the harvest of tomato and maize crops of particular interest for the agri-food industry.

2. Materials and methods

The core of each of the two custom-made systems was composed of an array of four chemoresistive Metal-Oxides sensors (MOXs). The implementation of this well-established technology in a hardware that allows a simple data treatment could represent a good alternative to complex eNose in terms of cost-benefits, especially for agri-food applications.

The experimental activities were organized in four phases, as follow:

1 Preliminary: study of the literature to identify gaseous emissions related to water stress conditions in tomato and maize crops, i.e. ethylene, ethanol, isoprene, methanol, acetaldehyde [11–16], production and characterization of chemoresistive gas sensors based on different sensing films, potentially sensitive to these chemical compounds. Successively we tested the MOX-based sensors to prove their potential effectiveness to detect the target gases in their proper concentration range, of interest for the case of study. Finally, we designed the two gas detectors to employ in tomato and in maize fields.
2 On-field: experimental measurements of gaseous emissions in a tomato and in a maize yield by two portable sensing units (Fig. 2) based on two different arrays, each composed of four chemoresistive gas sensors. The response collected for the eight sensors over the whole growing season of a tomato and a maize yields, located in Emilia-Romagna Region of Italy [20], were compared to meteo-sat data and farming operations (e.g. irrigations, rainfalls or pesticide-based treatments) in order to identify a possible correspondence between water supply to the crops and their reaction in terms of gaseous emissions.
3 Lab-test: calibration of the eight sensors used in the in-situ monitoring systems, employing field conditions (temperature and humidity).
4 Field-lab comparison: sensors calibration parameters were obtained from lab-measurements and then applied to field measurements in order to select, for each crop, the most performing sensors to monitor gaseous compounds correlated to water stress conditions.

2.1. Preliminary activities

Literature provides various studies on gases secreted by tomato and maize plants. So far, these works have been carried out in controlled water conditions and a reliable interpretation of an in-situ monitoring of such crops emissions turns out to be far from the realization.

Table 1 reports the gaseous chemical species and their relative concentration ranges emitted by tomato and maize crops in controlled

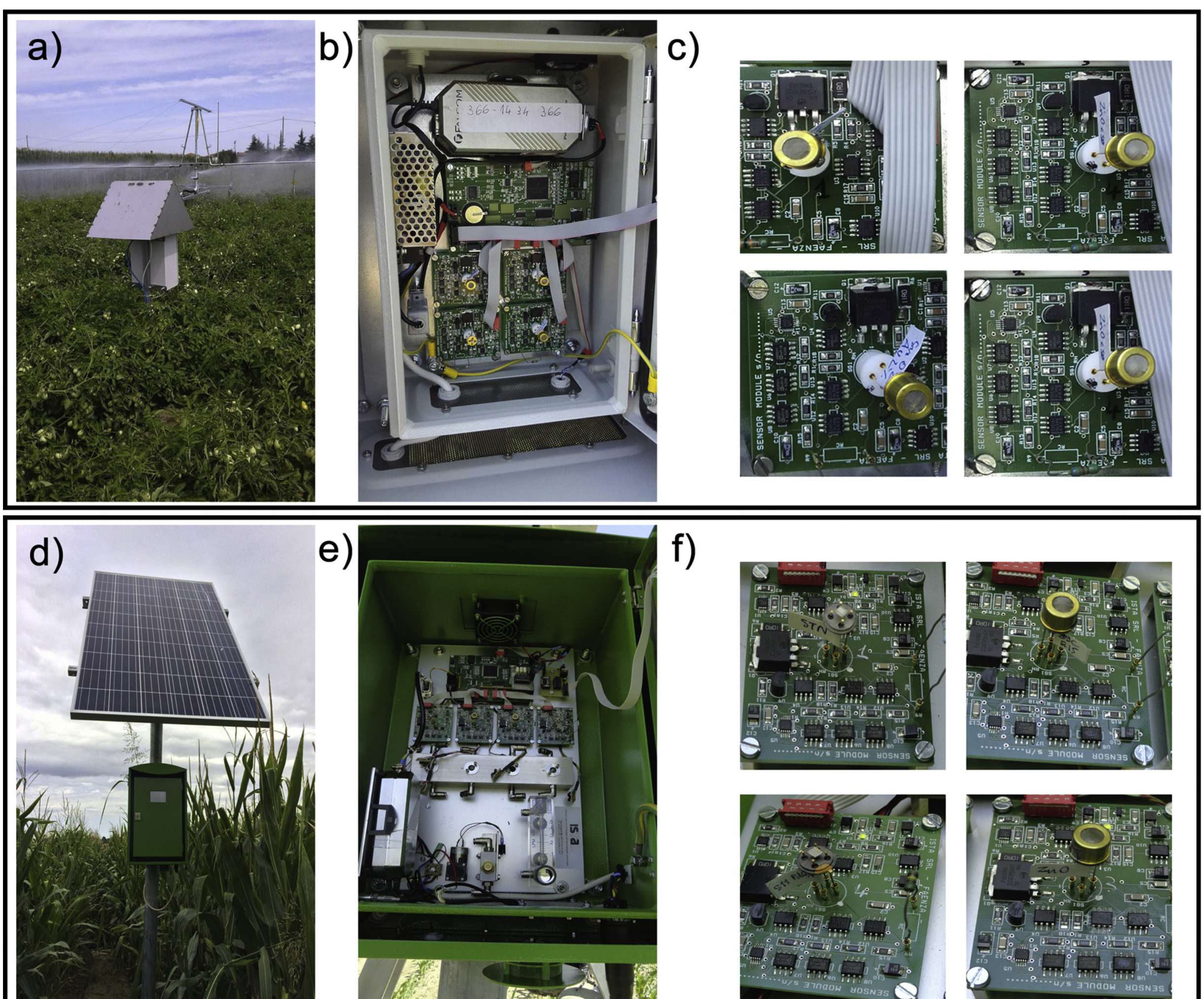

Fig. 2. Sensing units employed in tomato yield and maize yield. For each monitoring system one can see its placement in the field (a and d), the arrangement of the diverse components included in the designed prototype (b and e), and zoom on the 4 sensors– 1) SnO_2 + Pd 2%, 2) WO_3, 3) SnO_2 + Au 2% and 4) ZnO– employed in the prototype for tomato emissions monitoring (c), zoom of the 4 sensors– 1) STN (solid solution of SnO_2, TiO_2, Nb_2O_5), 2) SnO_2 + PdAl, 3) ZnO and 4) SnO_2 + Pt 2% –implemented in the prototype for maize emissions monitoring (f).

Table 1
Marker gases and relative concentration ranges secreted by tomato and maize under controlled water stress.

