Applying the electronic nose in the environment : requirements for the sensors

Jacques NICOLAS, Anne-Claude ROMAIN and Philippe ANDRE

Fondation Universitaire Luxembourgeoise (FUL)

Avenue de Longwy, 185

B-6700 ARLON

Belgium

Phone : +32(0)63 230857

Fax : +32(0)63 230800

nicolas@ful.ac.be

Abstract

For few years, the department "Environmental monitoring" at FUL applies the principle of the electronic nose equipped with tin oxide sensors to recognise and to monitor real life malodours in the environment and directly in the field.

For such emissions, the gas mixtures are very complex and only their odour should be of interest, and not their chemical composition.

Moreover, working in the field implies various constraints.

The obstacles of the monitoring of real life environmental odours with an electronic nose can be classified into three main areas : the final goal of the study (measuring an odorous annoyance), the analysed sample itself (influenced by the evolution of the process and of ambient parameters) and the operating conditions (necessity to transport the reference gas and the batteries in the field, influence of air humidity).

The paper describes the approach of FUL to the problem with various tests conducted in the field with home-made electronic noses based on tin oxide sensors and with very simple configurations. The conclusions, which can be extrapolated to any other sensor types, are promising, but the sensor performances (sensibility, reproducibility, electrical consumption, drift, etc.) should still be improved before reaching the final goal.

Keywords

Electronic nose – environment – odour

Introduction

For a dozen of years, the so-called electronic nose principle is used by many researchers in many labs in the world with the aim of recognising and, if possible, of monitoring gaseous ambiences.

Among all the applications of the electronic nose which are described in the literature, many are devoted to laboratory recognition of well defined ambiences, with reproducible operating procedures and with rather reproducible gas composition.

Some applications concern simple gas or simple gas mixtures [1, 2] : for example, recognising different concentration levels of methane or of ethanol or discriminating between carbon monoxide and hydrogen sulphide. Of course, for such simple ambiences, a single gas sensor is able to supply a signal proportional to the gas concentration.

The main interest of using a non specific gas sensor array for such measurements is to test its performance or to try different mathematical procedures or different operating conditions. Nevertheless, sometimes, when more specific sensors or instruments do not exist or if they exist, but if they are quite expensive, the use of a sensor array is justified. An example could be the ambience of BTX, for which the classic measurement methods are rather expensive.

Some other applications concern more complex ambiences.

For example, the applications in the domain of food industry have been widely reported. Examples include the identification of different types of cheese, different coffee qualities or different olive oil origin [3, 4, 5].

Obviously, the problem is even more difficult.

Now, the gas composition can vary from one sample to the other, but, globally, the main chemicals involved in the gas mixture are always the same. Moreover, for such application involving the volatiles generated by solids or liquids, the measurement is made in the lab on the head space created above the sample and in reproducible conditions.

Going a "step further" implies real atmospheres actually sampled in the environment. Such samples can be prepared for instance in Tedlar bags. Then, those bags are analysed by the electronic nose in the laboratory [6, 7]. The sampling of real atmosphere is sometimes difficult and limited by the risk and by the uncertainties of field operation. But, as for the measurement of food products the measurement itself can be performed with rigorous operating conditions in the lab, so that the results are generally good and reproducible.

The last step is the measurement of the real atmosphere at remote locations directly in the field, with a hand-held electronic nose. That is probably the more restricting situation, because all the difficulties are cumulated at the same time : the fluctuation of the quality of the studied atmosphere and the influence of external variables on the measuring instrument. So, measuring real ambiences directly in the field is really challenging.

Moreover, willing to detect an "odour" in the environment and not simply a gaseous ambience still adds an additional drawback in the procedure.

Such measurements should aim at a better understanding of the odour release, by relating it to the process which caused the emission. But the most interesting issue of the continuous monitoring of malodour in the field is the real time control of odour abatement techniques.

An example of odour abatement technique is the atomisation of neutralising agent around the odorous source. The neutralising products are generally based on natural plant essences and on essential oils which react with odours at a molecular level to neutralise the effect of the odour. Such products are quite expensive. So, controlling the spraying of the product by the measurement of the resulting odour in the vicinity of the process should constitute a real interest for the manager.

The problem is thus challenging and can't be compared with that of the monitoring of a single gas in the laboratory and many difficulties have to be overcome.

The chief obstacles of the monitoring of real life environmental odours with an electronic nose can be classified into three main areas : the final goal of the study, the analysed sample itself and the operating conditions

The final goal of the study.

When monitoring a malodour in the environment, the final variable to evaluate is a global odour annoyance, and not a concentration of some chemicals.

