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Can Electronic Noses be Used to Control Odour Abatement Measures in Sewers? – Approach by Testing 4 Multigas-sensor Systems under Realistic Conditions

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Four Multigas-sensor systems (so called electronic noses or e-noses) with different sensors and configurations were tested over a period of 6 months at a sewer research plant of the Berliner Wasserbetriebe. They were exposed to different realistic process conditions. The objective was to analyse the applicability of electronic noses for the control of odour abatement measures in sewer systems. In order to describe the relation of the sensor signals to the odour, olfactometric and hydrogen sulphide (H_2S) measurements were conducted. In the context of the data-mining process, the results were statistically evaluated. The best correlation coefficient for Linear Regression was 0.56 (e-nose D) whereas the results of Discriminant Analysis and Logistic Regression revealed that three of four e-noses are able to differentiate with regard to a level of 500 ou/m³. Results on response time and repeatability showed a general practicability of e-noses for dosage control. The performance of the e-noses seems to depend on the system configuration (gas preparation, type of sensors).

1. Introduction

Sewer operators are challenged to tackle increasing odour and corrosion problems arising in sewer networks. A variety of methods are available to avoid, reduce or control these problems. These are e.g. preventive measures in the liquid phase or measures to treat or conduct the odorous air after the transport to the gas phase (PREPARED, in preparation). Liquid phase measures are widely used and include the addition of chemicals to oxidize, bond or reduce the production of odorous and corrosive compounds. The dosage of chemicals however, often does not consider the problem (e.g. odour or problem of hydrogen sulphide H₂S) or the objective is not clearly defined. Empirical or static dosing and the lack to respond to changing odour conditions in sewers often leads to overdosage during periods with low odour levels or underdosage of chemicals – both cases being unfavourable in terms of costs for chemicals based upon online measurements of relevant parameters (e.g. odour) could achieve more cost-efficient control (Frey, 2010). Multigas-sensor systems (electronic noses, e-noses) which deploy several sensors may help to quantify and characterize odour problems for the control of odour abatement measures in sewer systems. Investigations (e.g. from Stuetz *et al.*, 1999; Giebel,

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The objective of investigation is to give a statement on the applicability of e-noses for the control of sewer odour abatement measures, especially the additive dosage. The possible added value compared to conventional measuring systems (e.g. H_2S measurements) should be identified.

2. Methods

2.1 Control of odour abatement measures and definition of requirements

An appropriate planning of measures involves an analysis in a first stage in order to define the problem (complex odour problem or problem of single substances; continuous or sporadic) and to identify the source of the problem (e.g. indirect dischargers). The choice of measure then needs to be based on the objective definition (e.g. reduction of odour nuisance, total elimination of odour sources). Finally, the efficiency of the measure needs to be monitored (Frey, 2008). Additive dosing based upon online measurements of odour could provide a valuable tool for an efficient application of chemicals.

Precondition for the application of electronic noses for dosage control is that they can deliver values which represent the actual odour. Further the e-noses should deliver reliable values and quickly respond to changing odour conditions. Finally the advantages to other (cheaper) measurement systems like H_2S -measurement devices must be checked. Provided that the criteria are positively answered, the e-nose systems are regarded as useful for controlling additive dosage.

2.2 Test of electronic noses

Four electronic noses with different sensors and configurations (key data see Table 1) were parallel tested in a sewer research channel from the Berliner Wasserbetriebe over a period of 6 months. The enoses were utilized in an offgas volume flow, measuring air, drawn from the sewer research plant, which consists of an accessible, 25 metre, DN 400 channel. The gravity channel was fed with real wastewater from a nearby pumping station. Two abatement chemicals (calcium nitrate and ferrous chloride) were dosed into the wastewater. The e-noses were connected to sealed openings from the sewer channel. Additional tests were conducted using sample bags filled with sewer air. In order to describe the relation of the sensor signals to the odour concentration, olfactometric measurements were conducted throughout the test phase. The sampling procedure was thoroughly documented and exactly synchronized to the different measuring cycles of the e-noses. Hydrogen sulphide (H₂S) was parallel measured with a specific sensor as well as grab samples for gas analyses (mercaptane, dimethyl sulphide, and ammonia) were conducted. The incoming wastewater was analysed for following parameters: pH, temperature, oxygen, COD, BOD₅, sulphide, sulphate, and conductivity.