Gas	Tomato	Maize
Ethylene	0–7.33 ppm/min [21,22]	/
Ethanol	0–0.23 ppm/min [23]	0–0.0002 ppm/min [24]
Isoprene	/	0–0.642 ppm/min [19]
Methanol	0–0.789 ppm/min [25]	0–0.762 ppm/min [25,26,27]
Acetaldehyde	/	Traces [24]

water stress conditions. We started from this information to identify potential sensing materials suitable for the detection of such target gases.

Among the wide palette of the potential nanostructured sensing materials, based on the experience and knowledge of our Sensors Laboratory, we tested seven MOX semiconductors vs. target gases to prove their capability to detect these chemical compounds [28–36].

The gas sensors, completely produced and characterized at our laboratory, were composed of thick sensing films of metal-oxide semiconductors, synthetized as nanostructured powders via sol-gel technique. After suitable thermal treatments, the powders were screen-printed onto an alumina substrates (substrate area $2.54 \times 2.54\,mm^2$ and thickness 200 μm, sensing film area $1 \times 1\,mm^2$ and thickness $20 \div 30$ μm) with gold interdigitated electrodes on the front side, for collecting material resistance variations occurred when exposed to chemical species, and platinum heater on the rear side, for applying the proper working temperature typically of each sensing material [36] (Figs. S1–S3, Supporting Information).

Table 2 lists the sensing materials chosen for the emissions monitoring linked to water conditions of tomato and maize crops. For each device, it is reported its proper working temperature, which was applied both in preliminary lab-tests and during in-situ monitoring, and the target gas for which it was selected.

After the preliminary lab-calibration, we employed 4 MOX gas sensors in each of the two custom-made portable units (Fig. 2), designed in our laboratory.

For the continuous real-time monitoring, each device requires a power supply of 30 W. The grey one, used for gaseous emissions from tomato crop, was designed to operate by a directly connection to the electricity grid, since sprinkling irrigation by a bar over the yield (see Fig. 2a) did not allow the use of a photovoltaic equipment for the power supply. Instead, in maize field, irrigation by means of aspersion with an equipment placed just outside the yield permitted the placement of a photovoltaic system (Fig. 2d). The panel ($1.65 \times 1.2\,m^2$) was fixed on a 3-meter-long pole. Inside the head-pole, it was placed a battery and charge control. The system in this configuration provided a power of 300 W.

Each custom-made device, composed of a double protection and compact size outdoor box (Fig. 2b and 2e), was fixed on a pole, at a height of 1 m in tomato crop and 2 m in maize crop, respectively. Since the grey unit in tomato was not shaded by the phovoltaic panel, as for the green one in maize yield, it was equipped with a suitable coverage to provide a shading (Fig. 2a). The grey sensing unit, employed in tomato field, is slightly smaller ($40 \times 30 \times 21\,cm^3$) than the green one ($49 \times 37 \times 21\,cm^3$). Each custom-made sensing unit contains: a power supply, 4 board for the implementation, heating and electrical signal acquisition of the 4 chemoresistive gas sensors exposed to a direct air flux (Fig. 2c and f), humidity/temperature sensors (Sensirion, SHT11) placed at the entrance of the box, a digital transmitter (GSM) for the remote data acquisition processed by a Labview-based program, and a microprocessor (Freescale MC9S12DP512, serial port RS232C) that manages the firmware for the real-time signal acquisition, the remote management of the measuring system, storage, data transmission, setting of the operating parameters (more details in Section 2 of Supporting Information, Figs. S4 and S5).

2.2. Field monitoring of gaseous emissions in tomato and maize crops

The experimental activities here presented were carried out during a two-year regional project [19]. Objectives of Hydro-intelligent Agrifood project were the development of an innovative technological platform, including systems sensitive to gases and gamma rays [37,38], able to operate on a permanent basis on the ground to increase the detail level on spatial data related to the water needs of the land, and the validation of the produced hardware through comparison and implementation with soil data.

Then, the two prototypes designed in the preliminary phase, were settled in tomato and maize yields (Fig. 2). The sensors signals were collected in continuous for four months, during the whole crops growing season, by a remote acquisition system. The electronic associated with the in-situ measurement prototypes is the same used in the lab-equipment [39] (Fig. S6, Supporting Information). Then, each sensor was employed inside a circuit, based on an operational amplifier, which collected the variation of the voltage signal that was proportional to the conductance variation of the sensing film. For such system, the sensor response is defined as $R = [G_{gas}\text{-}G_{air}]/G_{air}$, where G_{gas} is the conductance when the film is exposed to a gaseous compound and G_{air} is the reference conductance in presence of air [39]. We tested the stability of the sensors employed in this work and we can confirm that their drift is lower than 10% over the period of test [40].

Clearly, in an outside environment, such as a tomato and a maize yield, the chemical composition of the atmosphere is not simplified and controlled as in a laboratory test chamber. Therefore, in order to identify the reference conductance value (G_{air}) for on-field measurements, we considered two possible ways to determine the signals baseline. Indeed, we calculated the sensors response applying both the daily minima and the absolute minimum method. The first, the commonly method used for processing data acquired in environmental monitoring applications, considers the daily hourly averages of the collected signals compared to the minimum value of the same day. The latter is a data processing method that expresses the evolutionary nature of the emissions source, it consists of calculating the daily hourly averages of the collected signals compared to the minimum value measured in the whole period of data acquisition, i.e. the minimum of the whole period of growth of the crop. We highlight that the baseline does not lead to a “true zero” response of the sensors, but it represents their lowest signal linked to the lowest emissions concentration from

Table 2
MOX gas sensors and relative working temperatures selected for the implementation in the prototypes designed for the in-situ monitoring of emissions from tomato and maize yields.

Tomato			Maize		
Sensor	Working Temperature	Gas target	Sensor	Working Temperature	Gas target
SnO_2 + Pd 2%	450 °C	Ethylene [28]	STN solid solution of SnO_2, TiO_2, Nb_2O_5	500 °C	Isoprene [30,33]
WO_3	350 °C	Ozone [33]	SnO_2 + PdAl	450 °C	Methanol [34]
SnO_2 + Au 2%	400 °C	Ethylene [28]	ZnO	350 °C	Acetaldehyde/Ozone [31]
ZnO	350 °C	Ethanol [29]	SnO_2 + Pt 2%	450 °C	Ethanol [35]

the crop.

We applied these two methods to analyze data collected, in particular, we focused on three different weeks, each one characterized by significant changes in terms of conductance of the sensing films, in particular ascribable to a water supply variation, e.g. irrigation or rain. This approach allowed us to evaluate the strength of such methods and then to identify which was advisable for field data analyses.

Finally, we compared the sensors response with meteo-sat data and farming operations (e.g. irrigations, rainfalls) of each yield and, for each portable sensing unit, we identified which sensors demonstrated a robust correlation between their response and the variation of water conditions.

2.3. Calibration of the sensors

In order to calibrate the eight sensors employed in the two portable sensing units, especially those that exhibited better performance with respect to water supply variations during on-field monitoring, we planned an extensive lab-measurements campaign.