Of course, the tin oxide sensors react to many chemicals whether they smell or not. However, a suitable choice of the sensors can more particularly focus the responses on the detection of odorous compounds. For example, for a given configuration [11],

we have chosen 12 sensors from the Japanese company Figaro which are more sensible to odorous compounds : hydrogen sulfide, ammonia, solvents, air contaminants, fuel or odorous combustible gases, such as methane or propane. Of course, a similar selection could be made with another type of sensor (e.g. : thin film technology) or another trade mark [12].

When the adequate sensors have been chosen, the measured signals are processed with a pattern recognition technique. When a supervised method is used, one can indicate to the system that the target characteristic to recognise is the odour of the gas, and not an other property.

The following application concerns a study conducted in the vicinity of five typical real malodorous sources in rural environment [13] : a rendering plant, a paint shop in a coachbuilding, a waste water treatment plant, urban waste composting facilities, and a printing house.

The gas were sampled in Tedlar bags, near the sources, thus at the emission level and the tests were carried out in the laboratory with the 12 Figaro sensors.
A total of 59 samples are collected during a period of 7 months, between March and October, in various climate conditions, and sometimes at various operating conditions.
Using a supervised pattern recognition technique, such as the discriminant function analysis (DFA), and indicating to the method that the target grouping feature for the classification is, for instance, the time of the sampling in the year, it is possible to discriminate rather well the different months.

Now, with exactly the same data set, if the target groups provided to the DFA is the origin of the odorous emission, the system is still able to recognise rather well the different groups (figure 1).

Figure 1 : Results of a Discriminant Function Analysis in the plane of the two first roots for 59 samples from 5 odorous sources in the environment

That means that as long as the data set intrinsically contains the information about a given property, like the sampling period or the type of odour, a supervised method is able to classify the data according to that property.
Thus the odorous tonality of the sample can explicitly be introduced in the qualitative separation part of the study.

But it is also possible to introduce the odour in the quantitative part of the analysis, when trying to rely the sensor signals to the odour intensity. Again, if the dependant “y” variable is the odour intensity, a regression is able to construct a good prediction model from the sensor signals.
The following case concerns a study of the odorous emissions around a landfill site, with a mobile electronic nose made of 6 Taguchi sensors [14]. The operator performs measurements at some different locations on the landfill area : either in the vicinity of fresh waste, sometimes when the trucks pour out the refuse, sometimes when the waste is at rest, or at various distances from a landfill gas extraction well. At each location, he notes his feeling of odour strength on a 4 levels scale. A total of 141 observations were carried out with that procedure.

We have tried to rely the feeling of odour intensity to the 6 sensor signals. The best results are obtained with the Partial Least Squares regression (PLS). The model can predict the correct intensity level on the 4 levels scale in about 71 % of the cases.
Moreover, like the Principal Component Analysis (PCA), the PLS provides the separation of observations in two groups. Consequently, it should be used as sole tool, both to identify the source of the odour and to predicting its intensity.

In the same spirit, another interesting result can be presented. The signals provided by the Tagushi sensors were compared to the results of olfactometry measurements for the odour generated by the compost.
Olfactometry is a method that utilises a panel of people sniffing diluted odours to determine the odour strength or the odour concentration, expressed in odour unit per cubic meter.
The comparison concerns ambiences sampled in the vicinity of a compost area, at different locations, sometimes just near the compost pile and sometimes much farther.
The figure 2 shows that there is a relationship between the values of the odour strength (x axis) and the resistance of one sensor (here the TGS800, y axis). Of course, the reason of this relationship is that the odour intensity is linked to the concentration in chemicals, but that means that it should be possible to predict the odour intensity from the signal generated by the sensor array.

Figure 2 : Relationship between the strength of the compost odour (x axis), as measured by olfactometry, and the resistance of the TGS800 sensor.

The analysed sample.

The second specific feature of odour measurement in the environment is the fact that the analysed sample is highly variable, due to the process itself, which is not always exactly the same, and due to the influence of all the parameters in the environment. That leads to the scattering of the clouds of data points. The different groups overlap, and that is normal.

The figure 3 shows the result of a PCA carried out with about 400 observations made in the surrounding of 4 odorous sources and in odourless air sampled far from any source [15].

Figure 3 : PCA results, in the plane of the two first factors, for 4 odorous sources and odourless air (388 observations, 12 sensors).

