

A COMPARATIVE STUDY OF REAL-TIME MONITORING DETECTION AND ACTIVE SAMPLING MEASUREMENTS IN EVALUATING EXPOSURE LEVELS TO AMMONIA

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ABSTRACT

Occupational exposure to ammonia is an important issue in the waste management sector, especially in composting and anaerobic digestion plants. In this sector, operators can be exposed to high contents of ammonia which is important to assess. The aim of this work was to provide a comparative study of two ammonia measurement techniques in the workplace air. The first one is an offline active collection of air samples that are then brought to laboratory for analysis and whose results are comparable to OELs. The second one involves real-time monitoring which is easy to deploy, allows for data to be processed both quickly and directly and to explain exposure peaks relative to workers' activity. These two techniques were simultaneously deployed in several anaerobic digestion-composting plants to assess operators' potential exposure to ammonia, and data were compared. Results show that there are linear correlations between concentrations obtained from both methods, with a trend to overestimate real concentrations in ammonia for several real-time detectors. This trend could however be explained by the time needed for exposure peaks to decrease. Real-time gas detectors, if cautiously used, are good investigation tools to quickly confirm or invalidate the presence of ammonia in the workplace atmosphere, and for both studying and optimising the workplace. The combination of both online and offline methods facilitates the analysis of a work area or station in order to improve the efficiency of prevention measures and to provide an accurate quantification of operators' exposure for compliance checking of OELs.

1. INTRODUCTION

Ammonia is found in elements of the natural environment such as the air, soil, water, plants, animals, and humans. It is also present in many household and industrial cleaners, and used in many industries. Examples of sectors where workers are at risk of being exposed to ammonia are: agriculture involving soil fertilizer; industry entailing the manufacture of fertilizers, rubber, nitric acid, urea, plastics, fibres, synthetic resin, solvents, and other chemicals; mining and metallurgy; petroleum refining; and food processing where a commercial refrigerant is used or where ice is produced, and close to cold storage and de-icing operations (NIOSH, 2019).

In the aforementioned sectors, the use of ammonia is deliberate, but in several other industrial sectors, ammonia is an undesirable by-product, particularly in waste management which involves composting and anaerobic di-

gestion (ADEME et al., 2019; Dirrenberger, 2020a; Poirot et al., 2010). Anaerobic digestion includes various processes where microorganisms break down biodegradable material in oxygen-free conditions. It offers the advantage of double valorisation of organic waste with (i) agronomic valorisation by spreading or composting digestate and (ii) energetic valorisation by producing biogas for direct or indirect energy. In waste and organic effluent treatment processes, the biodegradation of organic matter leads to ammonium (NH_4^+) production: this is the ammonification stage (Molletta, 2015). The subsequent transformation of ammonium (NH_4^+) into ammonia (NH_3) followed by its volatilisation is a physicochemical phenomenon boosted by basic pH, temperature increases, extent of exchange surface, and air renewal (Beck-Friis et al., 2003; de Guardia et al., 2010a, 2010b; de Guardia et al., 2008; Fukumoto et al., 2003). The release of ammonia into the atmosphere generally occurs throughout the treatment of digestates by dehydration

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and/or composting. It is often detected in very small concentrations before anaerobic digestion because of waste pre-fermentation, and in higher quantities after anaerobic digestion. The different steps in the global anaerobic digestion process in anaerobic digestion-composting plants are presented in supplementary Figure S1 (online edition).

Operators working in anaerobic digestion plants face several risks, including biological and chemical hazards and the risk of asphyxia and explosion of flammable substances (INRS, 2013). Chemical hazard is due, in particular, to the emission and presence of toxic gases like ammonia, hydrogen sulphide, and carbon monoxide (Dirrenberger, 2020a). The assessment of exposure levels to ammonia is a significant issue and exposure levels can be compared to Occupational Exposure Limits (OELs; see supplementary Table S1 in online edition) (INRS, 2016b, 2018). The level of personal exposure depends upon dose, duration, and work being done (NIOSH, 2019). Acute exposure to ammonia leads to caustic lesions of skin, eye mucosa, and respiratory tract (INRS, 2018). It can be responsible for high bronchoconstriction (likened to an asthma crisis) which can become permanent with the development of bronchiectasis (Sundblad et al., 2004). In humans, for a concentration in the air above 5 volumetric parts per million (ppm_v), some subjective symptoms such as eye discomfort, headache, dizziness, and a sensation of intoxication were felt. In cases of concentrations between 25 and 50 ppm_v , more subjective symptoms were observed in voluntary subjects without physical exercise or with alternating times of break and physical exercise: sensations of eye, nasal, throat, or chest irritation, the need to cough, a penetrating odour, nasal drying, trouble breathing, headache, nausea, dizziness, and a sensation of intoxication (ANSES, 2018). The first irreversible effects appear over a few hundred ppm_v . Chronic exposure at lower levels can lead to sinusitis, irritation of mucosa and conjunctiva, chronic bronchitis, and asthma-like conditions (Sundblad et al., 2004), right from an exposure as low as 100 ppm_v .

The anaerobic digestion plants are usually large, so equipping work areas and following up operators are both complex tasks.

