Since January 2020 Elsevier has created a COVID-19 resource centre with free information in English and Mandarin on the novel coronavirus COVID-19. The COVID-19 resource centre is hosted on Elsevier Connect, the company's public news and information website.

Elsevier hereby grants permission to make all its COVID-19-related research that is available on the COVID-19 resource centre - including this research content - immediately available in PubMed Central and other publicly funded repositories, such as the WHO COVID database with rights for unrestricted research re-use and analyses in any form or by any means with acknowledgement of the original source. These permissions are granted for free by Elsevier for as long as the COVID-19 resource centre remains active.
A sensing approach for automated and real-time pesticide detection in the scope of smart-farming

Evangelos Skotadis,⁎ Aris Kanaris, Evangelos Aslanidis, Panagiotis Michalis, Nikos Kalatzis, Fotis Chatzipapadopoulos, Nikos Marianos, Dimitris Tsoukalas

ΔDepartment of Applied Physics, National Technical University of Athens, Athens 15780, Greece
NEUROPUBLIC S.A., 6 Methonis Street, Piraeus 18545, Greece

ARTICLE INFO

Keywords:
Gas sensors
Smart farming
Nanoparticles
Organophosphates
Chlorpyrifos

ABSTRACT

The increased use of pesticides across the globe has a major impact on public health. Advanced sensing methods are considered of significant importance to ensure that pesticide use on agricultural products remains within safety limits. This study presents the experimental testing of a hybrid, nanomaterial-based gas-sensing array, for the detection of a commercial organophosphate pesticide, towards its integration in a holistic smart-farming tool such as the “gaiasense” system. The sensing array utilizes nanoparticles (NPs) as the conductive layer of the device while four distinctive polymeric layers (superimposed on top of the NP layer) act as the gas-sensitive layer. The sensing array is ultimately called to discern between two gas-analytes: Chloract 48 EC (a chlorpyrifos-based insecticide) and Relative Humidity (R.H.) which acts as a reference analyte since it is anticipated to be present in real-field conditions. The unique response patterns generated after the exposure of the sensing-array to the two gas-analytes were analysed using a common statistical analysis tool, namely Principal Component Analysis (PCA). PCA has validated the ability of the array to detect, quantify as well as to differentiate between R.H. and Chloract. The sensing array being compact, low-cost and highly sensitive (LOD in the order of ppb for chlorpyrifos) can be effectively integrated with pre-existing crop-monitoring solutions such as the gaiasense.

1. Introduction

Agriculture currently faces many challenges that pose major threats for the resilience and sustainability of the sector. This includes, but not limited to, the intensification of agricultural production, increased use of pesticides and inefficient management of natural and energy resources. The impact of climate crisis, with extreme periods of droughts and precipitation events (Forzieri et al., 2018) across the globe, adds significant stress on the sector and indicates the urgent need to adapt to new dynamics for the cultivation of crops. This new era of uncertainty can potentially lead to a substantial increase of pesticide-application on crops, in an effort to sustain production rates and quality of products. This has been evident in many EU countries, e.g. in Greece the quantity of pesticide used in 2014 is estimated to be 2.58 kg/ha with the highest amount reported for Netherlands with 9.86 kg/ha (Sharma et al., 2019). Biological hazards (see COVID-19 pandemic impact) also highlight the need for advanced tools and smart farming solutions to remotely manage and assess farm activities, minimizing the need for field visits.

Chlorpyrifos (CPS) is an organophosphate pesticide and one of the most commonly used pesticides (Eastmond and Balakrishnan, 2010) in a range of in-door agricultural applications including tomatoes, corn, soybeans, broccoli, and apples but also applied in non-agricultural applications (e.g. structural pest control). However, the increasing use of CPS on crops has a significant impact on public health as it has been linked with the development of potential genotoxic and neurological effects, particularly evident in child population (Statement on the available, 2019; Hernandez and Menendez, 2016; Rauh et al., 2012). Despite the recent non-renewal of the approval of CPS in EU continent (EU, 2020), the substance still continues to be used in the vast majority of other countries. Advanced verification and certification methods are therefore considered to be of significant importance to remotely monitor and ensure that the use of CPS on agricultural products remain within safety limits (Mie et al., 2018).