First, we performed a humidity calibration for the eight sensors in order to assess possible water effects on their sensing performance (Fig. S7 and Tables S1 and S2, Supporting Information).

Then, considering both the concentration range identified in literature for the target gases under water stress (Table 1) and their Threshold Limit Values (TLV), for the calibration of the eight sensors we chose three concentration values for each gaseous compound (Table 3) included in a plausible interval of interest for their monitoring.

In order to achieve a robust sensors calibration, it was fundamental to recreate, in lab-test chamber (Fig. S6, Supporting Information), the same conditions of humidity and temperature occurred and then collected by dedicated sensors placed in the sensing units, during in-situ emissions monitoring in tomato and maize yields. Indeed, previous studies have shown the dependence of the chemoresistive sensors response from humidity. Moreover, it is important to define which type of humidity is measured by the monitoring systems. Absolute Humidity (AH) is the water content of air that does not take temperature into consideration, which directly affects the conductivity of a sensor. This because its response depends on the equilibrium of chemical-physical processes occurred at the surface and determined by type and concentration of gaseous compounds in the surrounding atmosphere, which in the case of water is AH. Relative Humidity (RH) is defined as the ratio between the partial pressure of water vapor and the level of saturation of humidity (at the same temperature and pressure). RH establishes, together with the temperature, the level of AH and therefore indirectly influence the sensor response [28].

In order to define temperature and humidity conditions to apply for sensors lab-calibration, we started from two important observations. First, during the preliminary lab-measurements (carried out in dry air) the temperature value in the test chamber was constant at 35 °C, while during the experimentation period the sensing units placed in tomato and maize fields collected temperature values ranged between 21.6 ÷ 52 °C and 10.6 ÷ 43.9 °C, with an average value of 35.5 °C and 26.9 °C, respectively, depending on day-night cycle. Latter, the commercial capacitive humidity sensors placed both in lab-test chamber (Honeywell HIH-4000) and in the two portable sensing units (Sensirion, SHT11) measured the relative humidity (RH).

Therefore, in order to evaluate the RH value to apply in lab-calibration of the 8 sensors, we started from Clapeyron equation, which defines absolute humidity as a function of time:

$$\mathrm{AH}(t) = \mathrm{RH}(T(t)) \bullet A \bullet e^{-(B/T(t))}$$

where $A = 1.39 \times 10^8\, kPa$ and $B = 5246\, K$ parameters are to be fit with the saturated steam diagrams of water in the temperature range of interest (20–40 °C). Then, by reversing the formula, it is possible to determine a RH percentage for a constant temperature.

Applying this approach to on-field RH and temperature data, we obtained AH range occurred in the two portable systems, then we calculated RH range at 35 °C, the aforementioned temperature induced in lab-test chamber during a measure. Unfortunately, with this method, the AH range obtained was too broad for identifying a plausible ranges of RH values for sensors lab-calibration.

Therefore, in order to take into account the natural daily temperature cycle, it was necessary to integrate the water saturation pressure P_{ws} in Clapeyron's equation for a constant temperature of 35 °C:

$$\mathrm{RH} = \frac{\mathrm{AH} \bullet T[K] \bullet 100\%}{C \bullet P_{WS}}$$

where

$$P_{WS} = A \bullet 10^{\left(\frac{m \bullet T[°C]}{T[°C]+T_n}\right)}$$

with $A = 6{,}116441\ kPa$, $m = 7{,}591386$ and $T_n = 240{,}7263$ for a temperature value within – 20 °C and 50 °C [41].

According to this approach, we obtained RH ranges of 28–74 % for tomato field and 26–63 % for maize field. In these ranges, we selected two RH values to apply in lab-calibration measurements, i.e. 33% and 52%, to evaluate the possible humidity effect on the sensors performance.

Then, the eight sensors were exposed to the three concentrations selected for each of the five target gases, applying in the test-chamber both relative humidity of 33% and 52%, and maintaining constant the temperature at 35 °C. Calibration curves (sensor response vs. gas concentration) were generated to identify the best sensitive sensor for each gaseous compound. Cyclic measurements were performed in order to prove the stability and repeatability of the sensing devices.

Moreover, cross sensitivity measurements were performed combining ethylene and ethanol in one case and isoprene and methanol in the other one, with a fixed gas concentration of 0.5 ppm and relative humidity equal to 52%.

2.4. Field-lab comparison

For the comparison between lab-and on-field measurements, we considered only sensors calibration curves obtained for each target gases at 52%RH, since the average RH% values collected in tomato and maize yields were 45.3 and 68.1%, respectively.

Then, for each lab-calibration curve, we applied an allometric function $y = ax^b$, where y is the sensor response and x is the gas concentration selected, and then we extracted a and b parameters. In the hypothesis of single-gas emission, we calculated plausible on-field gases concentration $x' = \left(\frac{y'}{a}\right)^{\frac{1}{b}}$ starting from the on-field sensors response y' and applying the above-mentioned fit parameters. In this way, for each sensor, it was defined a concentration range for each gas. These values were thus compared to those identified in literature (Table 1) and with the proper gases TLV (Table 3).

Table 3
TLV and concentration values of the target gases used for lab-calibration of sensors.

	Ethylene			Ethanol			Isoprene			Methanol			Acetaldehyde		
TLV [ppm]	200			1000			2			200			25		
Concentration [ppm]	14	10	6	1	0,75	0,5	0,5	0,3	0,1	2.7	1.35	0.6	4	2	1