Different methods are available in order to assess occupational exposure to ammonia, whether by air sampling followed by offline laboratory analyses or by direct measurement of concentrations with real-time detectors. The offline method consists of collecting air samples in the company, often trapped on sulfuric acid-impregnated filters, for subsequent analysis in the laboratory. Air samples can be taken from the worker's breathing zone when measuring personal exposure or at fixed points, at the height of the respiratory tract, when measuring ambient concentrations in work areas. They are analysed by ion chromatography (Bishop et al., 1986; INRS, 2016a; OSHA, 2002). A range of alternative methods is available with various sampling (acid-treated activated carbon tubes, acid-treated silica gel tubes, etc.) or analysis (spectrophotometry, ion selective electrode method) methods (Xu et al., 2020). The online method consists of recording instantaneous concentrations in ammonia with real-time detectors, before calculating average arithmetical values throughout the duration of

the measure (Bakhiyi et al., 2018; Dirrenberger et al., 2018; Pöther et al., 2021). To our knowledge, a link between offline (air sampling followed by laboratory analysis of samples) and online (real-time detection) methods for measuring atmospheric ammonia has not yet been investigated at occupational settings. To date, no comparative studies have been carried out for ammonia measurement techniques in the workplace air, including offline and online methods. However, such a study is needed to better appreciate the potential and usefulness of real-time measurement devices for assessing worker's exposure to ammonia, especially in occupational environments such as composting and anaerobic digestion plants.

The present study reports field measurement campaigns during which ammonia concentrations were measured by these two types of method (indirect active method for collection of air samples analysed "offline" in laboratory (INRS, 2016a); direct "online" method with registration of real-time concentrations by passive or active detectors (INRS, 2011)). The two methods were simultaneously carried out and compared for their measurements of ambient air, inside loader cabs, of personal levels on workers, and of the emissivity of matter. The use of real-time detectors highlighted a few advantages of these devices (manageable, easy to handle, immediate results acquisition, etc.), but also limitations (interferences, verification, calibration, data management, etc.). Some limitations, such as interferences for example, could be considered as advantages due to the possibility of a diverted use of the device, for a compound other than the one for which the device was intended.

The aim of the study was to compare and potentially correlate concentrations of ammonia in the air of anaerobic digestion plants measured by the offline method with those measured using real-time detectors. The objective was to develop a methodology which could be used in other sectors or extended to other contaminants, and adjusted according to the purpose of measurements. These elements were completed by an exploration of the limitations and advantages of real-time detectors for measuring occupational exposure to ammonia in the same sector, in order to take advantage of these good investigation tools without suffering their constraints.

2. MATERIALS AND METHODS

2.1 Description of sampling sites

The six anaerobic digestion plants (A to F) investigated in the present study were located in France (Table 1). They were chosen to give a proportionate sample of the variety of encountered processes and operation methods for waste treatment. Thus, these plants covered the whole types of dry anaerobic digestion processes used in France for domestic waste treatment (Dranco® [OWS, Belgium], Valorga® [Urbaser, Spain], Linde-BRV® [Linde-KCA-Dresden GmbH, Germany], Kompogas® [Vinci Environnement, Switzerland], BAL-HYBRID® [BAL Biogas, France]) (Damien, 2016; Dirrenberger, 2020b; Zeshan, 2012). They also use diverse pre-treatment and post-treatment methods.

2.2 Measurement strategy

The measurements were carried out in order to assess personal exposure levels and ambient concentrations for several airborne pollutants (ammonia, VOCs, bioaerosols, dusts, nitrous oxide, methane, carbon oxides, hydrogen sulphide). Stationary (work areas, loader cabs), personal, and emissivity measurements were performed. This paper presents results from ammonia sampling only.

Measurement campaigns took place between 2016 and 2018 in the six anaerobic digestion plants A to F (Table 2). They were performed in normal work conditions of the plants with possible short technical stops or failures. Each plant was visited once, except plant D, which was visited twice. Some concentrations of ammonia in the air of anaerobic digestion plants measured using an offline method were compared with concentrations obtained with online ones. The offline measurement method consists of sample collection and analysis after transportation to the laboratory as described in section 2.4.1. The online measurement method consists of measuring ammonia with real-time detectors; the 5 real-time detectors used in the study are detailed in section 2.4.2. Side-by-side comparison of online and offline methods was undertaken with both stationary and personal measurements. The comparison between data from the two techniques is validated for spatial and temporal accordance with the side-by-side measurements: cassette sampling and detectors must be positioned in the same place (tolerance of 20-30 cm) and for the same length of time (tolerance of maximum 2 minutes). Side-by-side comparison of online and offline methods was also performed for ammonia emissivity measurements taken from waste at various process phases.

Personal and ambient ammonia samples were collected over a continuous period varying from 3 to 8 hours during the same shift. As several real-time detectors were deployed at different steps of the anaerobic digestion process in parallel with the offline sampling devices, side-by-side comparisons of methods were possible. The measurement plan for these comparisons is presented in Table 2.

A total of nearly 400 measurement points were collected across six different plants over a period of almost two years. The number of samples collected at each site depended on several factors: number of premises, employees, or loaders, shift sometimes divided into several tasks inducing several samples for a same shift, etc. Emissivity measurements were performed at each site but offline method was used only at sites A and D (for campaign D2).

2.2.1 Personal exposure and ambient concentrations of ammonia

Stationary measurements of the ambient concentrations of ammonia were obtained in different work areas of the anaerobic digestion-composting plants in order to assess general contamination of the air at the premises (see supplementary Figure S2 in online edition). For that purpose, sampling and real-time measurement devices were generally positioned on tripods, at the height of the respiratory tract (i.e., to a height of about 170 cm from the floor) and in each work area (see supplementary Figure S2A in online edition). Measurement devices were also positioned in loader cabs, near the driver station (see supplementary Figure S2B in online edition).

