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Understanding Effectiveness of Material at Varying Depths in an Industrial Biofilter by means of an Electronic Nose

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Introduction

The studies reported here constitute an effort to prove the usefulness of electronic noses (supplied by E-Nose Pty Ltd, www.e-nose.info) to environmental pollution management. Whatever the political outcomes of current debates in Australia and elsewhere may be, emissions of industrial by-products and waste into the atmosphere, will remain a growing concern and priority.

Electronic noses or "artificial olfaction" offer real time continuous monitoring of complex mixtures of invisible compounds in the air – these are often detected by people and called "smells". E-Noses offer a method of monitoring whether, where, when and to what degree, air pollution by invisible chemicals, is happening.

Biofilters form an important part of odour control in large industrial operations which involve smell, such as landfills, waste treatment plants and food processing plants. They consist of large volumes of filter material, enclosed in a large, deep tank, usually of organic origin, such as bark and wood chips, seaweed, plant fibre, and the like. They may also contain inorganic mixtures, such as silicon sand and other minerals. The filter material is inoculated with proprietary organisms which live in the material and decompose odorant sources trapped by it. In brief, smelly industrial gases are delivered to the filter and gases without smell are released after the chemical-laden air passes through the filter.

The cost of each filter and its maintenance can be considerable. Community concern, prohibitions and penalties for air pollution mean that industrial operations described above are required to invest millions of dollars in odour filtration and abatement. In addition, weak, faulty or inadequate odour control can result in heavy fines and enforced requirements for compliance, meted out by governmental environmental protection agencies (EPAs).

The problem that currently exists for plant operators is that there is no gauge on the filters to show how close to spent the material in them is or indeed if they are effective at all. In some cases anaerobic processes in the filter add to the smell that they are supposed to be filtering (see: http://ptarpp2.uitm.edu.my/suhaimiabdultalib/fulltext/sewer%20microbial.pdf).

Occasionally a "spike" of odour is generated in the industrial operation that passes directly through the filter and out into the community, causing extreme concern in the community (as evidenced by the recent Orica emissions of ammonia at a plant in the Newcastle area, (see: http://www.smh.com.au/environment/the-untold-story-of-oricas-chemical-leaks-20111112-1ncup.html).

It is the aim of this study to bring E-Nose technology to address these problems, by continuously monitoring the potentially polluting air entering the filter and ascertaining the amount of odour removed by the filter and at what depth. A device that can monitor the efficacy of a filter in real time has the potential to alarm or set off a defensive action (dosing or secondary filtration) in the event of a "spike". This study tested whether any improvement in air quality could be measured at different depths of a biofilter, using an electronic nose (E-Nose Mk4) and if so, whether the observations were consistent across more than one device.

Figure 1: Bioaction Pty Ltd vertically structured biofilters with seven ports for extraction of air from varying depth in the filter. The E-Noses were housed in the adjacent trailer.

Figure 2: Odour from Yates operation piped to the two Bioaction biofilters.

Methods

Sample Collection for Human Test and Replication with 3 E-Noses

To control dilution of the raw odour from each outlet, odour samples were collected in duplicate in nalophan bags, from the ports located between each of the biofilter's levels. The bags were taken for analysis in Sydney within 24 hours.

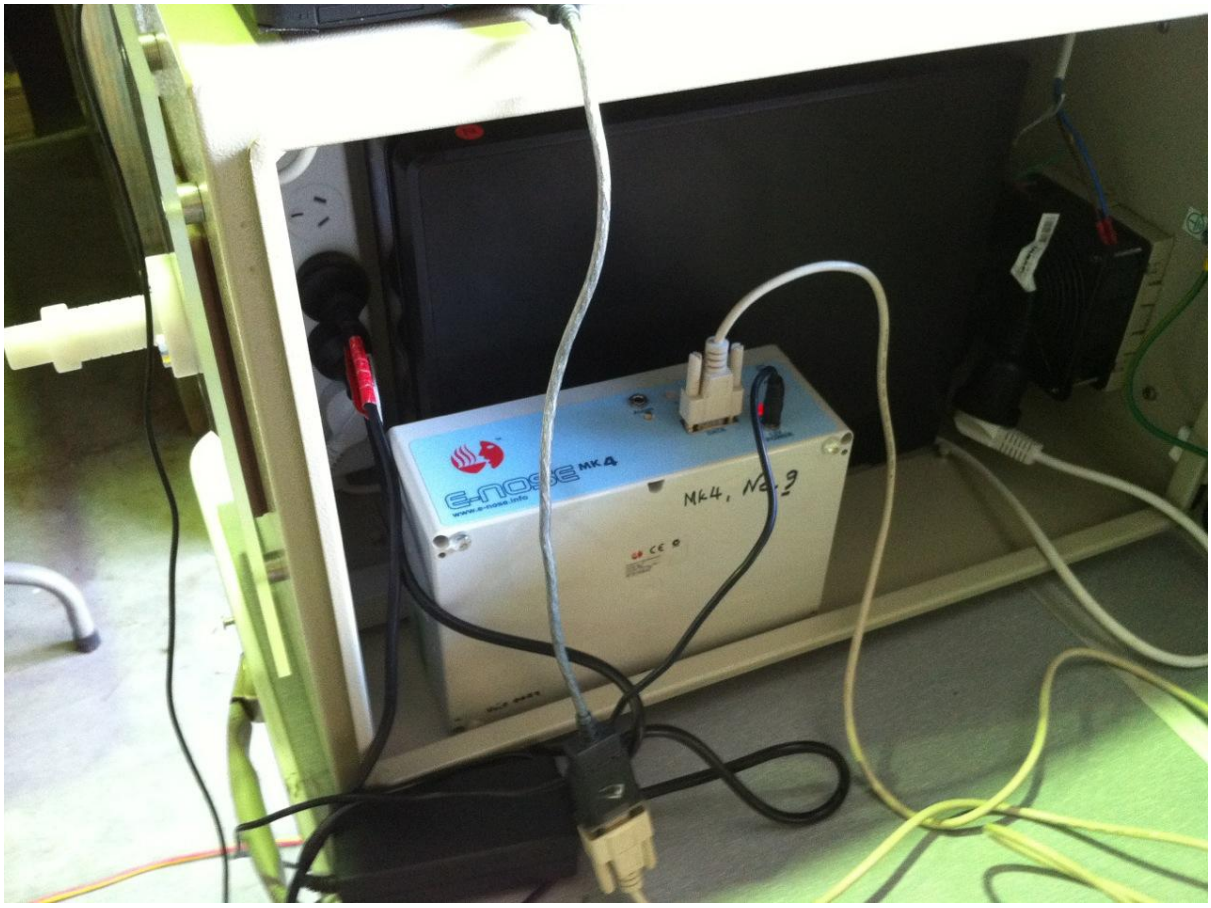

Figure 3: A Mk 4 E-Nose located in one of the cabinets.

Odour from the biofilters were also drawn into one of three customised steel cabinets inside the trailer parked next to the biofilters and continuously monitored for a period of four weeks.

Figure 4: Trailer with cabinets inside parked next to two Bioaction's Biofilter

E-Nose Measurements

Measurements of Total Chemical Load (TCL) by one Mk4 S2 E-Nose (see www.e-nose.info) were made in the E-Nose P/L Lab using the odour stored in the nalophan bags. The dependent variable, TCL, is the sum of the outputs in mV registered by the device's six chemical sensors. TCL represents the airborne molecules impinging on the surface of all the sensors and thus reflects the concentration of volatile molecules in the sample (odours and non-odours). The greater the TCL, the greater the concentration of volatile compounds in the sample.

