

Chapter Five - Results

5.1. Experimental development

5.1.1. Initial laboratory testing

A previous study by Stuetz *et al.* (1998) utilised an eNose model D (Neotronics Scientific, UK) to analyse raw and treated water samples for tainting compounds. As described earlier (Chapter one) this research had several limitations; the most limiting of which was the inability to operate continuously. To advance this study a temperature-controlled flow-cell was designed (Figure 4.2.2.2). The flow-cell emulates a remote heated sample chamber with the ability of processing several samples per hour. An internal chamber contains the sample while an external jacket regulates the samples temperature. The headspace samples are transferred to the sensor array via a gas transfer line. It was conceived that the flow-cell would operate on a cyclical and continuous program including; headspace generation, headspace analysis and sample change over.

Preliminary studies were used to establish the stability of the sampling apparatus for on-line analysis of RO water. The flow-cell was set up for batch sampling in order to collect data over periods of several days. Initial sampling parameters used to establish the flow-cell stability were;

Sparge flow = 100 ml/min; Sparge porosity grade = 0; Sample Temperature = 25 °C.

Figure 5.1.1.1 shows an example of the system stability using the preliminary sample parameters. The system showed several instabilities in the sensor responses; internal nose temperature and RH values. The system temperature is stable during the day but clearly decreases during the night (at around run 150). The peaks seen in the RH and sensor response were most likely the result of condensation in the headspace transfer line between the flow-cell and sensor array chamber, causing changes in the sensor chamber. Such fluctuations would be unsuitable in a continuous monitoring system where the aim is to detect sudden and slight changes in water quality due to sensor response changes.

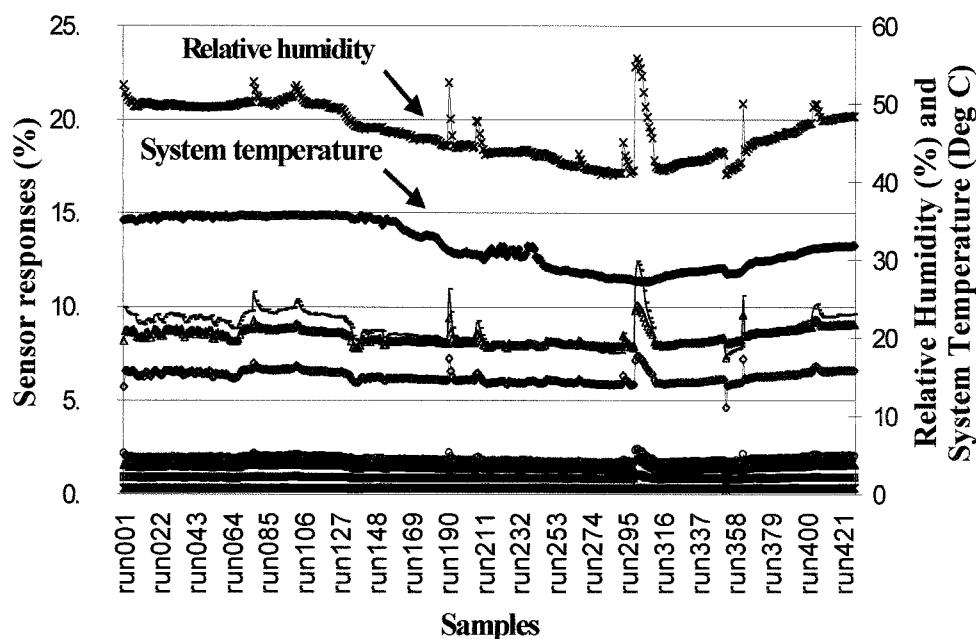


Figure 5.1.1.1 Plot of sensor responses showing instabilities in preliminary studies.

In order to produce a more stable system several modifications were introduced to the monitoring system in addition to operational parameters being changed;

- A temperature controlled heated tape was attached to the transfer line between the flow-cell and sensor array. The heated tape was controlled and set to 30 °C
- A temperature regulator was inserted into the sensor array module in order to maintain a constant temperature.
- The sampling methodology was modified to allow for purging of the sample transfer line between each headspace analysis.
- A statistical design was employed to determine the impact of the three controllable variables in the sampling system (Sample temperature, sparge gas flow rate and sparger porosity grade).

A photograph of the modified monitoring system showing sampling apparatus, temperature controlled transfer line and temperature controlled sensor array module is shown in Figure 5.1.1.2. A temperature gradient between the flow-cell and sensor array

was established to eliminate condensation buildup (the flow-cell being controlled at 25 °C, the heated transfer line at 30 °C and the sensor array at 35 °C). The transfer line was purged to enable flushing of the sample between acquisitions thereby reducing cross contamination between samples. A statistical design was carried out (as described in materials and methods section 4.4.3) after the physical modifications had been implemented. The results are summarised in Tables 5.1.1.1 – 5.1.1.8.

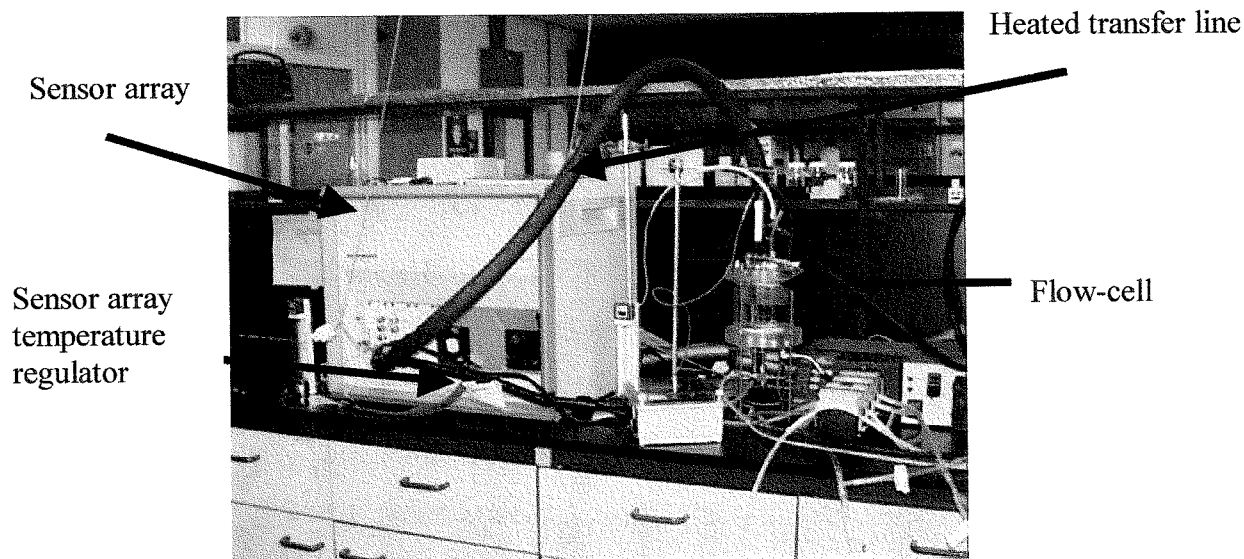


Figure 5.1.1.2 Modified laboratory set up including heated transfer line and temperature regulated sensor array.