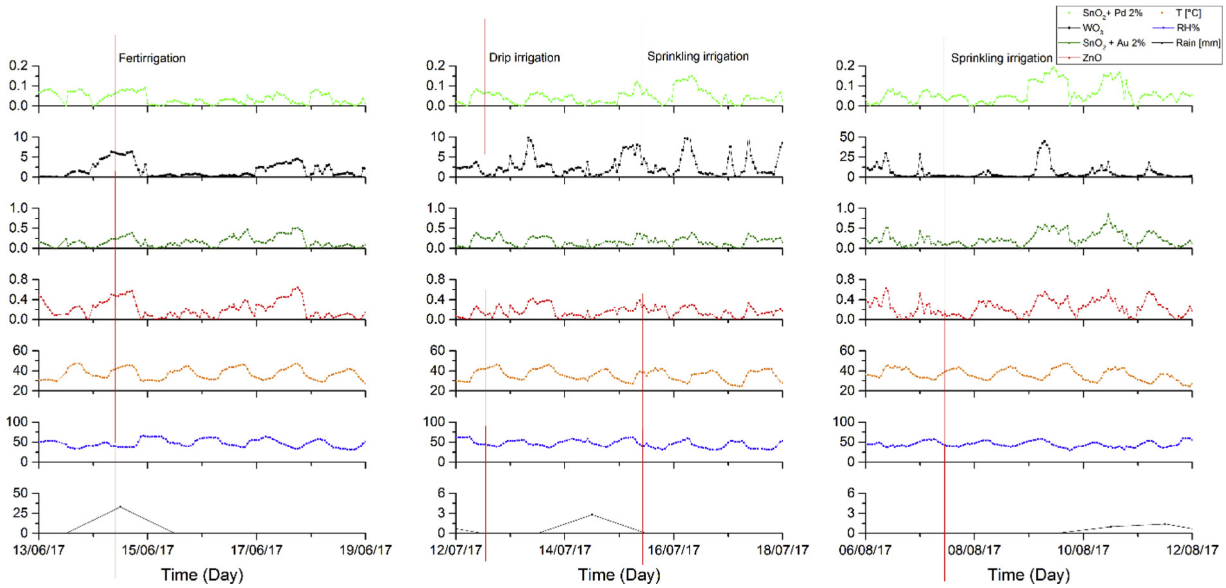

Fig. 3. Sensors response collected on tomato field during three particular weeks characterized by significant events: 13–19 June, fertirrigation (left), 12–18 July, switch from drip to sprinkling irrigation (center), 6–12 August, sprinkling irrigation (right).

3. Results and discussion

3.1. Field monitoring

The four sensor signals collected for each sensing unit were processed to calculate the devices response. In order to obtain a robust data treatment, the application of daily minima approach resulted more appropriate than the absolute minimum method.

Figs. 3 and 4 show three plots of the four sensors response calculated, relative humidity and temperature values collected inside the sensing units and rainfalls data given by weather station. These plots are referred to three different weeks characterized by significant events from meteorological and farming operations point of view.

Tomato crop was transplanted at the beginning of May and its data monitoring was processed starting from June until the end of August. In Fig. 3, we showed on-field measurements of three weeks of interest in which both rainfalls and farming operations occurred. First, one can observe (Fig. 3, left) that all the four sensors conveyed the effect of fertirrigation (potassium nitrate KNO_3) combined with rain (33 mm), both occurred on the 14th of June. Indeed, the four responses significantly decreased after these events then increasing at the previous value beyond two days. The switch from drip (12th July, total volume 2.4 h L) to sprinkling irrigation (15th July, total volume 40.5 h L) was valuable during the next twelve hours with a fall down of the responses, in particular for SnO_2 + Pd2% and WO_3 based sensors, even if the rainfall (14th July, 3 mm) seemed mainly to affect the sensors response (Fig. 3, center). When applied to ripe tomatoes (Fig. 3, right), sprinkling irrigation (7th August) resulted comparable or even major to rainfalls effect (10th - 11th August), although restrained, in terms of sensors response decrease. RH% and temperature trend followed the day-night cycle with values in the range of 30 ÷ 70% and 30 ÷ 50 °C, respectively. As expected, an increase in temperature corresponded to a decrease in relative humidity. Among the four sensors employed in gas sensing unit for on-field monitoring of tomato crop emissions, the two devices for

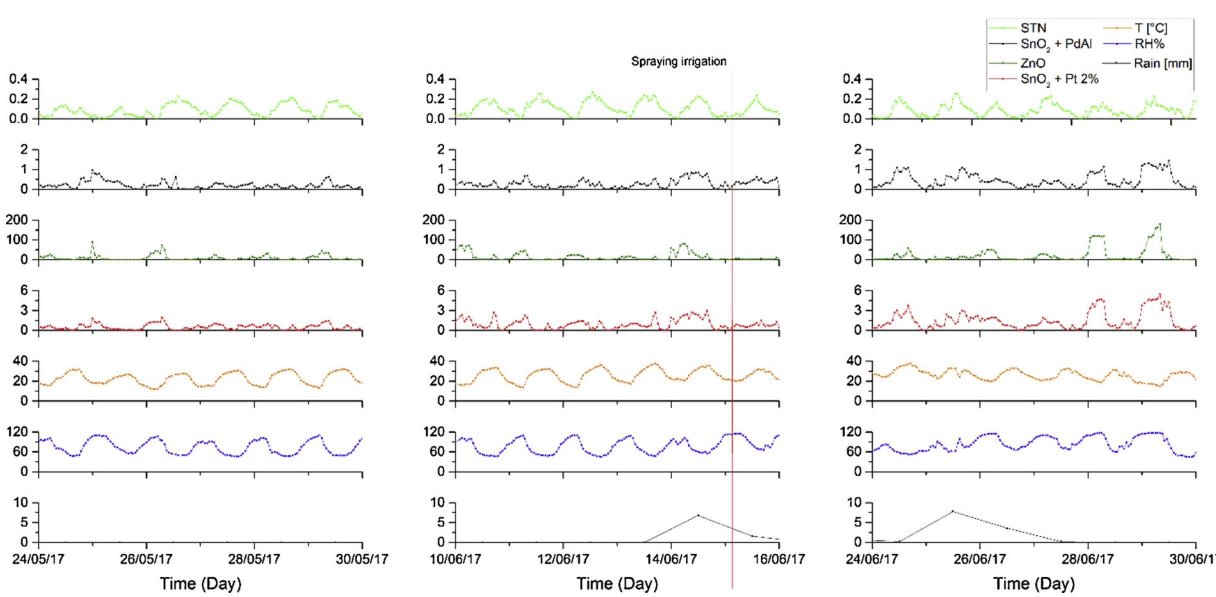

Fig. 4. Sensor responses collected on maize field during three particular weeks characterized by significant events: 24–30 May, first growth phase of maize (left), 10–16 June, 50 mm irrigation on the whole yield (center), 24–30 June, three raining days (right).

which the electrical activity showed a marked dependence on water supply were SnO_2 + Au2% (dark green line) and WO_3 (black line). The intensity of WO_3 response became three times higher from the first week taken into account (Fig. 3, left) than the last one (Fig. 3, right), following the increasing ripe grade of tomatoes. In addition, SnO_2 + Au2% response increased during tomato growth, moreover, it showed a better capability to discriminate the effect of different type of water supply, irrigations or rainfalls. It is important to highlight that no sensors response dependence occurred on relative humidity and temperature variations inside the sensing unit.

Maize crop was sowed at the end of March and its data monitoring was processed starting from May until the end of August. In Fig. 4, three graphs show the sensors response trend during three different moments of cultivation. The first plot (Fig. 4, left) is referred to a preliminary phase of maize growth in which no specific events occurred, the sensors response was low and STN-based device seemed to follow relative humidity trend. Combination of rain (14th June, 7 mm) and spraying irrigation (15th June, 50 mm on the whole yield) significantly reduced sensors response, apart from STN-based film, which seemed to follow again RH% variation (Fig. 4, center). The effect of rainfalls (25th - 26th June, between 8 and 4 mm) appeared more evident in the third week of interest (Fig. 4, right), in which all the four sensor responses decreased when rain occurred.