For personal measurements, operators were equipped with a pump and a sampling head mounted in the workers'

TABLE 1: Summary of the main characteristics of the anaerobic digestion plants investigated and climatic conditions measured during the measurement campaigns.

Plant	Type of waste (tonnage)	AD ⁵ process	Sampling period	Mean T°C *	Mean HR % *
A	70,000 t MSW ¹ 30,000 t varied BW ²	Valorga®	October 2017	18°C	74%
B	30,000 t MSW ¹ 6,000 t varied BW ²	BAL-HYBRID®	March 2017	16°C	75%
C	70,000 t MSW ¹	Dranco®	May 2017	25°C	59%
D	30,000 t domestic BW ² 5,000 t varied BW ² 10,000 t GW ³	Kompogas®	December 2016 (D1)	8°C	78%
			September 2017 (D2)	19°C	87%
E	20,000 t OFMSW ⁴ 20,000 t GW ³ 4,000 t varied BW ²	Linde-BRV®	April 2017	15°C	72%
F	85,000 t MSW ¹	Valorga®	November 2018	21°C	70%

¹ Municipal Solid Waste; ² BioWaste; ³ Green Waste; ⁴ Organic Fraction of Municipal Solid Waste; ⁵ Anaerobic Digestion

* Measured in ambient air on site during the campaigns

TABLE 2: Number of side-by-side comparisons through offline/online methods for ammonia measurements performed during the different campaigns in the anaerobic digestion composting plants.

Campaign	A	B	C	D1	D2	E	F
Stationary sampling	7	6	9	9	8	-	8
Personal sampling	14	14	9	27	6	6	14
Loader sampling	3	6	8	-	2	7	9
Emissivity sampling	17	-	-	-	12	-	-
Total measurements	41	26	26	36	28	13	31

breathing zone (see supplementary Figure S2C in online edition). All workers under observation held several real-time detectors in addition to the aforementioned offline measurement devices and passive badges.

2.2.2 Measurement of ammonia emissivity from waste

In order to better understand the origin of ammonia concentrations in the air of the workplace, it is important to measure ammonia emissivity from waste stored in the different premises at various steps of the process. These measurements allow to assess or explain pollution levels of premises as a function of quantities of stored materials, premises volume, and air renewal. Emissivity measurements were performed to better understand pollution of the premises and provided another opportunity to perform side-by-side comparisons between offline and online methods.

For that purpose, a measuring device was designed from elements used to measure exposure: sampling pumps, a real-time detector, and a plastic bucket with a lid (see supplementary Figure S2D in online edition). Emissivity measurements were therefore obtained using the online method. In two campaigns, sampling measurements were also collected in parallel on filters using an offline method, to ensure that real-time NH₃ concentration measurements were valid, allowing side-by-side comparisons of methods.

2.3 Transport and preservation of samples

Ammonia sampling cassettes were stored in closed boxes at ambient temperature during the campaign (maximum 3 days) and until they were analysed (maximum 2 months).

2.4 Methods for the measurement of ammonia

2.4.1 Offline active method

Ammonia was sampled on a sulfuric acid-impregnated quartz filter mounted in a two-stage 37 mm diameter closed-face cassette (CFC). The CFC was connected to a portable sampling pump (Gilian 5000, Sensidyne, USA) and sampling was performed at a 1 L/min flow rate and for up to 8 hours. Occasionally, a 2 L/min flow rate was used and the sampling time was reduced to a maximum of 4 hours. Thus, the average volume of air sampled is generally close to 0.5 m³. After sampling, impregnated filters were desorbed with 20 mL of Ultrapure Water. After filtration (MILLEX

filters 0.22 µm) and 10-fold dilution, analysis was performed by means of ion chromatography (METROHM 881 COMPACT IC PRO with METROSE0 C3 column), without a suppressor device and with a conductivity detector (INRS, 2016a). The linearity range for this device is between 0.40 and 660 mg/L in solution, the detection limit is 0.04 mg/L and the quantification limit is 0.11 mg/L. Average ammonia concentrations (C_{moy}) were calculated after analysis, expressed in mg.m⁻³ of air sampled, and then converted into ppm_v through calculation, using the molar volume/molar mass ratio.

2.4.2 Online method

Real-time detectors deployed during the measurement campaigns were chosen for their different characteristics (measuring range, weight of the device, portability, etc.), which led to assign each model to a specific task:

- Multi-gas active detectors (MultiRAE®, RAE, France) were mainly used for ambient air measurements. Indeed, they are heavier than others and less suitable for being held by workers.
- Other multi-gas active detectors (QRAE3®, RAE, France; BW GasAlertMicro5®, BW Technologies Honeywell, France) and VOC passive detectors (CUB®, ION Science, France) were used for individual measurements. They are lightweight devices and their portability is well-suited to obtaining individual samples. CUB® detectors are especially designed for VOCs but are sensitive to ammonia.
- Ammonia passive micro-sensors (Cairsens®, Envea, France) were used for loader cab measurements. Their weaker measuring range provides greater accuracy and is well adapted to cabs, assuming that they contain lower concentrations.

