D3.1.4.a:

Tests of odour sensors

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Tests of odour sensors

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Summary

This report briefly summarizes the results of the tests of electronic noses for measurement of odours from sewer systems. Tests have been conducted with real wastewater in Berlin at a sewer research plant of the Berliner Wasserbetriebe over a period of 8 months.

The methods are briefly described in Chapter 3. Electronic noses have been tested, two in the frame of PREPARED. Eleven evaluation criteria have been defined to evaluate the electronic noses - the correlation of sensor signals to olfactometric measurements was in the fore.

The investigations revealed that the e-nose could deliver sensor signals which are related to odour (up to 87 % odour prediction capabilities). The versatility and practicality of the devices however appear limited at the current status. For an active participation in a real scale application, further implementations as e.g. software with direct access to odour values, delay reduction, robust casings, etc. should still be done in order to meet requirements for specific sewer odour applications.

The transferability of the results and especially of established models is a crucial open question.

Contents

1 Sensor tests within Prepared

Sensors to be tested within PREPARED have been selected based on the needs of the partner cities.

Odour sensors have been selected as this parameter is expected to become more critical with climate change. Realistic tests have been conducted in Berlin by KWB.

Complementary Deliverable 3.1.1 provides a market review of sensors, including a list of available electronic noses for odour measurement (PREPARED, 2011a).

2 Odour measurement

Odour in sewer systems is caused by a mixture of volatile gas compounds. Usually no single compound is responsible for an odour but a combination of substances and their interactions.

Two broad classes of odour measurement can be distinguished (Psillakis, 2006):

- measurement by analytical instruments which refer to odorants and
- sensory measurements which employ the human noses and are related to odours.

The disadvantage of all analytical methods is that they tell very little about the perceived effect of odour. They are however preferred in terms of accuracy and repeatability.

Multi-gas sensor systems (electronic noses, e-noses) are interesting for environmental monitoring because they can offer an objective observation and provide online monitoring. They combine different sensor types or several sensors of one sensor type for chemical gas analysis in one device. Thus, e-noses can cover a wide spectrum of substances thanks to the unspecific sensors.

After training (referencing) with olfactometric analysis (analysis deploying human noses), e-noses can be able to deliver information about the odour concentration either thanks to a data analysis module integrated in the e-nose or through an external data analysis. This requires appropriate data analysis methods (e.g. multivariate analyses, neuronal networks). The high variation of the gas matrix and complex gas compositions require that the analysis is done with real experimental data and must be specific to the application and the electronic nose used (Röck *et al.*, 2008).

The principal sensory measurement method is threshold olfactometry (such as EN 13725:2003). It considers the effect perceived by humans. No information on the composition of the odour is given. Further it is affected by high inaccuracy. The uncertainty in measurement can be estimated between 25 % and 400 % (+/- 6 dB_{OD}) (Boeker & Haas, 2007). Another study has calculated an average uncertainty of 1.8 dB_{OD} (Both and Müller, 2011).

Different investigations (e.g. Stuetz *et al.*, 1999; Giebel, 2007; Frey, 2008) show that e-nose can present a suitable environmental monitoring solutions. But the number of trials under realistic conditions is limited (Bourgeois *et al.*, 2003).

3 Odour sensor tests

The Kompetenzzentrum Wasser Berlin (BWB) tested four commercially available electronic noses over a period of 8 months at the large-scale sewer research plant of Berliner Wasserbetriebe. Two of the e-noses have been tested in the frame of PREPARED (this report), two other ones in the frame of the KWB-project ODOCO-ARTNOSE.

The project was sponsored by Veolia Water, Berliner Wasserbetriebe and PREPARED. Cooperation partners were Berliner Wasserbetriebe, Evado engineering and the University of Kassel.

The report containing further information is available at www.kompetenz-wasser.de (project acronym: ODOCO-ARTNOSE).

The objective of the investigations was to assess the applicability of e-noses for sewer odour management at current technological status.

Within D 3.1.3 PREPARED (2011b) delivered a report on common protocol for sensor testing. This protocol could not be applied to these odour sensor tests as no lab conditions or standards were available. An ad-hoc strategy was thus developed to consider the local conditions at the sewer research plant.