However, nowadays there exists a lack of monitoring instruments and suitable methodologies for in-the-field automated detection of pesticide use on crops, mainly due to technical and cost issues. The use of compact, cost effective, low power and highly sensitive sensors poses as the main alternative to traditional pesticide/pollutants monitoring techniques (i.e. mainly chromatographic and coupled chromatographic-
2. PestGaS recordings are integrated with data from the already established sensing network.  
3. Pest management decision models generate more accurate recommendations.

**Fig. 1. Integration of Active Ingredient Detection technology within the gaiasense smart-farming solution.**

spectrometric procedures). Electrochemical, optical and piezoelectric biosensors (Zhao et al., 2015; Yan et al., 2015; Shang et al., 2011) as well as molecularly imprinted polymer sensors (Liu et al., 2015) are amongst the most common advanced methods for pesticide analysis and determination. Research interest for gas sensing of environmental pollutants is also steadily growing due to the fact that they are cheap, accurate, convenient, offer fast analysis of multiple analytes and most importantly they present reversible response and operate in room temperature (metal oxide gas sensors aside). In the field of micro and Nano gas-sensors in particular, nanomaterial devices have been studied thoroughly, providing promising results. One the most typical electrochemical gas-sensors are those relying on Metal oxide semiconductors (MOS), commonly based around p-type or n-type MOS materials fabricated in the nanoscale (Kim and Lee, 2014). Carbon Nanotube (CNT) based gas sensors have been also proposed for the detection of gases such as NH₃, NO₂, CO, CO₂ etc. (Bekyarova et al., 2004). On the other hand, Organic-Based Chemiresistive Gas Sensors are a very promising and emerging class of electrochemical sensors. These are usually based on organic materials (e.g. polymers) (Adhikari and Majumdar, 2004) that do not require heating elements or complex fabrication steps (this is the case for MOS sensors) and are therefore cost-effective and easily integrated with inorganic materials such as metallic Nanoparticles (NPs) so as to obtain devices with improved properties. Cross-linked Au NPs in particular have been used in order to prepare chemiresistors capable of detecting various environmental pollutants as well as VOCs for the detection of breath biomarkers for disease detection (Carvalho et al., 2017; Zhao et al., 2016). Limited results have been reported up to now for pesticide gas-sensors; dimethyl-methylphosphonate (DMMP, lab simulant of the toxic agent of sarin) has been successfully detected with a limit of detection (LOD) in the ppm range, using complex single-use sensors (Yu et al., 2015); Organophosphat vapour sensing via Peptide nanotube biosensors with a short life span (45 days) and a LOD in the ppb regime has been reported (Baker et al., 2014); a SnO₂ organophosphorus gas sensor operating at 250–300 °C, with a LOD of 1.053 μg/L has been also discussed (Huang et al., 2004); Finally a nanopore sensor (agarose gel-based chip) has been used for the detection of vaporized omethoate (LOD of 100 ppb) through the complex formation with a DNA aptamer, and its obstruction at the nanopore (Fujii et al., 2017).

According to the Food and Agricultural Organization of the United Nations, Integrated Pest Management (IPM) should be considered as an integral process of modern farming practices. IPM emphasizes on the sustainable and combined utilization of all available pest control techniques that will ensure the growth of a healthy crop with the least possible disruption to agro-ecosystems. Sensing technologies based on the IoT paradigm, data analytics, intelligent decision support systems, end-user applications and devices are already in use in the context of Smart Farming to advance farm management and decision making, minimizing financial costs and environmental impact (Brewster et al., 2017). However, there is a gap on close-to-real-time pesticides detection systems that are feasible to be deployed at the field as part of an integrated pest management system in the context of smart farming. The aim of this study is to evaluate the Pesticide Gas Sensing Array (PestGaS), a sensing-array comprised of four distinctive gas-sensors as discussed below, which is envisioned to become an autonomous low-cost sensing technique capable to be integrated with operational frameworks in the context of smart-farming.