The Biofilters

The Biofilters contained material with a proprietary formulation developed by Bioaction Pty Ltd (www.bioaction.com.au) in collaboration with the Environmental Biotechnology Cooperative Research Centre in Australia (http://www.ebcrc.com.au/). The mechanism of filtration involves a hydrophobic micropore filtration medium which effects mass transfer of organics and oxygen from inlet gases into the liquid phase, thereby removing nuisance odorants such as H_2S, ammonias and low level VOCs (see http://www.odours.com.au/Search.aspx?searchtext=FiltaOdor&searchmode=ExactPhrase). The medium is contained in vertical and modular structured vessels which require less space on site than traditional bed biofilters. The vertical structure made it possible to sample at varying depths, from ports in the wall of the biofilter. Each filter unit contained a variant of the material formulation.

Human Threshold Measurements

Duplicate samples and room air samples were given "blind" to 9 healthy non-smoker adults (7 females and 2 males all aged between 25 and 50y) to sniff. The objective of the human measurement was to determine which if any sample of odorous air lay above, below or at human detection threshold or recognition threshold of the odour. The odour was delivered in 50ml syringes drawn from the sample bags, to both humans and the machine. The human subjects were told that the odour in the syringes, if present, would be the smell of fertilizer. There were two sets of 9 syringes, 8 with odour and one with unfiltered Sydney office air. Subjects were asked to mark a questionnaire for each randomly presented sample, firstly if they could smell any odour at all, and if so, how strong it was on a scale of 1 to 10 (from very weak to strongest imaginable). They were also to indicate which bag smelled of fertilizer.

Sampling of air from the inlet and outlet of a biofilter was made by the independent supplier of dynamic olfactometry (DO) measurement (The Odour Unit Pty Ltd, Sydney - TOU). These two points were the only ones in common with the present study, although other DO measurements were made on site.

Replication with Three E-Noses

Each sample bag collected from the biofilter was tagged by letters from A to I to indicate which stage the air come from, with A being the air exiting the final stage of the Biofilter and H being the air before it enters the biofilter. The samples tagged as I were ambient room air at E-Nose office to be used as a control sample. It was the same ambient air being breathed by the human subjects during the sniffing test.

A 50 ml syringe was used to take and deliver the samples into the E-noses. As shown in the figure below. The samples were then delivered into the E-nose over the course of 5-8 seconds. The next sample was injected into the E-nose 3 minutes after the previous sample. Each experiment was performed twice.

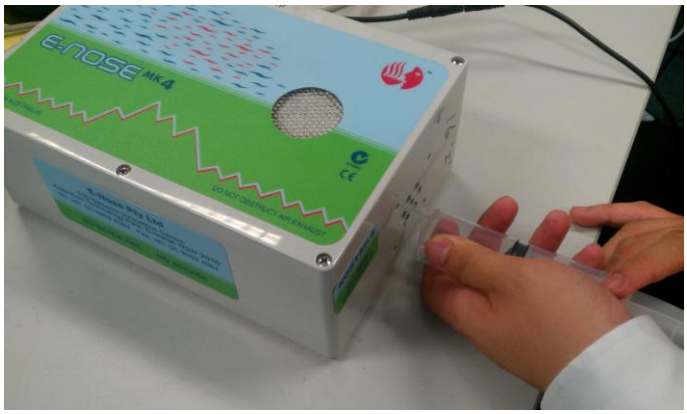

Figure 5: Delivery of each odour drawn from each sample bag with a clean syringe, then injected into one nostril of the E-Nose.

Data were recorded using Picolog software and analysed using Microsoft Excel. The E-Noses used for this experiment were the same units used previously at the fertilizer Plant. In this replication test, total peak heights were measured instead of TCL. Unlike TCL which sums all of the sensor readings, peak height value is calculated by measuring the difference between the sensor value before the sample injection (sensor baseline) and the highest value on each sensor after sample injection

Results

Direct flow from the filter ports into the E-Nose cabinets sent the instruments off-scale at lowest sensitivity settings and caused some acidic corrosion in one of the cabinet fans. This confirmed that a systematic dilution is necessary for measurement at the filter ports. It does not rule out using e-noses directly at the filter ports, provided an appropriate dilution can be effected before the air enters the device. Corrosion on the fan also raises safety issues when the raw gases are fed directly into electrical apparatus. Development of sample delivery is required to address these issues.

Experiment 1: TCL Measurement

The experiment was performed by using 50ml samples drawn from the bagged air, allowed for a small sample of odour to be applied into the devices and mixing with the constant volume of air inside the device, without overburdening the sensors. The result of the TCL measurement is shown below at Figure 5. The TCL measurement (the sum of the outputs in mV registered by the device's six chemical sensors after samples are delivered) shows that the TCL levels went down as the odour passes through the filter. This shows that the biofilter greatly reduced the amount of odorous chemical.

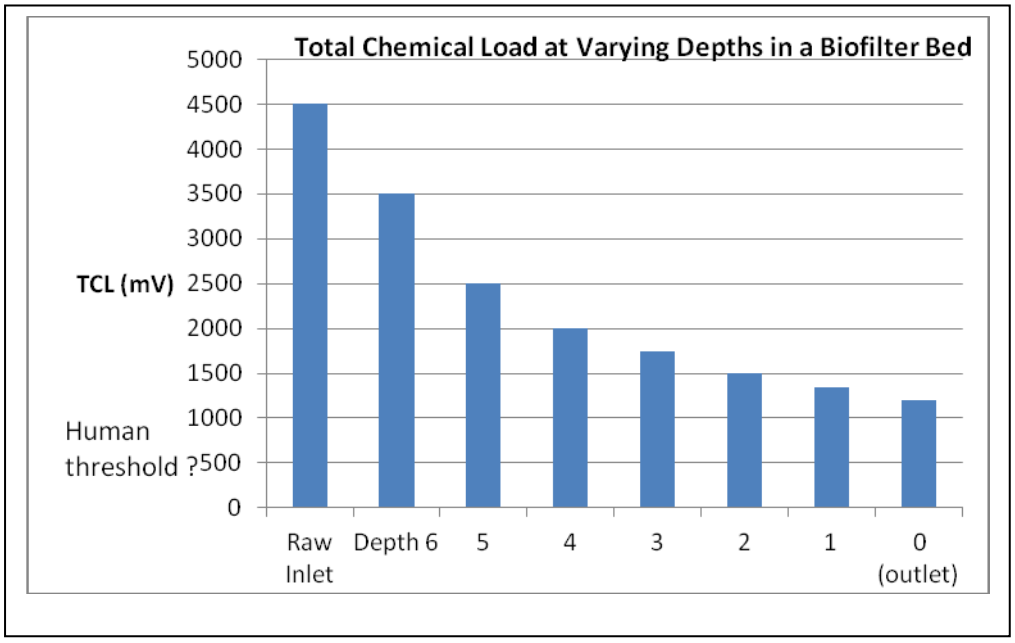

Figure 6: Data of odour (total chemical load on all E-Nose sensors) at varying depths in the biofilter, showing most chemical load near the inlet and least near the outlet. Depth 6 (Sample G) is closest to the raw inlet (H),Depth 1 (B) is near the outlet or bed surface at Depth 0 (A).

