# Chapter Six - Discussion

## 6.1. System development

System optimisation, through statistical and operational approaches, identified the most appropriate way to monitor for risk compounds in a controlled laboratory environment. The interference effects that temperature and humidity can produce have been reported by (Gardner and Bartlett, 1999) and are known to affect the response patterns and characteristics of conducting polymer sensors. Understanding the influences minimal changes in the control and monitoring of variables such as sample temperatures, sample-pollution temperature interaction, RH and gas flow variations have enabled the production of meaningful results and will hopefully supplement the knowledge base for further studies.

## 6.2. Laboratory based assessment

Tables 5.2.2.1 and 5.2.2.2 collate the results from extensive laboratory testing using 2-chlorophenol and diesel spiking under varied conditions, tabulated in Results section 5.2.2.

The 2-chlorophenol (Table 5.2.2.1) and diesel (Table 5.2.2.2) testing matrices show that RH has a general high and low of 45% and 30%, respectively. Trends are evident in the magnitude of the sensor responses gained from each combination of variables. The observed trends in RH are in accordance with initial statistical design trends (Results section 5.1) with sample temperature being key in producing the result. For the 2-chlorophenol and diesel spiking the magnitude of the sensor response change increased with a corresponding increase in both pollutant concentration and sample temperature. As the combination of flow sparge gas flow rate, sample temperature and pollutant concentration increased, more sensors responded to the test solutions. The effects that these three variable changes had upon the magnitude of the sensor response and the trends observed in the RH profile offer insight into sensor behavior and reproducibility

for the changing parameters. Introducing the pollution mid-way through data set collection eliminates the possibility of cross-dataset comparison difficulties as highlighted in Results section 5.1.3. The effects of pollution introduction are supplemental to any changes occurring in ambient conditions. Any change occurring within a monitored dataset other than what is considered to be 'drift' is reflected in the graphical representation. This inter-process observation method should be applied as the standard approach for future trials.

### 6.2.1. Addressing levels of detection

It has been shown that with the current set-up detection down to and including low ppm levels are attainable. This is in keeping with similar research using conducting polymer sensors (Hodgins *et al.,* 1995, Misselbrook *et al.,* 1997, Doleman and Lewis 2001). Stuetz *et al.* (1988) have reported lower levels of detection in the ppb and ppt region are attainable.

It is generally thought that human olfaction is more sensitive than the electronic nose, however this generalisation is subjective and will depend on the type of odourant being analysed and the manner in which it has been analysed. Doleman and Lewis (2001) show the similarity between the detection levels for a human and electronic nose for a range of alkanes and alcohols with different vapour pressures. For nine of the ten compounds tested the electronic nose had a lower detection threshold. Whereas the results from this study suggest that the electronic nose coupled with our sampling methodology are far from being able to detect down to the odour threshold values for 2-chlorophenol or diesel.

To enhance the detection thresholds in this study several modifications could be addressed, however not all are viable or practical. Due to either limitations of the sensor array or cost and time constraints required to enable marketing of the unit as a fast, affordable and reliable piece of monitoring equipment.

To improve taintant detectability ideally the laboratory and field units would be operated at sample temperatures similar to those used for smell bell (60 °C) or flavour profile analysis (45 °C) where the increase in sample temperature promotes volatility (Crompton 2003). However our system is limited to the operational temperature of the CP sensors, which operate at 30 °C. If the sample reaching the sensors were hotter than 30 °C condensation would form upon the sensors and render them useless.

Stuetz *et al.* (1998) reported that concentrations in the ppb to ppt range could be detected when using static sampling. They allowed headspace equilibrium to occur yet did not have to consider trying to implement a continuous monitoring flow-through system. The time taken for the natural headspace to reach equilibrium will depend upon the volumes of liquid and gas, the concentrations and vapor pressures of the pollutants experienced, none of which can be assumed leading to unknown equilibrium times.

By allowing headspace equilibrium to form between the liquid and trapped volume of air above it any resultant dilution effects caused by sparging the sample with a flow rate of $N_2$ will be removed. This requires investigation as it is highly likely that the passing of $N_2$ gas through the sample promotes sample volatilisation due to gas stripping but it may also dilute the sample by as many factors as head space volumes of gas that sparge the liquid. Another means of transferring the gas sample to the sensor array would need to be considered if the carrier gas were to be removed.

It has been established that sensor responses are susceptible to changes in RH, temperature and flow rate (Gardner and Bartlett, 1999) although the authors claim that ideally odour sensors should be insensitive to these effects and that steps should be taken to minimise their impact. However the nature of any application may direct and limit the operational control of the sensors and the parameters, under which measurements are made. It is important to understand and monitor the effects of these parameters rather than minimising their effects. The RH sensor should be treated as another sensor in the array. Any RH or sample temperature fluctuation could be a product of the changing sample and be indicating a transformation in water quality. Subduing any effect, such as

dehumidifying a sample (Oshita *et al.*, 2000) or statistical data compensation (Gardner and Bartlett, 1999, Gardner *et al.*, 2000, Bourgeois *et al.*, 2003) could lead to an involuntary minimisation and therefore a masking of an abnormal occurrence.

## 6.3. Field based assessment

### 6.3.1. Monitoring frequency

Typical analytical systems such as CLSA with GC detection can analyse low ng/l levels of target compounds (Khiari *et al.*, 1992 Palmentier *et al.*, 1998, Hasset and Rohwer, 1999) but when should these units monitor the process? It is neither practical nor cost effective to operate them 24 hours a day, seven days a week. Drage (1998) reports that the operational cost from a monitoring station upon the River Trent, UK are £350K per year while Bode and Nusch (1999) report the combined annual operational costs for two monitoring stations in the Ruhr River, Germany is just over DM200K. These figures could be significantly reduced if the operational time of major pieces of analytical equipment were lessened and systems similar to the unit described in this study were used to screen the water. It is anticipated that an operating eNose system could be commissioned for about £30K, maintenance costs are minimal. The information in Table 2.5.1 compares the key variables associated of standard on-line monitoring techniques. The eNose system is best compared to that of biomonitoring. Neither system is capable of providing specific contaminant information but indicates the presence of an abnormality. The benefit of the Enose over biomonitoring is the time taken to react to the pollution occurrence. Biomonitoring, although relatively rapid, will involve a lag period following the pollution occurrence, as the behavioral changes of the monitor have to be detected. The eNose's response will be immediate in the form of a resistance change. Conventional parametric methods and techniques such as GC, LC and spectroscopic techniques are more costly and require more maintenance yet are more useful at detecting and classifying pollution events.