For ammonia detection, the most common form of sensor is electrochemical, which is the case for all cells used for ammonia in this study (ammonia cells from MultiRAE®, QRAE3®, BW GasAlertMicro5® and Cairsens® detectors). In this type of sensor, ammonia leads to a redox reaction which induces an electric current that is proportional to quantity of ammonia molecules entering the cell (INRS, 2011). For VOC detection, PID lamps were used (BW GasAlertMicro5PID® and CUB®). The main specifications of the different detectors used are given in Table 3.

TABLE 3: Main specifications of real-time gas detectors used for ammonia and VOC measurements during the measurement campaigns.

Gas	Model	Measuring range (ppm _v)	Resolution	Weight (g)	Autonomy (h)	Recording interval (s)	Measuring technique	Mode
NH ₃	MultiRAE®	0-100	1	880	12	1-3,600	Electrochemical	Active
	QRAE3®	0-100	1	410	11	1-3,600	Electrochemical	Active
	BW GasAlert Micro5®	0-100	0.1-1.0	370	15	1-127	Electrochemical	Active
	Cairsens®	0-25	0.5	55	> 24	60-3,600	Electrochemical	Passive
COV	CUB®	0-5,000	0.1	110	16	1-3,600	PID	Passive
	BW GasAlert Micro5PID®	0-1,000	0.1-1.0	370	15	1-127	PID	Active

The devices are provided with an internal clock, which is synchronised with a single source. They also have an internal recorder whose frequency is configurable (see “recording interval” in Table 3). Before each campaign, detectors were verified and calibrated, if necessary, with two points: (i) “zero point” performed in clean air (calibration) and outside in the field (verification); and (ii) “reference point” performed with a bottle of standard reference gas - NH₃, 50 ppm_v air balance – equipped with a pressure control valve. During each campaign, this procedure was reiterated at the end of each shift, when the workday was over. This step is time-consuming, insofar as each verification needs several minutes due to the response time of an ammonia electrochemical sensor being in the order of a minute. In addition, before any verification, the detector must have run in clean air for at least five to ten minutes. If the second verification was compliant (gap lower than 10%), recorded measurements were validated and used. Otherwise, measurements were rejected.

The arithmetical average (C_{moy}) value of a relevant detector was calculated and expressed in ppm_v.

2.4.3 Emissivity offline and online methods

The measuring device implemented for emissivity measurements used the following elements: sampling pumps (Gilian GilAir Plus®, Sensidyne, USA), a real-time detector (BW GasAlertMicro5®, BW Technologies Honeywell, France) (INRS, 2009), and a plastic bucket with a lid (15 L dosing bucket available from DIY shops). A pump was used to draw air from the container (with an air flow rate $Q_{\text{spl}} = 1$ L/min), and then one or more additional pumps diluted the sample (up to 15 times) to reduce the moisture content and ammonia concentration, ensuring non-saturating values for the analyser. To ensure that the inlet air was not charged with pollutants, the measurement device was installed outdoors. Whatever the material analysed, the container was always filled to the same level (15 cm) and swept at the same sampling rate ($Q_{\text{spl}} = 1$ L/min). Consequently, in the absence of other changes, the emissivity of materials was comparable between sites.

Concentrations were measured after the container outlet had reached a steady state. The time required to attain this state was governed by the time constant of the air exchange in the dead volume of the bucket ($V_m = 8$ L). Under the hypothesis of perfect mixing type flow, a duration equivalent to three time constants (V_m/Q_{spl}) would be required to reach 95% of the final concentration value, i.e., 24 min. Thus, a waiting time of approximately 30 minutes was systematically applied.

In two of the campaigns, ammonia emissivity levels from matter were also measured with an offline active method (INRS, 2016a) to allow comparison between data from the two techniques and to potentially correlate them.

2.4.4 Complementary measurement methods

Temperature and relative hygrometry of the air were monitored using a thermo-hygrometer device (Testo 635®, Testo, France) which operates at temperatures ranging from -20 to +50°C (resolution 0.1°C) and at the hygrometry range from 0 to 100%HR (resolution 0.1%HR).

From a measurement cost point of view, offline measurement requires consumables, pumps that need to be maintained and an analytical chain based on ion chromatography (which also requires skilled employees for this analysis). The investment needed for offline measurement can represent several tens of thousands of euros, plus a few thousand euros for maintenance, calibration and consumables. Online measurement represents much lower investment costs (a few thousand euros depending on the instrument) and, even with the addition of maintenance and calibration costs, will remain at a more advantageous cost price.

2.5 Statistical analysis of data

For each type of measurement (ambient air of work areas, on workers, in loaders), mean concentrations collected on filters were plotted as a function of values obtained with real-time detectors in the same place and at the same time. Linear correlations were drawn to calculate slopes and coefficients of determination R^2 . In brief, when methods were equivalent, slopes would be close to 1 in each case and the straight line should cross the abscissa axis near zero. The closer the coefficient of determination is to one, the better the linear correlation.

To complete this analysis and determine statistical significance, Fisher's test and Student's t-test were used. Differences were considered significant if the p-value was 0.05 or lower.

3. RESULTS AND DISCUSSION

3.1 Side-by-side comparison of online and offline methods

Results from the approximately 200 comparison points between offline and online methods were gathered by measurement type, namely ambient air, individual, loader cabs and emissivity measurements.

Note that in the case of ammonia measurements, measuring range does not exceed 100 ppm_v for MultiRAE®, QRAE®, and BWGasAlertMicro5® detectors. Results presented on Figure 1d show concentrations up to 250 ppm_v due to dilution of the sample – up to 15 times (cf. section 2.4.3).