3.1 Electronic noses

The electronic noses have been chosen based on their target application fields (wastewater emissions) and experiences with sewer air. They basically differ from each other in gas preparation, sensor amount and types and measurement mode. Table 1 lists the specifications of the tested e-noses.

Table 1 : Specifications of the e-noses used in the PREPARED tests

	E-nose B	E-nose D
Sensors*	6 QCM, 2 EC	10 MOS
Measurement mode**	Batch mode, desorption cycle	Continuous with interrupting purging phases
Gas preparation	Cooling, dustfilter, preconcentration	Automatic dilution

** MOS...Metaloxide sensors; EC...electrochemical sensors; QCM...Quartz crystal microbalance*

*** Continuous measurement method: data acquisition more often than every 5 min*

The e-noses were tested as provided, including all gas preparation provisions. Hence, not the sensors themselves are evaluated, but the whole measurement chain (without data analysis module). Data analyses by the vendors were not considered.

3.2 Test conduction

The tests have been conducted in the large-scale sewer research plant of Berliner Wasserbetriebe (BWB) (see Figure 1). The plant consists of two parallel gravity sewers (DN 400) with a length of 25 m. The system is fed with wastewater from a nearby pumping station. The wastewater comes from a combination of a separate and combined sewer system. It is a mixture of industrial and domestic wastewaters.

Figure 1: Sewer research plant of the Berliner Wasserbetriebe

Different conditions were established in the sewer research plant during the test period from June 2011 to February 2012. Tests were conducted with wastewater, and with applying odour abatement methods, such as

- dosage of calcium nitrate,
- dosage of ferrous chloride.

Thus different operation conditions were established. All e-noses experienced the same conditions.

The measured concentrations ranged from 0 to 2,000,000 ou_E/m^3 (0 to 250 ppm H_2S). Thus the e-noses were facing harsh conditions.

Following tests have been conducted:

1. Measurements from sewer channel

The e-noses were each connected to sealed openings in the sewer channel (see Figure 2). Additional openings next to the e-nose openings were available to draw air samples for olfactometry or other analyses.

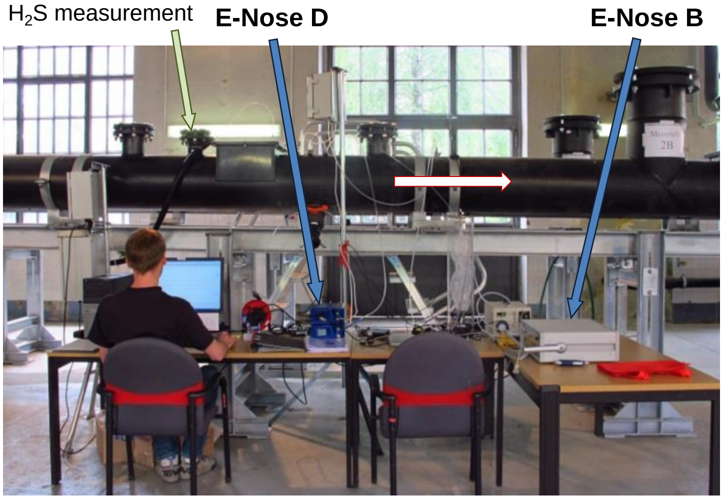


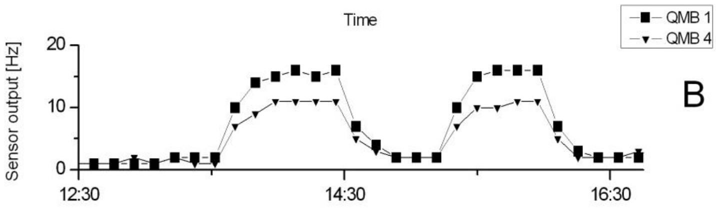
Figure 2: Measuring site of the e-noses at the sewer research plant; flow direction of the wastewater is indicated.

2. Measurements from sample bag

Sample bags were filled with sewer air to be afterwards measured by the e-noses (see Figure 3). The aim was to expose the e-noses to a homogenous gas sample to

- induce a step increase (for determining response times),
- repeat the measurement with the same gas sample (for determining the repeatability),
- investigate the effect of temperature and humidity by changing these parameters within the sample bags.

a)



b)

Figure 3: a) Measurement from sample bag by the e-nose; b) Example of repeatability test: measurement curves for sample bag measurements for 2 sensors of e-nose B.