The eNose system can be left to run with the fine tuned units left on stand-by until triggered by an erroneous sensor response. Upon pollution detection an auto sampler

could be triggered enabling the pollution to be categorised and quantified using the sensitive analytical techniques.

### 6.3.2. Detection levels

Is it necessary to be looking for threshold levels prior to water treatment? Conventional drinking water treatment can remove 35-50% of all taste and odours (Anselme *et al.*, 1988, Kim *et al.*, 1997), with granular activated carbon (GAC) and pre-ozonation typically removing a further 75-90% (Kim *et al.*, 1997). The GAC removal efficiency depends on the type and pore size of the material used (Kim *et al.*, 1997), the bed characteristics, the contact time allowed and recovery solvent used (Crompton, 2003). Hepplewhite *et al.* (2001) suggests that an expected MIB concentration would be ~100ng/l (ppt) and Kim *et al.* (1997) reports that an average of 15 ng/l would be typical with highs of 85 ng/l not unusual. Van Der Hoek *et al.* (1999) achieved 100% removal for three pesticides at concentrations of 5 ug/l (ppb). On this basis if our laboratory finding could be replicated in the field we are an order of magnitude away from achieving such levels.

It should be remembered that although it would be ideal if no pollution entered the works there would be a set level of pollution that the treatment process will be able to successfully remove. Severn Trent has addressed this area using fertilisers as the problem compounds (Brian Drage, Personal communication). They dosed the inlet of the works with a known concentration of fertiliser, 3 ug/l. The treatment works was observed to see how well it eradicated the compound. After one pass through the treatment works a value of 1.5 ug/l was detected in the effluent. This data gives an idea to the safe-level limit for fertilisers entering the plant that can be successfully treated to give a final effluent that is in accordance with the governing regulations.

The attainable levels of detection in the field are going to be higher than those obtained under laboratory conditions. The experimental design analysis of the 2-chlorophenol and diesel testing showed that although sample concentration was the most significant variable sample temperature was nearly as significant. Temperature regulation on-line is

not practical and complications could be expected relating to fluctuations and sample blending also the additional cost implications have to be considered. Alternative methods of obtaining similar or better results are sought.

### 6.3.3. Preconcentration

Preconcentrating the sample prior to analysis could increase the levels of detection. The basic methods rely on either concentrating the sample by removing water from the sample (e.g. membrane) or by isolating the sample from the water (e.g. solvent extraction).

Bruzzoniti *et al.* (2000) reviews preconcentration techniques for use in water analysis yet does not mention the cost or time implications required to reach set concentration factors, both of which are of great importance when considering an affordable real time operation. In a river system where the type of pollutant is unpredictable a universally effective method of preconcentration is required, with the maximum concentration factor achievable for a particular chemical being proportional to its octanol-water coefficient (Petty *et al.*, 2000). Segal *et al.* (2000) have shown that a membrane extraction with a sorbent interface can increase the sensitivity of a micro-GC system by a factor of over 100 with a concentration time as short as 1 minute. The sample volume required for GC analysis is significantly less then for our eNose analysis, therefore longer sample preparation times would be expected. SPMD (semi permeable membrane devices), in general, concentrate all neutral hydrophobic chemicals having molecular masses <600 from water. No other sampling approach offers this broad range of applicability with respect to chemical class or molecular mass, but care should be taken to avoid contamination (Petty *et al.*, 2000). RO is currently the most useful method for preparing large quantities of non-volatile organic concentrates, yet if 1000's of litres per day are to be processed a simpler method should be developed (Jolly and Suffet 1987). Although smaller volumes would be required (<200 litres per day) the limiting factor would be the time taken to produce to concentrate. The longer the time taken to produce the sample relates to the further any pollution has traveled along the river.

Advantages and disadvantages of available methods for either concentrating or isolating organic compounds from water are shown in Table 6.3.3.1. Picking our requirements from Table 6.3.3.1 and incorporating the associated time constraints for each approach does not leave many options if the aim is to maintain a fast and effective prerequisite.

Guadarrama *et al.* (2001) have shown that the responses of conducting polymers can be masked by the water and ethanol content of wines but after the SPME method is applied the discriminability of the array is enhanced. The SPME fibres they used had a low affinity to ethanol and water so therefore adsorbed the minority volatiles responsible for the aromatic characteristics of the wines. SPME has a typical extraction time of 50 mins an equilibrium time of 60 mins plus GC analysis takes ~30mins. SPME is labour and cost efficient, sample sizes are small and ppb levels of detection are attainable (Watson *et al.*, 1999).

Purge and trap, headspace analysis and solid-phase extraction are designed for laboratory analysis of discrete samples and are not suitable for continuous, on-line monitoring (Guo and Mitra 1998). It is also time-consuming and requires large sample sizes (Watson *et al.*, 1999). Isolation of the contamination is another valid option however since we would be dealing with relatively large sample if there is an option to reduce the time factor then this is another viable option, see Figure 5.12.2.1 for a proposed schematic for a possible preconcentration unit. Concentration of the river sample will provide a better representation of the river system. At present our 100ml sample, once every fifteen minutes, is a minute fraction of the mega-litres per hour of water passing the monitoring station each day and unless we assume the river to be totally homogenous we are not monitoring effectively.

Table 6.3.3.1 Advantages and disadvantages of methods used for either concentrating or isolating organic compounds from water (Adapted from Jolly and Suffet 1987)

| Method | Type of compound concentrated | Advantage | Disadvantage |
|---|---|---|---|
| Freeze concentration (C) | Polar and non polar | Low temperature | Litre volumes, limited concentration, salt concentration |
| Freeze drying (C) | Non volatile | Low temperature, high concentration, low contamination | 1-100 litre volumes, salt concentration |
| Vacuum distillation (C) | Non volatile | Ambient or near ambient temperature, high concentration, low contamination | 1-100 litre volumes, salt concentration |
| Reverse osmosis (C) | Molecular weight >200 | Ambient temperatures, ≥100 litre volumes | Salt concentration, contamination |
| Ultrafiltration (C) | Molecular weight >1000 | Ambient temperatures, ≥100 litre volumes | Limited throughput |
| Gas stripping (I) | Volatile, semivolatile | Small samples | Low volumes |
| Solvent extraction (I) | Nonpolar, volatile, semivolatile | Ambient temperature, large volumes, low salt concentration | Solvent contamination, specificity, concentrate storage |
| Activated carbon (I) | Nonpolar, volatile, nonvolatile | Ambient temperature, large volumes | Limited recovery of adsorbed organics, concentrate storage artifacts |
| Ion exchange (I) | Polar, nonpolar | Large volumes, organic recovery 70-90% | Resin preparation and elution |
| XAD resin (I) | Nonpolar to polar, volatile, nonvolatile | Convenient, ambient temperature, large volumes | Contamination, limited recovery of adsorbed organics, resin preparation |
| Precipitation (I) | Humic materials, specific chemicals | Suitable for large masses | Specificity |
| Centrifugation (I) | Macromolecules | _ | Specificity (i.e., large molecules, low volumes) |

(C) Concentrating technique, (I) Isolating technique.