3.1.1 Ambient air sampling

Comparison between stationary measurements of ammonia using the online method (detector type MultiRAE®) and the offline method (CFC method with impregnated filters) is shown in Figure 1a. The results show a significant and positive linear correlation ($n=39$; $R^2=0.98$; $p=0.68$) between the average response provided by real-time detectors and measurements from impregnated filter samples. They also reveal an overestimate of 30% in average of ammonia concentration given by real-time detectors, as compared to the average determined by the offline method developed at the institute and described in section 2.4.1 (INRS, 2016a).

3.1.2 Loader cab sampling

Samples were taken in loader cabs using the Cairsens®

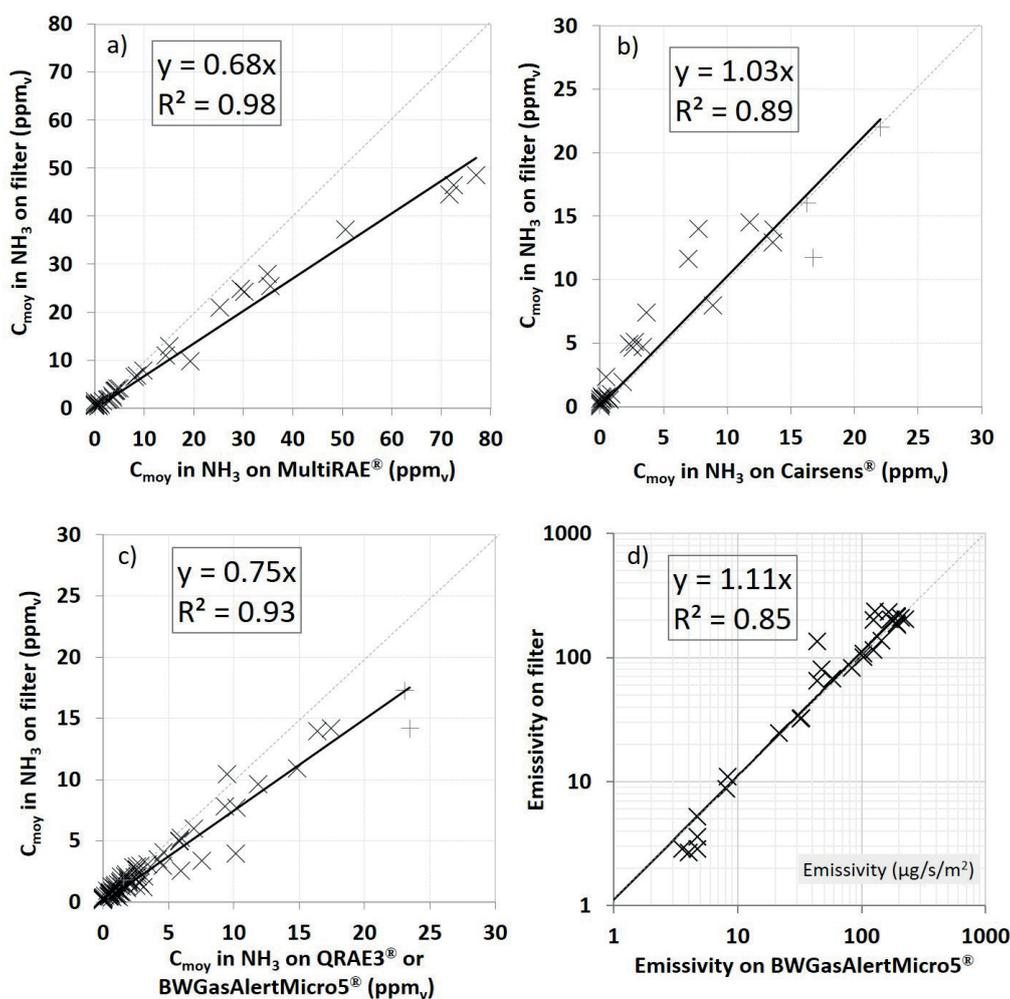


FIGURE 1: Comparative offline/online measurements of ammonia in anaerobic digestion plants. a) Stationary measurements performed in ambient air for MultiRAE® active detectors vs NH₃ CFC cassettes (n = 39). b) Stationary measurements performed in loader cabs for Cairsens® passive detectors vs NH₃ CFC cassettes (n = 29+3). c) Individual measurements performed close to workers' respiratory tracts for QRAE3®[cross symbol]/BW GasAlertMicro5®[plus symbol] active detectors vs NH₃ CFC cassettes (n = 88). d) Emissivity measurements from materials for BW GasAlertMicro5® active detectors vs NH₃ CFC cassettes (n=29).

detectors, except for three additional measurements (represented by plus markers) which correspond to ambient samples with average concentrations higher than 15 ppm_v. A comparison of side-by-side measurements shows a linear relationship (Figure 1b) between the average response provided by real-time detectors and measurements from impregnated filter samples (n=29+3; R²=0.89; p=1.03). Insofar as the calculated slope is close to 1, that implies that performed measurements by both online and offline methods give comparable concentrations. It is worth noting that this sensor model has a lower measurement range (0-25 ppm_v) and works in a passive mode (a small air stream ensuring a simple air brewing).

3.1.3 Personal sampling

When measuring personal samples, pairs of data are correlated (Figure 1c) and a linear relationship can be defined (n=88; R²=0.93; p=0.75) between averages calculated from online measurements (detector type QRAE3® and BW GasAlertMicro5®) and averages from offline corresponding

samples on filters for NH₃. Based on the overall measurements, this trend line illustrates an overestimate of about 30% in average of ammonia concentration that is given by detectors, in comparison to the average determined by the offline method (INRS, 2016a).