Such model is able to detect the presence of the compost odour with respect to odourless air and to any other odours : that seems an obvious result, but it is sometimes sufficient for many applications. We see that some observations belong to the “no man’s land” between the groups : that is normal, those are either observations made around the odorous atmosphere, but far from the source, or observations made in the air, but which was not really pure. These different kinds of points can be confused.

But the scattering of the observations can also be due to the sensor drift, which mainly induces the elongation of the clusters into curvilinear shapes.

The figure 4 shows the evolution of the classification performance for 4 environmental sources during a four years period, from 1998 until 2001 [15].

We have calibrated a recognition model in 1998 with 12 sensors, and we have tried to apply it to validate more recent observations. Obviously, the model is no longer applicable : there is a long term drift effect which exclude the possibility of accurate recognition of the four sources. The total percentage of correct classification decreases from year to year : 97.9 % for the observations of 1998 which were used for the model calibration, 81.8 % for the observations of 1999, used for validation purpose, and only 20 % for the observations of 2001.

Figure 4 : DFA results for 97 observations around 4 odorous sources : model calibrated with data of 1998 and validated with all observations, from 1998 until 2001

With classic gas concentration measurement, such problem can be solved quite easily by calibrating the sensor with a standard gas. Here, such standard gas could also be used to calibrate the sensor array, for example ethanol, but it not the ideal solution, because ethanol is a single gas and the responses of the sensors to that single gas cannot be extrapolated to the signals of the sensor array in the presence of real complex gas mixture.

Nevertheless, ethanol was used for calibrating, and the problem was approached by finding an equivalence between the "concentration" of the odour and the concentration of ethanol.

The common points between the complex gas mixture and ethanol is the individual responses of the sensors in the array.

For each sensor, the calibration curve for ethanol can be obtained by exposing the sensors to different known concentration levels of ethanol.
On the other hand, the same step can be applied for various dilutions of the studied gas mixture.

Such an approach has been applied to the array of 12 TGS sensors in the case of the compost odour.
Such a procedure leads to rather good results and let us hope to compensate the sensor drift by a suitable calibration with ethanol before each measurement campaign.

At least, the procedure allows to assess the "concentration" of the gas mixture and also to estimate the detection threshold of our sensor array (figure 5).

Figure 5 : Equivalence between the ethanol concentration and the dilution of the compost odorous sample for the sensor TGS2620.

The figure shows that the order of magnitude of the "concentration" level of the non-diluted odorous compost sample is about 25 ppmv of "ethanol-equivalent". But sometimes, when the sample is taken farther from the source, the concentration can fall to about 1 ppmv. That means that, even by sampling the odour in the vicinity of the emission source, the detection threshold of the Taguchi sensors is often reached.

And that is an additional drawback of the measurement in the field : the very low levels of chemical concentration in the real atmosphere. That means that it should

be quite impossible to identify an odour farther from the source, in the environment. A possible solution to such problem should be to improve the sample uptake, for example, by pre-concentrating the analytes prior to investigation. Some design of "field preconcentrators" are proposed in the literature. Generally, the trap is an adsorption tube, filled with a sorbent material, such as Tenax or charcoal, and a small thermo-desorption unit is placed just at the entry of the sensor chamber.

The operating conditions

The third specific feature which characterises the odour measurement in the environment is the conditions of operation in the field : the investigated sites (landifll areas, settling ponds of sugar factories, …) are sometimes far from any building and not easy to reach. So the instrument must be simple and transportable and its maintenance must be reduced.

In particular, one of the constraint is the necessity to use the reference to the base line, that is to say, to the response of the sensor to a pure air. That is generally recommended in the literature when using a tin oxide sensor array : the classic way is to work by cycling between a reference air, free from any contaminant, and the odorous sample. The response of the sensor is generally the difference between the signal, after equilibrium in the odorous ambience and the base line generated in pure air.

But the use of a pure air cylinder is not convenient for field applications : that is heavy and cumbersome. Alternatively, filtering the ambient air with charcoal or molecular sieves leads to frequent regeneration of the adsorbing medium. So, a

continuous monitoring in the field should impose very restricting maintenance conditions.

For real life operation with the electronic nose, we decided not to work with perfectly pure air, but with the ambient air, coarsely filtered and not dried. The goal is not to create a base line for the measurement reference, but simply to purge the sensor vessel, so as to regenerate the sensors from time to time.

Moreover, the results show that the best classification of odorous sources is always obtained with the raw resistance, and not with the difference between the signal and the base line [16]. Indeed, as the "reference" is not a very pure air, small variations of the concentration of trace elements in the reference air influence the classification.

A second constraint of the operating conditions in the field is that the electrical supply network is not available, which forces the operator to transport very heavy batteries in the field, sometimes, under rather difficult conditions.