The data in Table 5.1.1.1 presents the recorded RH values from the statistical design experiments. The design was repeated over a period of three days to establish repeatability in the chosen parameters.

Table 5.1.1.7 Main effect coefficients and interaction coefficients generated for the 3x8 RH experiments on DI-water

Coefficient	Day 1	Day 2	Day 3	Average
A1	0.56	1.50	0.87	0.98
A2	0.98	0.25	-0.5	0.24
A3	-5.57	-5.79	-6.75	-6.04
A12	-0.43	-0.01	-0.51	-0.32
A13	-0.86	-0.22	-0.65	-0.58
A23	0.43	-0.47	-0.88	-0.31
A123	-0.36	0.11	-0.36	-0.20
A0	38.65	37.44	36.97	37.69

The results for each coefficient were averaged over the three days to provide one set of generalised coefficients. The significance of the averaged interactions can be calculated by dividing each of the coefficients by averaged A123 value (the interactions between all three components) (Table 5.1.1.8). The magnitude of the value indicates its significance.

Table 5.1.1.8 The significance of the averaged main effect generated for the three days of the 3x8 RH experiments on DI-water

Coefficient	Average for the three days	Significance
A1	0.98	-4.82
A2	0.24	-1.19
A3	-6.04	29.71
A12	-0.32	1.56
A13	-0.58	2.84
A23	-0.31	1.51
A123	-0.20	1

Where

A1 = The main effect coefficient for V1 (Gas flow rate)

A2 = The main effect coefficient for V2 (Sparger porosity)

A3 = The main effect coefficient for V3 (Sample temperature)

The data in Table 5.1.1.8 implies that the sample temperature has the most significant effect on the value of RH produced with gas flow rate second and the interaction of temperature and flow rate ranking third.

Figure 5.1.1.3 (provided by Neil Collins (courtesy of Marconi Applied Technologies) using Statistica statistical package) summarises the interaction effects of the three variables from the statistical design experiments. The plots indicate where a developing region of RH stability (desirability) can be observed. The data implies that the model is improving as the system is entering a region where the linear approximation holds well. The desirability function is the relationship between predicted responses and the desirability of the responses. The profiling of desirability in such plots involves assigning predicted values a score from 0 to 1 (very undesirable and very desirable respectively). In each of the three contour plots the interactions of each component provide a consistent picture; as flow and temperature increase with a decrease in porosity a stable and reproducible RH is attained. These plots determined the value of each parameter to be used as the starting point for future studies:

Sparge flow = 168 ml/min; Sparge porosity grade = 0; Sample temperature = 25.5 °C.

The monitoring system was re-tested for stability using the above parameters. Figure 5.1.1.4 shows that over a period of 900 runs (~5 days) a more stable sensor response profile was achieved compared to Figure 5.1.1.1 as no sudden changes in RH or sensor response are present. Some gradual fluctuations over time are still observed in the RH and response profiles. These may be the result of minor environmental changes in the monitoring system due to the sample being analysed or slight changes to the environment in which the equipment is housed.

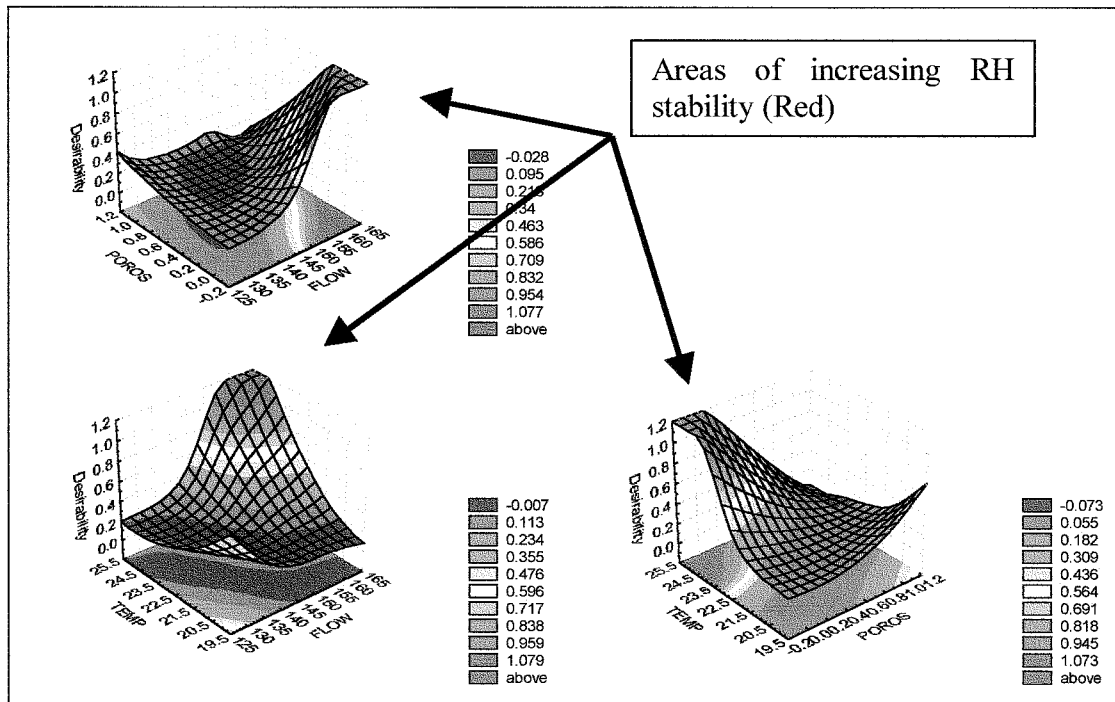


Figure 5.1.1.3 Statistical design plots showing areas of increased stability in RH generation.

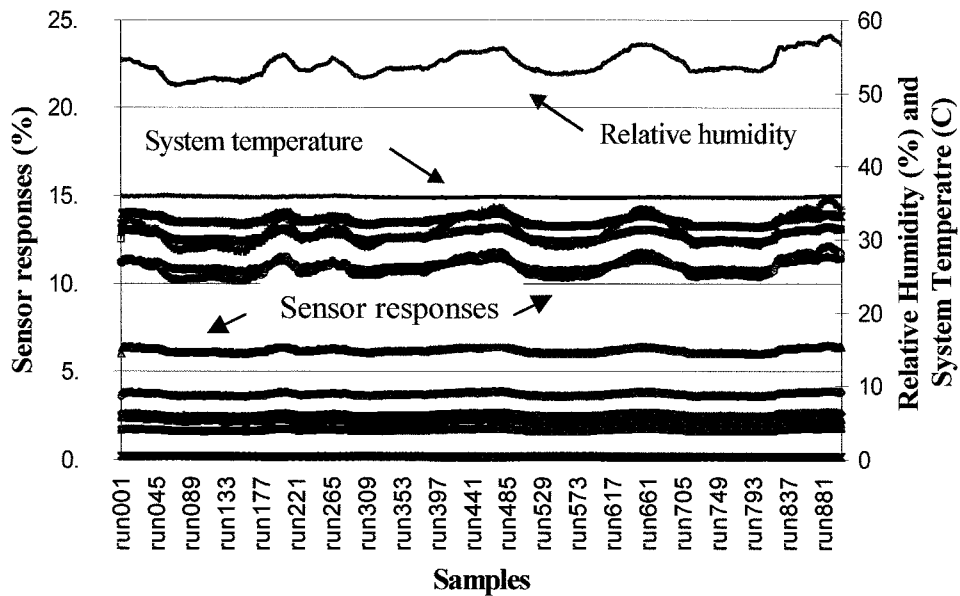


Figure 5.1.1.4 Plot of sensor responses and RH showing improved system stability due to the implementation of a statistical design.