Among the four sensors employed in gas sensing unit for on-field monitoring of maize crop emissions, the two devices for which the electrical activity showed a marked dependence on water supply were SnO_2 + PdAl (black line) and SnO_2 + Au2% (red line). Moreover, one can observe that their response increase, collected during the three weeks of interest, corresponded to an increase of metabolic activity of the crop. RH% and temperature trend followed the day-night cycle with values in the range of 30 ÷ 100% and 10 ÷ 40 °C, respectively.

3.2. Lab-calibration

Sensing performance of the eight sensors employed on tomato and maize fields were investigated making a deepened lab-calibration.

The humidity calibration performed with the eight sensors highlighted a response trend similar to that of capacitive commercial sensor integrated in the lab-test chamber for the monitoring of relative humidity (Fig. S7, Supporting Information). Only for WO_3 sensor, the response seemed not to be affected by water, whereas STN sensor showed a continuous response increase to increasing humidity concentration without well-defined variations between the different concentrations applied. It is important to highlight that, starting from 40% RH, for the other six sensors the response variation resulted negligible. Moreover, the percentage variation of the sensors conductance measured at 50%RH and 35%RH ranged almost within the limited value of 15% (Tables S1 and S2, Supporting Information).

For each gas, we show dynamic response and calibration curve of sensors tested at two different relative humidity values, 33 and 52%. As for on-field measurements (Figs. 5 and 6, Fig. S8–S10 Supporting Information), the sensor response was calculated as $R = [G_{gas}\text{-}G_{air}]/G_{air}$, where G_{gas} is the conductance when the film is exposed to a gaseous compound and G_{air} is the reference conductance in presence of air (Tables S3, S5, S7, S9 and S11 Supporting Information). The response and recovery times of the sensing films were calculated as the time necessary to attain 90% of steady-state sensor response and as the e-folding response, respectively, and both ranged between 5 min and dozens of minutes (Tables S4, S6, S8, S10, and S12 Supporting Information).

We compared the response values and the sensing performance of the eight devices but, considering the information from literature (Table 1), we focused our attention especially on ethylene (Fig. 5) and isoprene (Fig. 6) as gaseous markers of tomato and maize, respectively.

For all gases, (Figs. 5 and 6, Fig. S8–S10 Supporting Information), SnO_2 + Pt2% sensor exhibited at the same time high sensitivity and poor selectivity. The last could make this device inadequate to discriminate gases of interest. SnO_2 + PdAl and SnO_2 + Pd2% sensors showed good performance even if the trend of calibration curve was quite flat, then it would be difficult to identify possible significant water stress correlated to gases concentration. Only with ethylene (Fig. 5), SnO_2 + Pd2% showed slightly better performance. WO_3 and ZnO sensors showed lower performance in terms of both sensitivity and selectivity, with a further lacking response variation vs. gas concentration. Therefore, the two sensors that exhibited a differentiation of response and sensing performance for the five gases tested at three concentrations were SnO_2 + Au2% and STN (solid solution of SnO_2, TiO_2, Nb_2O_5).

Stability and repeatability of the sensors at the three-gas concentrations selected were investigated carrying out measurements in two different ways: starting from the higher, in the first case, we directly switched from a concentration to another, in the second one, between the injections of each gas concentration we restored the baseline through an air flux at the proper %RH. Approximately, the percentage variation of the response at the same gas concentration is in the order of 2 ÷ 15% at 33%RH and 1 ÷ 10% at 52%RH, respectively, between the two responses values collected for each of the three gas concentrations selected for each target gas. The percentage variation of the response times for the higher gas concentration is in the order of 1 ÷ 7% at 33%RH and 3 ÷ 13% at 52%RH, whereas the recovery times for the lowest concentration is in the order of 1 ÷ 9% at 33%RH and 2 ÷ 13% at 52%RH.

In addition, possible interfering effects were investigated exposing the eight sensors to mixture of two gases at the same concentration of 0.5 ppm: ethylene and ethanol (Fig. S11, Supporting Information), isoprene and methanol (Fig. S12, Supporting Information). For mixture of ethylene and ethanol, any overlaps occurred indeed the sensors response to ethanol is the same in presence of pure ethanol or in its combination with ethylene. Instead, for mixture of isoprene and methanol, the response to the first increased when the latter is added even if it is not a linear addition. This confirmed the difficult to monitor such complex gaseous emissions in real environments, but in any case an analytical identification of chemical compounds was out of the topic of this work.

3.3. Field-lab comparison

The performance of each of the eight sensors were evaluated from different points of view: on-field, with respect to the capability to highlight potential water stress conditions, i.e. irrigations and rainfalls, in laboratory, with respect to their intrinsic sensing properties towards the detection of five gases identified as markers for water stress status in tomato and maize crops.

Table 4 clearly summarized which sensors resulted useful in the two cases of study, as discussed in the previous paragraphs.

Among the seven sensing materials tested, WO_3 and ZnO based sensors demonstrated good performance during on-field measurements, otherwise, their lab-calibration with target gases highlighted a lack of selectivity and poor sensitivity with respect to the other sensing materials. The on-field behavior of WO_3 and ZnO based sensors should be ascribed to the increasing ozone concentration, arisen during the summer season. Indeed, it is well-documented the sensitivity of these two materials to ozone molecule, which often acts as interfering in environmental monitoring [42,43].

Finally, the ZnO sensor that was employed in maize crop showed slightly better performance than the other one used for tomato emissions monitoring due to a different nanostructured morphology: nanorods in the first case and nanograins in the second one [44].

About SnO_2 + PdAl sensor, its discrete capability to detect gaseous emissions variations linked to water stress did not found a robust correspondence with target gases used in lab-tests.

Based on the just discussed observations, in order to carry out a strength field-lab comparison, we selected four sensors: SnO_2 + Pd2%