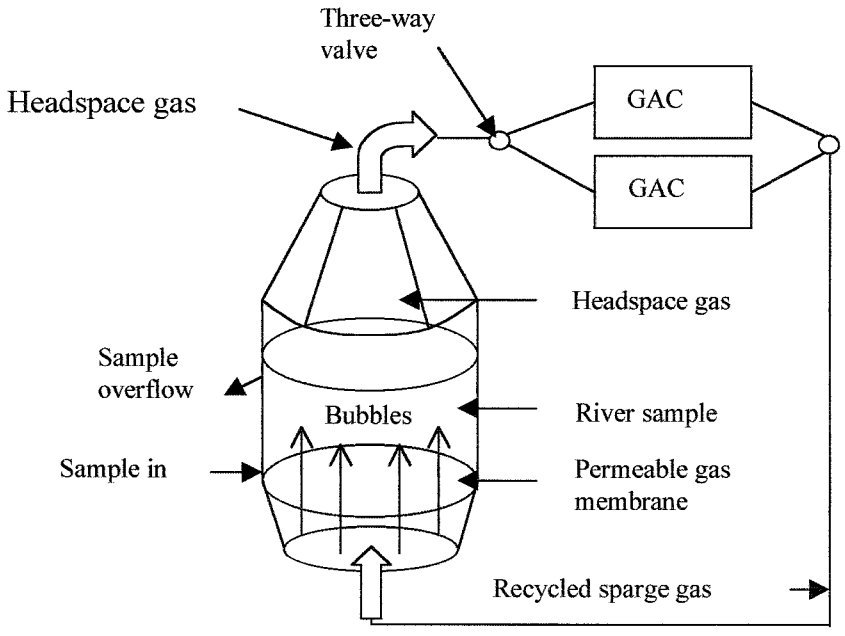


Figure 6.12.2.1 Schematic for proposed preconcentrator

Figure 6.12.2.1 shows a schematic for a proposed preconcentration unit for our set up. The vessel would be roughly fifteen litres in volume (10 litre sample, 5 litre headspace). This is based upon purge and trap with closed loop stripping similar to approaches implemented by Hasset and Rohwer (1999) and Knepper *et al.* (1999). The recirculating sparge gas passes through the gas permeable membrane and produces bubbles that strip the organics from the solution and promote sample volatility and concentration within the headspace. The sample stripping time allowed affects the recovery attainable. One hour is sufficient for relatively volatile compounds whereas two hours could be required for less volatile compounds (Crompton 2003). The resultant headspace is carried to the GAC beds where the pollutant molecules become trapped in the carbon. The two beds allow one to be collecting whist the other is de-sorbed, reducing downtime and increasing the speed of the process. The sample can be desorbed using a small amount of a suitable solvent and analysed using the eNose and flow-cell as described in previous sections.

The flow rate of the stripping gas, the particle size of the carbon and the choice of desorption solvent all effect the carbon's efficiency to retain the organic pollutants. A

carbon particle size ranging from 0.35- 0.12 mm diameter provides a percentage recovery range from 91-97 % while the choice of solvent can vary percentage recovery from 88-100%, this is dependant on the organic being recovered (Crompton, 2003).

Any addition to this existing on-line operation is highly likely to increase unit and operational costs whist reducing sampling frequency. It is undesirable to detract from the real-time status of this operation, as it is a key feature and novelty.

## 6.4. Data analysis

### 6.4.1. Parametric compensation

Parametric compensation has been used to sharpen graphical response (Gardner and Bartlett 1999, Bourgeois *et al.,* 2003). Both authors have used data normalisation techniques to clarify the effects upon their sensors. This can produce clear results although it is not necessarily as desirable as it may seem. Gardner and Bartlett (1999) normalise the sensor with respect to itself to produce an auto-scaling effect with the resultant ranging from 0 to 1. This technique can be used as a preparatory step to PCA analysis (Gardner and Bartlett 1999). This allows each sensor to be considered as an equal to all others in the array when considering an abnormality, however some sensors may or may not react to the presence of pollution so all sensors within the array should be considered individually. Gardner and Bartlett (1999) have also normalised the sensor array response to set the array vector length to unity. By doing this they are able to remove the effects of gas concentration and classify the sample by type. This could be extremely useful for applications where a yes or no answer is required such as hazardous gas detectors or in our case indicating the presence of pollution. It should be noted that in a changing environment different compounds could yield very similar sensor response profiles, therefore indicating that sample RH or temperature can mask the classifying ability of this method. The inclusion of more than one sensor into the array therefore reduces the chances of misclassifying a compound. The sensors produce an odour profile of a sample, an odour 'fingerprint'. The greater number of sensors in the array the better the chance of classification. The nature of this normalisation means that in each set of

processed data there will be at least one value that when normalised equals 1. This does not necessarily indicate that pollution is present at this point, just that it had the largest sensor response from the data set analysed (i.e 100% of the magnitude variation). This method is suitable if it is known that pollution is included in the analysed data, if there is no pollution then a false positive will be recorded. We have shown that the sensor response varies due to ambient conditions (Figure 5.1.2.1) and that in certain circumstances the magnitude of the baseline response also varies. Therefore we cannot set a suitable base-line limit for such normalisations.

Bourgeois *et al.* (2003) have plotted RH verses sensor response, which is in effect the same as normalising the sensor with respect to the changing RH. Figures 6.4.1.1 and 6.4.1.2 show the before and after of such a representation. Figure 6.4.1.3 shows a plot of the sensor response where each point has be divided by the corresponding RH value obtained. A similar profile is obtained as in Figure 6.4.1.2. The three plots illustrate how a clearer picture of sensor change can be obtained. This is only viable however if there is no corresponding change in the values of RH. If the sensors and RH respond in a similar way to a change in water quality then this classifying technique becomes meaningless.