5.1.2. Reducing RH and gas flow effects

Conducting polymer sensors are known to be sensitive to changes in RH and gas flow rates (Gardner and Bartlett 1999) which can result in slight fluctuations in sensor response profiles (as observed in Figure 5.1.1.4). Figure 5.1.2.1. shows a more detailed plot of 4 sensor profiles and RH for 999 data points (approx. 4 days) which indicates the a diurnal drift is evident in the RH and sensor response profiles as the monitoring system, sample generation temperature, headspace transfer and sensor array module are maintained at 25.5°C, 30°C and 35°C, respectively. The repeated fluctuation suggests that some external factors are effecting/changing the RH of the sample, but the fluctuation is a gradual change (i.e. not rapid).

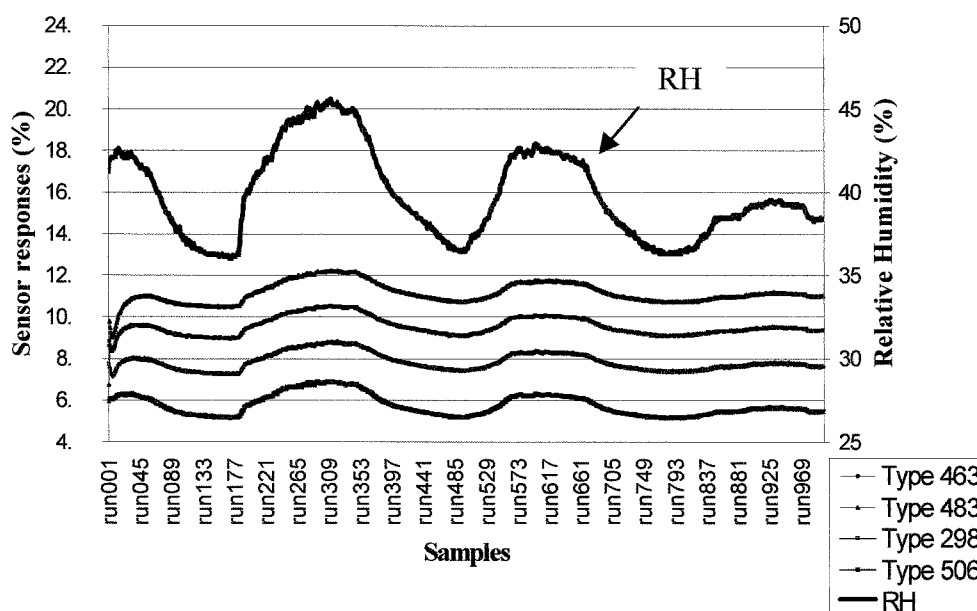


Figure 5.1.2.1 Plot of diurnal drift in sensor and RH Profiles over a 4 day sampling period.

Figure 5.1.2.2 illustrates the same plot as Figure 5.1.2.1 (except minus the sensor responses) and with the addition of the gas flow recorded during sampling. The plot shows that the gas flow has an opposite diurnal effect to that observed in the RH profile, when the gas flow increases the RH decreases and vice versa. The gas was supplied from

a zero grade nitrogen (N_2) bottle, which was stored external to the laboratory (outside the building). Therefore as the outside temperature fluctuates (between night and day) a corresponding change in flow and therefore RH, is observed. A flow increase of 40 ml/min (from 200 ml/min to 240 ml/ml = 20% increase) leads to a dilution of the headspace gas resulting in a 5% decrease in RH.

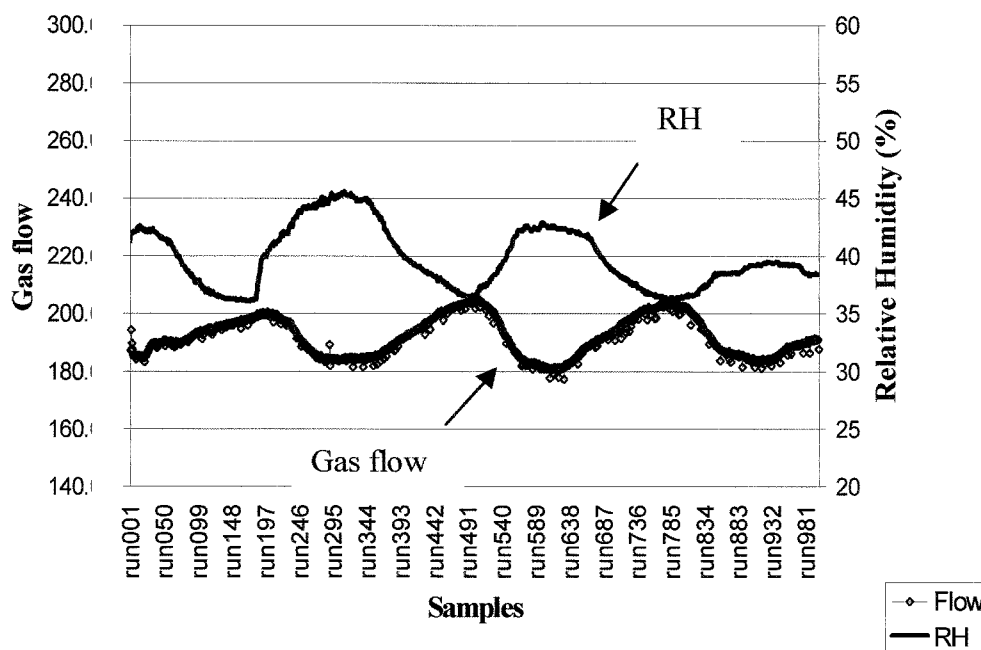


Figure 5.1.2.2 Plot of relative humidity and gas flows for an 85 hour sampling period showing fluctuations in response profiles.

By drawing on the ideal gas principles ($pV=nRT$) in which pressure and volume are inversely related and both pressure and volume are directly related to temperature it can be deduced that a change in gas bottle/supply line temperatures can cause changes in supply pressure and therefore gas flow rates. An increase in gas flow of 20 ml/min leads to a ~10% reduction in sample RH (as observed in Figure 5.1.2.2). To reduce N_2 gas temperature changes prior to sample sparging a supply loop was introduced to buffer the supply line using a temperature controlled water bath at 30 °C. Additionally, the gas supply bottle was relocated to the laboratory to reduce temperature-related fluctuations. Figure 5.1.2.3 shows an example of the reduced, yet still present, fluctuations after the

modifications had been made. A flow increase of 20 ml/min now leads to a RH reduction of ~5%.