The E-Nose measurements shown in Figure 6 show that the biofilter removed 73.33% of the airborne chemicals entering the filter. Most of the filtration is done by the first 3 levels of the filter. The questions now remaining are: What is the relationship between TCL and human perception of the odour? Is the remaining chemical load coming out of the filter smelly? Is it below human detection or recognition threshold?

Table 1: Identification of human thresholds for detection (green) and recognition (blue) of odour sampled at different depths of two biofilters

% Subjects rating sample as *zero* odour

Sample	Ambient Control	A	B	C	D	E	F	G	H
Unit 1	44	33	22	22	11	11	0	0	0
Unit2	56	33	44	11	22	0	0	0	0
Mean	50	33	33	16.5	16.5	5.5	0	0	0

% Subjects rating sample as *zero or level 1* odour

Sample	Ambient Control	A	B	C	D	E	F	G	H
Unit 1	89	66	22	56	4	33	11	0	0
Unit2	66	56	56	22	56	0	11	0	0
Mean	77.5	61	39	39	50	16.5	11	0	0

The data in the above table shows that around half the group could not detect odour in the samples I (ambient), A and B. Around half of the group could detect some odour and recognise it in samples D and E. The detection threshold for the odour is therefore close to the concentration of odorants in sample B and reaches a recognition threshold in the higher concentrated sample D. The Odour Unit value of sample B is, by definition, at 1 Odour Unit.

Dynamic Olfactometry (Odour Units) Data

The Odour Unit Pty. Ltd. (TOU) sampled and measured odour in terms of Odour Units/m3 at the following points: raw Inlet, Stacks, Biofilter unit 1 and Biofilter Unit 2. Each measurement was repeated (two measurements per sampling point). The measurement for Stack sample (Odour from the outlet of the pre existing filtration system) were not the subject of study here so the data cannot be compared to the E-nose results, nor were the Odour Units measured at different depths in the biofilters. However, two data were relevant: the inlet and outlet corresponding to sample H and I respectively.

Table 2: E-Nose and TOU Results Compared

	E-nose TCL Reading (mV)	Odour Units Repetition 1 (ou)	Odour Units Repetition 2 (ou)
Raw Inlet	4500	10800	12400
Biofilter Unit 1 (Outlet)	1200	892	832
Biofilter Unit 2 (Outlet)		892	892

Experiment 2

Replication Test of 3 E-Noses

After the first experiment, fresh samples were collected in duplicate from the site corresponding to samples A to H. These samples are then injected to the 3 different, but closely matched E-Noses previously used in the monitoring study.

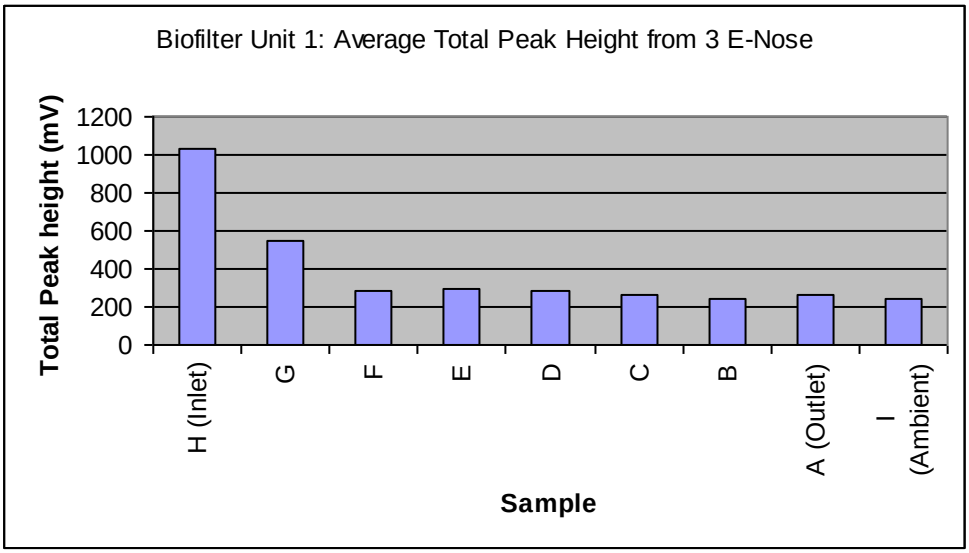

Figure 7A: Averaged responses from Biofilter Unit 1, by three E-Noses

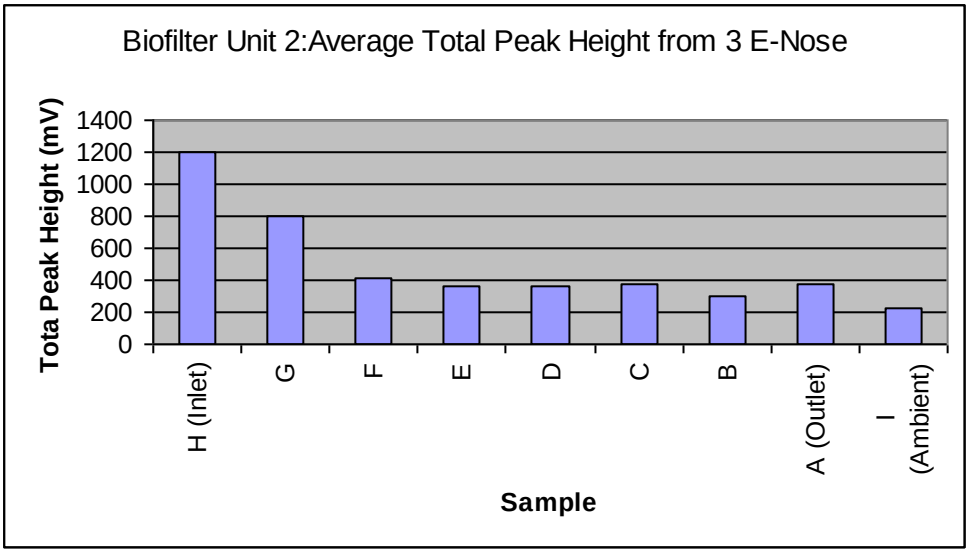

Figure 7B: Averaged responses of 3 E-Noses from Biofilter Unit 2.

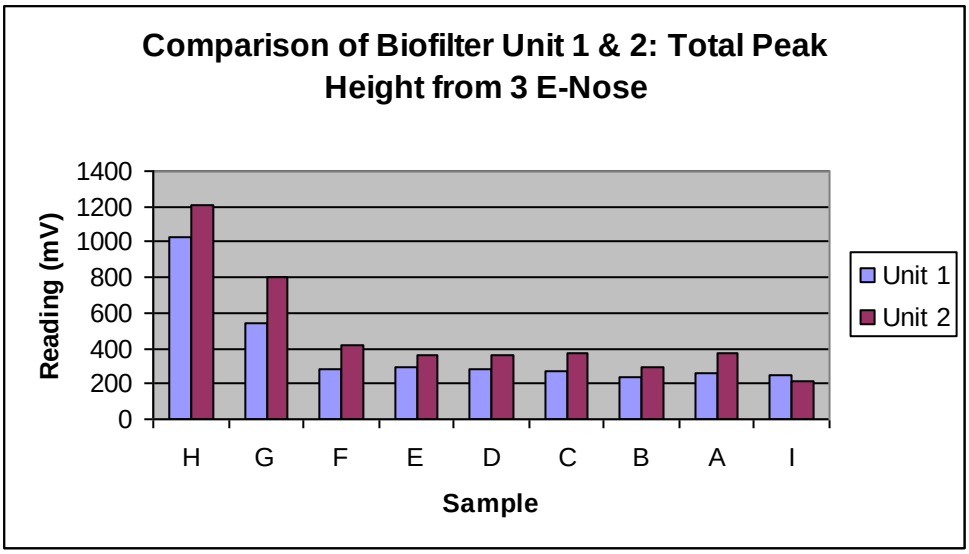

Figure 8: Comparison of Average Responses by three E-Noses on Unit 1 and 2

Radar Plots for the bagged air samples

Radar plots of the peak heights for each sensor are used to show the overall "fingerprint" of the sample odour. This plots allows us to compare how the odours change over time as it moves through the filters. It also allows us to compare the readings from the 2 filters.