So, any improvement of the electrical consumption of the sensors will be appreciated by the user of a field electronic nose.

For example, using 12 sensors from the Figaro TGS series 800 needs about 10 watts. Using the new 2000 series already allows to divide the consumption by a factor 3, but, obviously, a thin film technology allows to lower still much more the electrical consumption. In a given configuration used for indoor pollution monitoring, a thin film sensor micro array from the Swiss company Microsens was used : a 12 sensors arrangement consumes less than 100 mW [17].

And the last constraint of working in the field is the influence of ambient parameters, such as air humidity, temperature or wind speed. Particularly concerning the

humidity, the conditions of the ambience cannot be modified without changing also the quality of the odour, and so, the sample cannot be dried or saturated in humidity. Now, the sensors are also sensible to the water vapour : the semiconductor resistance variation is modified or even reversed when humidity changes. However, we have shown that, as long as the humidity level don't vary outside a "reasonable range", it can be considered as a "neutral variable" for the learning procedure.

Such observation can be made in the frame of the following experiments conducted in the laboratory with synthetic odours, using an array of 12 "Figaro" sensors in the lab, in dynamic conditions [18]. Some synthetic odours are transferred into the sensor chamber. They are made of chemical compounds, typical of environmental odours : that is alcohols, esters, amines, aldehydes, ketones and sulfides. Each sample is prepared in a Tedlar bag, but under uncontrolled external conditions, and thus under various humidity levels. The pattern recognition technique is a neural network with 18 log-sigmoïd neurons and a backpropagation algorithm. In a first scenario, the network learning step is based on a training set of signals generated by the odour at any humidity level. In such conditions, the network is able to recognise 6 new samples. New samples means : 6 validation samples, not used for the calibration procedure.

In a second scenario, the same operation is performed with the same samples, but this time, the training involves only those samples with low water content. And now, the model so calibrated is no more able to recognise more humid sample.

Thus, those experiments show that, as long as sampling and learning are carried out under many different humidity conditions, and not under particular ones for a given source, the classification remains relevant, and the humidity may be considered as a "neutral" variable.

That finding was confirmed with real odours sampled in the environment at different seasons, with different humidity conditions.

Conclusion

The various tests conducted in the field with home-made electronic noses, with very simple configurations, lead to very promising results. They allow to explicit the specifications of a portable instrument, able to predict an unknown odour in the environment, and to monitor it continuously, on the basis of the classification model calibrated during the learning phase [19, 20].

The monitoring of environmental odour is really a challenge, but for environmental use, there is no need for very accurate response : a rough detection is sufficient for most applications.
Consequently, there is no need for operating conditions as restricting as laboratory electronic nose ones.

Such conclusions are promising, but further works are still needed before reaching the final goal and to point out the boundaries of the method. More particularly, the sensor performances should be improved : sensibility, reproducibility, electrical consumption, drift, in order to consider the use of electronic nose in the field and for a long period.

References

[1] G. Faglia, F. Bicelli,, G. Sberveglieri, P. Maffezzoni, P. Gubian, P., Sensors and Actuators B 44 (1997) 517-520.

[2] J. Orts, E. Llobet, X. Vilanova, J. Brezmes, X. Correig, Sensors and Actuators B 60 (1999) 106-117.

[3] E. Schaller, J.O. Bosset, F. Escher, Chimia 53 (1999) 98-102

[4] J.W. Gardner, H.V. Shurmer, T.T. Tan, Sensors and Actuators B 6 (1992) 71-75

[5] C. Di Natale, A. Macagnano, S. Nardis, R. Paolesse, C. Falconi, E. Proietti, P. Siciliano, R. Rella, A. Taurino, A. D'Amico, A., Sensors and Actuators B 78 (2001) 303-309

[6] R.M. Stuetz, R.A. Fenner, G. Engin, Water Res. 33 (1999) 442-452

[7] B.G. Kermani, PhD Dissertation, Department of Electrical Engineering, North Carolina State University, Raleigh, 1996.

[8] F. Di Francesco, B. Lazzerini, F. Marcelloni, G. Pioggia Atmospheric Environment 35 (2001) 1225-1234

[9] R. Menzel, J. Goschnick Sensors and Actuators B 68 (2000) 115-122

[10] A. Perera, T. Pardo, T. Sundi, R. Gutierrez-Osuna, S. Marco, J. Nicolas, Proceedings of the 8th conference Eurodeur, Paris, 19-21 June 2001.