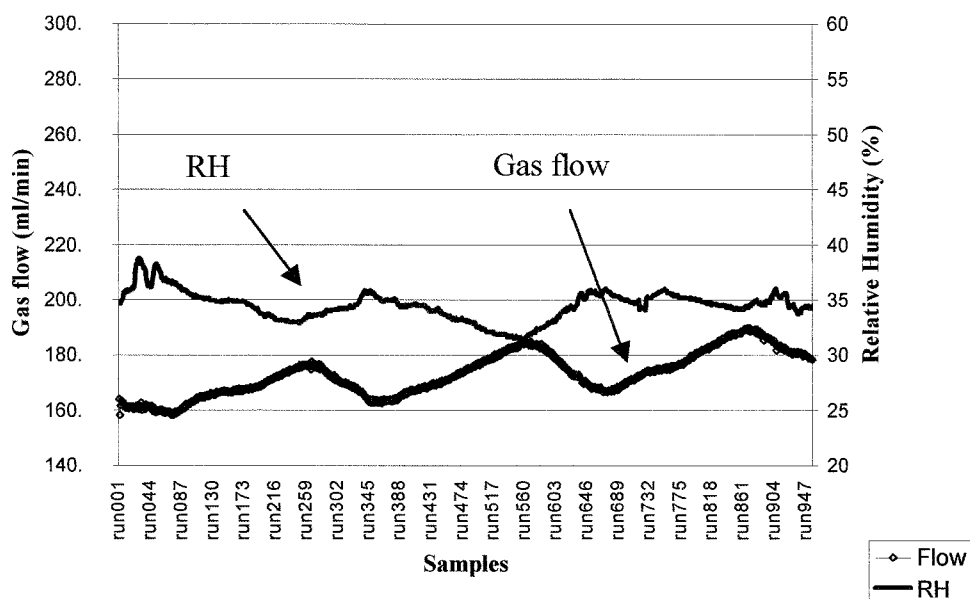


Figure 5.1.2.3 Plot of relative humidity and gas flows for an 85 hour sampling period showing reduced fluctuation in profile variation.

The RH fluctuations are still present due to variability in both laboratory and gas bottle temperatures. The temperatures change as the laboratory warms during the day and cools during the night. To eliminate these observations the monitoring equipment would need to be placed in a temperature controlled laboratory, an extravagance that might be unavailable when in use as an in-field on-line application.

5.1.3. Selecting a suitable sampling window

The eNose based monitoring system can generate large data sets when operated continuously. Identifying pollution episodes within these sets where diurnal changes are apparent may be difficult. To optimise analysis and increase the probability of detecting a pollution event protocols need to be developed to detect changes in the sensor responses. Two analysis approaches could be to generate a large data bank so that data sets can be compared back to known events or patterns or analysis of individual data sets

independent of previous events. To compare the data generated during on-line analysis it is essential to be able to compare data from one run to the next. Grouping sets of data collected from different runs can introduce inconsistencies in compared data sets; these could be mistaken for the presence of pollution (Figure 5.1.3.1). This occurs when data sets are joined that have not been collected concurrently, when there has been a significant time gap between sampling where ambient conditions may have altered effecting either the gas flow or sample temperatures and therefore RH. This leads to either slightly increased or decreased sensor response values. Therefore data needs to be analysed sequentially.

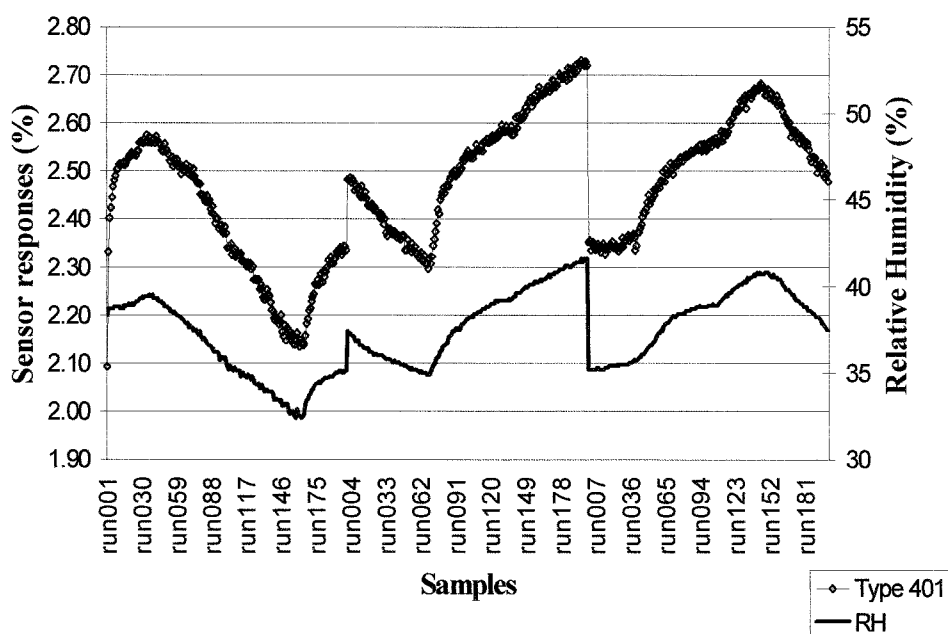


Figure 5.1.3.1. Disjointed data sets showing the problems associated with cross-comparison of data that has not been collected concurrently.

5.1.4. Identification of pollution

To function as an on-line pollution monitor the ability to discern the presence of pollution in a passing water matrix is vital.

Once a stable sampling system was established the flow-cell was spiked with a known concentration of pollutant. Figure 5.1.4.1 shows an example of a 10ppm spike of 2-

chlorophenol. The sharp increase in sensor response profile shows the point where the 2-chlorophenol was injected direct into the flow-cell prior to sparging at run 396. 2-chlorophenol was used solely in order to attain an idea as to the behavioural changes of the system when attempting to integrate spiked compounds. The peak is not present in the flow-cell for long as it is flushed through the system. A blank spike was injected at run 316 showing that the system is definitely detecting the presence of a pollutant and not a disturbance due to the spiking procedure.