Although PestGaS is designed as an autonomous and interoperable sensing system, it is initially planned to be integrated and piloted with the “gaiasense” Smart Farming solution which already incorporates a wide range of sensing and data analytics technologies in order to offer next generation advice to farmers (Kalatzis et al., 2019). A cornerstone for the “gaiasense” SF solution is the infrastructure of telemetric autonomous stations which collect data from sensors installed in the field; the sensors are used so as to record atmospheric (air temperature, relative moisture, wind direction and velocity, rain,) soil (temperature, salinity, moisture) and plant (leaf wetness, leaf humidity, leaf temperature) parameters. As it is illustrated in Fig. 1, the envisioned integration of the PestGaS sensor in a homogenized approach with sensors that are already operating in a typical smart farming system is going to fill the existing gap of automated pesticide application detection and advance significantly the information and decision making at farm management level.

In the heart of the PestGaS monitoring system lies a gas-sensing array comprised of self-assembled nanoparticle networks (tuning the conductivity of the sensor) that are covered by 4 different polymeric...
materials (acting as the gas sensitive layer). This component can be easily integrated in the gaiasense system since it is compact, has low power requirements and hybrid chemiresistors based on Pt NPs and polymeric coatings have been developed in the past by this group and have been used for the detection of humidity and other organic analytes (Skotadis et al., 2012, 2010, 2013; Tang et al., 2012), as well as of a standard-solution containing CPS and p-xylene (appropriate solute for CPS) (Madianos et al., 2018). However, such experiments have focused on the sensors’ ability to discern between the actual pesticide active-substance (namely CPS) and the solutes (p-xylene and water). The current study aims to establish the potential of the proposed sensor array to be used in actual in-the-field applications. For this reason a commercial CPS based pesticide, and not a laboratory synthesized standard solution, has been selected for the first time as one of the target analytes to be tested in a laboratory environment. The main objective of the study is to discern between the commercially available pesticide and Relative Humidity (R.H.), which is considered to be the most common amongst the environmental variables that occur in green house environment. The proposed sensor features important advantages related to its competitors since it is a reusable, highly sensitive (detection in the ppb regime), cost-effective, low-power and reliable gas sensing device, that is capable but not restricted to the detection of a commercially available pesticide solution. In addition, it is suitable for easy integration in smart farming solutions aiming to provide advanced tools, incorporated into a holistic management platform for real-time and remote monitoring of crops.

2. Materials & methods

The hybrid chemical sensors are based on the combination of metallic nanoparticles and polymer films. As a first step Platinum (Pt) NPs of 5 nm in diameter are deposited on top of oxidized silicon wafers that have been previously patterned with gold interdigitated electrodes (IDEs, as can be seen in Fig. 2), having an inter-finger gap of 10 μm and a thickness of 30 nm. Optical lithography, the e-gun technique and lift-off have been employed in order to produce the IDEs. The NP layer has been fabricated and deposited on top of the IDEs in a single step, using a modified magnetron sputtering technique which allows for easy and precise control of the NP surface coverage as well as NP size; the experimental process for the fabrication of similar sensors to the ones reported herein has been discussed in length in previous publications by this group (Skotadis et al., 2012, 2013). The surface coverage of the devices discussed in this paper, has been selected according to previous results (Bekyarova et al., 2004) and for maximum sensitivity; for this reason devices with a mean resistance in the range of 700 kΩ have been used (Fig. 2c). It’s important to note that all of the aforementioned steps were performed in room temperature (25°C).

Polymeric solutions were prepared using the following materials that were bought from Merck: Poly(ethyl methacrylate) (PEMA), Poly (2-hydroxyethyl methacrylate) (PHEMA), poly(isobutyl methacrylate) (PIBMA) and poly(butyl methacrylate) (PBMA). The selection of the polymeric materials was based on their susceptibility towards humidity absorption (Oikonomou et al., 2011). All polymeric solutions were prepared using a high precision micro-balance; the solvent of choice was PGMEA in the case of PEMA, PIBMA and PBMA while Methanol was used in the case of PHEMA. The resulting polymer solutions were then spin-coated on top of the nanoparticle functionalized substrates so as to obtain a ~500 nm thick polymer layer.

Commercially available Chloract 48 EC solution (a CPS based insecticide) was purchased from a local agricultural supplies store. According to Chloract’s manufacturer, 100–250 c.c. of Chloract should be used per one acre of crop; in addition, a total of 65 L of Chloract/water solution should be used per acre. For all experiments reported herein a medium approach has been followed, by fabricating a test solution having the following concentration: 175 c.c. of Chloract in 65 L of Chloract/DI water solution. The actual volume of the finalized test-solution used in the experiments was 30 ml, corresponding to 0.081 c.c. of Chloract dissolved in a total solution volume of 30 ml. As far as the actual synthesis of the Chloract 48 EC is concerned, its documentation reports that 44.4% corresponds to CPS while 55.7% corresponds to auxiliary substances. This translates to a solution that is 0.12% CPS, 0.15% auxiliary substances and 99.73% H2O in concentration.