[11] J. Nicolas, A.C. Romain, V. Wiertz, J. Maternova, J, in : Sensors and chemometrics (Ed.: M-T. Ramirez-Silva), Research Signpost, Kerala, pp. 75-90.

[12] K. C. Persaud, S. M. Khaffaf, P. J. Hobbs and R.W. Sneath, Chemical Senses, 21 (1996) 495-505.

[13] A.C. Romain, J. Nicolas, V. Wiertz, J. Maternova, P. Andre, Ph. Sensors and Actuators B 62 (2000) 73-79.

[14] J. Nicolas, A.C. Romain, D. Monticelli, J. Maternova, P. André, Proceedings of abstracts ISOEN2000 - Brighton - 20-24 July 2000 - 127-128

[15] A.C. Romain, P. André, J. Nicolas, Sensors and Actuators B 84 (2002) 271-277

[16] J. Nicolas, A.C. Romain, V. Wiertz, J. Maternova, P. André, Sensors and Actuators B 69 (2000) 366-371

[17] J. Maternova, A.C. Romain, J. Nicolas, J., Proceedings of the 8th conference Eurodeur, Paris, 19-21 June 2001.

[18] A.C. Romain, J. Nicolas, P. André Semin. Food Analysis 2 (1997) 283-296

[19] J. Nicolas, A.C. Romain, V. Wiertz, J. Maternova, P. André, Proceedings ISOEN 99, Tübingen, September, 20-22, 1999 – 368-371

[20] R.M. Stuetz, J. Nicolas, Proceedings of 1st IWA International Conference on Odour and VOCs: Measurement, Regulation and Control Techniques - Sydney, Australia - 25- 28 March 2001

List of figures captions

Figure 1 : Results of a Discriminant Function Analysis in the plane of the two first roots for 59 samples from 5 odorous sources in the environment.

Figure 2 : Relationship between the strength of the compost odour (x axis), as measured by olfactometry, and the resistance of the TGS800 sensor.

Figure 3 : PCA results, in the plane of the two first factors, for 4 odorous sources and odourless air (388 observations, 12 sensors).

Figure 4 : DFA results for 97 observations around 4 odorous sources : model calibrated with data of 1998 and validated with all observations, from 1998 until 2001.

Figure 5 : Equivalence between the ethanol concentration and the dilution of the compost odorous sample for the sensor TGS2620.

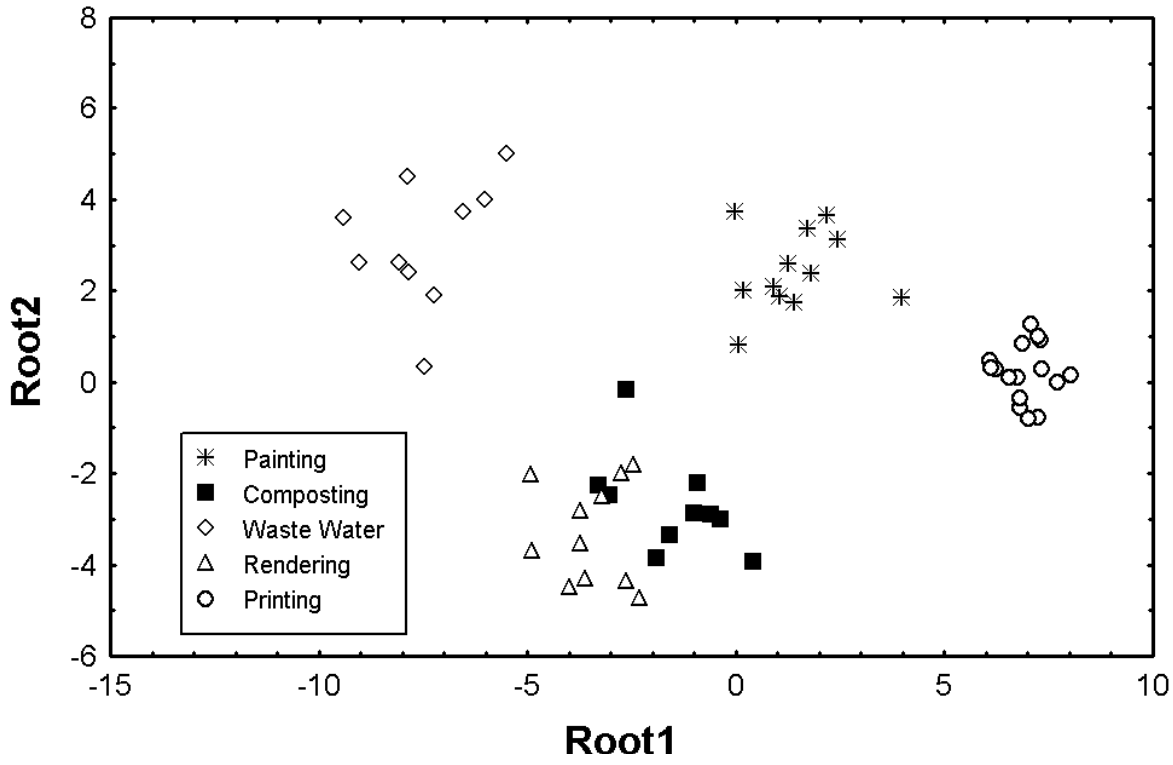
Root2
Root1
8
6
4
2
0
-2
-4
-6
-15
-10
-5
0
5
10
Painting
Composting
Waste Water
Rendering
Printing