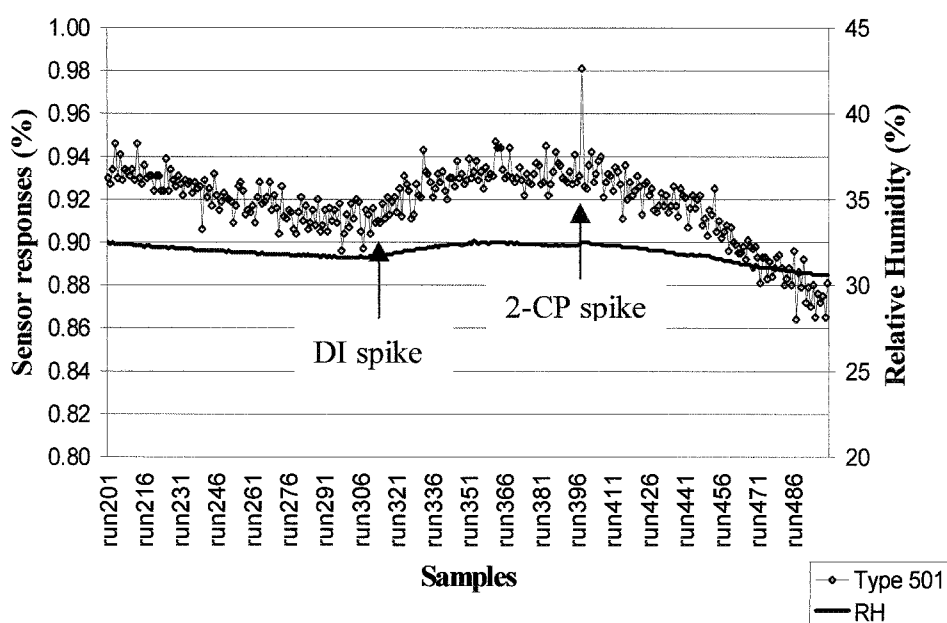


Figure 5.1.4.1 Sensor 501 between runs 200-500 using DI water as matrix. 10 ppm 2CP spike at sample number run396. Blank DI spike at sample number run316.

This single injection spiking approach shows that the system is able to detect changes in water quality however is not indicative of a true pollution event. Therefore rather than utilising a flow-through system with the pollutant being injected direct to the flow-cell the supply waters were recirculated and spiked. This enabled the pollution to remain present in the waters for longer rather than being flushed away after one analysis. Figures 5.1.4.2 and 5.1.4.3 show plots of 2-chlorophenol spikes that were injected into the recirculating stream. The sensor response peaks are almost identical and show the pollution entering the system and the sensor responses gradually decreasing, to pre-spike background levels, as the pollutant is sparged from the solution (over a period of ~9 runs,

45 mins). These monitoring trials show that the system is able to detect sudden changes in water quality and track to presence of pollution during a prolonged event.

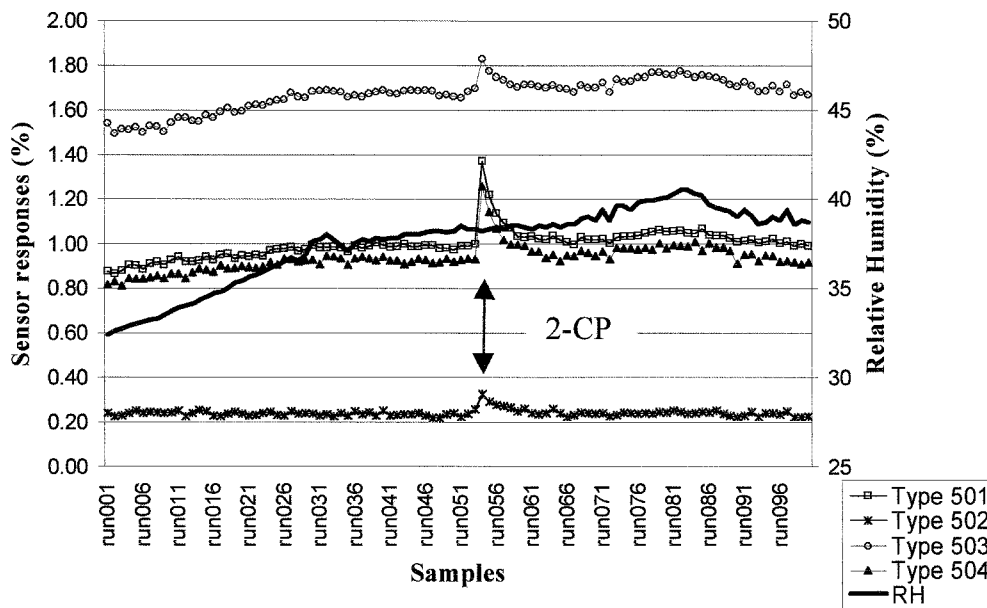


Figure 5.1.4.2 Plot of four sensors and RH between runs 1-100.
10 ppm 2-chlorophenol injection at run 55.

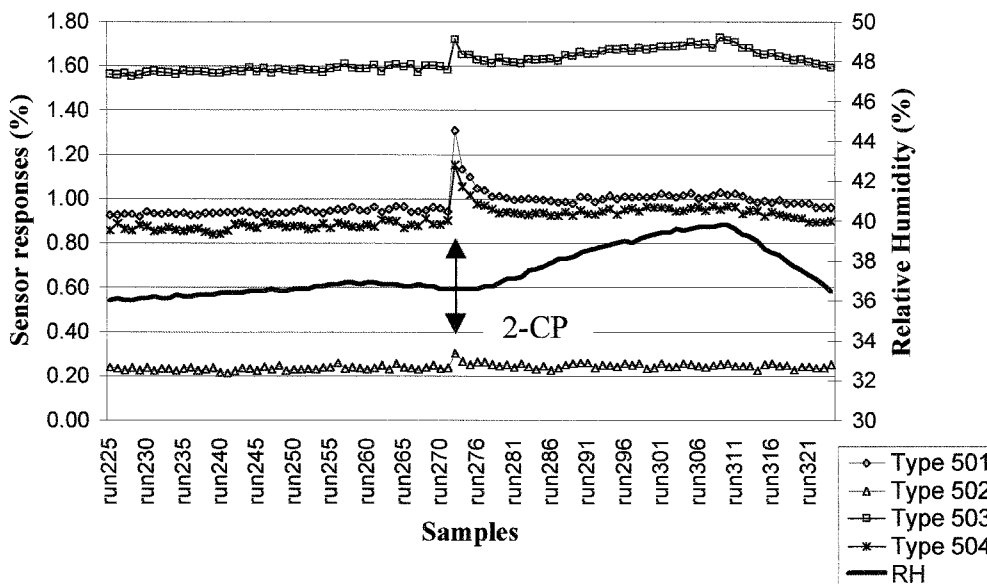


Figure 5.1.4.3 Plot of four sensors between runs 225-324.
10 ppm 2-chlorophenol injection at run 273.

5.1.5. Sample temperature blending

During a period of isolation testing a notable change in sample temperature was observed during sample acquisition. Figure 5.1.5.1 shows that false positives occurred due to temperature differences between the sample and flow-cell. The heated jacket on the flow-cell maintains a stable temperature of 25.5°C throughout the system whilst recirculation is occurring but once the cell is isolated for analysis, the jacket only heats the trapped sample and overcompensates heating the sample above the desired temperature. This effects the sample characteristics and gives rise to an increase in sensor response values (Figure 5.1.5.1).