3. Measurements from ambient air

Additionally, e-noses were exposed to air in the hall were the sewer research plant is located to measure non- and low-odorous air.

3.3 Olfactometry

To identify if the e-nose sensor signals are in any relation to the odour, olfactometric analyses according to DIN EN 13725:2003 have been conducted throughout the test period.

To check for a correlation of e-nose sensor signals and odour concentration, paired values of e-nose signals and olfactometry were needed. For this purpose, air samples were drawn from the sewer channel (see Figure 4 and Figure 5) and sent to an olfactometric laboratory.

A mathematical model should be developed for each e-nose to describe the function between the sensor signal and the olfactometric values.

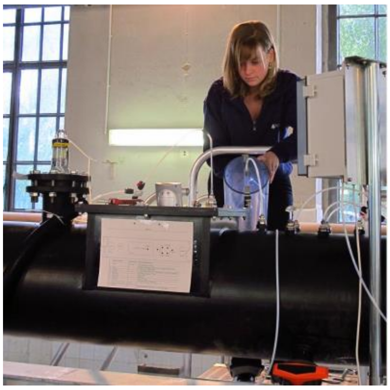


Figure 4: Sampling from the headspace of the sewer research plant

Figure 5: Air sample bag to be send to the laboratory for olfactometric analysis

3.4 Evaluation criteria

To assess the performance of the electronic noses at the sewer research plant, 11 evaluation criteria (quantitative and qualitative; as listed in Table 2) were defined. The criteria were defined by considering

- basic evaluation of e-noses regarding odour measurement (is there a relation between e-nose signals and odour?)
- general performance criteria for chemical sensors (based on DIN ISO 9169:2006) which can also characterise the sensor responses under real conditions (for example response time)
- functionality under real conditions (like effects of temperature)
- experiences from operation during the test period

- intrinsic properties.

Table 2: Evaluation criteria for the test of electronic noses

No.	Criteria	Description
1	Odour explanation and prediction capabilities	Correlation of sensor signals to odour concentration (olfactometry)
1 a	Odour explanation and prediction (total data-set)	
1 b	Odour explanation and prediction (dependency on test conditions)	
2	Repeatability of measurements	Ability to provide similar indications for repeated measurements with sewer air under the same measurement conditions
3	Response time	Determination of time span from the beginning of a measurement until the sensor value is within +/- 10 % of the final value; using sewer air samples
4	Effect of humidity and temperature	Estimation of interference of humidity and temperature on sensor signal based on trials
5	Stability of sensor signals	Estimation of signal stability based on repeated measurement with test vials and development of baseline frequencies/resistances during tests
6	Memory effect	Estimation of trend of response time over test period; difference between rise and fall times
7	Availability	Percentage of time when data was recorded over the test period
8	Strength of casing	Provisions for protection against water, pollution or explosion
9	Operation and maintenance*	Appraisal on installation easiness, maintenance efforts and easiness, handling, software availability, possibilities of remote control, support from vendor
10	Possibility of instant monitoring	Possibility of direct display of signals and odour concentration values
11	Availability of conditioning system	Provisions for compensation for temperature and humidity influences and sensor protection

** Criteria "Operation and maintenance" includes 9 sub-criteria*

4 Results of odour sensor tests

The main results of tests for both electronic noses are presented. In the full report (available at www.kompetenz-wasser.de) the findings of all four e-noses are presented.

Please notice that each location has its own conditions and characteristics: the presented results are only valid for the test conditions, the transferability of the results and especially of established models is a crucial open question.

4.1 Odour explanation and prediction capabilities

To identify if the e-nose sensor signals are in any relation to the odour, mathematical analyses have been conducted. It was then checked if a correlation can be established between the sensor signals and the odour concentration. This criterion is presented separately from the other criteria (as listed in Table 2) as it is a precondition when applying e-noses for sewer odour monitoring.