All gas-sensing experiments have been conducted in the gas-sensing characterization setup that is available at the School of Applied Physics of the NTUA; a schematic of the specific setup used for the Chloract vs.

![Fig. 2. Sensor Schematic and Microscopy images (a) cross section of the sensing device (b) Top-down view of the sensor (c) Transmission Electron Microscopy Image, the Pt nanoparticle distribution and size can be seen.](image-url)
Humidity experiments can be seen in Fig. 3. The Chloract test-solution as well as DI water (30 ml for both analytes) have been placed inside two separate gas bubblers; their respective vapours have been collected by feeding the bubblers with a separate Nitrogen gas-line, externally controlled by two Nitrogen Mass Flow Controllers (MFCs). Varying concentrations of Chloract test-solution or Humidity (corresponding to varying Nitrogen flow-rates: 32–1300 ml/min) were then superimposed over a continuous flow of nitrogen which eventually flowed inside the sensors’ measurement chamber. All of the following experiments correspond to a comparison of the sensors’ response between Chloract test-solution and Humidity, for identical carrier-gas (Nitrogen) flows. The sensors have been packaged inside a small volume 3D-printed measurement chamber that ensures sufficient isolation from the rest of the measurement setup; R.H. and temperature were controlled to within 0.1% and 0.1 °C respectively while a commercial R.H and Temperature sensor was also used in order to monitor the chamber. All sensing evaluation experiments have been conducted at a temperature of 25°C and the sensor’s resistance has been monitored using the Keithley 2400 multimeter.

3. Experimental results/discussion

Chemical sensors based on Pt NPs have been developed in the past by this group and have been used for the detection of humidity and other organic analytes (Skotadis et al., 2012, 2010, 2013; Tang et al., 2012) as well as of a standard-solution containing CPS and p-xylene (Madianos et al., 2018). However, such experiments have focused on the sensors’ ability to discern between the actual pesticide active-substance (namely CPS) and the solute (p-xylene). The current study aims to establish the potential of the proposed sensor array to be used in actual in-the-field applications. For this reason a commercial CPS based pesticide and not a standard solution has been selected as one of the target analytes; in addition this study’s goal is to discern between the commercially available pesticide and the most common and ever-present gas in greenhouses as well as in open crops, namely humidity.

The mechanism for the detection of gaseous analytes by hybrid NP/polymer based sensors has been discussed extensively in previous publications (Skotadis et al., 2012, 2010, 2013; Tang et al., 2012; Madianos et al., 2018). In brief, the polymer layer acts as the gas-sensitive and transducing layer of the device by absorbing gases that are present in its vicinity; different polymers present different selectivity/susceptibility towards different gases. The absorption of vapours leads in turn in a swelling of the polymer layer which in turn translates in the deformation/stress of the underlying NP layer and in the increase of the mean inter-nanoparticle distance. The result of this process is the increase of the as-measured sensor Resistance, when exposed to varying concentrations of target analytes. However, polymer coatings feature one inherent disadvantage when used as sensitive gas-sensing layers in composite gas mixtures: poor selectivity. This leads to increased uncertainty over the identity of the gases responsible for the sensors’ response; this can in turn be bypassed by applying statistical analysis techniques such as Principal Component Analysis (PCA) for target identification (Facure et al., 2017; Lu et al., 2017).

It is also worth noting that our proposed gas-sensors have been optimized (Skotadis et al., 2012) in terms of the available fabrication parameters, where the nanoparticle surface coverage and the IDE gap have been found to have the most prominent effect on sensor performance. In fact, optimum sensing performance has been observed for devices with conductivity that lies in the intermediate transition state, just below the percolation threshold. The percolation threshold, for devices such as the ones discussed in the current paper, has been previously reported to be in the range of 600 kΩ to 1–10 MΩ in terms of device resistance or in the range of 42–46% in terms of nanoparticle surface coverage (Scher and Zallen, 1970). For the needs of this paper all of the above mentioned results have been taken into account: all of the sensors used in the current experimental setups were designed with an IDE inter finger spacing of 10 μm and a nanoparticle surface coverage of 46% (5 sensors for each of the four distinctive polymer coatings).