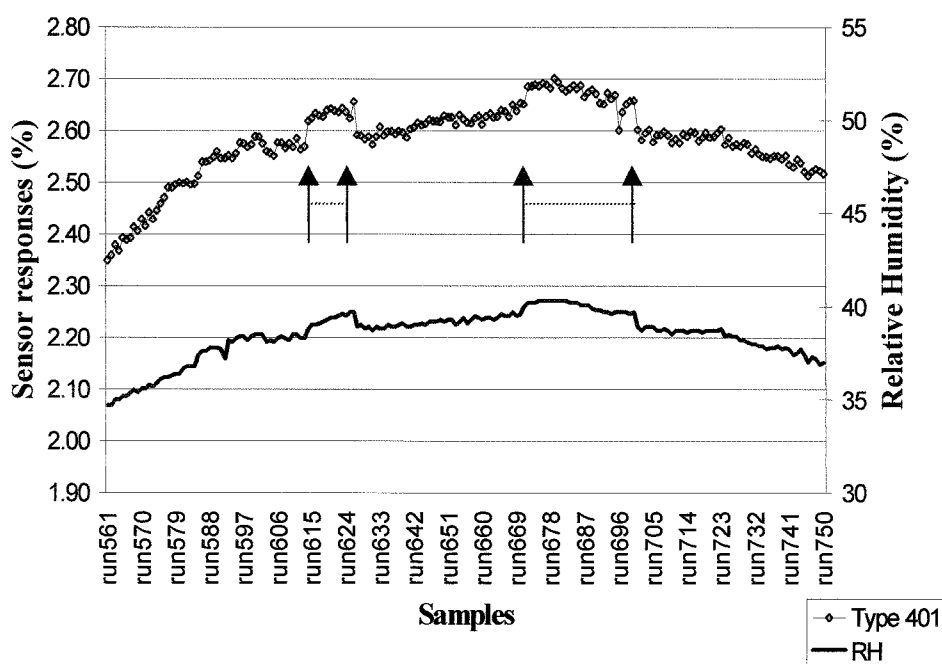


Figure 5.1.5.1 Sensor 401 and RH between runs 561-750.

Blank spike introduced between sample numbers run613-623.

1 ppm 2-chlorophenol spike introduced between sample numbers run670-700.

When simulating pollution events it is necessary to blend the unpolluted and polluted water samples together prior to analysis whilst attempting to keep all temperatures constant. As seen earlier (Figure 5.1.3.1) slight changes in ambient or sample temperature can produce false peaks that could be mistaken for polluted waters.

To overcome this a water bath, held at 30°C, was used as the simulated river into which the spiked waters were submerged and allowed temperatures to equilibrate, thus removing fluctuations in the sensor response due to mismatched sample temperatures. Once a stable and reproducible system was attained the system could be tested with a range of pollutants.

5.2. Laboratory based assessment

5.2.1. Test matrix

A range of compounds and sample concentrations were selected to assess the monitoring systems ability to detect sudden changes in water quality. The compounds chosen were 2-chlorophenol, 2-MIB, diesel, 1,2-propandiol, ethanol, 1,4-dioxane and atrazine which were tested at 5, 10 and 20 ppm. The flow-cell, simulated river and pollutant sample temperatures were regulated using the water bath and heated jacket. The effects of sparge gas flow rate, at a sample temperature of 30°C, were investigated for each compound at concentrations of 5, 10 and 20 ppm. The sparge gas flow rate was set at 200 ml/min for the first period of experimentation then reduced to 100 ml/min for the second. Each compound and concentration thereof, was spiked into the running system while the sensor data was continuously logged. The sensor responses were monitored for each flow rate to see whether they increased or decreased the system's ability to detect sudden changes in water quality. Table 5.2.1.1 lists the sensors that showed a change in resistance during the spiking period.

Table 5.2.1.1 Responding sensors from initial testing matrix.

Pollutant concentration	5 ppm		10 ppm		20 ppm	
	100 ml/min	200 ml/min	100 ml/min	200 ml/min	100 ml/min	200 ml/min
Sparge gas flow rate						
1,2-propandiol	No response	No response	No response	No response	No response	601
1,4-dioxane	No response	No response	No response	No response	No response	No response
2-chlorophenol	501	501	501	501, 502, 504	501, 502, 503, 504	501, 502, 503, 504
2MIB	N/A	N/A	N/A	N/A	N/A	501, 502, 503
Atrazine	No response	No response	No response	No Response	No response	No response
Diesel	501, 502, 503, 504	501, 502, 503, 504	501, 502, 503, 504	501, 502, 503, 504	501, 502, 503, 504	501, 502, 503, 504
Ethanol	No response	No response	No response	No response	No response	No response

Sensors 501, 502, 503 and 504 detected the majority of all the pollution episodes for runs using 2-chlorophenol and diesel. Figures 5.2.1.1 and 5.2.1.2 shows the effects that a 5ppm 2-chlorophenol spike at 100ml/min sparge rate and a 10ppm 2-chlorophenol spike at 200ml/min sparge rate have upon sensor 501. Both peaks are identifiable above the background sensor responses and show comparable RH values therefore the difference in sensor response magnitude could be attributed to the pollutant concentration. The declining response of the 5ppm sample suggests that the pollutant is removed from the water matrix or is near its limit of detection whereas the 10ppm sample is still within the detection range of sensor 501 and is stable throughout.

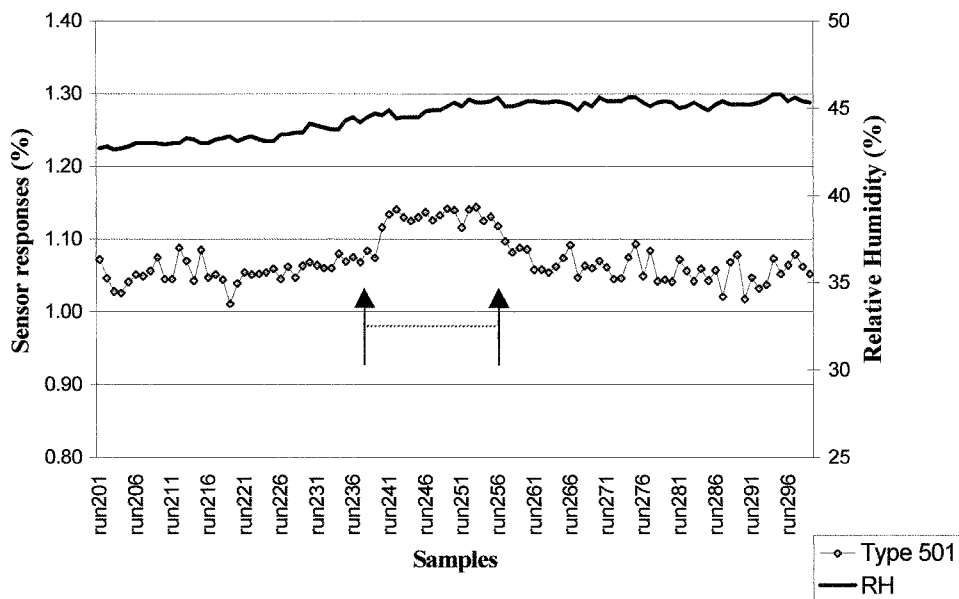


Figure 5.2.1.1 Sensor 501 between runs 201-399. 100ml/min sparge rate.
5 ppm 2-chorphenol spike between sample numbers 238-256.

