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Blind Prediction of Odor Concentration in Deodorization Process in Wastewater Treatment Plant Using E-nose and Dynamic Olfactometry

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This project presents the capacity of e-noses to predict with good accuracy odor concentrations based on training with reference method using dynamic olfactometry procedure (EN 13725: 2022) in a variable environment like deodorization sources at SIAAP wastewater treatment plant. It shows how optimization with a reduced training allows to achieve 90 % of correct predictions of odor level from blind samples collected in channelled sources.
IOMS (Instrumental Odor Monitoring Systems) WT1 were deployed in the Ellona dryer cabinet at the outlet of deodorization units and raw air sampled in real-time. The training of analyzers consists in quantifying odor emissions from sources with dynamic olfactometry data during 5 days of campaigns over a 3 months period.
The hardware deployment, training method, protocol and signal optimization are presented, as well as the data pipeline: from data collection to modelling with IOT platform using multivariate statistics. A linear regression model (Partial Least Squares) allows to build calibration curves for both sites (with resulting R^2>0.93) and to validate instrumental correlation with olfactometry scores to implement algorithm in electronic noses for olfactory nuisance monitoring. After the training step, we discuss perspectives of fulfilling real-time monitoring considering operations at source, olfactory nuisances and gases at emissions points with odor forecasting of emissions impact to control operations and improve environmental survey.

1. Introduction

The SIAAP (Syndicat Interdépartemental de l'Assainissement de l'Agglomération Parisienne) transports and treats the wastewater of 9 million inhabitants, i.e., 2,600,000 m3/day of wastewater, at 6 treatment plants in the Paris region, interconnected via a dense 440 km sewer network. This wastewater is highly charged with organic matter. Water and sludge treatment processes generate odors, source of nuisances for nearby residents.
This is why the SIAAP, at the instigation of the State authorities, set up its first "Environmental Observatory" at the Seine Aval plant in 1991 in charge of the SIAAP's olfactory problems. The birth of nose juries and committees of volunteer local residents in 1993 have enabled a better understanding of odor phenomena. They are responsible for taking odor measurements in their homes and reporting nuisances. Still today, this system allows to be quickly informed of the nuisances experienced by residents and to objectify the nuisance (Diallo & al., 2018).
In order to comply with all regulatory requirements, the SIAAP has started a large program of redesign of the Seine aval plant. This program includes the containment of installations that were previously in the open air. It also includes setting up new treatment processes.
The installations containment drastically reduces the fugitive emissions from the equipments, however other problems remain. Indeed, a change in odors' nature was observed: sulfur or ammonia compounds are not always the main odor tracers originating from the new plant units (Laura Capelli & al, 2008).

Also, a change of paradigm becomes necessary, by evolving the plant measure network towards the identification of an olfactory imprint specific to each installation. For this purpose, the SIAAP's Impact Management Service (Service Maîtrise de l'Impact) decided to test an innovative technology, the electronic nose, on its Seine aval plant (Giorgio S. & all). The electronic nose Ellona Watch Tower (WT1) associates several non specific gas sensors (mainly Metallic Oxyde Sensors : MOS) with data treatment techniques using multivariate statistics (A. Panzitta & al, Nose 2022).

The test implemented at the Seine aval plant consisted of installing two electronical noses in channelled sources: one in the water treatment area, at the deodorization outlet of the nitrification-denitrification process (UPEI), one in the sludge treatment area, at the outlet of physico-chemical deodorization (UPBD). These two plants have diametrically different exhaust air treatment processes, both in terms of odor intensity and nature. The test objectives are to better characterize and quantify continuously the odor emissions of these two installations, while assessing the noses reliability and to use the obtained results to supply the SIAAP's odor emission model (SYPROS : Système de Prévision des Odeurs du SIAAP) (Ho Tin Noe I. & al, 2012).
As technical specifications, after a tuning phase, the prediction of odor concentration samples from each emission must be conducted in a blind way to match dynamic olfactometry results. The correlation algorithm will be accepted if 80% of the results predicted by the nose correspond to the odor measurement NF EN 13725 in EOU/m3, considering an extended olfactometric measurement uncertainty of ± 50%. Among 10 samples tested in the validation phase, 8 must fall within the correct measurement range, for a success rate of 80% minimum.