3.1.4 Emissivity measurements

Results obtained show that the two methods are equivalent (n=29; R²=0.85; p=1.11) in the case of emissivity measurements (Figure 1d). It is worth reminding that a waiting time of approximately 30 minutes was applied to reach the steady state before starting offline and online measurements. This delay, necessary for the stability of the measurement, allows to avoid potential overestimation from real-time detectors which seems to be observed with ambient air and personal sampling.

No significant differences were observed between offline and online values with Student's t-test.

These correlations consolidate the possible use of such a device in quickly assessing, and with a wider safe-

ty margin, the presence of problematic concentrations of ammonia for occupational safety and health of operators.

3.2 Overestimation of the ammonia concentration with various detectors

The comparison of average ammonia concentrations provided by direct reading devices and results from offline method samples shows a linear correlation between the two techniques for all measurements. Nevertheless, the observed trend is that real-time active detectors overestimate ammonia concentrations for ambient and individual measurements, compared to the offline method.

A possible explanation for this overestimation is the time required for the concentration to decrease to zero after exposure. This time is directly connected to electrochemical cells. Figure 2 shows an example of an exposure peak of ammonia during a worker's follow-up. The gap between the recorded (detector data) and theoretical (if increasing and decreasing of the signal were equivalent) profiles could explain that average ammonia concentrations calculated from the values stored by real-time active detectors is about 30% higher than concentrations obtained from filter analysis. This explanation is supported by emissivity measurements, for which a waiting time of approximately 30 minutes is required to obtain equivalence between offline and online methods.

Then again, the results seem to depend upon which detector was in use, as offline and online methods are approximately equivalent in the case of loader cab measurements, for example, with Cairsens® detectors (Figure 1b). It is therefore useful to have a good working knowledge of the used devices and their characteristics and to ensure that the measurements are robust by using several control offline samples. A possible overestimation is, however, consistent with prevention.

3.3 Advantages and limitations for the use of detectors in occupational settings

3.3.1 Advantages of real-time detectors

The examination of the real-time profile allows the observation of peaks of concentrations.

As shown on Figure 3, a real-time detector profile provides a common approach to a worker's exposure: ammonia concentration is time stamped. It is also possible to link an exposure peak to a specific task or to the specific location of an operator. The use of video or spatio-temporal positioning tools allows for this peak analysis to be automated. In Figure 3 of the example, the worker is exposed over more than six consecutive hours to an ammonia concentration of 2.3 ppm_v according to the offline method and 2.6 ppm_v according to the online method (QRAE3® detector), both methods being simultaneously deployed. Although global exposure to ammonia is rather weak, real-time detection highlights three main peaks responsible for this measured content, with high values that could be deleterious for the operator being observed (the two first peaks, higher than 80 ppm_v, are due to emptying of plenums in a technical gallery).

The study allows to summarise the main advantages of real-time detectors as follows:

- Manageable, easy to handle, light devices. Modern devices are continuously improved to be smaller, lighter, easier to deploy, and used with user-friendly software (Table 3).
- Measurement of ammonia concentration is nearly instantaneous. The standard response time for electrochemical cell sensors is about one minute. They are also suitable for ensuring a function of safety detectors for operators. To help with this, a configuration of the alarm setpoint with a reference value is required. Thus, the chosen setpoint could be the STEL value (see supplementary Table S1 in online edition), provided detailed instructions are observed when the alarm goes off, such as area evacuation or installation of Respiratory Protective Equipment (RPE).

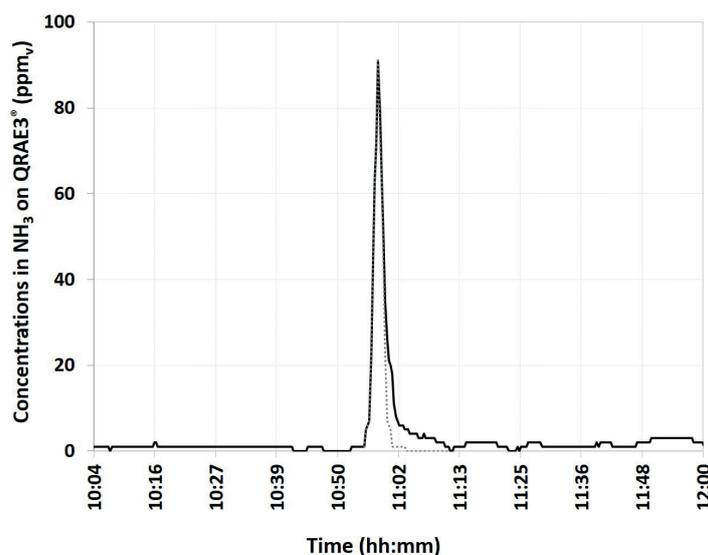


FIGURE 2: Example of an exposure peak of ammonia during a worker's follow-up. Detector signal = black solid line ; Theoretical profile = grey dotted line.