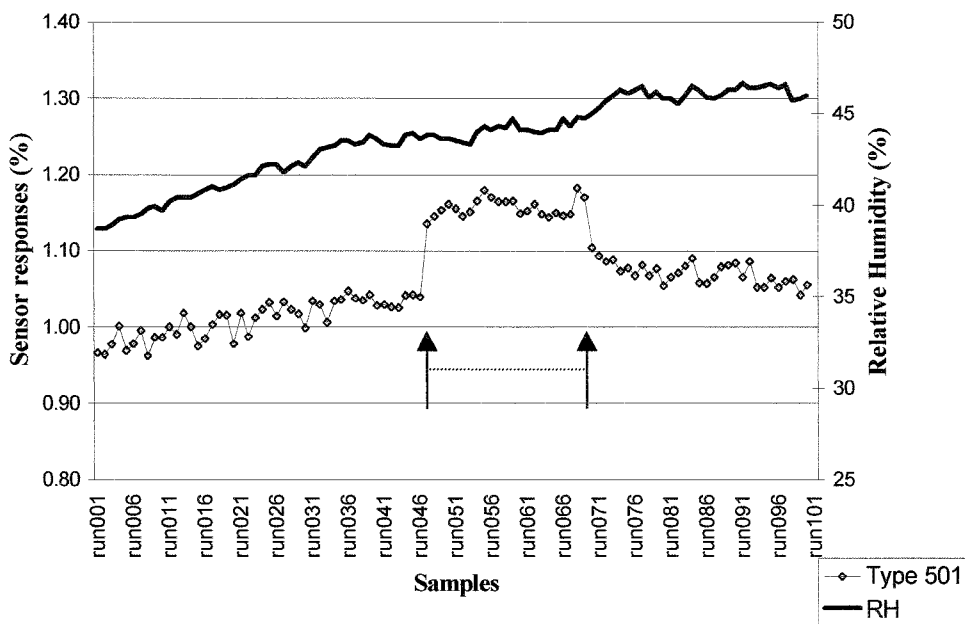


Figure 5.2.1.2 Sensor 501 between runs 1-101. 200ml/min sparge rate.
10 ppm 2-chorphenol spike between sample numbers 47-69.

Figure 5.2.1.3 and 5.2.1.4 show that 2-methylisoborneol spikes at 20 ppm are clearly identifiable for sensors 501 and 502, respectively. In each case there is a noticeable change in the sensor response which soon begins to fade as if the concentration of the pollutant in the flow-cell decreases. It is unclear as to exactly why this happens but the most likely reason is that the N₂ bubbles from the sparger are assisting the equilibrium changes between the sample and the headspace thus stripping the odour from the liquid phase and reducing the concentration in the liquid phase. The less hydrophilic and more volatile the compound the faster this reduction in concentration would be expected (Crompton 2003).

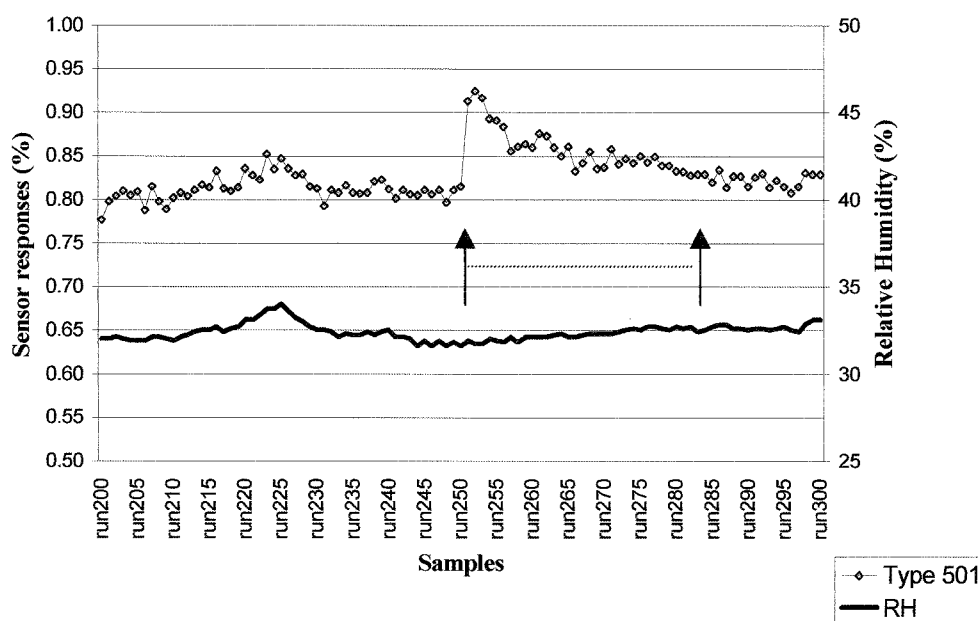


Figure 5.2.1.3 Sensor 501 between runs 201-300. 200ml/min sparge rate.
20 ppm 2-MIB spike between sample numbers 251-284.

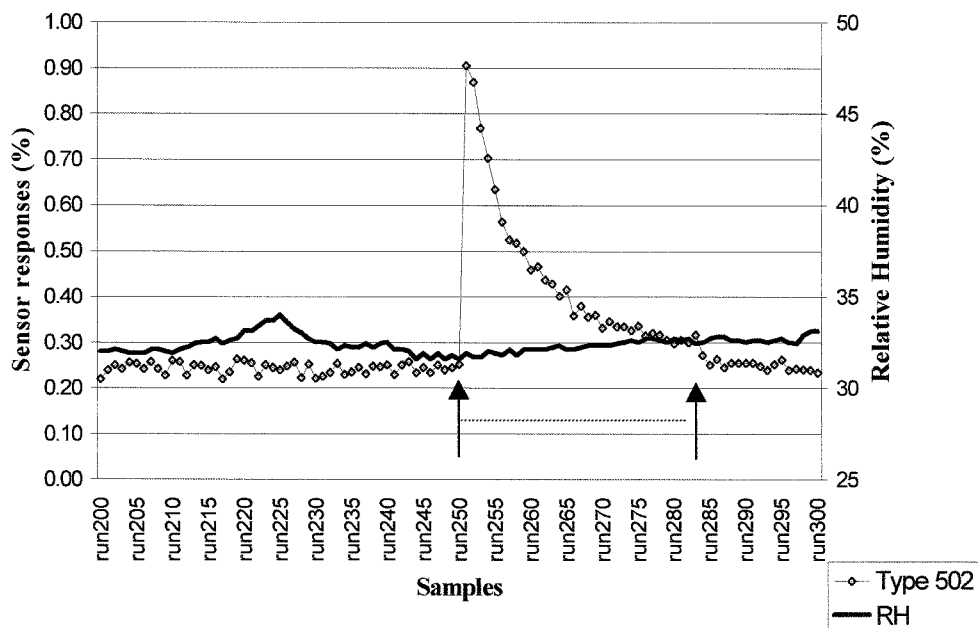


Figure 5.2.1.4 Sensor 502 between runs 201-300. 200ml/min sparge rate.
10 ppm 2-MIB spike between sample numbers 251-284.

Figures 5.2.1.5 and 5.2.1.6 shows the introduction of a 20 ppm diesel solution and the sensors 501 and 504 respectively. In a similar situation to the plots obtained using 2-MIB a clear step up is evident but this soon declines to a stable level above that of the preceding background response for the DI water. The pollution does not completely disappear but would if left in the system for a longer period.