2. Materials and methods

2.1 SIAAP means for pollutants and odor monitoring

To follow up the nuisances generated by the SIAAP installations, the Impact Management Service uses different tools such as sensorial means, fixed sensors (follow up of the sulfur and ammonia compounds), mobile devices (laboratory trucks) and communications means used by the public to signal nuisances. Finally, the SYPROS tool enables to follow up odor emissions in almost real time and to make predictions (Venanci A & al, 2013).

2.2 Ellona solutions

Two dryer cabinets with WT1 e-noses (ELLONA) are installed at the Seine Aval facilities in channelled sources at the following locations (Figure 1). These two chemical deodorization processes work on the same principle of chemical washing of the stale air against the current and transfer of odorous compounds from the gaseous phase to the liquid phase (in the baths at the foot of the tower).

(a)

(b)

Figure 1. (a) Biofiltration zone (nitrification process); (b) Connection of Ellona dryer eated line to UPEI deodorization source

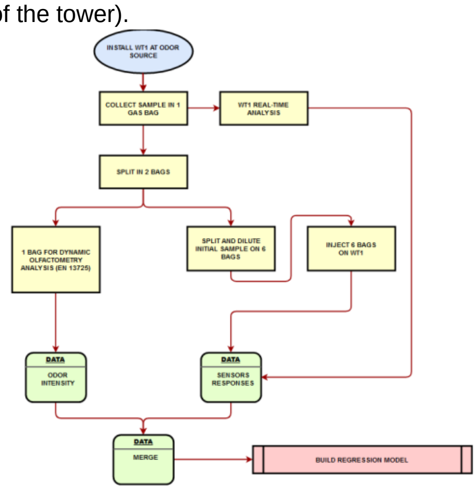


Figure 2. A diagram of the protocol designed by Ellona to ensure the training of the e-noses

Both installations consist of a single air treatment line with 4 washing towers each. However, it should be noted that these two installations have quite different modes of operation:

The nit-denit facility operates with softened water in towers 2, 3, and 4. Tower 1 is empty. The nominal flow rate is 89,000 N/m^3/h. The exhaust air to be treated is mainly composed of H_2S. The installation on the UPBD sector treats the exhaust air from the filter press building. Its nominal flow is about 5 700 Nm^3/h. Ammonia is the main gas present in the exhaust air to be treated. The system works with softened water in the 4 towers, and soda is added in tower 3.

The Dryer developed by Ellona is an accessory to the WT1 dedicated to the monitoring of air pollution in channelled sources. The solution enables sampling and conditioning of hot and humid gases and includes: a self-regulating heated transfer line of 2-meters length , a cooling dryer allowing to lower the dew point of the sample to +5°C and the elimination of the condensates thanks to a peristaltic pump, a sampling pump, and a WT1 analyzer.

For sampling, it offers a remotely controlled sample/reference air selection valve which enables to perform training of devices in controlled condition, an air purification cartridge to produce reference air and an input for the analysis of samples packed in nalophan bags by the WT1. The device switches the sample circuit between the sample channel (transfer line) and a reference air channel free of odorous compounds with a 3-way solenoid valve controlled by the WT1.

The reference air is produced from ambient air filtered on a cartridge packed with activated carbon and impregnated alumina beads. The cartridge ensures the removal of VOCs and oxidizing pollutants. The filtered air is then directed to the drying unit and the WT1 analyzer.

In this case, the WT1 IOMS's configuration for each unit contains 4 Metal Oxide Sensors (MOS) for odor prediction, a set of Electro-chemical (EC) sensors for Hydrogen Sulfide (H_2S), Ammonia (NH_3), mercaptans (RSH) for online quantification (Zarra T & al.2008), Photoionization Sensor (PID) with a UV lamp of 10.6 ev for Volatile organic compounds (VOCs) concentration and noise, temperature, humidity, and atmospheric pressure sensors. It is connected to the antenna mounted on the bottom plate of the dryer instrument, and connection to the data network is done with LTE-M communication using a local sim card.