Figure 6 summarizes the evaluation results which were derived from the correlation of odour concentration to the e-nose signals for odour explanation and prediction. Linear and non-linear models have been applied. Prediction capabilities were determined by splitting the data-set into one training data-set with which the model was created and applying the other part of the data set to this model. Only this can give indications on the quality of the model (see also Frechen & Giebel, 2010).

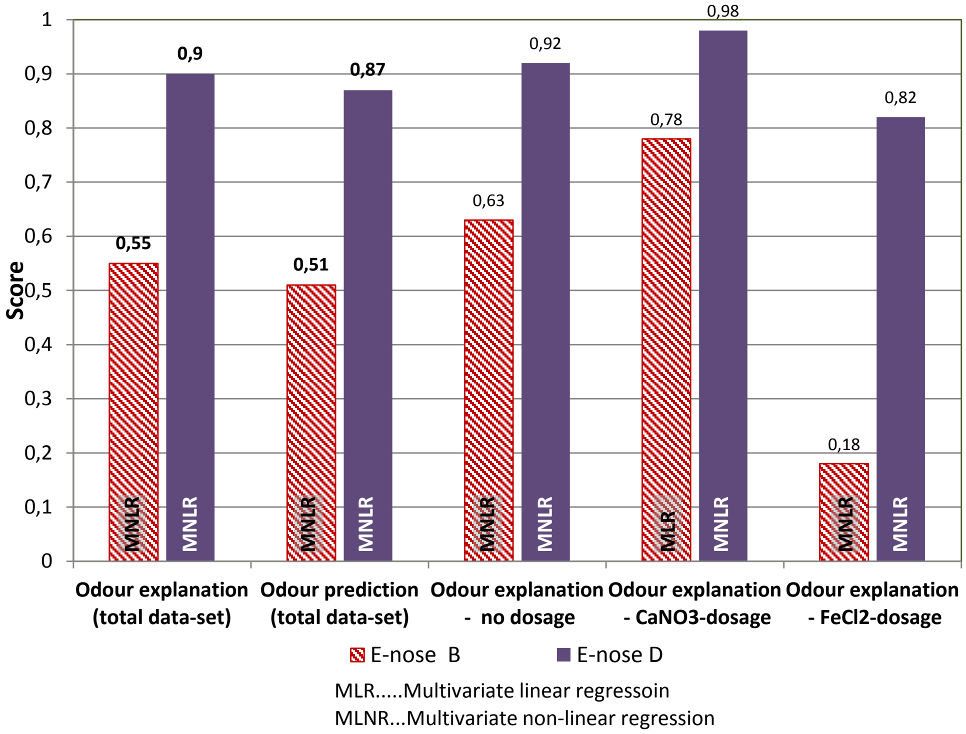


Figure 6: Results of investigations for "Odour explanation and prediction capabilities"; Comparison of two e-noses dependent on categories (total data-set, no dosage, $CaNO_3$-dosage, $FeCl_2$-dosage). The score represents the best correlation coefficient R^2 found by mathematical analyses (linear and non-linear regression models were used). The prediction abilities for the total data-set were determined by a random 50/50 data split. Results are based on analyses by the Department of Sanitary and Environmental Engineering of the University of Kassel.

Very good results for odour explanation and prediction capabilities were found for e-nose D when applying a non-linear model (up to 98 % of odour explanation). Thus, at the test site, the e-nose was able to measure in relation to odour. E-nose D also showed good correlations to odour for the measurements when odour additives for odour abatement were dosed into the sewer, thus indicating that its performance is independent from test conditions.

The capabilities of e-nose B were in the medium range with a maximum of 78 % odour explanation. The e-nose performance appears to depend on the test conditions applied; the result for the total data set is below those in the category "no dosage" and "$CaNO_3$-dosage". Thus, the poor overall explanation capability at the test site (< 60 %) does not rule out the practicability of the e-nose for other locations but it needs to be investigated thoroughly.

In Stuetz *et al.* (2000), a correlation coefficient of 0.88 was found between odour concentration and e-nose output by canonical correlation when measuring wastewater emissions. By applying neuronal networks Giebel (2007) could determine prediction capabilities of 77.6 %. Thus other models than the ones used in these tests could be further investigated.