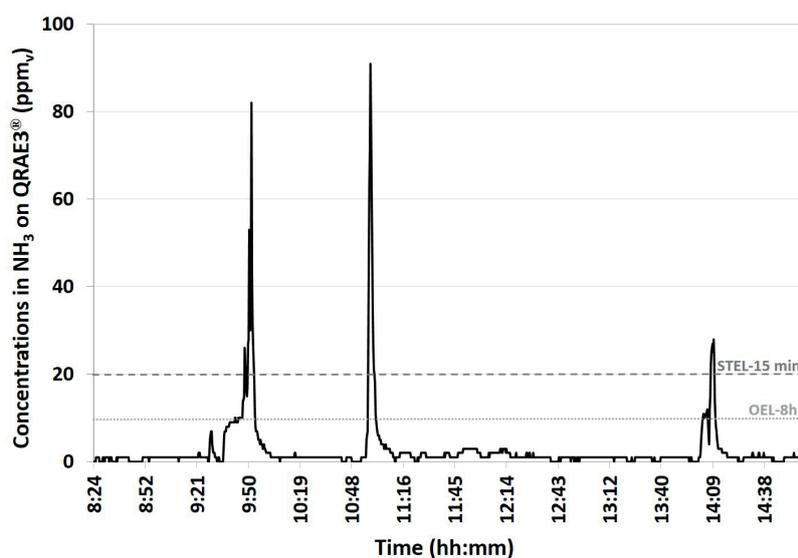


FIGURE 3: Example of a worker's exposure profile (online QRAE3® vs offline NH₃ CFC cassette).

- Determination of an operator's exposure profile or a specific area pollution profile.
- Immediate results acquisition. All the detectors deployed during these measurement campaigns are configurable via their own software interface. The recovery and treatment of recorded data takes only a few minutes for each device.

3.3.2 Limitations of real-time detectors

The use of real-time detectors also presents a few disadvantages that can produce meaningless results if they are not taken into account:

- Occurrence of possible interfering substances. The knowledge of all present gaseous compounds in investigating atmosphere is essential. Indeed, a fully selective sensor does not exist: some compounds can positively or negatively affect a measurement. The list of main interfering substances is not always accessible to users, but suppliers of devices must be able to positively comply with any such request. Thus, for example, according to the manufacturer's documentation, the sensor used in QRAE3® detectors is sensitive to the presence of a few ppm_v of hydrogen sulphide and of large quantities of carbon dioxide (> 5%V). It is not sensitive to gases such as carbon monoxide or dihydrogen. These elements are true in the case of new and fit sensors.
- Need to verify and calibrate detectors according to the best practice rules. These operations require skilled staff and specific material: standard gas, expansion valve and suitable pipes, calibration mask or automated test station. It is essential to periodically verify devices and to set a tolerance concerning detector response during the verification step. If the verification result is outside of the documented tolerance, it is impossible to use the measurements to discern exposure levels. For example, in the case of this study, detectors were verified with two points: a "zero" or without ammonia atmosphere point and a "reference point" performed

with a bottle of standard reference gas - NH₃, 50 ppm_v air balance. Verification is validated if a given detector response is between 45 and 55 ppm_v.

3.3.3 Investigation of interference occurring with PID

The study of the evolution of concentrations over time provided by the real-time detectors has allowed to identify important characteristics that need to be taken into account when deploying such instruments in occupational settings. In the present study, the detection principle of the detectors used was based on an electrochemical sensor or Photo Ionization Detectors (PID). Indeed, two models of PID were used: BW GasAlertMicro5® and CUB® (10.6 eV lamp, calibration with isobutylene 100 ppm_v, measurement range of 0 to 1000 ppm_v for BW GasAlertMicro5® and 0 to 5000 ppm_v for CUB®).

The measurements made with the BW GasAlertMicro5® detector provided interesting data. The BW GasAlertMicro5® detector was mounted with an electrochemical sensor for ammonia quantification and a PID sensor for the estimation of organic vapours. The two sensors had the further advantage of being synchronous. The deployment of this detector equipped with these two types of sensors was carried out on a maintenance operator during campaign D1 (Table 1). The result showed that both sensors present very similar concentration profiles, with a proportionality factor close to 7 in favour of the PID (Figure 4a). In such a situation, the PID sensor response can be attributed only to the presence of ammonia in the work atmosphere. Another side-by-side comparison was also carried out with a PID (CUB®) and an electrochemical sensor (mounted on QRAE3® detector) operating synchronously for ammonia quantification during all campaigns. The example presented in Figure 4b corresponds to a maintenance operator in plant C. The result showed that both sensors also present similar concentration profiles, with a proportionality factor close to 8 in favour of the PID but with two strong differences when considering concentration peaks revealed by the

PID (Figure 4b). Indeed, the two peaks occurring near 6:40 and 7:55 can be explained by the presence of organic vapours and were not therefore due to ammonia contribution.

The most common form of sensor used to detect ammonia is an electrochemical sensor (Timmer et al., 2005). PID such as the CUB® detectors are especially designed for VOCs (INRS, 2009; Spinelle et al., 2017) but are sensitive to some inorganic gases such as ammonia (ionization energy for ammonia: $10.070 \pm 0,020$ eV (Handbook of chemistry and physics - CRC, 2008). Note that PID response is given in isobutylene equivalent (C_4H_8), this gas being used for verification and calibration of this type of sensor. Thus, the exploitation of PID results is complex in the present case, insofar as it is not possible to determine whether a PID sensor reaction is due to ammonia or organic vapours. Two solutions allow to overcome this potential problem. The first is to use detectors that deploy both an electrochemical sensor for quantifying ammonia and a PID sensor for estimating organic vapour levels (for example BW GasAlertMicro5® detectors). The second solution is to use two distinct detectors, but to synchronise them with the

same time reference (for example QRAE3® and CUB®).