Figure 1

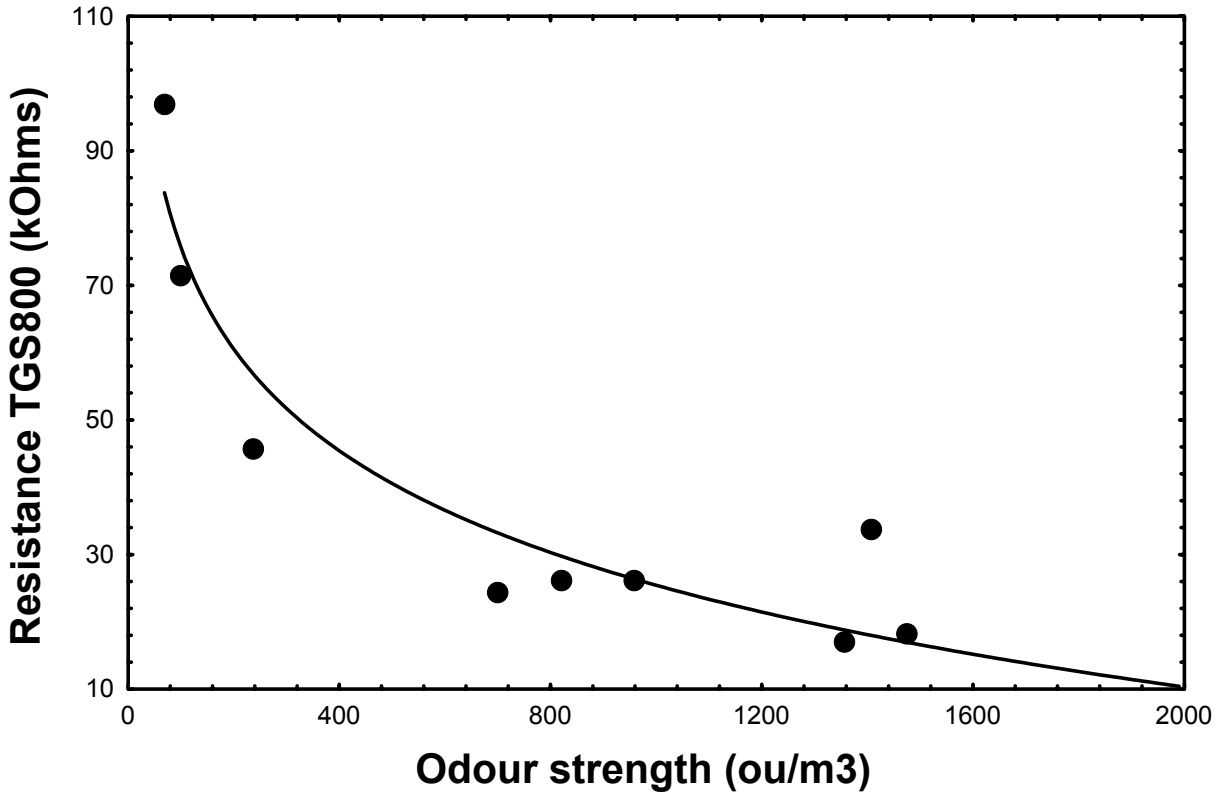
Resistance TGS800 (kOhms)
110
90
70
50
30
10
0
400
800
1200
1600
2000
Odour strength (ou/m3)