4.2 Overall evaluation of e-nose B

The results of the evaluation criteria for e-nose B are presented in Figure 7.

Repeatable measurements are delivered by the e-nose (89 %) whereas this tends to decrease in the lower concentration range.

A very fast response cannot be expected from this e-nose, due to the batch-mode operation and some delay times due to the pre-concentration step. A response time of 4 measurement cycles was determined. As one cycle typically takes 4 to 10 minutes, a minimum time of 16 minutes must be anticipated until the sensors reach their final value.

Medium to low effect of temperature and humidity show that the high sensitivity of quartz crystal microbalance sensors (QCM) could be overcome to a large extend.

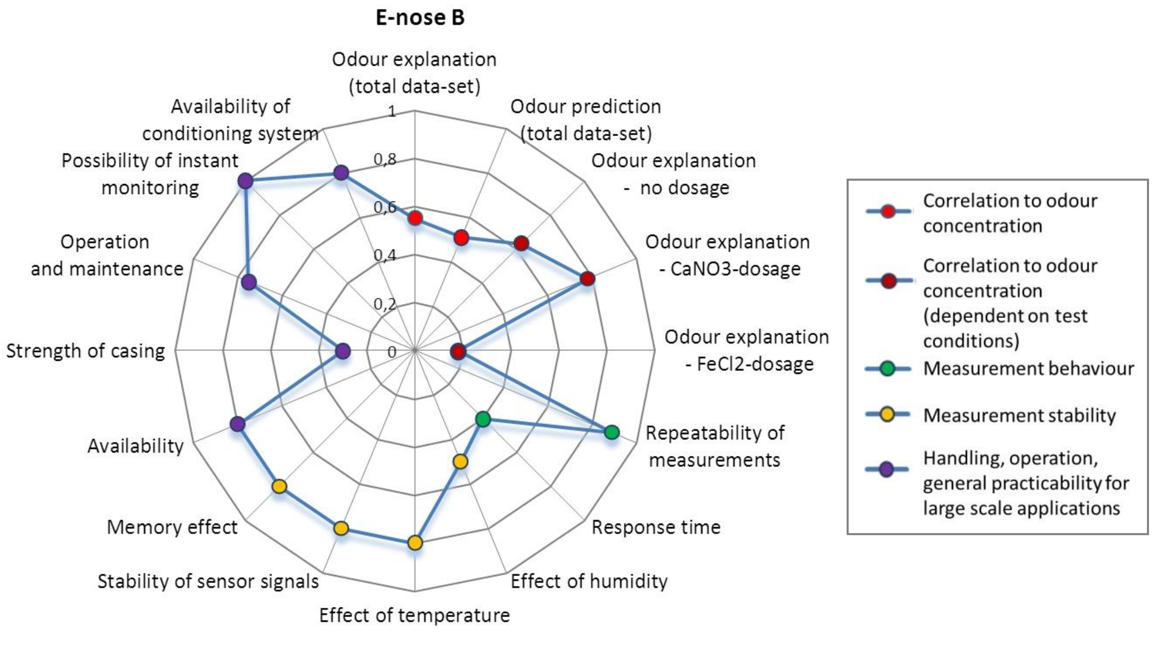


Figure 7: Results of evaluation for e-nose B. Colours indicate groups of criteria.

Additionally the measurements are stable (low drift effects within 5 months) and showed no effect of previous measured values on the next values (memory effect). This good performance can be ascribed to the fact that the QCM sensors are not based on a chemical reaction on the sensor surface but on a reversible reaction after which the sensors can recovery.

Apart from the fact that the device currently does not have provisions for outdoor applications (for example protection against water intrusion) the handling and practicability is rated high. E-nose B is already equipped with some features which meet the requirements for an application in a dosing system (i.a. output signal, full remote control). The applied industrial gas pump has a long lifetime.

Analysis software for the user is not available. But the device provides possibilities to integrate a model in the system (with support from the vendor) in order to give directly information on the odour concentration.

4.3 Overall evaluation of e-nose D

Results of e-nose D are provided in Figure 8.

A very high repeatability was found for e-nose D (95.0 %).