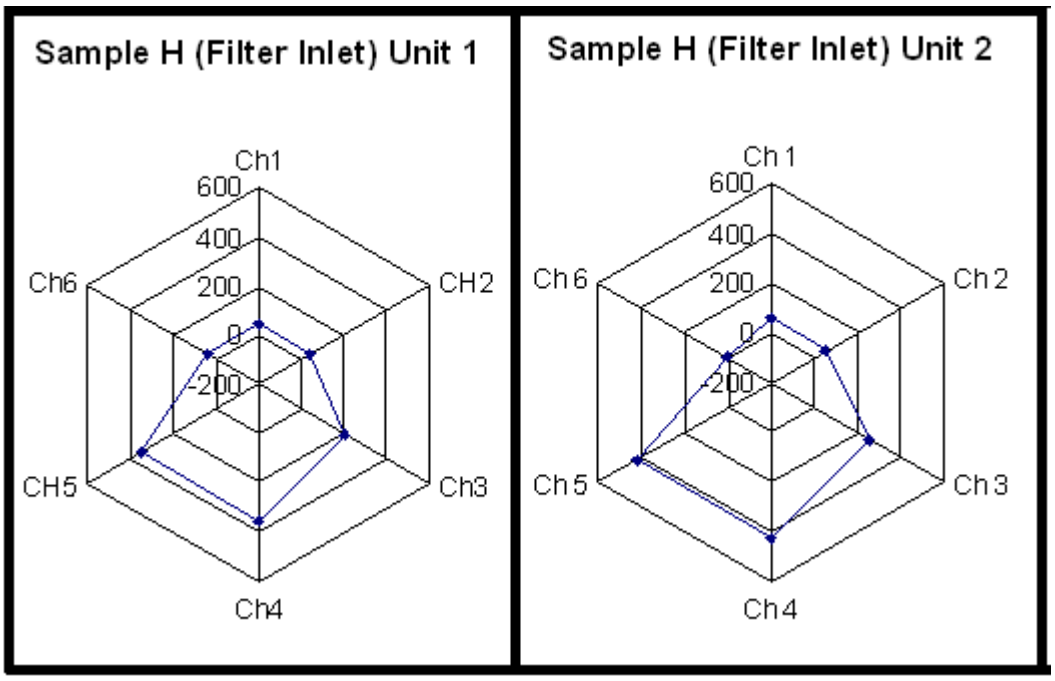

Figure 9: Radar Plots of quality of odour at portal H (inlet) of Units 1 and 2

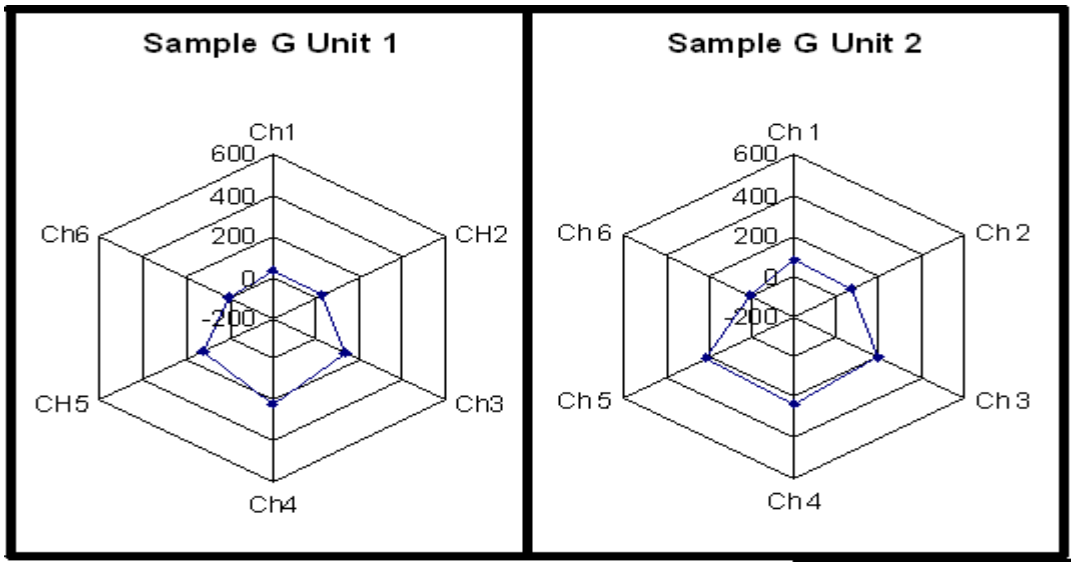

Figure 10: Radar Plots of quality of odour at portal G of Units 1 and 2

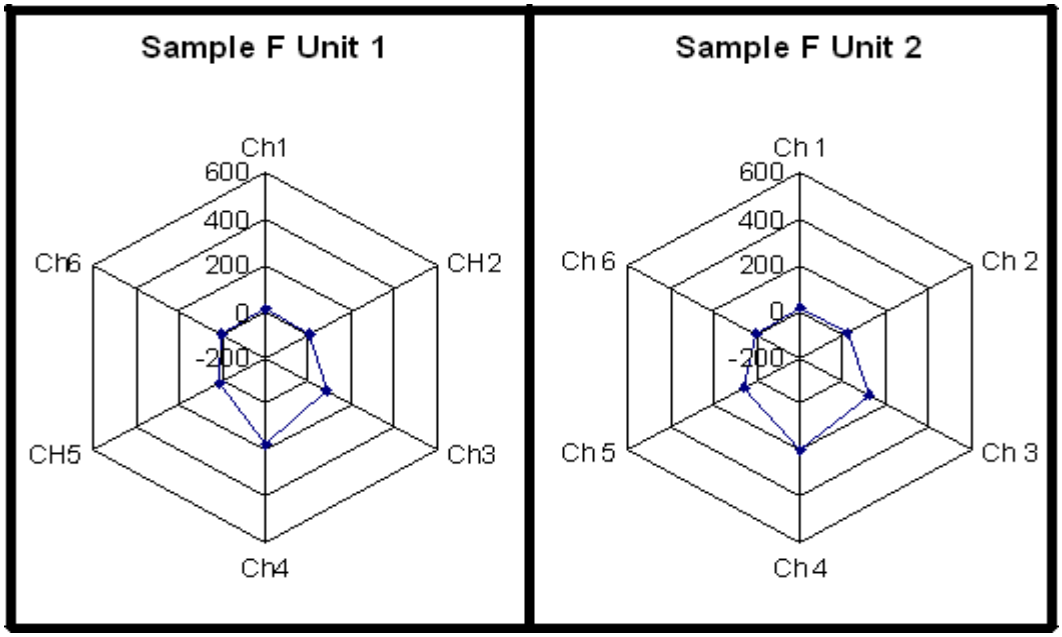

Figure 11: Radar Plots of quality of odour at portal F of Units 1 and 2

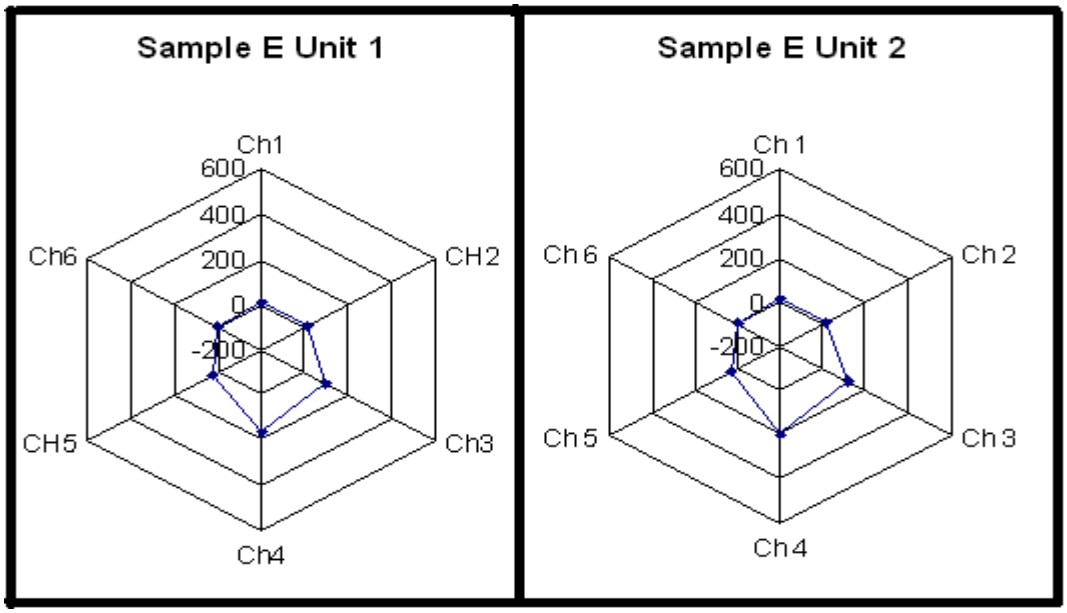

Figure 12: Radar Plots of quality of odour at portal E of Units 1 and 2

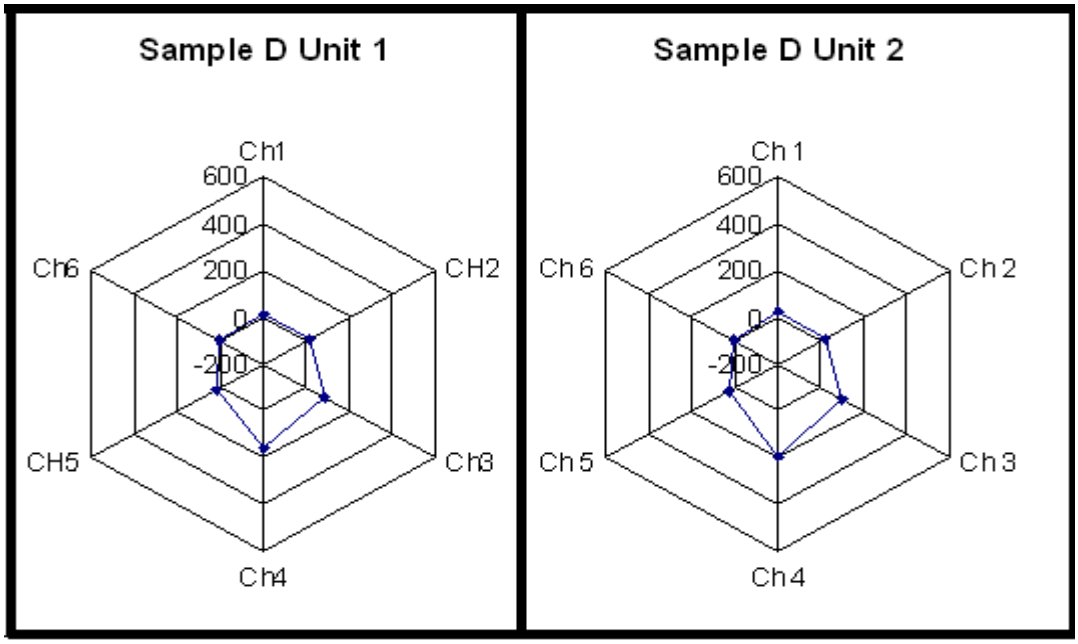

Figure 13: Radar Plots of quality of odour at portal D of Units 1 and 2

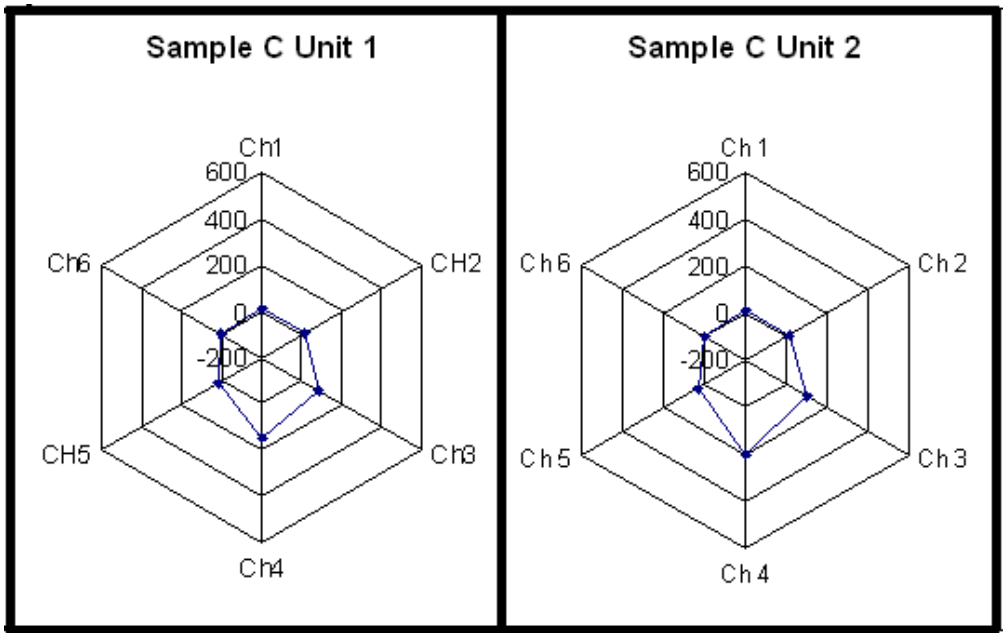

Figure 14: Radar Plots of quality of odour at portal C of Units 1 and 2

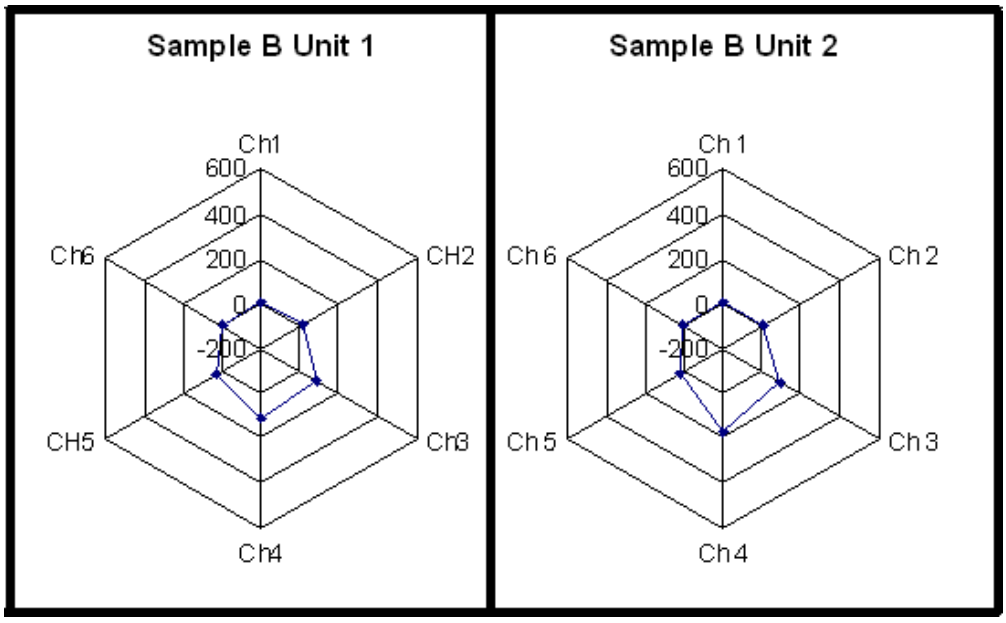

Figure 15: Radar Plots of quality of odour at portal B of Units 1 and 2

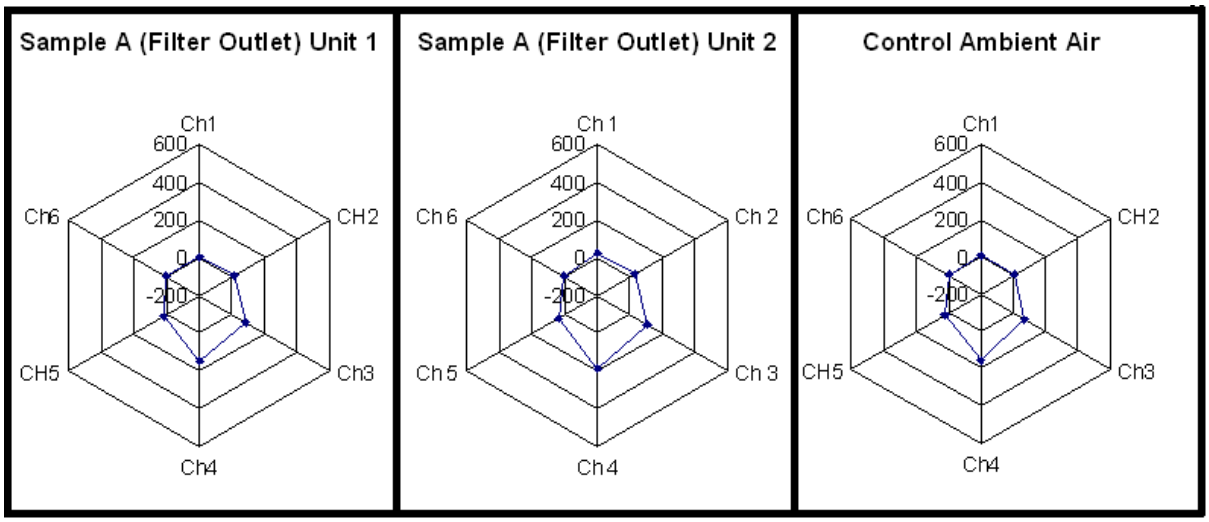