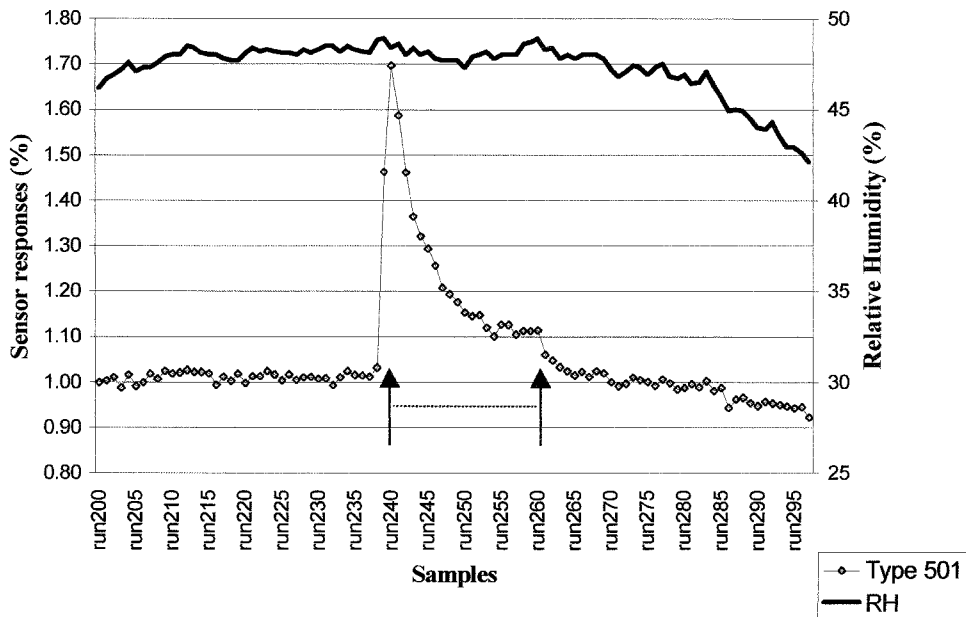


Figure 5.2.1.5 Sensor 501 between runs 201-300. 200ml/min sparge rate.
20 ppm diesel spike between sample numbers 240-260.

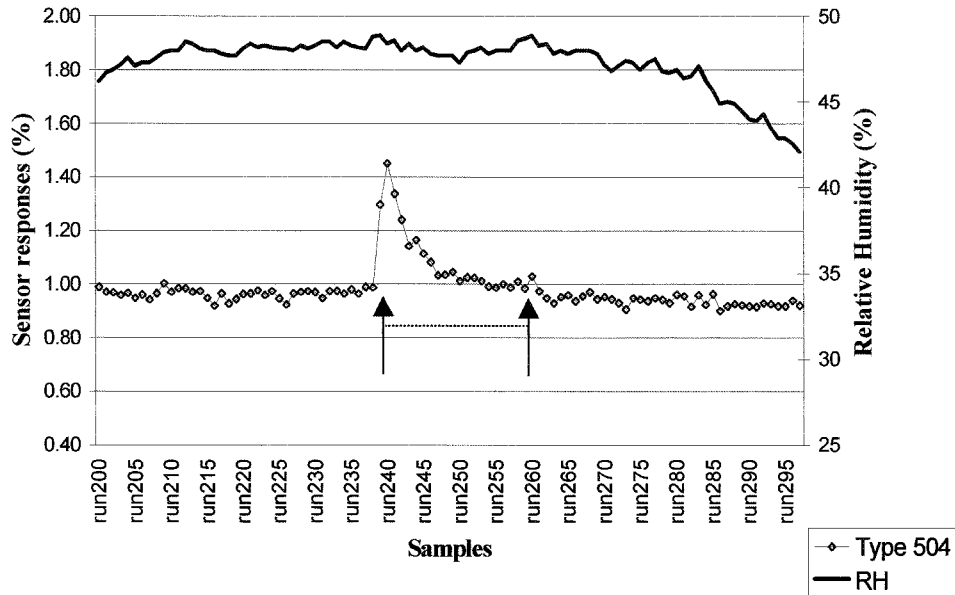


Figure 5.2.1.6 Sensor 504 between runs 201-300. 200ml/min sparge rate.
20 ppm diesel spike between sample numbers 240-260.

Figure 5.2.1.7 shows the introduction of a 20ppm 1,2-propanediol spike and the response of sensor 601. This sensor was a prototype sensor of unknown composition and instead of a peak being observed we can see an induced period of stability in the response profile. This was unexpected but shows how different sensors can behave for a variety of polluting compounds, adding to the benefits of using an array of sensors.

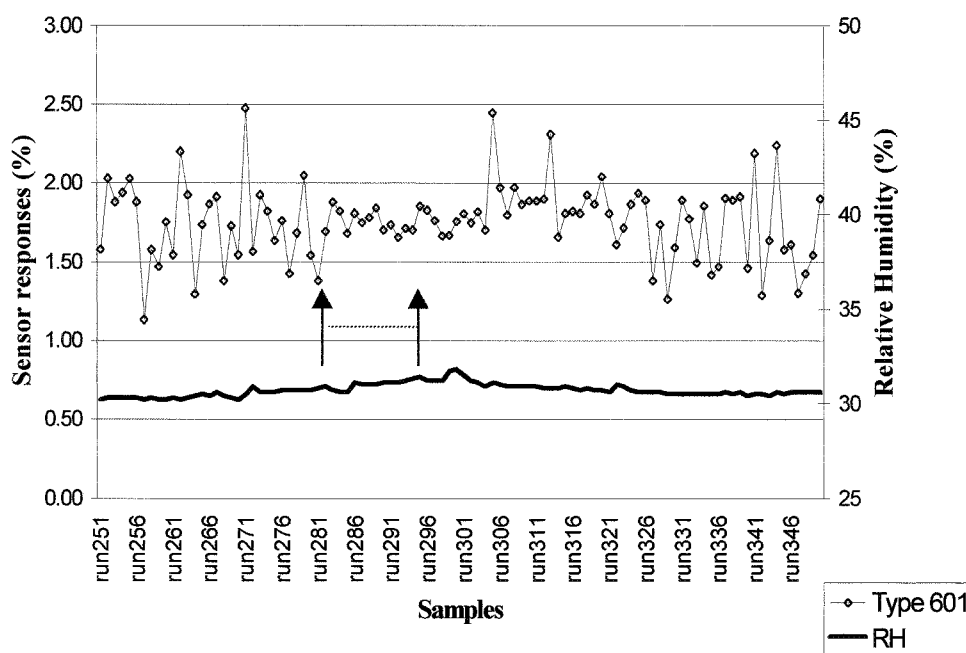


Figure 5.2.1.7 Sensor 601 between runs 251-350 200ml/min sparge rate.
20 ppm 1,2-propanediol spike between sample numbers 282-293.

The matrix testing showed that 2-chlorophenol and diesel are the most detectable compounds under these sampling conditions. On this basis further experimental work concentrated on a more detailed study where the detectability of these two compounds was assessed under differing parametric conditions.