E-nose	A	В	C (Usage of 2 identical e noses in serial*)	D
Type & amount of sensors	3 MOS, 2 EC, 1 PID	8 QMB, 2 EC	8 MOS, 2 EC	10 MOS
Measuring mode	Continuous	Batch-mode	Continuous	Continuous with purging phases
Measurement interval	Adjustable (from 1s)	Depends on settings of measuring cycle	Adjustable (from 1s)	1 s (purging for 5 min every 90 s)
Sample gas preparation	Filter, Heating, Drying, Dilution	Cooling, Filter, Thermal desorption	none	Automatic dilution

Table 1: Key data of the four tested electronic noses

* Later indicated as e-nose C (lower), e-nose C (upper)

3. Results

3.1 Odour measurement with e-noses

Within the field of odour measurement with e-noses, the validity and the reliability of a measurement has to be checked. Concerning validity, the question arises whether the sensor values are in any relation to the odour. The answer to this question can partly be given by the results of a mathematical evaluation, when sensor signals are compared to olfactometric analyses (odour concentration). It is important to keep in mind that the uncertainty of olfactometric analyses can be estimated to be 50 % (Boeker, 2004). The results of a mathematical analysis also depend on the experimental design, on the e-nose signals assigned to the odour measurements and on the odour substances. For the mathematical evaluation, Linear Regression, Logistic Regression and Discriminant Analysis were used. Before application of a procedure, it has to be proven that the respective hypotheses are acceptable. Normally, in the case of Linear Regression a normal distribution and no interaction between the explaining variable, here each sensor, are assumed. The target variable, here the odour concentration, should be metric. For the use of Discriminant Analysis and Logistic Regression, the target variable can only be used in categories. This means that these procedures are able to decide whether the odour concentration is above or below a given level. Table 1 lists the total data set used for mathematical evaluation.

Table 1: Overview of the number of paired values (parallel olfactometric samples and e-nose readings)

E-nose	А	В	C (lower)	D
Number of samples	147	152	161	232

First of all, the samples differ in size for each e-nose (see Table 1). Hence, only under the condition of similarity between the samples in regard to the odour substances the comparison between them is possible. Furthermore, the different number of sensors has to be considered by correcting the measurement of correlation R^2 . The R^2 has to be understood as a measurement of correlation between sensor data and odour measurements. The range of R^2 is normally between "0" and "1". After correction of the number of sensors it could be even negative. Table 2 summarizes the results.

E-nose	R²
А	0.27
В	0.36
C (lower)	0.35
D	0.56

Table 2: Overview of the results of the Linear Regression

E-nose D is able to explain at least 55 % of the variance of odour measurement. The other e-noses show correlations with R^2 below 0.36.

Another possibility to use e-noses in combination with odour abatement measures is to define thresholds which e.g. should not be exceeded. For the application of the Discriminant Analysis and the Logistic Regression a level of 500 ou_E/m^3 was chosen as air with an odour concentration below the level of 500 ou_E/m^3 is regarded as not problematic concerning odour nuisance (Giebel, 2007; Frey, 2008). The results of both procedures are listed in Table 3. They show that e-nose A is not able to differentiate with regard to the level 500 ou_E/m^3 with the current models used (only five measurements lower than 500 ou_E/m^3 are available). That means, that the model is not able to differentiate between the categories in the sample. As the performance of e-nose B, and C was poor concerning Linear Regression, it can be assumed here that the good results with Discriminant Analysis and Logistic

Regression (94 % to 100 %) depends on the level chosen. First results from analyses with one neural network and Multilayer-perceptron are similar to those presented.

Table 3: Results of the classification

E-nose	Discriminant Analysis	Logistic Regression
A	-	-
В	94.1 %	94.7 %
C (lower)	99.4 %	100.0 %
D	100.0 %	100.0 %

The above described evaluation only deals with linear regression and explanation of the data. However, as has been highlighted by Frechen and Giebel (in press), explanation solely is of poor use considering the ability of e-noses to predict correctly. Only in the case of a good result of the model used on unknown data the applicability of the e-nose in combination with the model is given. In further analyses, non-linear models will be applied and the prediction capabilities of the e-noses will be examined by using data-splits. According to DESEE (2007), it has to be checked whether models derived at one location can be transferred to other locations.

3.2 Response time tests

Flexible abatement strategies to control the amount of additives according to the level of odour require that e-noses can quickly respond to changing conditions in the sewer. Hence short response times are regarded as being valuable for an efficient dosage control. Response time is defined as the time span from the beginning of the measurement (i.e. when the sample gas enters the e-nose) until the sensor value is within +/- 10 % of the final value [*settling time* in DIN EN 61298 (2008)]. For determining the response time, odorous air (sewer air) with concentrations between 4,000 ou_E/m³ and 470,000 ou_E/m³ was collected in a sample bag. To induce a step change of signals the e-noses were measuring from this odour sample after being exposed to ambient air. For the analysis 23 to 38 tests could be considered. The measurement time was 29 minutes for continuously measuring e-noses (A, C), and 5 cycles for e-nose B (batch-mode). For e-nose D one measurement took 180 seconds (recommended by vendor) with purging phases before and after.

The response time can only be evaluated if the sensor converges to a final value. This was considered true when the considered final value (after the measurement time) was below 5 % of the mean of the last 40 % of the measurement. Results were only considered usable when the induced change of a sensor signal was above 10 %. The response time was calculated for each sensor per measurement. The slowest sensor (mean value of all measurements) is defined to determine the response time of the e-nose.