Data acquisition, storage, and processing for online visualization are done on the Ellonasoft remote cloud platform that allows visualization of the electronic noses data with a record of one point every 10s, the creation of alert notifications, and algorithms using statistical mathematical models.

Ellona designed a protocol (Figure 2) to inject a sampling fraction collected from the sources, in order to ensure the training of the e-nose considering its range of variation. This is done with the preparation of a dilution fraction from the raw source to build a calibration curve with dynamic olfactometry data. The first e-nose learning process campaign (which took place simultaneously with dynamic olfactometry), included 5 days of learning campaigns from 17/03/2022 to 10/05/2022, followed by a validation campaign on 30/05/2022.

A second campaign to complete the data was performed on 26/07/2022 for UPBD and on 01/08/2022 for UPEI. The second validation campaign took place on 29/08/2022. Note that for this second campaign Ellona provided very precise sampling instructions, which allowed the sampling of significant data in only one day per site. This subject is further detailed in Section 3.1.

2.3 Monitoring Dynamic Olfactometry & regulatory method

The sampling protocol, allowing the e-noses to be trained following Ellona guidelines, was carried out by the EGIS Structures and Environment team, which has a laboratory accredited by COFRAC (French Accreditation Committee) in Aix-en-Provence (France). All the general provisions to be respected by the laboratory are described in the quality standard NF EN ISO/CEI 17025. The sampling and analysis method are detailed in the technical standard NF EN 13725. The air samples from the channelled sources were taken by tapping into the existing pipes. Once the sampling device is installed on the source, the sampling is carried out with a lung box system avoiding any contact between the sampled air and the pumping system. The sampled air is stored in odorless Nalophan bags (20L, 60L to 130 liters) and sent to laboratory for analysis.

Standardized olfactometric analysis is used for the learning phase of the e-nose and for the controls of the device's functioning. The olfactometric analysis finds the dilution factor to be applied to each sample to bring its odor to the detection threshold.

By definition, the detection threshold corresponds to 1 European Odor Unit per cubic meter of air (1 ouE/m3). The odor concentration of an odorant mixture (Cod) is obtained by multiplying the dilution factor (F) by the European Odor Unit (1 orE/m^3).

$$Cod = F \times 1 \text{ orE/m}^3 \qquad (1)$$

3. Results

3.1 Calibration and Models integration

Campaign 1 provided 24 samples from the UPEI sector. Among those samples, only 41% were coming from the outlet of deodorization source (raw emissions or dilution) with a range of odor concentration from 88 to 227 UO/m3. For UPBD, it provided 20 samples. Only 35% of them were coming from the outlet of deodorization source among which 2 samples at 181 and 1316 OU/m^3 , 2 batches were below 50 OU/m^3 and three batches' around 60 OU/m^3. Therefore, the dataset sampled during Campaign 1 was too poor to build a calibration curve covering the variation of odor intensity from each source. The results on blind validation for this dataset showed that out of the 10 blind batches, only three were coming from each channelled source and 2 scores from the prediction of the nose matched the olfactometry data (67% instead of 80%).

The second calibration campaign allowed to enrich existing data sets. The protocol was optimized by Ellona for one day for each sector and samples were collected at different periods of the day. Eight new samples (including raw, diluted fraction of raw emissions and duplicate) from UPEI deodorization were injected to WT1 and submitted to dynamic olfactometry, and 10 from UPBD considering filter press operations and debatizing were sent to laboratory.
The selection of data points for building a Partial Least Squares regression (PLS) on Ellonasoft allowed to reach a correlation score R^2 =0.94 for UPEI with an instrumental standard deviation of 39 OU/m3. For UPBD, the results showed R^2=0.97 with a fair SD (111 OU/m3) which can be improved by optimizing the time selection. Each model is stored in the device configuration as a new virtual sensor to transmit in real-time values in odor units from the source where the WT1 is located. This feature will provide prediction of odor units for the 10 blind samples.

3.2 Blind prediction validation

Table 1 and 2 present the results of blind sampling at each emissive source. The new algorithm allows validation of 100% of UPBD samples for odor concentration and 4 samples out of 5 for UPEI source, which fulfil technical specifications imposed by the contract, as 90% of success was reached. Sample 6121 is overestimated compared to the estimated odor unit. Since it is a mixed batch not directly measured by the analyzer in the source, some axis of investigation (sample preparation, injection) should help to understand the gap.