Figure 16: Radar Plots of quality of odour at portal A (Outlet) of Units 1 and 2

Table 3: Unit 1 Average Results

Sample	Unit 1 Total Response 3 E-Nose Average (mV)	Response Reduction at depth compared to unfiltered sample (sample H)
I	243.9448	
H	1031.837	
G	544.25	47.25%
F	279.5817	72.90%
E	295.61	71.35%
D	287.6133	72.13%
C	267.2467	74.10%
B	236.995	77.03%
A	258.8133	74.92%

Table 4: Unit 2 Average Results

Sample	Unit 2 Total Response 3 E-Nose Average (mV)	Response Reduction at depth compared to unfiltered sample (sample H)
I	219.515	
H	1205.713	
G	800.0767	33.64%
F	414.6167	65.61%
E	364.535	69.77%
D	360.6983	70.08%
C	368.7767	69.41%
B	298.6383	75.23%
A	368.84	69.41%

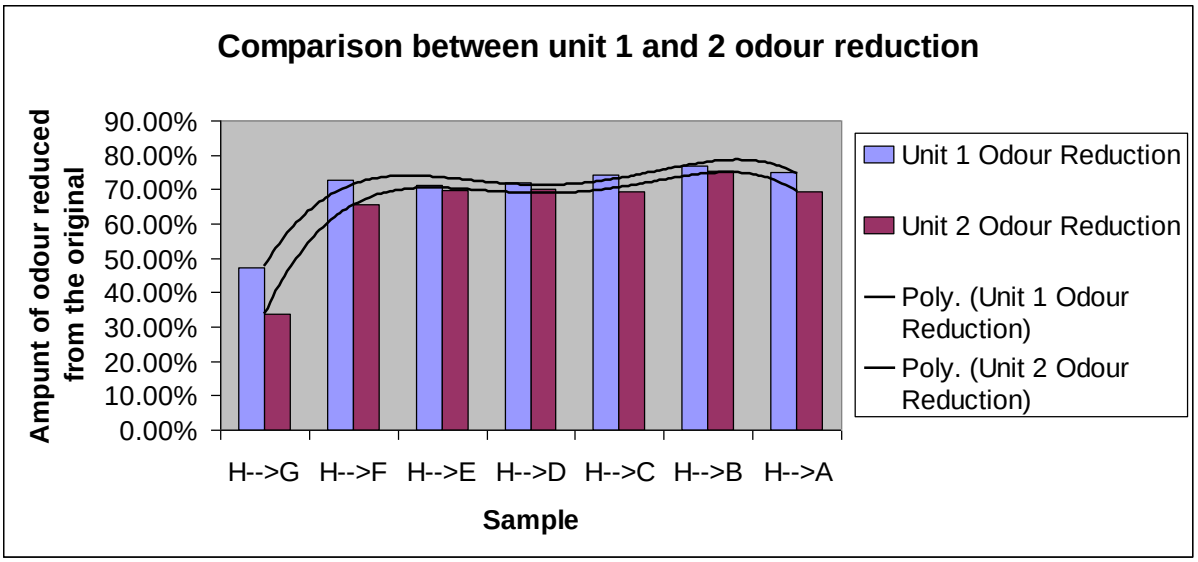

Figure 17: Odour Reduction Comparison between Biofilter Units 1 and 2

Table 5: Biofilter Outlet Air Result: How much cleaner/dirtier than room air?

Biofilter Unit 1	**Total Response (mV)**	**Value Compared to Room Air Average Total Response (Perfect Match Value = 100%, <100%= Cleaner, >100%=Dirtier)**
E-Nose 0001	136.33	58.83%
E-Nose 0005	309.14	133.41%
E-Nose 0009	330.97	142.83%
Average	258.8133	111.69%
Biofilter Unit 2		
E-Nose 0001	291.035	125.59%
E-Nose 0005	415.43	179.27%
E-Nose 0009	400.055	172.64%
Average	368.84	159.17%

Discussion

Experiment 1

A significant number of the human panel judged that Sample A (outlet) and sample B (a level above the outlet) had no odour. By Sample C detection of presence of odour was made by majority of subjects. In sample D most subjects could still not recognise the odour. This indicates that the human odour detection threshold is at air loaded with molecules at level B in the biofilter, but they remain difficult to identify as having any particular quality until they reach a load down at level D.