In Fig. 4 the typical transient sensing response of a NP based gas sensor can be seen, over the course of a gas-sensing characterization experiment (here the transient response of a PEMA coated sensor is shown as a typical result). In this case the sensor is first exposed to incrementally increasing concentrations of Chloract test-solution and as a second step to a corresponding range of R.H. concentrations. The nitrogen flow-rate values that were employed so as to achieve R.H. concentrations in the range of 10–58.3% were also used in the case of the Chloract solution and as can be seen in Fig. 4 for identical nitrogen concentrations in the range of 10–58.3%.
flow-rates the sensor responds in a different manner. In particular, all four different polymeric coatings systematically show increased sensitivity towards the Chloract solution. It is worth noting that all experiments have been repeated by inverting the introduction order of the two analytes (Chloract and Humidity), in the measurement chamber; in every case the sensors showed increased response towards the pesticide solution.

In Fig. 5, the % Relative resistance response ($\Delta R/R_0\%$) for sensors coated with each of the four polymeric coatings, towards the Chloract solution and R.H., can be seen; $R_0$ is the resistance of the sensors during pure Nitrogen flow. The mean response of the 5 sensors coated with each polymer can be seen as error bars; their standard deviation (in the case of R.H.) was between 0.25% and 1.1%, 0.35% and 1.2%, 0.32% and 0.88%, 0.35% and 1.53% for PBMA, PIBMA, PEMA and PHEMA polymers respectively. In the Case of Chloract, the sensors had a standard deviation between 0.32% and 1.31%, 0.34% and 1.42%, 0.40% and 1.12%, 0.40% and 2.2% for PBMA, PIBMA, PEMA and PHEMA polymers respectively. Precision measurements revealed that the sensors had a standard deviation, in the case of R.H., between 0.12% and 0.65%, 0.17% and 0.53%, 0.15% and 0.45%, 0.16% and 0.71% for PBMA, PIBMA, PEMA and PHEMA polymers respectively. In the Case of Chloract, the sensors had a standard deviation between 0.29% and 0.52%, 0.15% and 0.42%, 0.18% and 0.48%, 0.18% and 0.96% for PBMA, PIBMA, PEMA and PHEMA polymers respectively. The mean response time for all 16 sensors has been found to be 20 sec (response time is the time needed for the sensor to reach 70% of equilibrium state). All sensors showed a quasi-linear response towards Chloract while PBMA and PEMA sensors exhibited two regions of different linearity towards humidity, for concentrations in the range between 10 and 50% of R.H. and for concentrations higher than 50%. The sensors’ resolution (minimum change in R.H. or pesticide that can be detected) was found to be equivalent to 0.48% of R.H. (or 150 ppm). As far as the limit of detection (LOD) of the sensors is concerned all sensors are able to detect R.H. and Chloract for flow-rates as low as 7.8 ml/min, corresponding to concentrations as low as 250 ppm and 18.95 ppb respectively, while the minimum flow-rate for which the sensor array can successfully separate R.H. from Chloract is 32 ml/min (corresponding to a Humidity concentration of 1000 ppm, a R.H. of 3.2% and a CPS concentration of 73.95 ppb). It is worth noting that CPS cannot be measured separately from the rest of the auxiliary substances included in the commercial Chloract 48 EC solution, as well as water which is used in order to further dilute the initial solution. The LOD for CPS has been approximated by calculating the partial vapour pressure of CPS in the Chloract 48 EC solution and by approximating the partial vapour pressure of the auxiliary substances (proprietary materials of unknown identity) using that of a common solute for CPS, namely p-xylene. Using Raoult’s law, a good approximation for dilute solutions, the aforementioned LOD for CPS (73.95 ppb), has been determined. This CPS LOD, corresponds to a Nitrogen flow-rate of 32 ml/min and 1002 ppm of CPS Test-solution. The saturation pressure of the Chloract solution is 23.7356 Torr, which is slightly different than that of Water in the same temperature (23.7413 Torr). This results in slightly different...
concentrations between Chloract and Humidity, for the same flow-rates; e.g. the maximum flow-rate that can be achieved by our system (1300 ml/min) produces a R.H. concentration of 58.3% at 25 °C, this flow-rate translates to 18225 ppm of Humidity and 18220 ppm of Chloract solution.