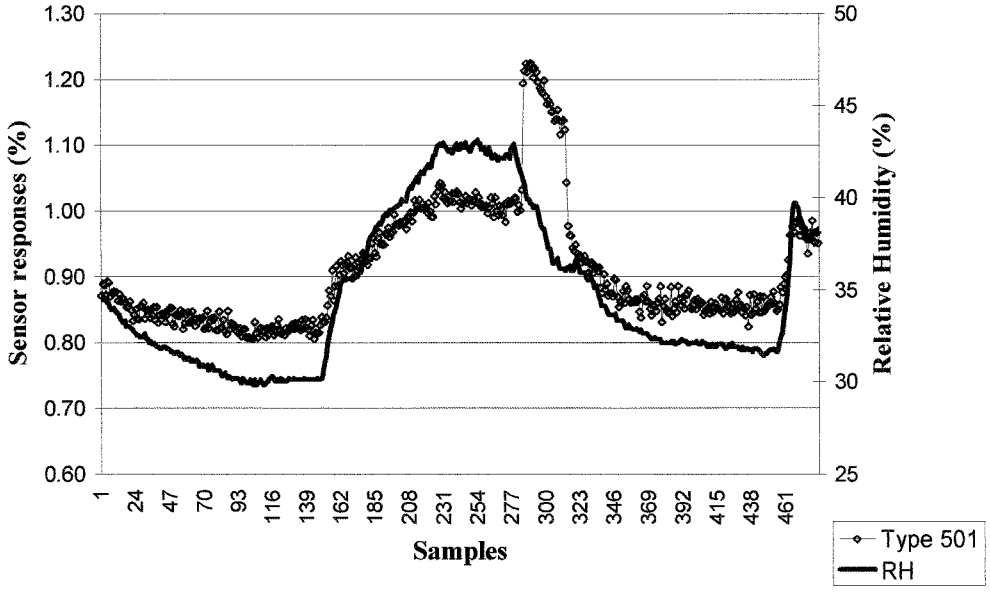


Figure 6.4.2.1 Sensor 501 between runs 0-483. 200 ml/min sparge rate. 20 ppm 2-CP spike between runs 284-314. Liquid temperatures at 30 °C.

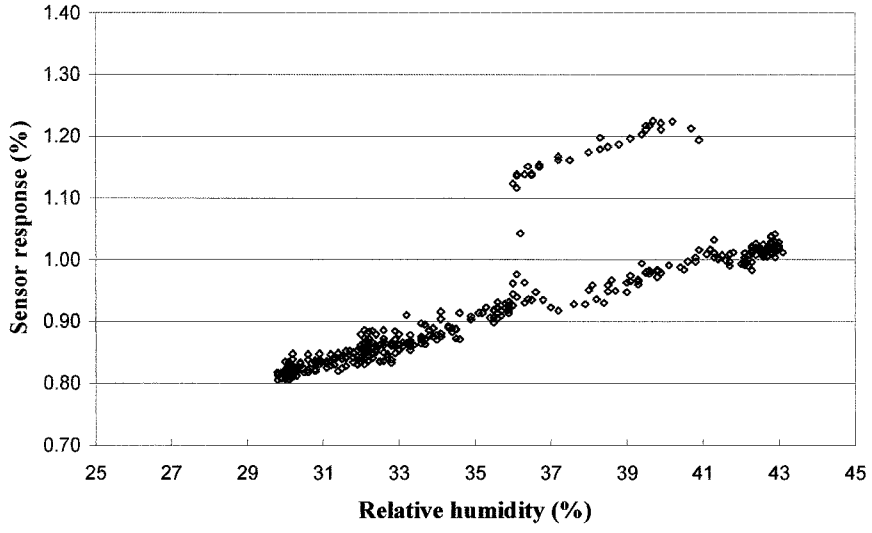


Figure 6.4.1.2 Sensor 501Vs RH between runs 0-483. 200 ml/min sparge flow rate. 20 ppm 2-CP spike between runs 284-314. Sample temperatures at 30 °C.

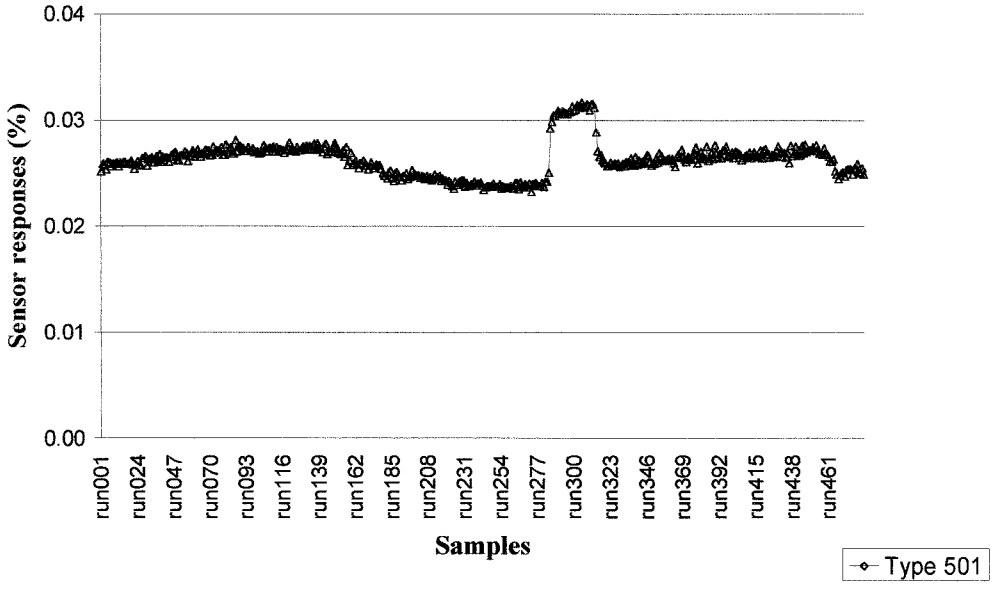


Figure 6.4.1.3 Sensor 501 Normalised with respect to RH between runs 0-483. 200 ml/min sparge rate. 20 ppm 2-CP spike between runs 284-314. Liquid temperatures at 30 °C.