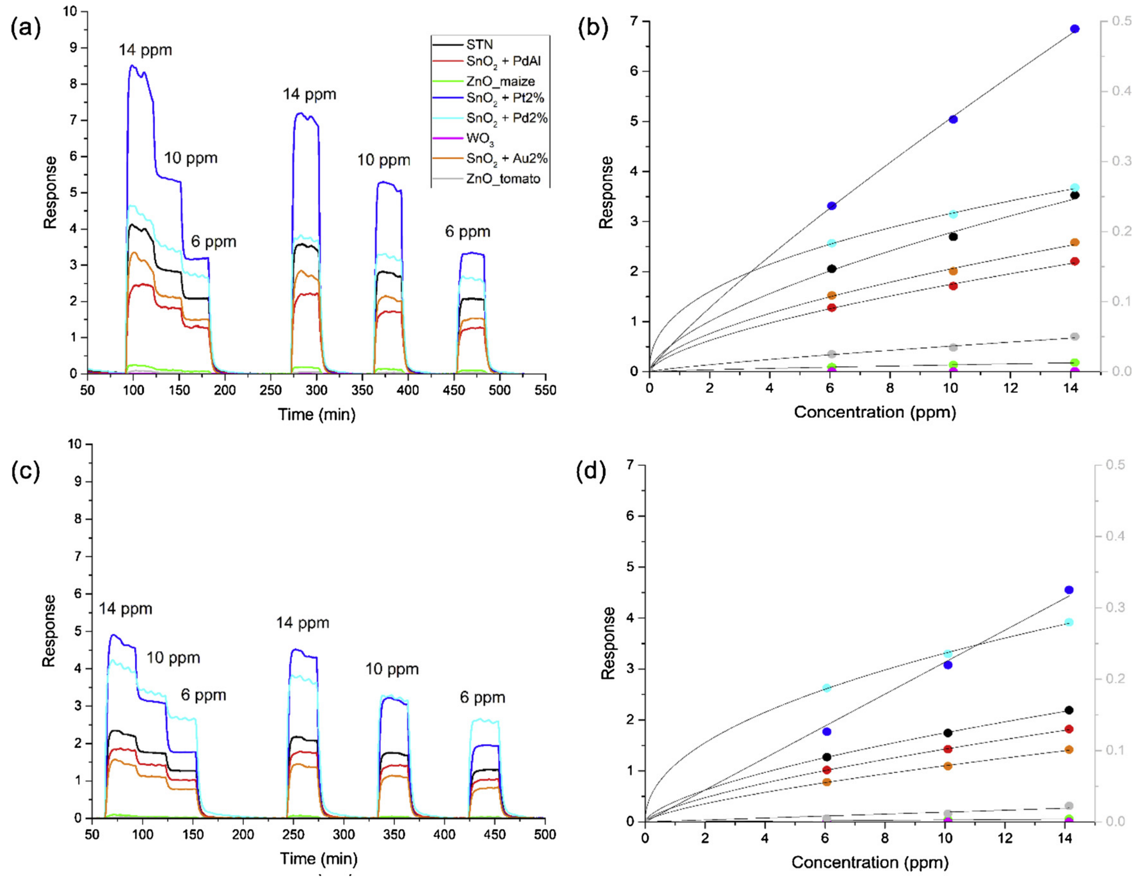

Fig. 5. Dynamic response and calibration curve of sensors tested with 14, 10 and 6 ppm of ethylene at 33%RH a) and b), at 52%RH c) and d).

and SnO_2 + Au2%, employed in sensing unit for the tomato emissions monitoring, STN and SnO_2 + Pt2% used in sensing unit for the maize emissions monitoring. For each of these sensors, we produced a set of calibration curves vs. target gases (Fig. S13, Supporting information). Knowing the sensors response (y) and selected gases concentration values (x), we fitted each curve of each sensor with an allometric function, $y = ax^b$, in order to obtain a and b fit parameters of that sensor exposed to a specific gas target (Table S13, Supporting Information). Applying these parameters to on-field response (y') of the four selected sensors, we obtained a plausible calibration for the five-target gases concentrations (x') in tomato and maize crops (Figs. 7 and 8). These values were compared to concentration ranges identified in literature and with the proper gases TLV (Tables S14–S17, Supporting Information).

Fig. 7 shows the variation of gaseous emissions concentration measured by SnO_2 + Pd2% and SnO_2 + Au2% sensors during the three weeks of interest identified for on-field monitoring of tomato crop.

For the first one, it can be notice that the gases concentration increased with the tomato growth while, for the second one, the concentration trend seemed to decrease. In the first week (Fig. 7, left), for both sensors, the combination of fertirrigation and rainfall led to a moderate increase of gases concentration, ascribable to an increase of tomato metabolic activity. During the second week (Fig. 7, center), in all likelihood, the succession of drip irrigation, rainfall and sprinkling irrigation reduced the plants metabolism and then their gaseous emissions secreted. In particular, the effect of sprinkling irrigation resulted more effective than what was observed by preliminary sensors response analysis (Fig. 3). Sprinkling irrigation and rainfall, occurred in the third week (Fig. 7, right), confirmed their reducing effect on gases concentration, although tomato crops was in an advanced stage of ripening.

The effect of water stress on tomato crop were well-highlighted especially by SnO_2 + Au2%. Indeed, concentration range of gaseous emissions detected by this sensing device was higher than that observed by SnO_2 + Pd2% sensor. Moreover, the response times of SnO_2 + Au2% to water content variation were lower than those of SnO_2 + Pd2% sensor.

Fig. 8 shows the variation of gaseous emissions concentration measured by STN and SnO_2 + Pt2% sensors during the three weeks of interest identified for on-field monitoring of maize crop.

The trend of gaseous emissions monitored by STN sensor in maize seemed to decrease with the crop growth, contrary of what obtained with SnO_2 + Pd2% and SnO_2 + Au2% in tomato, and it resulted to be similar to response trend of the same sensor previously discussed in the study of in-situ monitoring (Fig. 4). Indeed, STN sensing film seemed to follow relative humidity daily cycle.

Instead, gases concentration detected by SnO_2 + Pt2% sensor resulted low during the first week (Fig. 8, left), corresponding to the preliminary phase of plants growth, then during the next weeks (Fig. 8, center and right) emissions concentration slightly increased, in line with emissions occurred in tomato field. No effect of relative humidity daily cycle occurred for SnO_2 + Pt2% sensor, but one can observe that the detection of water content variations by this device proved more effective by response analysis (Fig. 4) than by emissions concentration study (Fig. 8). In any case, despite the poor selectivity showed by lab-calibration, SnO_2 + Pt2% sensor demonstrated high sensitivity that, at this point, leads to reconsider its performance during maize on-field monitoring.

Moreover, it becomes necessary to reconsider also SnO_2 + PdAl sensor that, although it showed average sensing performance in lab-tests, it gave good result in terms of response analysis (Fig. 4). Fig. 9 confirms the similar trend of SnO_2 + PdAl to SnO_2 + Pt2% sensor for emissions concentration (Fig. S14 and Table S13 and S18, Supporting