Therefore a PID sensor sensitivity to ammonia makes this a useful tool for evaluating workers' exposure to this deleterious gas. Indeed, in the absence of an electrochemical sensor for measuring ammonia concentration, the use of a PID which is equipped with a 10.6 eV lamp can allow to estimate ammonia concentration (by multiplying by a factor 8-10), provided that there are no organic vapours in ambient air.

In summary, the advantages and possibilities offered by real-time detectors make them essential to occupational health and safety experts as part of their mission to assess operators' exposure to gaseous compounds. Nevertheless, the use of these devices and the exploration of the results arising from them require technical means and trained personnel. If all precautions are taken, the use of real-time detectors, associated with some reference samples collected following the method developed at the institute (INRS, 2016a), enables a reduction in the number of lab analyses and therefore quickly obtains spatial and temporal information. However, it is worth noting that only

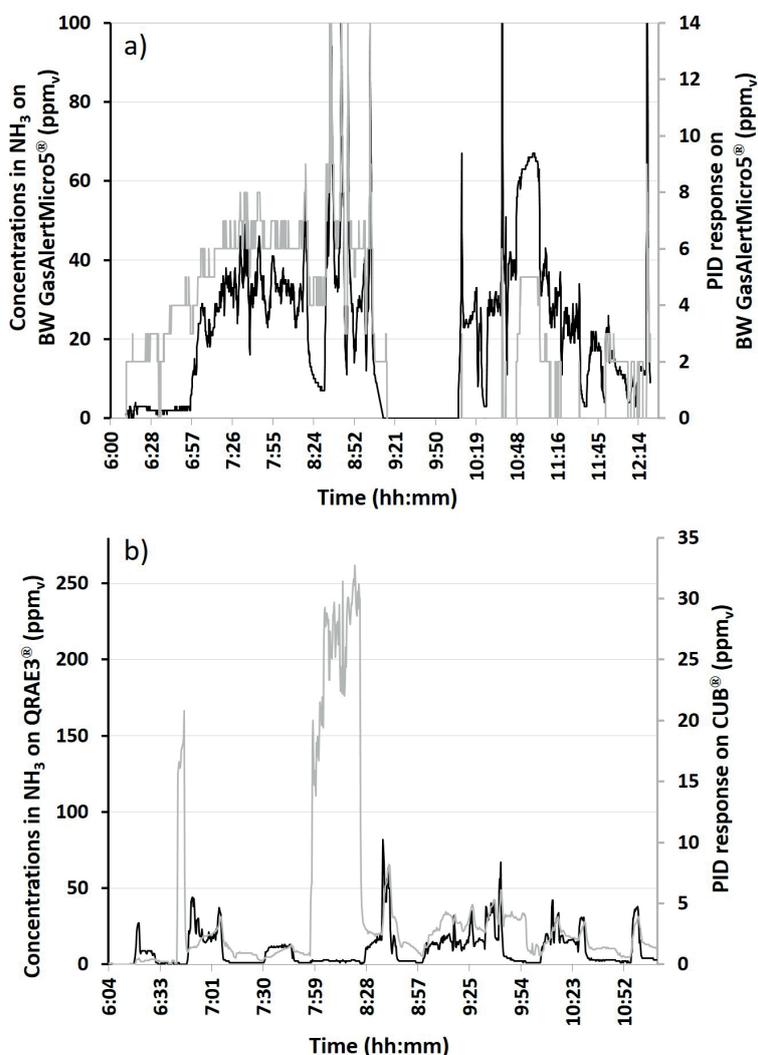


FIGURE 4: a) Examples of a worker's exposure profile : a) from a BW GasAlertMicro5® detector (NH_3 /PID sensors) ; b) from QRAE3® (NH_3) and CUB® (PID) detectors. NH_3 sensor response = black line ; PID sensor response = grey line.

the offline method provides measurements that are comparable with OEL values. Detectors could also not fully substitute offline methods, namely due to the unidentified interfering substances present in the workplace atmosphere which could impact sensors.

4. CONCLUSIONS

Correlations between concentrations of ammonia in the air of anaerobic digestion plants measured by both offline and online methods were investigated. Measurements allowed to calculate linear correlations between concentrations obtained from both methods, showing that it is possible to use real-time gas detectors equipped with ammonia electrochemical sensor to assess potential exposure of an operator or pollution of a work area with ammonia, insofar as these devices have been verified and calibrated beforehand.

Real-time gas detectors are good investigation tools for occupational health and safety experts who would like to quickly confirm or invalidate the presence of potentially expected gases in the workplace atmosphere. They are also useful tools for both studying and optimising the workplace.

The limitations and advantages of real-time detectors have been highlighted in the case of assessment of occupational exposure to ammonia in the anaerobic digestion sector. These detectors are easy to use and to deploy and provide nearly instantaneous measurements associated with exposure profiles. However, substances in the atmosphere might interfere with them, thus distorting exposure measurements. If aware of this possible limitation, a user might take advantage of this feature, for example, by using a detector to find a pollutant it is not primarily designed to detect.

The combination of both online and offline methods facilitates the analysis of a work area or station on the one hand in order to improve the efficiency of prevention measures, and on the other hand to provide an accurate quantification of operators' exposure for compliance checking of OELs. This methodology could be used in other sectors, such as the food industry, and could be extended to other contaminants.

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