Figure 6.4.1.4 shows changes recorded at the on-line monitoring station where the RH, sample temperature and RH all peaked during the presence of pollution. Figure 6.4.1.5 shows the normalised plot of the sensor and RH shown in Figure 6.4.1.4, the corresponding temperature and RH fluctuation at the time of pollution masks the benefits of data normalisation. In an on-line system, where the type of pollutant, and the effects it may have upon the sensors in the array, is unknown it is not acceptable to be using such a process for pollution identification as it can clearly mislead.

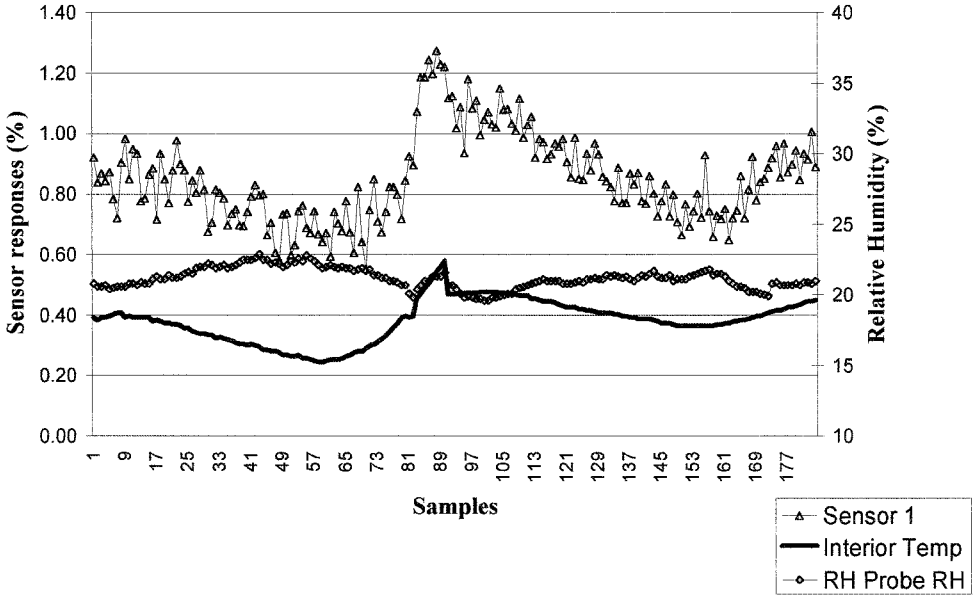


Figure 6.4.1.4 Sensor 1 (501) between 15.17 pm (15-5-02) and 13.09 pm (17-5-02). 20 ppm 2CP spike introduced between runs 85-90. ProSAT @ River Trent Monitoring Station.

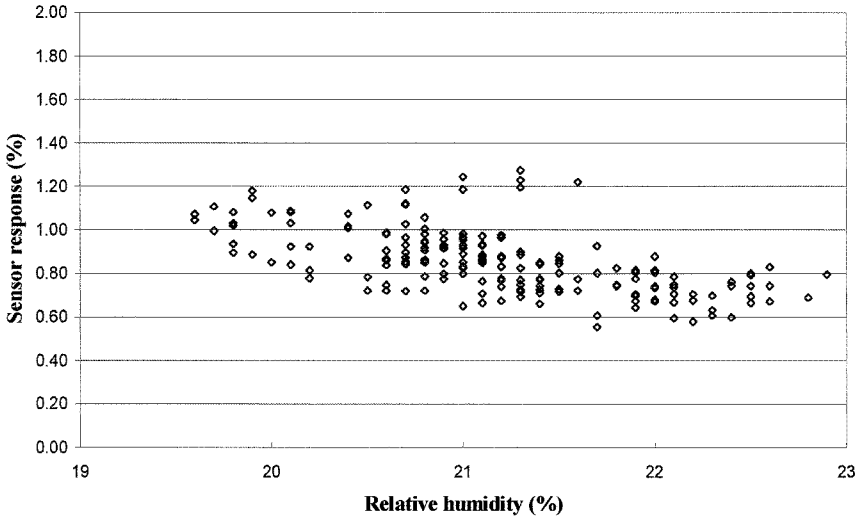


Figure 6.4.1.5 Sensor 1 verses RH. 20 ppm 2CP spike introduced between runs 85-90. ProSAT @ River Trent Monitoring Station.

When plotting sensor response verses the corresponding RH value it should also be noted that as the concentration of the pollutant, the sample temperature and gas flow decrease the likelihood of the sensor registering a response also decreases. Figures 6.4.1.6 and 6.4.1.7 show such plots for 5 and 20 ppm 2-chlorophenol spikes. The distance separating each cluster of response values with decreasing sample concentration. In a noisy environment the lower levels of pollution could be reduced and become lost in background RH fluctuations. Figure 6.4.1.8 gives a direct comparison of sensors 501, 502, 503 and 504 all plotted against the corresponding RH value. As the response magnitude decreases so does the separation between baseline values and spiked samples.

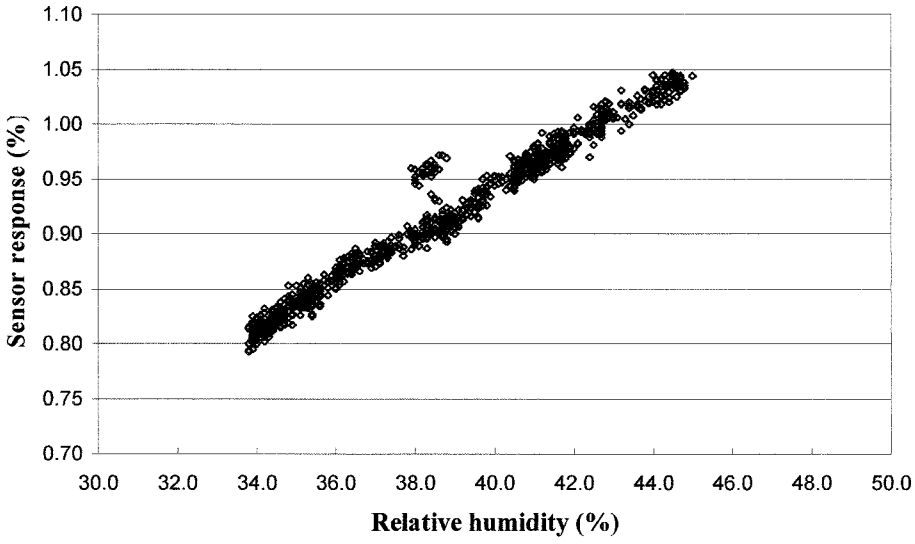


Figure 6.4.1.6 Sensor 501Vs RH between runs 0-483.
5 ppm 2-CP spike between runs 284-314. (24 Jan 2002)