The operation of the sensor-array as a potential e-nose, capable of discerning between R.H. and the commercial Chloract solution can be seen in Fig. 6, where distinctive “fingerprints” in terms of sensing response for each polymer are produced for varying R.H. and Chloract solution concentrations. Since each polymer is characterized by its own unique diffusion rate and therefore swelling for humidity and Chloract solution, distinctive responses are obtained for the same nitrogen flow-rates of the two analytes. Fig. 6(c) reveals that there is a shift in the sensors’ response when they are exposed to Chloract 48 EC vapours. However, since in real-life conditions target-gases are of unknown origin, concentration and identity, the sensors need to discern between the two analytes of the study. A unique “fingerprint” type response such as the one recorded in Fig. 6, is an essential prerequisite in order to apply pattern recognition and statistical techniques in the post-processing of the existing experimental data-sets. To that end PCA has been performed over our existing data-set using R and Rstudio. PCA is a well-established statistical analysis technique that is commonly used in order to discriminate between target analytes (Huang et al., 2004; Fujii et al., 2017), by analysing the output of a sensing-array. Herein, a sensing array coated with 4 different polymeric films has been employed; the ability of the array to discern between the two test-gases is examined by taking into consideration either two, three or all four polymeric coatings that were available, in every possible combination. In Fig. 7, PCA results can be seen by using an increasing number of discrete polymer coatings in order to extract them. As is to be expected, the gradual increase in the number of distinctive polymeric coatings used for the PCA, signals an increase in the degree of separation between Chloract and R.H. (Fig. 7a–c); for increasing target-gas concentration there is an increase in the separation between Chloract and R.H., regardless of the number of polymeric coatings. However, it is important to note that in all results shown in Fig. 7, a necessary condition for successful separation is to always include in the PCA, the response of a PHEMA coated sensor. Typical PCA results using 2 polymer coatings, without including a PHEMA coated sensor can be seen in Fig. 7(d), where the separation between Chloract and R.H. is reduced; in addition the placement/location of pesticide and R.H. response-points in the two component PCA analysis diagram seems to be of a random nature. Similar results are obtained by using 3 polymeric coatings and regardless of the combination of choice. The hydrophilic nature of the PHEMA coating (by far the most hydrophilic amongst the polymers used in the current study (Manoli et al., 2010) and its specific susceptibility towards Chloract and R.H. vapours, seems to play a key role in target-gas identification as well as gas quantification.

Fig. 6. Distinctive fingerprint-patterns after the response of sensors with all four different polymeric coatings towards (a) Relative Humidity (R.H.) from 3.2% to 58.3% (b) Chloract test-solution, for N₂ carrier-gas flows from 32 to 1300 ml/min (identical N₂ flows with the ones used to achieve R.H. from 3.2% to 58.3%) and (c) combined response to both analytes.
4. Conclusions

The main goal of the current paper was to evaluate the performance of a gas-sensing array (PestGaS) based on self-assembled metallic nanoparticles coated by 4 different polymeric films, as a potential smart-farming tool that will be eventually used in actual in-the-field autonomous crop-monitoring systems. This is the main reason why a commercially available chlorpyrifos based insecticide (Chloract 48 EC) and not a standard solution has been used as one of the two test gases employed in the frame of the current study. The sensing array has been put to the test by its introduction to varying concentrations of Chloract and Relative Humidity (R.H.); R.H. has been chosen as a reference gas since it is omnipresent in any farming environment.

The sensing array has successfully responded to both test-gases, while each of the 4 distinctive sensors (different polymer coatings) has shown a differentiated response towards R.H. and Chloract vapours. This formed the basis for successful target identification and quantification; to that end, a commonly used statistical analysis technique, namely Principal Component Analysis (PCA), has been employed in order to analyse the convoluted response of the sensing array. The use of the PCA technique has resulted in separating between Chloract and R.H. as well as determining the concentration of each target/gas component. It is worth noting that the sensors showed a low limit of detection for chlorpyrifos (73.95 ppb), while by employing the PCA technique the total number of identified individual gases can be further expanded.