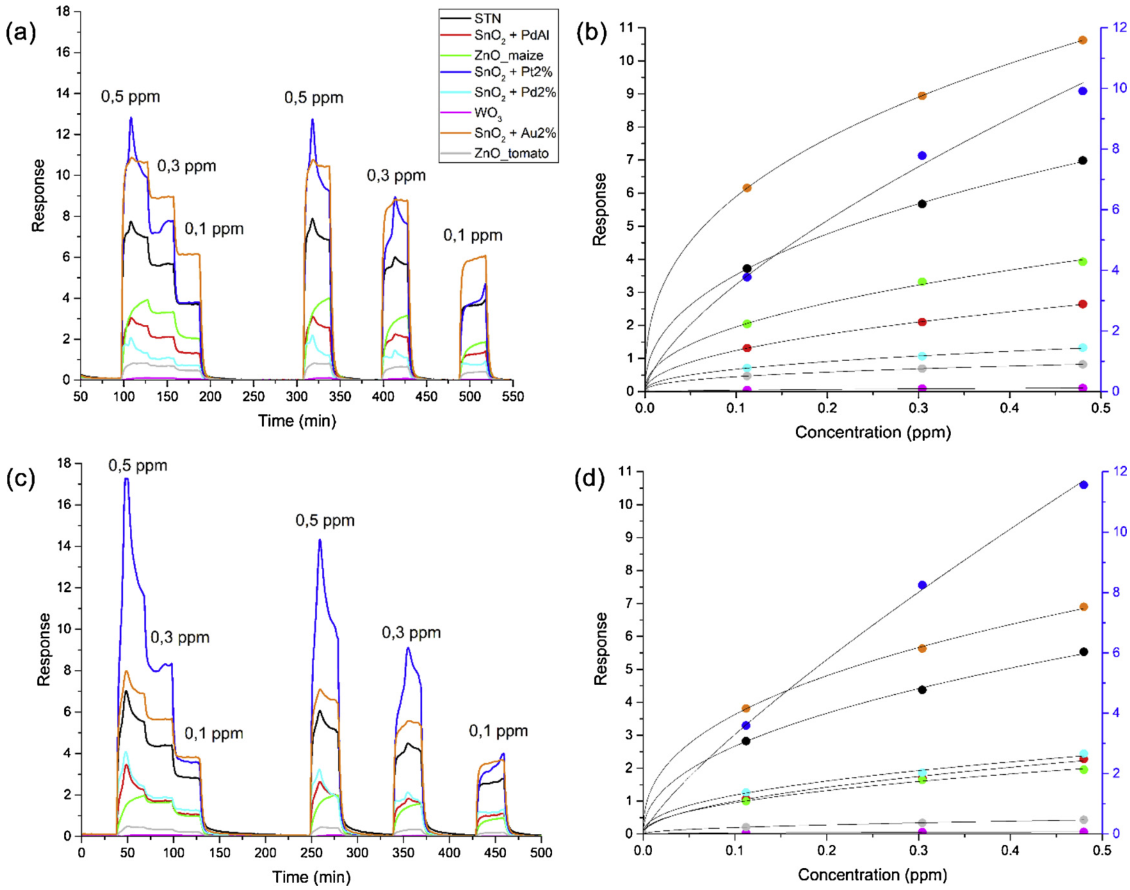

Fig. 6. Dynamic response and calibration curve of sensors tested with 0.5, 0.3 and 0.1 ppm of isoprene at 33%RH a) and b), at 52%RH c) and d).

Table 4
Sensors selected for tomato and maize emissions monitoring, sensors that demonstrated a significant electrical activity during on-field measurements, sensors that showed good sensing performance during lab-calibration vs. target gases at proper concentrations.

Tomato			Maize		
Sensor	On-Field	LAB	Sensor	On-Field	LAB
SnO_2 + Pd 2%	X	✓	STN solid solution of SnO_2, TiO_2, Nb_2O_5	X	✓
WO_3	✓	X	SnO_2 + PdAl	✓	X
SnO_2 + Au 2%	✓	✓	ZnO	✓	X
ZnO	X	X	SnO_2 + Pt 2%	X	✓

Information). In the case of SnO_2+PdAl the increase of emissions concentration with the maize growth was clearer, but the assessment of water content variation remains more available from on-field sensor response analysis. In addition, as for gases concentration, the response study (Fig. 4) of SnO_2+PdAl and SnO_2+Pt2% sensors highlighted a comparable behavior during on-field measurements.

A deep understanding about the mechanisms that regulate water stress plays a fundamental role in the water balance determination and represents a great challenge for the agri-food panorama, in particular for an efficient irrigation scheduling. The main idea of this work was placed in the necessity to identify a palette of sensing materials which feature to recognize, at a macroscopic level, variations of gaseous emissions correlated to water stress suffered by crops. In this perspective, we wanted to develop an inclusive study and not a compartmental investigation between on-field and lab-test data, since the latter approach would have led to an aseptic dissertation of the devices sensing performance, to the detriment of a practical interpretation of the possible stress manifestations from the crops. However, we are conscious that our study is affected by some limitations. First of all, the complexity of emissions from the soil-plant-atmosphere system represents the main brake for the design of a gas detector based on a number of sensors restricted maximum at two, although, the arrangement of electronics and the remote data processing make this sensing unit more cost-effective and easy to use than an eNose. A programmed series of analytical chemical analyses (GC–MS), carried out during the whole growth season, would help the identification of the main gaseous compounds secreted as stress marker. This study should be supported by the definition of the ground reference parameters by agronomists, who could also plan a controlled stress induction in the crops, tuned following their significant growth phases. Another important limitation of this work is the understanding about the correlation between water stress extent and the associated biological effects on the plants, certainly linked to a variation of gaseous emissions both as type and as concentration. From this point of view, it would be functional to interact with a biological research team, which could lead the identification of possible stress markers and of their effect on the metabolic activity of the crops.

4. Conclusions

In this work, we presented an extensive investigation arranged in on-field and lab-activities. We monitored gaseous emissions in tomato and maize yields for a whole campaign by using two sensing units, specifically designed and produced in our laboratory, based on MOX sensors. Data collected were processed and compared with meteo-sat information and occurred farming operations. The sensors employed in the monitoring systems were calibrated in the laboratory by exposing