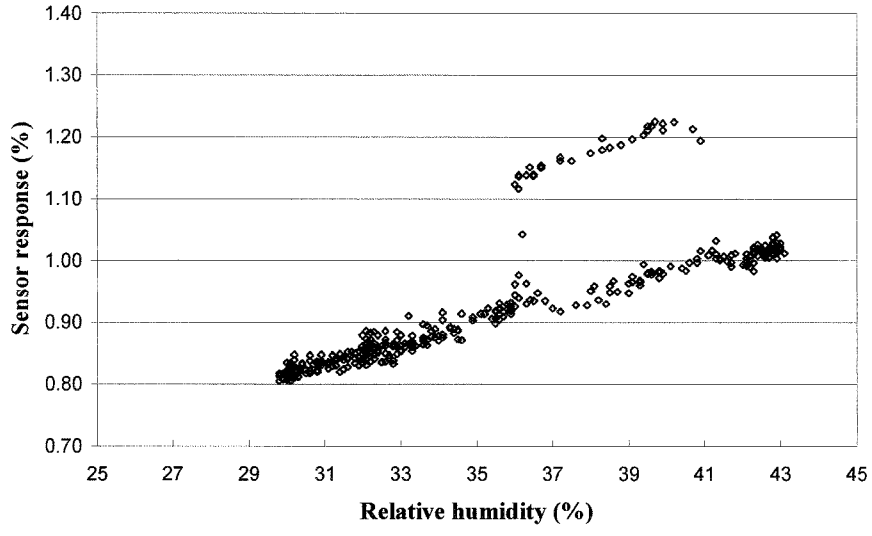


Figure 6.4.1.7 Sensor 501Vs RH between runs 0-483. 200 ml/min sparge flow rate.
20 ppm 2-CP spike between runs 284-314. Sample temperatures at 30 °C.

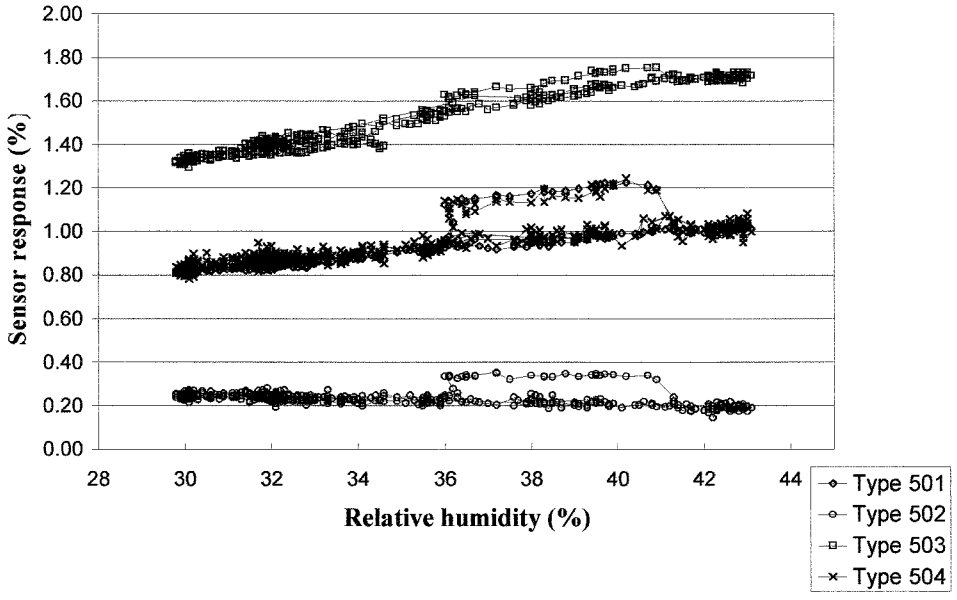


Figure 6.4.1.8 Sensors 501, 502, 503 and 504 Vs RH between runs 0-483. 200 ml/min sparge flow rate.20 ppm 2-CP spike between runs 284-314. Sample temperatures at 30°C.

Figure 6.4.1.9 shows sensor 501 during a 20 ppm diesel spike. When the sensor responses are plotted against their corresponding RH values the drift from peak back to baseline concentration is clearly observed (Figure 6.4.1.10). As the response magnitude decreases so does the separation between baseline values and spiked samples. This is the same as the trends observed for the diesel pollution when viewing with PCA (Figure 5.4.1.5).

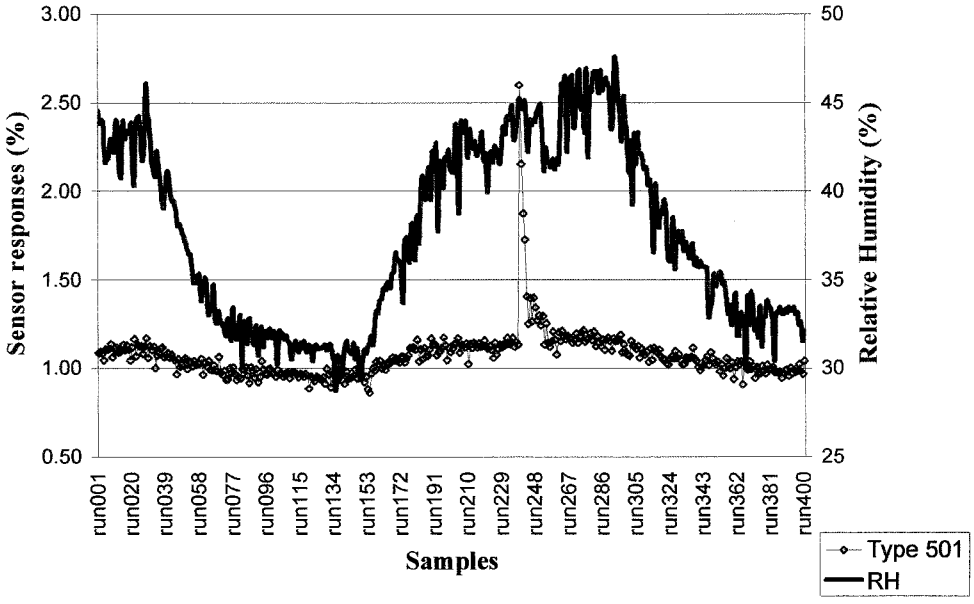


Figure 6.4.1.9 Sensor 501 between runs 0-400. 200 ml/min sparge flow. 20 ppm diesel spike between runs 240-260. Liquid temperatures at 30°C.