E-nose	А	В	C (lower)	C (upper)	D
Measurements	23	24	23	23	38
Measuring time	29 min	5 cycles (≈43 min)	29 min	29 min	3 min
Usable results	33.9 %	61.5 %	88.6 %	87.5 %	47.3 %
Response Time	14.4 min	4 cycles (≈34 min)	5.7 min	6.1 min	2.6 min

Table 4: Average response time of the e-noses	(note: e-nose D has shorter measurement times.)

The results (as summarized in Table 4) reveal that response times of the e-noses differ considerably. E-nose A and e-nose B have average response times of up to 34 minutes. This response might be too slow to react to peak loads arising in a sewer system. Both e-nose systems are equipped with an extensive sample preparation (see Table 1). The duration of one batch cycle of e-nose B can however be reduced. E-nose C which is designed without gas pretreatment reacts faster with a response time of around 6 minutes. As first finding this can be considered as appropriate response time to adapt dosing rates of additives or to changing sewer conditions. The shortest response time was found for e-nose D, whereas the proportion of usable results is low (47.3 %) which indicates that the sensors often did not converge to a final value. Very low responses were found for e-nose A, resulting in a very low number of usable results (33.9 %).

3.3 Repeatability tests

For reasons of reliability the e-noses should be able to provide closely similar indications for repeated measurements under the same measurement conditions. Around 20 air sample bags from the sewer channel could be considered. For ensuring a short storage time of the samples only two measurements of each sample per e-nose were carried out. The second measurements took place between 10 to 110 minutes after the first measurements. The repeatability was calculated as percentage difference between the two measurements under the same measurement conditions for each sensor. The repeatability score for the whole e-nose is the mean over all repeated measurements.

Table 5 summarizes the results. All e-noses seem to produce repeatable measurements with a repeatability between 89 % and 96 %.

E-nose	А	В	C (lower)	C (upper)	D
Measurement pairs (samples)	22	23	14	14	22
Repeatability	94.6 %	89.1 %	95.5 %	96.2 %	95.0 %

3.4 Comparison of odour to H₂S measurements

For wastewater applications the parameter H_2S is often used as surrogate parameter for odour measurements. This is e.g. due to its relatively easy and inexpensive measurement method. For the justification of applying e-noses instead (or additional), their added value need to be examined. Besides correlating the e-nose signals to odour concentration (see chapter 3.1) also the relation of H_2S concentrations to odour concentration was assessed. 152 paired values could be used. As seen in Figure 1 the coefficient of determination R^2 using a linear fit was only 0.20. Comparing this figure to the findings in chapter 3.1 it can be seen that the measurements by e-nose B, e-nose C, and e-nose D are in a better correlation to odour ($R^2 = 0.36$, 0.35 and 0.56 respectively; see Table 2) than the H_2S measurements.



Figure 1: Linear correlation of H_2S values to odour concentration (olfactometry); (range of values: 0 - 236 ppm H_2S ; 2,580 - 2,064,260 ou_E/m³)

4. Conclusions

First results of the data-mining process show that only one e-nose tested at the given location with real wastewater revealed a correlation coefficient R^2 to odour greater 0.50 (e-nose D with 0.56). For the other e-noses the correlation was below 0.36. Besides these not satisfying results, the findings of Discriminant Analysis and Logistic Regression seem more promising. All e-noses, except e-nose A, could distinguish if a measurement lies above or below the defined limit of 500 ou_E/m³. When an

abatement measure is applied this ability of the e-nose could be conducive to e.g document the longterm effect of a measure (< 500 ou_E/m^3 are regarded as non-critical for nuisance; Frey, 2008). Dynamic dosage control however requires more then only a yes or no feature, but e-noses need to find the corresponding odour concentration. Further work will deal with other models and the prediction capabilities of the e-noses (using data splits).

Regarding the response time, two e-noses (e-nose D and e-nose C) can be considered to fulfil the requirements (with response times between 3 and 6 minutes). Sensors of e-nose A and D however do often not show a distinct response or do not converge to a final value within the recommended time of the vendor. Repeatability tests revealed that all e-noses can conclude on similar output for measurements under the same conditions.

In general the benefit of applying e-noses in the sewer instead of (or additional to) H_2S measurements, needs to be assessed already in the planning stage. In the case of the here described tests, it can be concluded that solely H_2S measurements could not represent the odorant spectrum in the sewer in a satisfactory way (correlation of 0.20). The e-noses could provide a clear better performance (correlation coefficients above 0.27).

All e-noses tested differ in their configuration, with different amount and types of sensors as well as different sample preparations (drying, dilution, etc.). This seems to play a role in the performance of the e-noses. E-nose A and B which are equipped with extensive sample preparation tend to come off worse than the other e-noses (especially regarding correlation to odour and response time). Hence, e-nose systems and models should ideally be adapted to the specific tasks or location.

Further results of the investigations will be presented in the project report of the project Odoco-Artnose (available from August 2012 on the website of Kompetenzzentrum Wasser Berlin, <u>www.kompetenz-wasser.de</u>). This project is sponsored by Berliner Wasserbetriebe and Veolia Water.

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