The use of gas sensors with key-properties such as miniaturization, reusability, low power requirements, high-sensitivity and low-cost, for the detection of environmental pollutants such as pesticides and insecticides is of great importance; this holds especially true if the scarcity of the already reported results found in the literature is taken into account. The current sensing array fulfils all of the aforementioned criteria, which promote its easy integration in the context of already existing crop-monitoring solutions such as the gaiasense. The combination of an advanced gas-sensing detection tool such as the PestGaS with a state-of-the-art crop-monitoring tool is invaluable; this would significantly upgrade the added-value of the integrated system, elevating it into a powerful multi-purpose, smart-farming platform with unique capabilities, for real-time and remote monitoring of crops. An expansion in the number of individual gases identified by the system (e.g. detection of new pollutants), the modification of environmental parameters such as background humidity and temperature and the eventual incorporation of the sensor in the context of the commercial gaiasense system are only a few of our future goals.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Acknowledgments

This project has been funded by NEUROPUBLIC S.A. under program ID: 62381800. The authors acknowledge the help of Dimitra Bouzani, M.Sc., in processing the Figures of this paper as well as Dr. Konstantinos Giannakopoulos for the TEM images.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compag.2020.105759.

References

Adhikari, B., Majumdar, S., 2004. Polymers in sensor applications. Prog. Polym. Sci. 29, 699–766.
Baker, P.A., Goltz, M.N., Schrand, A.M., Yoon, D.Y., Kim, D.S., 2014. Organophosphorus vapour detection on gold electrodes using peptide nanotubes. Biosens. Bioelectron. 61, 119–123.
Bekyarova, E., Davis, M., Burch, T., Ikits, M., Zhao, B., Sunshine, S., Haddon, R., 2004. Chemically functionalized single-walled carbon nanotubes as ammonia sensors. J. Phys. Chem. B 108, 19717–19720.
Brewster, C., Rousk, I., Kalatzis, N., Doolin, K., Ellis, K., 2017. IoT in agriculture: Designing a Europe-wide large-scale pilot. IEEE Commun. Mag. 55, 26–33.
Carvalho, W.S., Wei, M., Ipko, N., Gao, Y., Serpe, M.J., 2017. Polymer-Based Technologies for Sensing Applications. Anal. Chem. 90, 459–479.
Eastmond, D.A., Balakrishnan, S., 2010. Genotoxicity of Pesticides. In: Krieger, R. (Ed.), Hayes’ Handbook of Pesticide Toxicology. Academic Press, San Diego, pp. 357–380.
European Commission Implementing Regulation (EU) 2020/18 (2020) 14-16.
Faccure, M.H.M., Mercante, L.A., Mattose, L.H.C., Corre, D.S., 2017. Detection of trace levels of organophosphate pesticides using an electronic tongue based on graphene hybrid nanocomposites. Talanta 167, 59–66.
Forzieri, G., Bianchi, A., Silva, F.B., Marin Herrera, M., Forzieri, G., 2016. Linking pesticide exposure with pediatric leukemia: potential underlying mechanisms. Int. J. Mol. Sci. 17, 461.
Huang, X., Liu, J., Pi, Z., Yu, Z., 2004. Qualitative and quantitative analysis of organophosphorus pesticide residues using temperature modulated SnO2 gas sensor. Talanta 64, 538–545.
Kalatzis, N., Mariano, N., Chatzipapadopoulos, F., 2019. IoT and data interoperability in agriculture: A case study on the giuseense TM smart farming solution. In: Proceedings of 2019 Global IoT Summit (GIoTS), pp. 1–6.
Kim, H.J., Lee, J.H., 2014. Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview. Sens. Actuators B Chem. 192, 607–627.
Luo, W., Dong, X., Qiu, L., Yan, Z., Meng, Z., Xue, M., He, X., Liu, X., 2017. Colorimetric sensor arrays based on pattern recognition for the detection of nitroaromatic molecules. J. Hazard. Mater. 326, 130–137.