Further a fast response time could be determined for e-nose D (< 5 min). The data sheet of the device states response times of typically 1 to 2 seconds. However, the tests with sewer emissions at the sewer research plant revealed that only a low proportion of sensors could converge to a final value within 3 minutes.

The stability of sensor signals was rated low as a sensitivity loss (for 6 of 10 sensors above 30 %) was observed even within 3 months of measurement.

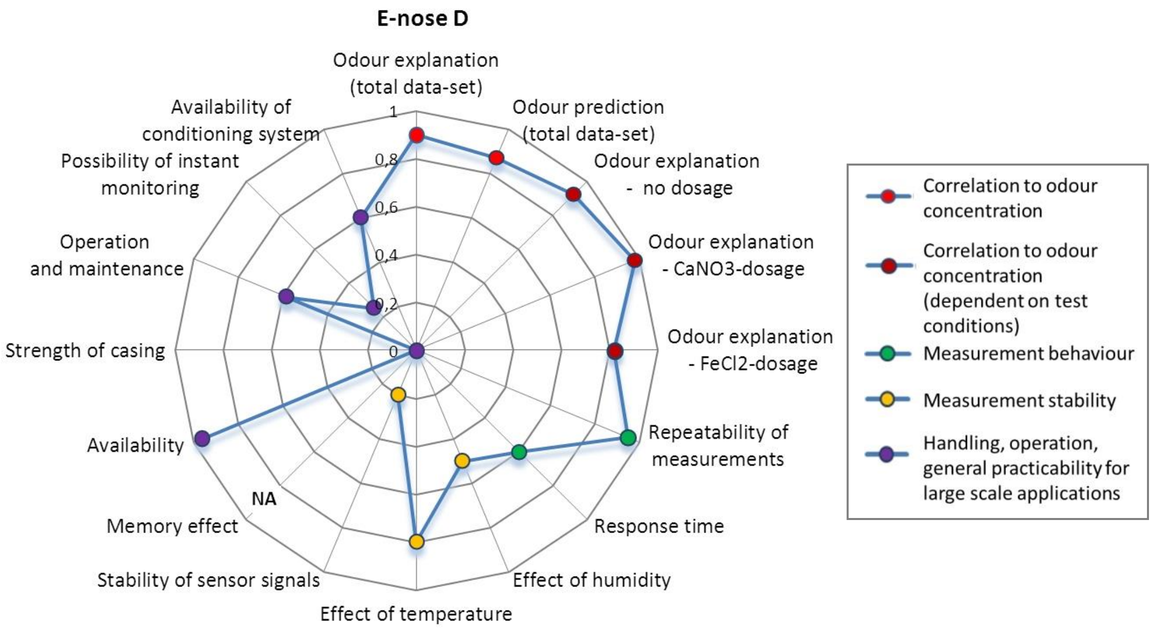


Figure 8: Results of evaluation for e-nose D. Colours indicate groups of criteria.

Figure 8 clearly illustrates that despite the very good correlation of the sensor values to odour concentration, the general practicability is not provided for large scale applications in the sewer. This is due to limitations regarding provisions for outdoor applications, no possibilities for remote control or instant odour monitoring, and necessary maintenance activities (exchange of filters, tests with vial).

5 Conclusions

Generally it can be mentioned that the results are promising and that e-noses show good potential for measuring odours in sewer systems. However some drawbacks exist for each e-nose. For an active participation in a real scale application, further implementations as e.g. software with direct access to odour values, delay times reduction, robust casings, etc. should still be done in order to meet requirements for specific applications. It is only possible when vendors have possibilities and motivation to adapt the system.

The transferability of the established models has not been investigated but is a crucial aspect when an e-nose should be used at different locations with different conditions (wastewater matrix). The re-establishment of a model for another location involves expenditure of time, personnel and money (for olfactometric analyses and data analyses). A model which has been produced under a wide range of operating conditions in the first place can be beneficial. Dynamic models (such as neuronal networks) could be subject of further investigations.

The findings are based on the tests, thus only valid for the conditions at the sewer research plant.

The findings suggest that the actual practicality of e-noses depends on the requirements based on the target application. A fast response might be desirable when dosage control is in the fore. Whereas for monitoring purposes it might be sufficient to have a stable system which is easy to handle and requires low maintenance.