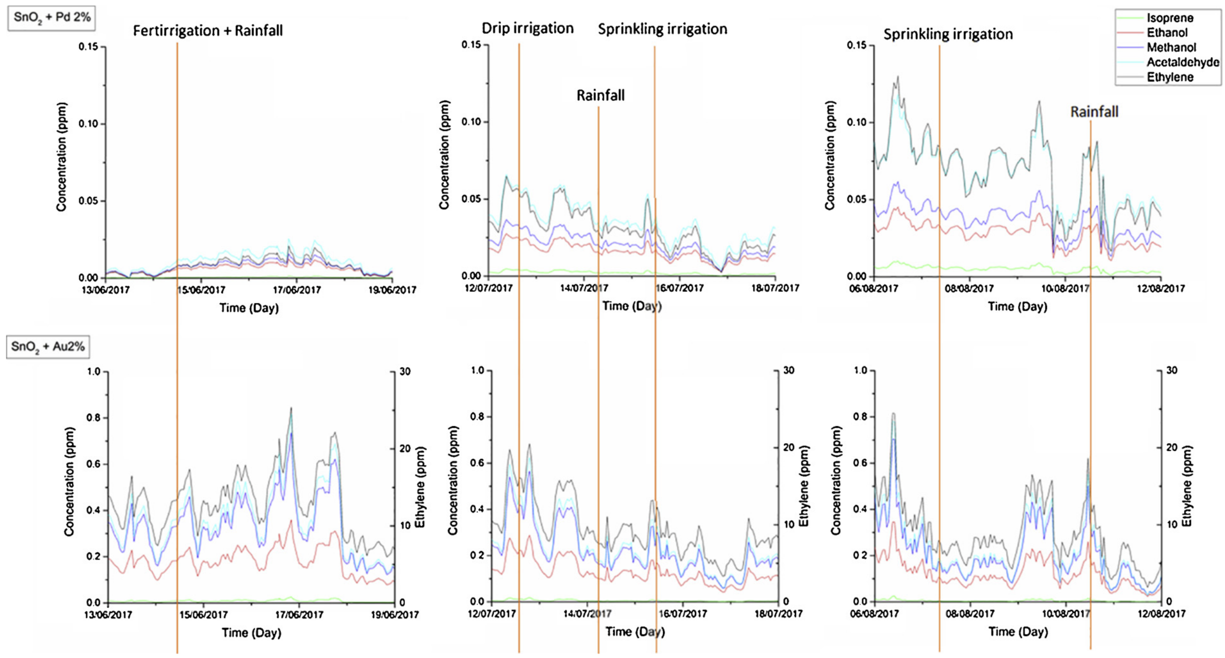

Fig. 7. On-field tomato gaseous emission concentration detected by SnO_2 + Pd2% and SnO_2 + Au2% sensors, during the three weeks of interest: 13–19 June, fertirrigation (left), 12–18 July, switch from drip to sprinkling irrigation (center), 6–12 August, sprinkling irrigation (right).

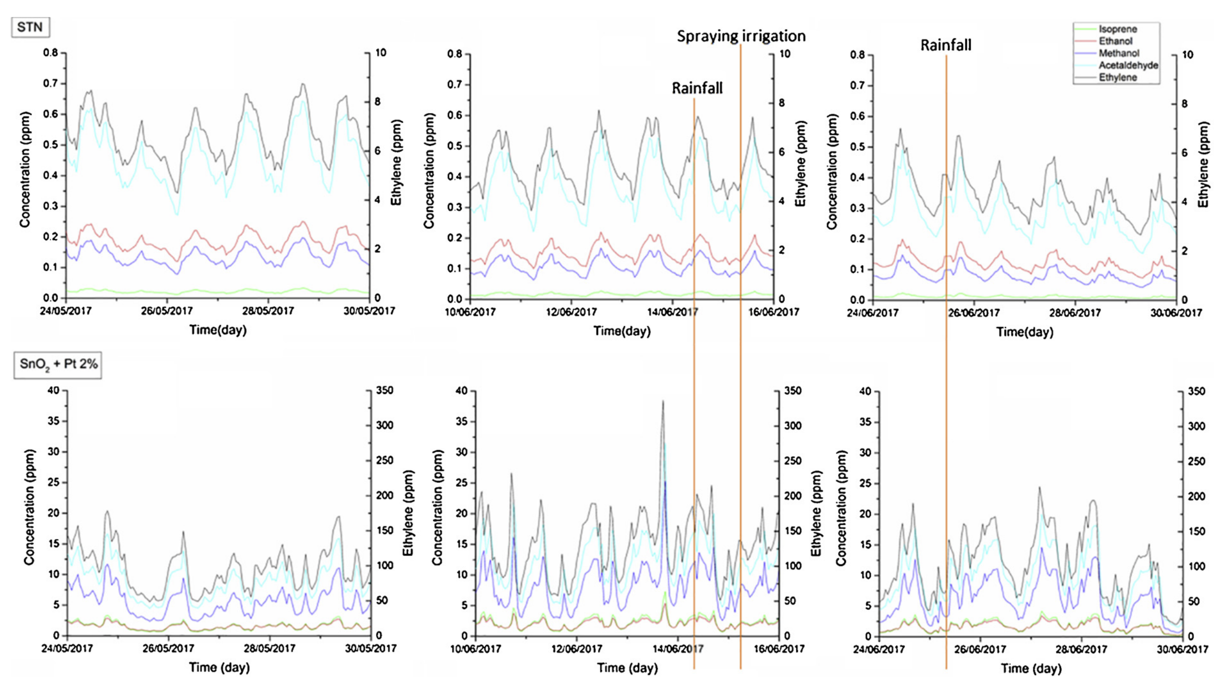

Fig. 8. On-field maize gaseous emission concentration detected by STN and SnO_2 + Pt2% sensors, during the three weeks of interest: 24–30 May, first growth phase of maize (left), 10–16 June, 50 mm irrigation on the whole yield (center), 24–30 June, three raining days (right).

them to gases identified as markers for water stress in tomato and maize crops so as to determine plausible concentration ranges for the on-field monitored emissions.

The number of sensors necessary for the application in question was reduced from four to one or two devices. The results obtained open up to the production of more compact and cost effective sensing systems for water stress monitoring in agri-food field, which making them competitive with respect to the devices currently in use; moreover, they should represent a huge potential in the technological panorama related to agricultural industry. In this sense, the preliminary results obtained with this work should open up to the definition of diverse water management solutions. Indeed, from a technological point of view, the highlighted information may provide irrigation advices about the time of intervention and the volumes to be used in order to obtain a quality product, whereas, from a biological point of view, it could be possible to investigate the correlation between morphological changes in plants and their water stress, getting at the root cause.

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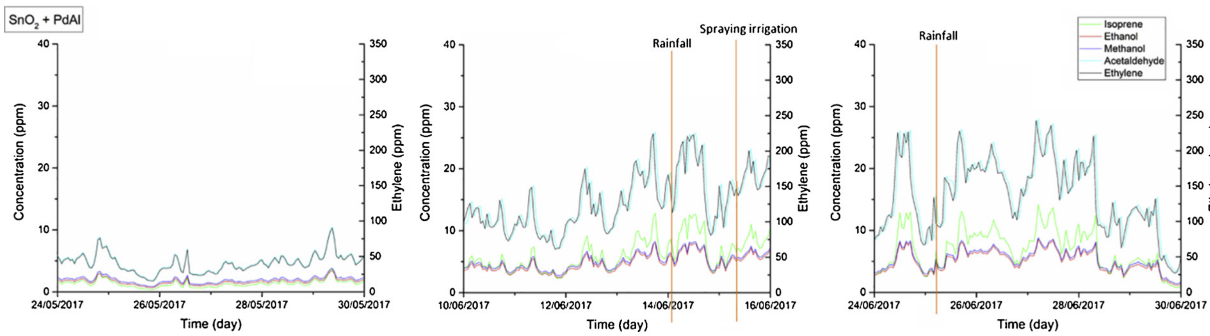

Fig. 9. On-field maize gaseous emission concentration detected by SnO_2 + PdAl sensor, during the three weeks of interest: 24–30 May, first growth phase of maize (left), 10–16 June, 50 mm irrigation on the whole yield (center), 24–30 June, three raining days (right).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2019.127227.

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