Figure 2

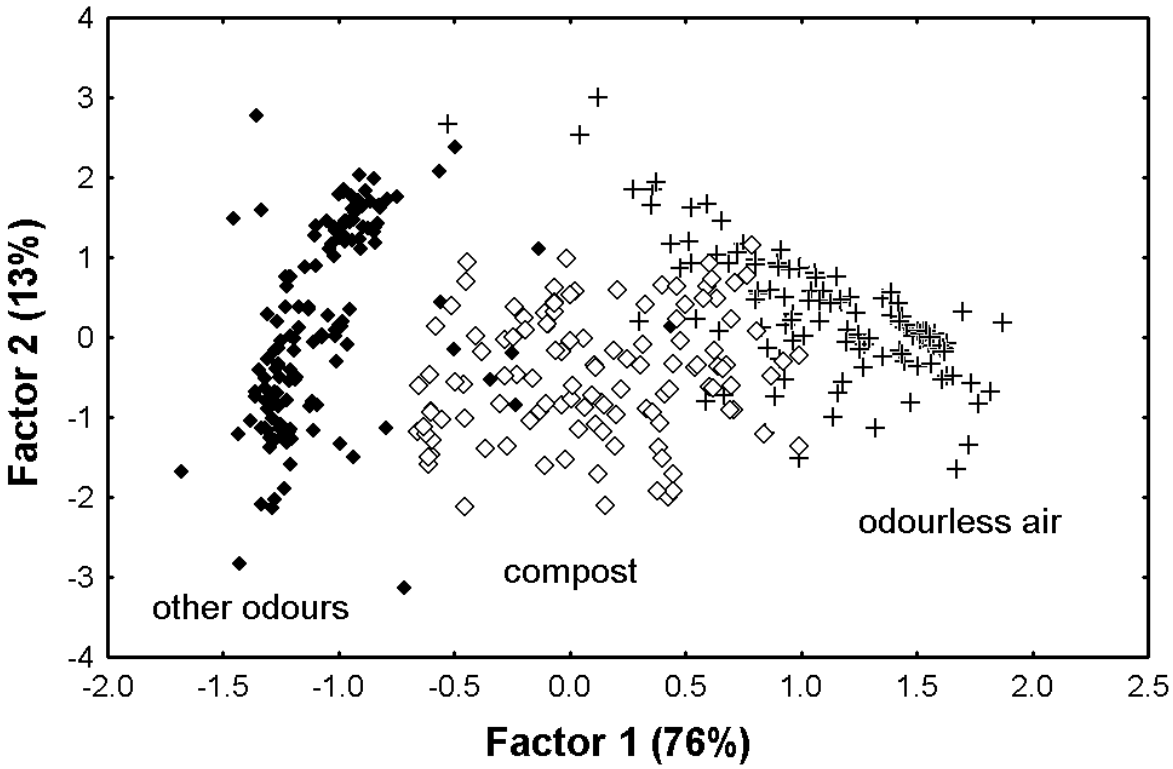
Factor 2 (13%)
Factor 1 (76%)
4
3
2
1
0
-1
-2
-3
-4
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
other odours
compost
odourless air

Figure 3

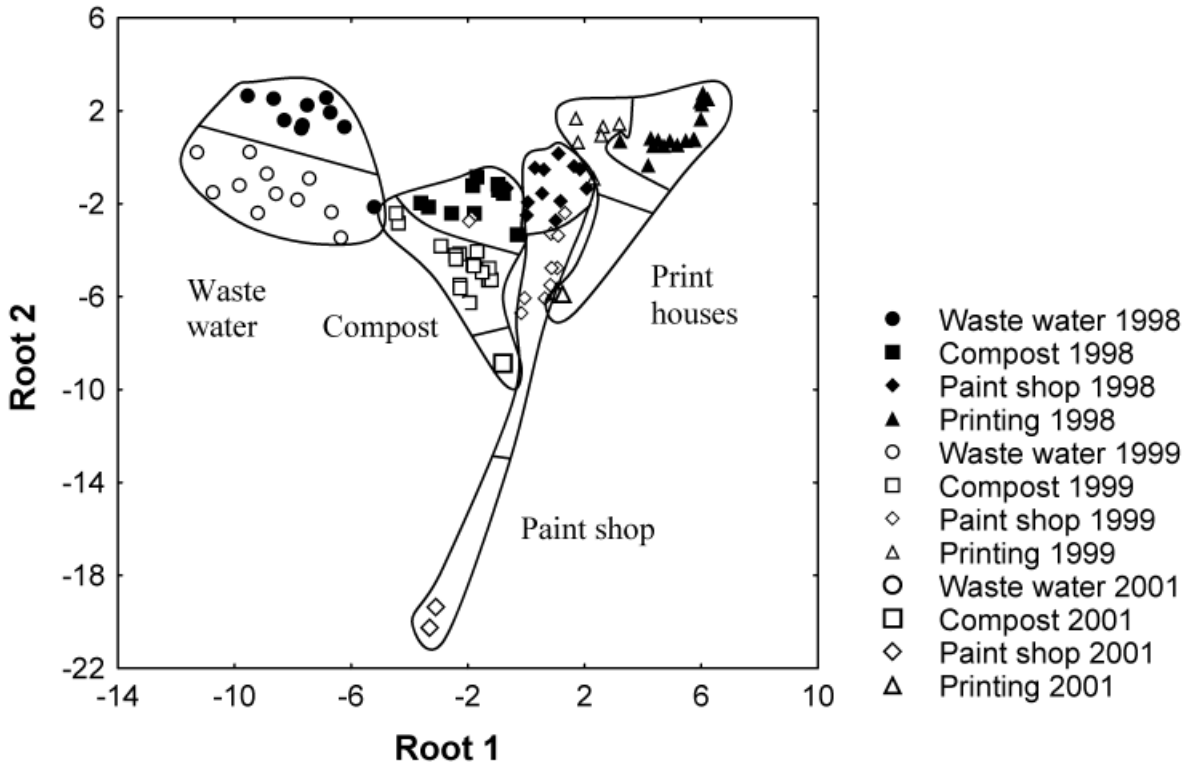
6
2
-2
-6
-10
-14
-18
-22
-14
-10
-6
-2
2
6
10
Root 2
Root 1
Waste water
Compost
Print houses
Paint shop
Waste water 1998
Compost 1998
Paint shop 1998
Printing 1998
Waste water 1999
Compost 1999
Paint shop 1999
Printing 1999
Waste water 2001
Compost 2001
Paint shop 2001
Printing 2001