Madianos, L., Skotadis, E., Patsiouras, L., Filippidou, M.K., Chatzistrandoulis, S., Tsoukalas, D., 2018. Nanoparticle based gas-sensing array for pesticide detection. J. Environ. Chem. Eng. 6, 6641–6646.
Manoli, K., Goustouridis, D., Raptis, I., Valamontes, E., Sanopoulou, M., 2010. Vapor-induced swelling of supported methacrylic and silicone polymer films: determination of interaction parameters. J. Appl. Polym. Sci. 116, 84–90.
Mie, A., Rudeen, C., Grandjean, P., 2018. Safety of safety evaluation of pesticides: developmental neurotoxicity of chlorpyrifos and chlorpyrifos-methyl. Environ. Health 17, 1–5.
Oikonomou, P., Patiss, P., Botsialas, A., Manoli, K., Goustouridis, D., Pantazis, N.A., Kavadias, A., Valamontes, E., Ganetos, T., Sanopoulou, M., Raptis, I., 2011. Performance simulation, realization and evaluation of capacitive sensor arrays for the real time detection of volatile organic compounds. Microelectron. Eng. 88, 2259–2263.
Raul, V.A., Perera, P.F., Horton, M.K., Whyatt, R.M., Bansal, R., Hao, X., 2012. Brain anomalies in children exposed prenatally to a common organophosphate pesticide. Proc. Natl. Acad. Sci. U.S.A. 109, 7871–7876.
Scher, H., Zilien, R., 1970. Critical density in percolation processes. J. Chem. Phys. 53, 3759.
Shang, Z.J., Xu, Y.L., Gu, Y.X.Z., Wang, Y., Wei, D.X., Zhan, L.L., 2011. A rapid detection of pesticide residue based on piezoelectric biosensor. Procedia Engineer. 15, 4480–4485.
Sharma, A., Kumar, V., Shahzad, B., Tanveer, M., Sidhu, G.P.S., Handa, N., Kohli, S.K., Yadav, P., Bali, A.S., Parihar, R.D., 2019. Worldwide pesticide usage and its impacts on ecosystem. SN Appl. Sci. 1, 1446.
Skotadis, E., Tang, J., Tsouvi, V., Tsoukalas, D., 2010. Chemiresistive sensor fabricated by the sequential ink-jet printing deposition of a gold nanoparticle and polymer layer. Microelectron. Eng. 87, 2258–2263.
Skotadis, E., Tanner, J.L., Stathopoulos, S., Tsouvi, V., Tsoukalas, D., 2012. Chemical sensing based on double layer PHHEMA polymer and platinum nanoparticle films. Sens. Actuat. B Chem. 175, 85–91.
Skotadis, E., Mossoudakos, D., Katsabrookou, K., Stathopoulos, S., Tsoukalas, D., 2013. Flexible polymide chemical sensors using platinum nanoparticles. Sens. Actuat. B Chem. 189, 106–112.
Statement on the available outcomes of the human health assessment in the context of the pesticides peer review of the active substance chlorpyrifos, 2019. EFSA J. 17, 5809.
Tang, J., Skotadis, E., Stathopoulos, S., Roussis, V., Tsouvi, V., Tsoukalas, D., 2012. PHEMA functionalization of gold nanoparticles for vapor sensing: chemi-resistance, chemi-capacitance and chemi-impedance. Sensors Actuat. B Chem. 2170, 129–136.
Yan, X., Li, H., Han, X., Xu, X., 2015. A ratiometric fluorescence quantum dots based biosensor for organophosphorus pesticides detection by inner-filter effect. Biosens. Bioelectron. 74, 277–283.
Yu, F., Xu, P., Wang, J., Li, X., 2015. Length-extensional resonating gas sensors with ICfoundry compatible low-cost fabrication in non-SOI single-wafer. Microelectron. Eng. 136, 1–7.
Zha, W., Al-Nasser, I.F., Shan, S., Li, J., Skee, Z., Kang, N., Loo, J., Lu, S., Zhong, C.J., Grausgruber, C.J., 2016. Detection of mixed volatile organic compounds and lung cancer breaths using chemiresistor arrays with crosslinked nanoparticle thin films. Sens. Actuators B Chem. 232, 292–299.
Zhao, H., Ji, X., Wang, B., Wang, N., Li, X., Ni, R., 2015. An ultra-sensitive acetylcholinesterase biosensor based on reduced graphene oxide-Au nanoparticles-ß-cyclodextrin/Prussian blue-chitosan nanocomposites for organophosphorus pesticides detection. Biosens. Bioelectron. 65, 23–30.