The human sniffing experiment, showed *that the remnant TCL leaving the biofilter is below the human threshold of detection of odour from the biofilter*, as measured by a panel of 9 adults sniffing bagged odour from the various biofilter ports. This means that 50% of people will not be able to detect any odour leaving the biofilter at the outlet, nor at depth 1 (in this figure, port B on the filter). This also indicates that, by definition, odours from sample B is equal to 1 odour unit.

At depth 3, (Port D on the filter) air at this depth is above the human *detection* level but below human *recognition* threshold. This means that 50% of people while being aware of an odour could not recognise its quality. This allows the placement of the cut-offs shown in figure 18.

Supra-threshold levels of TCL informs the operator (or a control system) that action is needed, such as activity change, dosing, or refreshing filtration material.

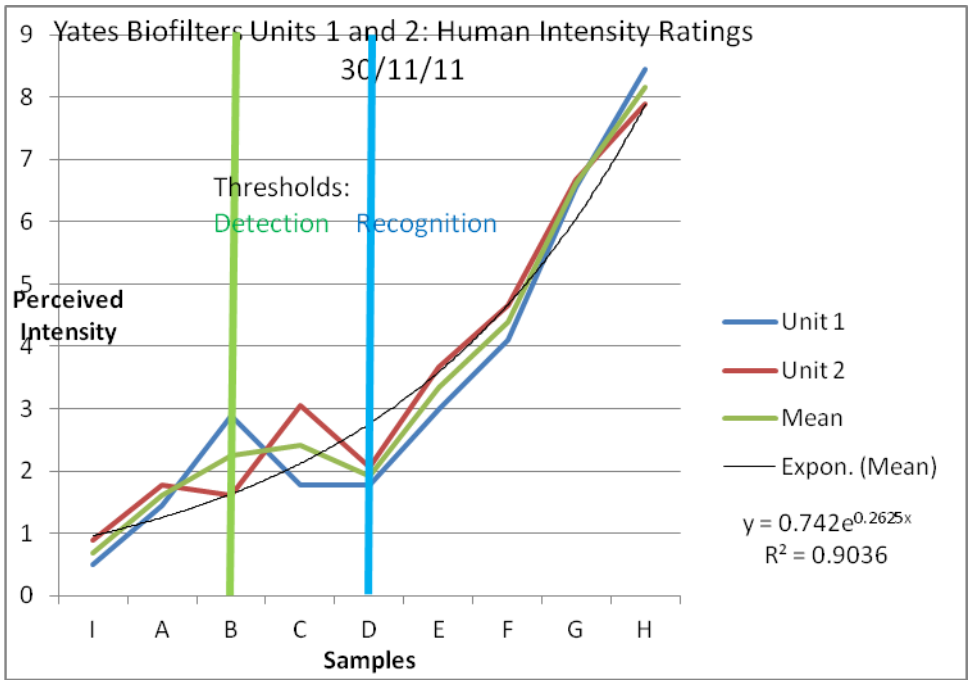

Figure 18: Human assessments of the two sets of air samples from Biofilter Units 1 and 2.

Linear calibration was derived from the two measurement points made by both methods. Once other points are made (at different depths in the biofilter by DO, the non-linear (better predictive) relationship and calibration equation can be derived. Using the available OU data, namely, data from the inlet odour provided by TOU and the odour level determined for sample B (1 OU). The following linear relationship between E-Nose and DO can be seen in Figure 19.

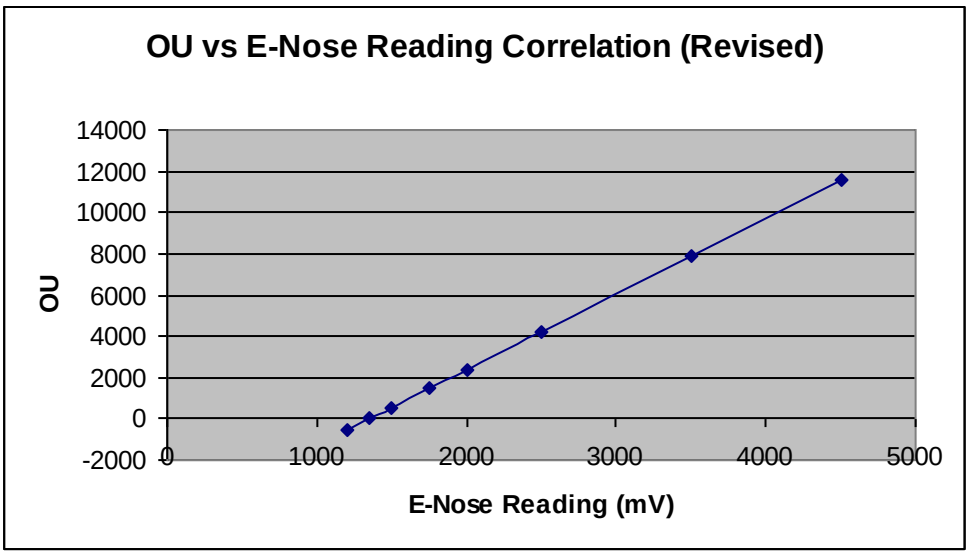

Figure 19 : An independent company's Linear Model after taking into account human panel test and TOU data for inlet OU Values

In terms of dynamic olfactometry (OU) measurements, the outlet from Bioaction's Biofilter still requires about 892 more unit volumes of dilution before the odour level falls below the human detection threshold. However, the human sniffing experiment performed by E-Nose P/L showed that the TCL measurements at the outlet (A) and at the port below the outlet (B) were below human detection threshold. This corresponds to an OU measurement no greater than unity. The calibration curve based on the E-nose measurement at G&H corresponds to odour removal by the biofilter of 100% shown in figure 19. Both biofilter units were removing odoriferous volatiles to below threshold. By the time the fertilizer odour had reached the biofilter outlet, it was below 1 OU. The relationship sought in Figure 6 can now be shown in figure 20.

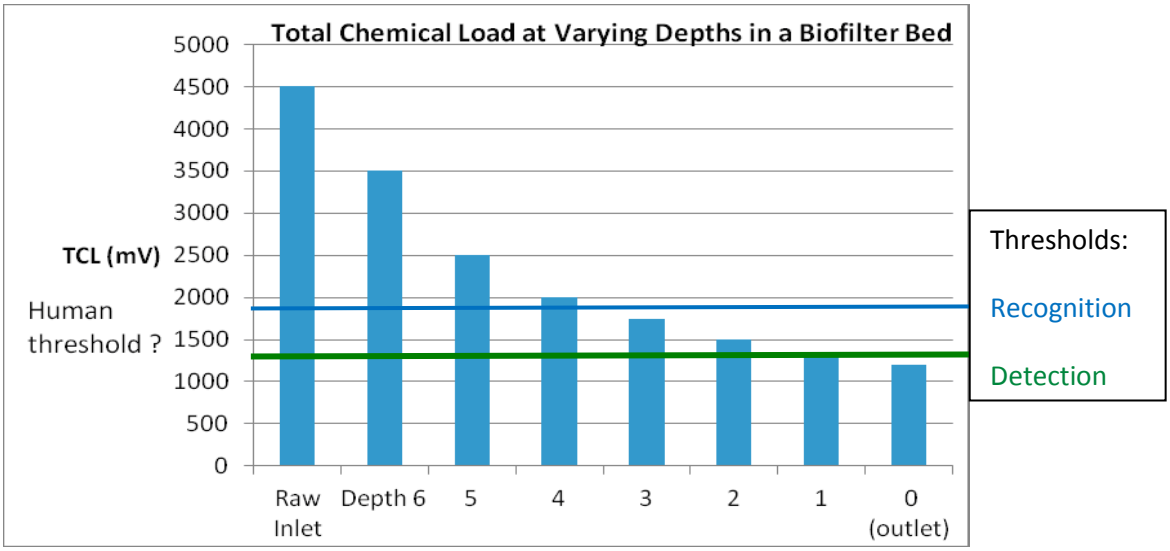

Figure 20: Superimposition of human thresholds found in this study on the data from duplicate samples applied to the E-Nose. After level 4, odour fumes passing through the filter have been reduced to below human recognition threshold and by level 1 they no longer can be detected at all by 50% of normal adults.