Figure 4

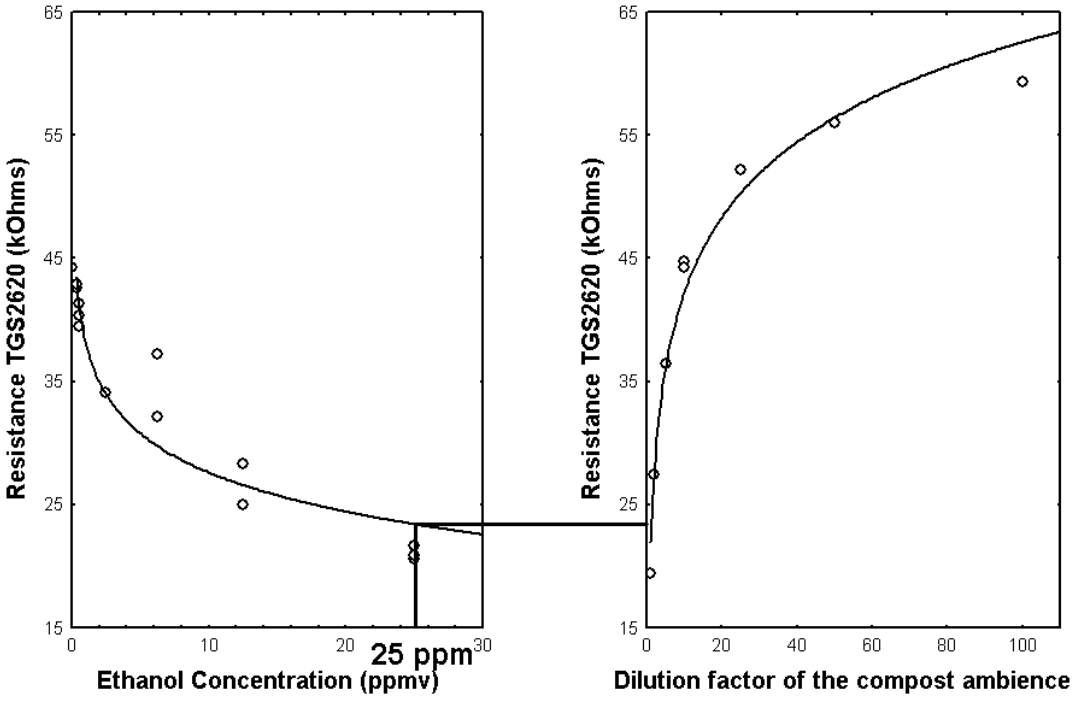
Resistance TGS2620 (kOhms)
65
55
45
35
25
15
0
10
20
30
25 ppm
Ethanol Concentration (ppmv)
Resistance TGS2620 (kOhms)
65
55
45
35
25
15
0
20
40
60
80
100
Dilution factor of the compost ambience

Figure 5