Table 1: Results of OU prediction for blind batches by the Ellona e-nose at UPBD sector

Label	Odor concentration measured by COFRAC laboratory (EOU/m3)	Lower limit for odor concentration to be predicted	Upper limit for odor concentration to be predicted	Odor concentration predicted by ellona nose (EOU/m3)
9378	<50	0	75	66
7429	120	60	180	79
6979*	213	106	319	252
6121*	95	47	142	274
1238*	239	119	358	294

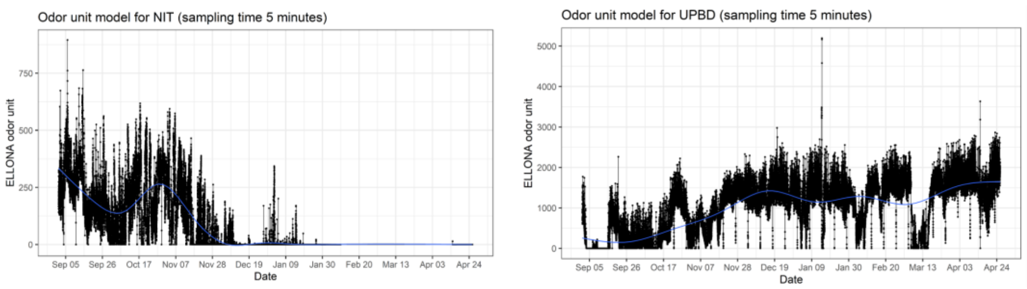
* Mixed batches.

Table 2. Results of OU prediction for blind batches by Ellona e-nose at UPEI sector

Label	Odor concentration measured by COFRAC laboratory (EOU/m3)	Lower limit for odor concentration to be predicted	Upper limit for odor concentration to be predicted	Odor concentration predicted by ellona nose (EOU/m3)
4305	782	391	1173	810
7579	1469	735	2204	1113
9257	1107	554	1661	1198
9415	930	465	1395	1164
9499	585	293	878	839

3.3 Online monitoring results

The validated algorithm allowed performing continuous measurement since September 2022. Figure 3 (plotted with R) shows the trends of odor unit concentration (OU/m3) at each source.



(a) *(b)*

Figure 3. (a) History of odor concentration (OU/m3) from September 1st,2022 to April 24th, 2023 at UPEI-nit (b). History of odor concentration (OU/m3) from September 1st,2022 to April 24th, 2023 at UPBD.

A campaign for odor unit evaluation at UPBD was carried out on 21/11/2022, at 13:30. The value read on the e-nose was in the range of the acceptability interval defined in the technical specification (490-1370 OU/m^3). The e-nose detected 1150 OU/m^3 versus 980 UO/m^3 from dynamic olfactometry. This value will be added to the existing model in the Ellonasoft platform to enrich the algorithm sample base.

For UPEI sector facility from September 2022 to February 2023 the average value is 196 OUE/m^3, corresponding to an odor concentration estimated as "very little persistent in the environment". The average concentrations of H_2S and mercaptan are also low: 0.03 ppm and 0.09 ppm, respectively. From the end of November onwards, an overall drop in odor concentrations at the deodorization outlet was observed. This phenomenon can be explained by a reduction in bacterial activity in the biofiltration basins connected to the drop in seasonal temperatures. Indeed, bacterial metabolisms decrease with the temperatures and this installation only treats the air extracted in the biofilters environment. This hypothesis will, however, have to be verified at the end of 2023.

For the UPBD sector, odor concentrations measured by the e-nose are slightly higher over the considered period: the value is 322 OUE/m^3 (454 OUE/m^3 from the beginning of November to April 25th, 2023) but remains below 500 OUE/m^3. They are therefore considered "very little persistent". Average concentrations of NH_3, H_2S, and mercaptan also remain low: 0.41 ppm, 0.01 ppm and 0.06 ppm respectively.