Experiment 2

The aim of this experiment is to compare the general performance of 3 E-Nose and the two biofilters.

The radar plots constructed from the sensor readings of each sample allows us to obtain a representation of odour quality. As observed from the Figures 9-15, channel 3, 4, and 5 were the most sensitive to the fertilizer odour. Another notable difference that can be observed from the graph is that channel 5 no longer measures significant odours at depth F. This implies that the biofilter has successfully eliminated the volatile organic compounds detectable by this sensor at depth F. Both filters are in the same condition, as proven by figure 8, where there are no significant differences between the average readings between the 2 different biofilter units.

It also can be seen from the graphs, that the results are not exactly similar across all 3 E-noses. These dissimilarities can be attributed to uncontrollable variations in the syringe, the delivery method and by minor variations in sensor properties and internal factors such as fan speed. Nevertheless, the results also show that at least 2 E-noses gave a relatively similar reading at any given sample.

The overall Results of the experiment can be seen from the average of 3 E-Nose comparing Unit 1 and Unit 2 (Figure 7 and 8).

In both filter units, the same effects of filtration on odour could be seen. The most noticeable reduction in airborne chemicals happened at both the first and the second stage of the biofilter (H-> G and G-> F, see Figure 6-8). From Figures 9-10, analysis on air exiting from 1st stage of filtration (G) and the 2nd stage of filtration (F) shows a great reduction in peak height in channels 1,2,3,4, and 5.

However, channel 6 remains flat (no noticeable increase in value) throughout the entire experiment. This was also observed in both biofilters.

After the second stage, the reduction in airborne chemical become less noticeable in both filter units (Figures 11-15), most of the sensor's reading (channel 1,2, and 5) shows that the some of the chemicals present in the samples quantity have dropped into room air level. This is shown by the fact that the injection of the samples only triggers a very small peak height on most channels from sample F onwards. The radar plots for each sample also show little or no change after stage F, in both filter units. Channels 3 and 4 are an exception due to the fact that their peak heights are still above 100 mV, however it also should be noted that their peak heights fluctuate slightly suggesting that the chemicals captured by the two sensors are not being removed by the biofilter after the 2nd stage (or removed at a very slow rate). Similar result can be seen from the radar plot, after the drastic change in "odour fingerprints" shown in Figures 9-10. These quality measurements remain mostly the same from Figures 10-16. In all of the above, there is a striking consistency between biofilter units 1 and 2.

As shown by Table 1, the human test shows that most the panellists rate the odour as 0 (no smell at all) or 1 (very weak) after the 4th level of filtration (D). The result from the machine (E-Nose) experiment differs slightly from the human experiment result showing that the sensor value stabilized after filter at depth 5 (F) and there are no significant difference between the chemical concentrations in the air leaving the filters at depth 5 (F) and the air leaving the biofilter, besides small random (unaccounted for) fluctuations. However, the human panel reported a strong smell at depth 5 (F) , weak smell at depth 3 (C) and no smell at the outlet. The variation in machine readings appears to have not matched this sensitivity in the human, suggesting that ultimately the human nose is the best available measuring instrument. This issue can be addresses by setting the machine threshold for "clarity" (no odour) of filtration at a conservatively low level, as shown on Figure 20, where a TCL of around 1300 represents human detection threshold for odour.

Further calculations also show that the first two stages on average remove between 69-72% of the detectable airborne chemicals. The first 2 stages are therefore responsible for more than 90% of the removal process since the entire system only removes, on average, between 69-75% of the detectable airborne chemicals (as measured by the sensor array). The highest chemical removal recorded was 89.27% and the lowest was 37.15%. The biofilter does not remove every airborne molecule (if it did, these percentages would be around 100%). The outlet air was more heavily laden with airborne molecules than the ambient room air at the lab (Figure 16 and 17). The key point, however, is whether the filter removes enough of the smelly compounds for them to be no longer detectable by the human nose at the exit point of the filter. The answer is shown to be "yes": the filter reduced odorant output to below human threshold and did most of this work within the first depth-layers of the filter.

The variation in the data from repeated samples and across the three instruments can be attributed to sample delivery variation as well as non-uniformity in the chemical sensors. The way chemical sensors are constructed, using surface layers of rare earths (or other proprietary materials) on flat plates, no two chemical sensors can be expected to be perfectly identical.

Another result shown in Figures 9 -16 is that even after 7 stages of filtration, the remaining chemical level in the air is still slightly higher compared to room air as can be seen from Table 5. We assume this is the difference between ambient air on site and room air in Sydney.

It is worth noting that the E-Nose shows that most airborne chemicals entering the filter bed are removed between Level 6 (nearest to the inlet) and Level 4 (about midway into the filter). This predicts that the deeper material is doing most of the work and that deeper material is likely to become exhausted sooner than material closer to the outlet. This informs maintenance is needed at the levels nearest the inlet earlier than near the outlet. This may confer economic advantage to the plant management, in term of filter maintenance.

Lastly, there is no significant performance difference between the two units of Biofilter. Difference in performance is so small it can be simply attributed to other factors such as sample deliver speed and difference in airflow within the E-Nose. Figure 17 shows that the parallel trendlines of the two biofilter units.

Conclusions

The E-Nose offers a continuous real-time monitor of what is happening inside the filter and how much volatile chemical material is being removed by the filter. The method can be applied to testing of current and future technical developments in filtration media, to managing filter efficiency and for early warning of fugitive odours (“spikes”) breaking through the filter.

Using both e-nose and dynamic olfactometry on at the same sampling points, the relationship between them can be expressed as an equation. The equation can be used to convert E-Nose measurements to Odour Units automatically.

Further work aims to show that the E-Nose can directly control variables in real time, to keep the biofilter optimally effective. Material changes or exchanges of shallow for deep material will optimise filtration efficiency and costs and minimise the risk of fugitive odours. E-Nose measurement of the filter outputs can also control a dosing system, routeing odour to a special emergency system or other odour-abatement regime.

This study has shown the usefulness of an electronic nose in monitoring odour from a biofilter.

The data from the E-Nose matched the human data in a predictable way and showed that once calibrated with human perception, it can be used to inform an operator what is happening to odour going into, inside, and coming out of biofilters. The data was consistent when measured by three independent e-noses.

The data showed that there was no difference in performance between the two biofilter units. This informs the designers that proprietary formulations used in each are functionally equivalent, and guides them to decisions based on the other factors such as cost and longevity of filter materials.

The electronic nose is likely to play an important part in the control of odours in this and other chemical engineering contexts, with benefit to plant operators in terms of cost and social responsibility.

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