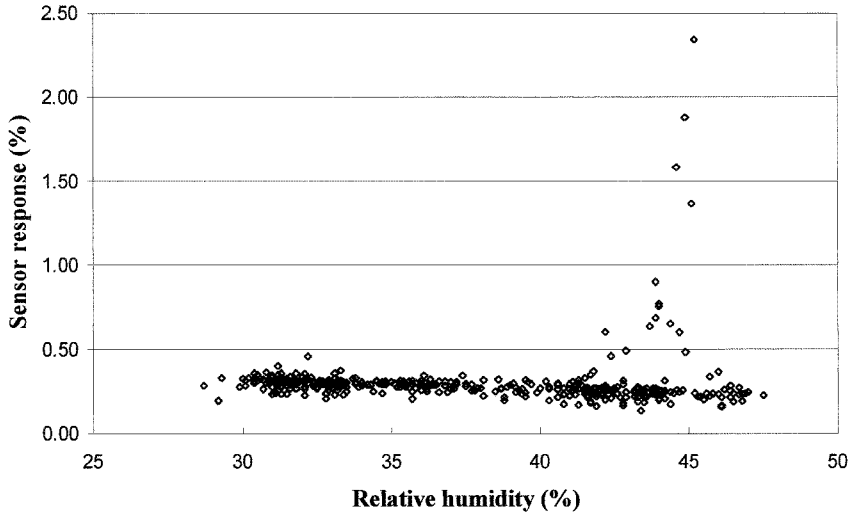


Figure 6.4.1.10 Sensor 501vs RH between runs 0-400. 200 ml/min sparge flow. 20 ppm diesel spike between runs 240-260. Liquid temperatures at 30°C.

### 6.4.2. Addition of sensor response values

The values from each sensor acquisition could be added providing a combined effect. Therefore when pollution enters the system the total response change would be more pronounced making data analysis and PCA representation clearer. However, although promising, this cannot be applied without further testing and analysis. As shown earlier (Figure 5.2.1.7) some sensors behave in different ways to varying pollutant compounds. To this point only a few compounds have be detected using our system. It is possible that for other pollutant compounds negative and positive effects could be seen in the sensor response profiles, therefore adding responses may produce clearer result yet could also produce subdued effects. Once we have a better understanding of how other compounds effect the sensors an addition procedure could be implemented.

## 6.5. Potential for real time analysis

As suggested by Lloyd *et al.* (1998) there is often a trade off between instrument sensitivity and time required to obtain the result. This is pertinent to our application where detection levels are not as low as those attainable by GC and LC techniques yet the sampling time and sample processing times are faster offering a more regular and representative analysis of the water. Once the presence of pollution has been detected abstraction can be suspended whilst the time consuming techniques are applied for quantification. At an unmanned remote monitoring station these techniques will not know when to operate unless they can be activated automatically when a significant change in water quality is detected by the sensor array.

A means of classifying the water quality is required. Once an abnormality has been confirmed supplemental analytical techniques can be deployed. But what would be a suitable method for achieving this? It is not suitable to use a simple gradient change from one sensor profile to the next due to the variations that are known to exist. A modification to a simple gradient change where any change is considered against previous data would be suitable. Ahring *et al.* (1995) employed a statistical significance

test to evaluate different Volatile Fatty Acid concentrations and to indicate process imbalance, they used:

$$Z = x - y/SD$$

Where: Z is the significance value, x is the value of the parameter being viewed, y is the average of the parameter values preceding x and SD is the standard deviation of the points used to obtain y.

The number of points used to calculate the y and SD value were investigated. Fewer points will enable a current picture of fluctuations but will not be representative of the bigger data set whereas more points will give a bigger picture of fluctuations, however more changes would be expected in the larger set increasing the risk of diluting the effect of the presence of pollution. Values from laboratory and field testing will be assigned to Z so that it is possible to see when the variation in Z is significant or can be attributed to acceptable fluctuations. Figure 6.5.1 shows a typical 20 ppm 2-chlorophenol spike within a 500 data point data set. The plot was chosen as the presence of pollution is clear providing a good test for the statistical significance application. The data presented in Figures 6.5.2, 6.5.3, 6.5.4 and 6.5.5 are calculated from Figure 6.5.1. The difference between the plots is the number of data point values used to calculate the y and SD values (10 ,20, 30 and 50 points, respectively). Figure 6.5.2 indicates a clear statistical change in the sensor profile as the pollution enters and then leaves the system. The more data that are incorporated into the averaged and standard deviation the statistical change becomes less distinct (Figures 6.5.3 – 6.5.5).

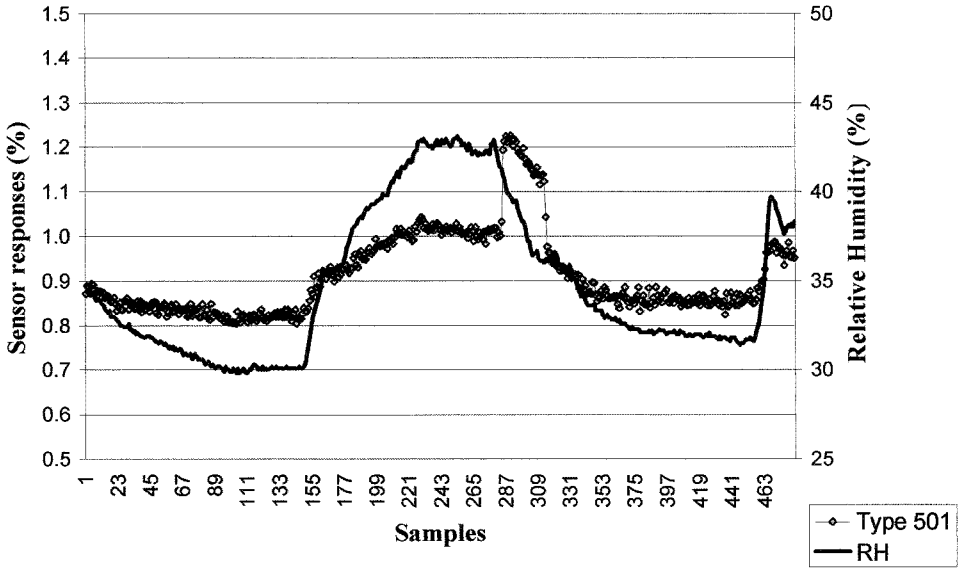


Figure 6.5.1 20ppm 2-chlorophenol spike within a data set of 500 sample acquisitions.