A closer examination of the operating conditions of the facility appears to show a variation in odor concentrations with the activity of the filter presses, with significant decrease in odor concentrations when there is no debatizing in the filter press building. Indeed, this process, allowing the production of "cake" is very emissive, especially in NH_3. These observations are aligned with the results observed during the first campaign of odor training that led to optimizing the sampling of emissions in the duct and adjusting sampling protocol considering debatizing cycles. In addition, since March 13^{th}, soda is no longer injected into the oxidobasic towers. The installation only works with softened water. The first results do not show increased odor concentrations at the process outlet. It is, however, too early to conclude on the relevance of this action.

Since the algorithms validation in September 2022, the e-noses enabled the initial objective of a continuous follow up of the installations, including automatic alarms when exceeding the regulatory thresholds. The odor concentrations issued from the e-noses are significantly more important at the UPBD area than at the UPEI area.

In the UPBD area, the majoritary component is ammonia of which 92% of data were validated for the period from September 2022 to January 2024, with an elevated variability in the measure, as the difference between minimum and maximum is high (0 to 7ppm NH_3). The concentrations of H_2S, CH_3-SH and NH_3 have in some periods great similitudes with odor concentrations. There exists a positive correlation between the number of debatizings and the concentrations in odor units. It is therefore a parameter that needs to be used to reduce odor emissions.

For the UPEI area, the e-nose data allowed the SIAAP to determine the abatement efficiency of this installation, with a 93% yield for H_2S. It has been shown that determining a correlation between the pollutants and the odor concentration is a more complex issue, due to the very low measured concentrations (< 1 ppm). The PLS algorithm also provided on the Ellonasoft platform might work better.

3.4 Odor modelling in Sypros platform

The expectation for the project is to enrich the data set of the current model from SIAAP's SYPROS platform and integrate e-nose odor measurements at channelled sources in the dispersion tool to predict the level of odor nuisance in the environmental area (Figure 5). This map shows odor perception at the location of a given resident with a prediction between 2 -3 OU. Simultaneously, the odor unit measured at UPBD was 1916 OUE/m^3.

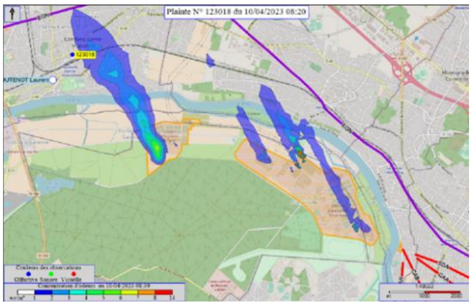


Figure 5. SYPROS Platform overview: example of mapping of source dispersion of SIAAP SAV sites and olfactory reporting of one resident (claim ID 123018) on April 10th, 2023, at 8:20.

4. Conclusions

Facing the evolution of odorant markers and to respond to a financial strategy, a progressive redesign of the existing measurement network of the Environment Department at SIAAP was undertaken. Ellona's WT1 electronic nose technology is identified as the most suitable to meet SIAAP's environmental monitoring needs. Indeed, these devices have real advantages: they are versatile and robust, allowing the continuous quantification of odors in situ. Equipped with MOS and electrochemical sensors, they can also quantify gases such as ammonia, VOCs, hydrogen sulphide and mercaptans. A gas dryer upstream of the equipment eliminates humidity problems. In addition, they are less expensive to purchase and require less maintenance compared to the traditional TRS measurement systems used at SIAAP for many years. Moreover, their quantification threshold is lower than that of the existing devices. The learning phase allowing the quantification of odors presents a certain number of operational and financial constraints given the cost of dynamic olfactometric analyses, and the required time and material to perform this operation. The learning methodology remains a key step to perform for a reliable operation of WT1.

The Ellona WT1 IOMS devices seem promising for the SIAAP's Impact Management Service: four new sources located at different places of the wastewater treatment plant Seine aval were also equipped with Ellona IOMS electronic noses. In parallel, some optimized sampling for dynamic olfactomettry will allow the training of these WT1.
Training IOMS devices requires a complete knowledge of source activity and its range of variation for odor concentration to optimize the preparation of sampling and prepare dilutions to inject in devices during collection of bags for dynamic olfactometry. For channelled sources, the results reflect the importance of using a DRYER allowing sampling at the emissions of sources for a better correlation between instruments and reference method with reasonable confidence.

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