6 Bibliography

Boeker, P., Haas, T. (2007). Die Messunsicherheit der Olfaktometrie. *Gefahrstoffe: Reinhaltung der Luft* 67(7/8): 331-340.

Both, R., Müller, F. (2011). Überlegungen zur Messunsicherheit bei olfaktorischen Messungen. Eine Auswertung der n-Butanoldaten von 19 Laboratorien. *VDI-Berichte: Gerüche in der Umwelt* 2141: 43-54.

Bourgeois, W., Romain, A.-C., Nicolas, J., Stuetz, R. M. (2003). The use of sensor arrays for environmental monitoring: interests and limitations. *Journal of Environmental Monitoring* 5: 852-860.

DIN EN 13725. (2003). *Bestimmung der Geruchsstoffkonzentration mit dynamischer Olfaktomietrie*. VDI/DIN-Handbuch Reinhaltung der Luft Band 1a.

DIN EN ISO 9169 (2006). *Air quality - Definition and determination of performance characteristics of an automatic measuring system*. Geneva (Switzerland): ISO, 31 p.

Frechen, F.-B.; Giebel, S.M. (2010). The New VDI Guideline 3885/1 for OEC Measurement and why we might need Electronic Noses. *Plenary keynote at the International Conference on Environmental Odour Monitoring and Control (NOSE2010)*, Sept. 2010, Florence, Italy.

Frey, M. (2008). *Untersuchungen zur Sulfidbildung und zur Effizienz der Geruchsminimierung*. [ed.] Franz-Bernd Frechen. Schriftenreihe des Fachgebiets Siedlungswasserwirtschaft der Universität Kassel. Kassel: Kassel University Press, 2008. Vol. 28. ISBN 978-3-89958-453.

Giebel, S.M. (2007). Schätzung der Geruchsstoffkonzentration anhand von Sensorarrays: Vergleich zwischen Logistischer Regression und Neuronaler Netze (Estimation of the odour concentration). *VDI-Conference "Odour in the Environment"*, Bad Kissingen, 13.-14.11.2007. VDI Report 1995, pp. 389-395, ISBN 978-3-18-01995-9.

PREPARED (2011a). *Deliverable D3.1.1: Market review for some sensors. Report n° 2011-017*. Seventh Framework Programme Theme 6 Project PREPARED Enabling Change, KWR, Nieuwegein, The Netherlands, 68 pp. Available at: http://www.prepared-fp7.eu/prepared-publications

PREPARED (2011b). *Deliverable D3.1.3: A common protocol for sensor testing*. *Report No. 2011.001*. Seventh Framework Programme Theme 6 Project PREPARED Enabling change, KWR, Nieuwegein, The Netherlands, 68 pp. Available at: http://www.prepared-fp7.eu/prepared-publications

Psillakis, E. (2006). Odour Measurement. In ISEKI-food "*Odours in the Food Industry*", editor: Xavier Nicolay. New York (USA): Springer Verlag, 176 p. ISBN 9780387341248.

Röck, F. , Barsan, N., Weimar, U. (2008). Electronic Nose: Current Status and Future Trends. *Chemical Review* 108, 705-725.

Stuetz, R.M., Fenner, R.A., Hall, S.J., Stratful, I., Loke, D. (2000). Monitoring of wastewater odours using an electronic nose. *Water Science and Technology* 41(6), 41-47.

Stuetz, R.M.; Fenner, R.A.; Engin, G. (1999). Assessment of odours from sewage treatment works by an electronic nose, H2S analysis and olfactometry. *Water Research* 33 (2), 453-461.

7 List of abbreviations

BWB .... Berliner Wasserbetriebe

$Ca(NO_3)_2$ .... Calcium nitrate

EC .... Electrochemical sensor

E-nose .... Electronic nose (also multigas-sensor system)

$FeCl_2$ .... Ferrous chloride

H_2S .... Hydrogen sulphide

KWB .... Kompetenzzentrum Wasser Berlin

MOS .... Metal oxide semiconductor

ou_E .... European Odour Unit

ou_E/m^3 .... Odour concentration

PID .... Photoionization detector

ppm .... Parts per million

QMB .... Quartz crystal microbalance