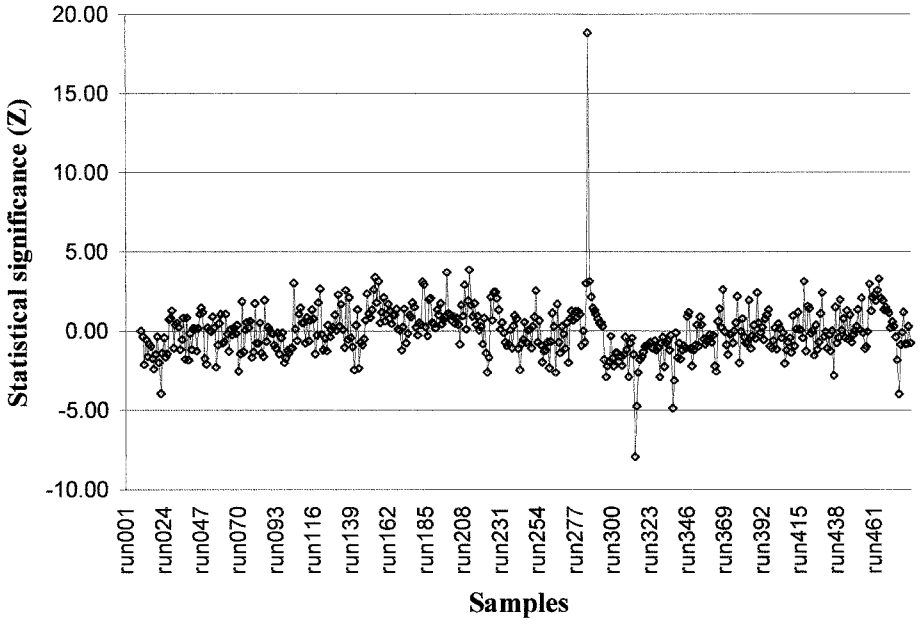


Figure 6.5.2 Statistical significance test using ten previous data point values to calculate the average and SD values for a 20ppm 2CP spike.

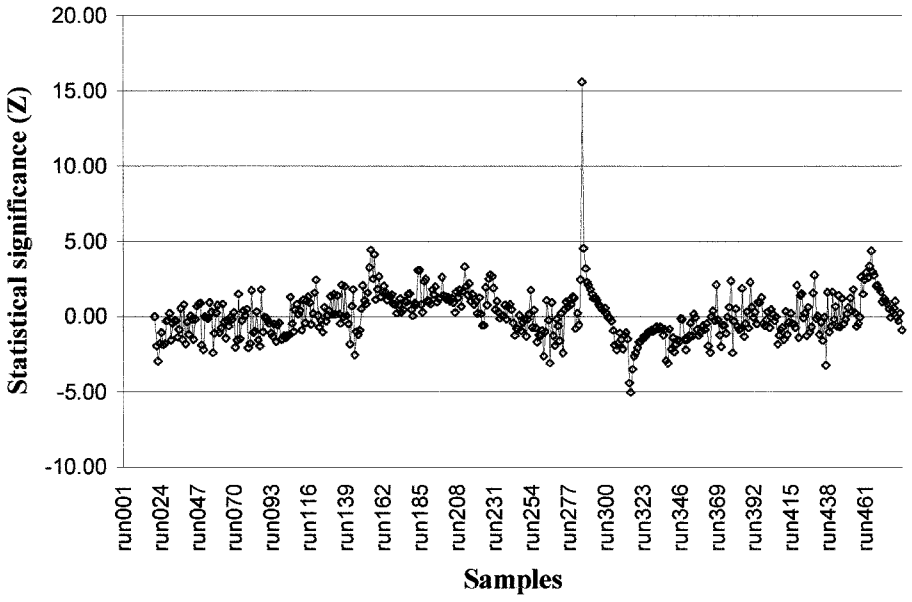


Figure 6.5.3 Statistical significance test using twenty previous data point values to calculate the average and SD values for a 20ppm 2CP spike.

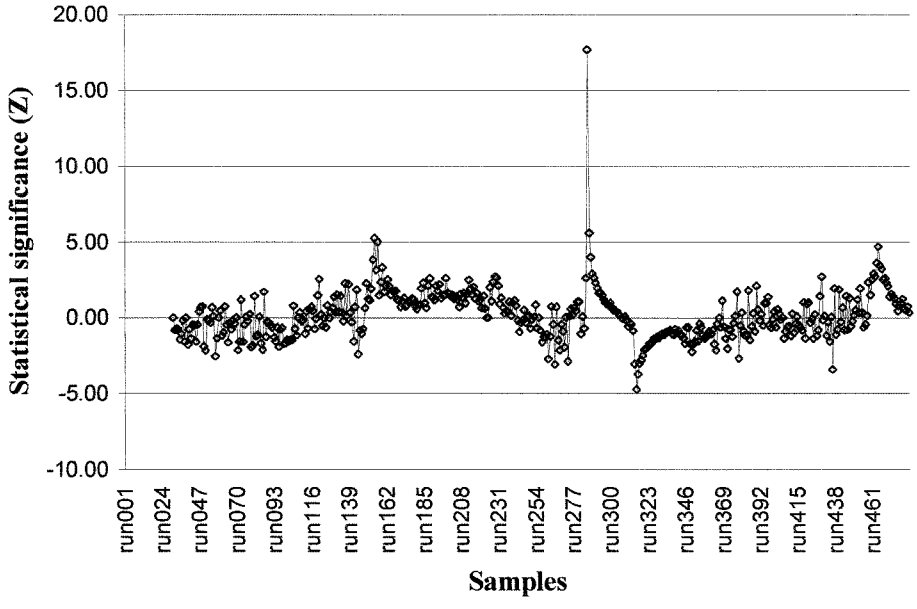


Figure 6.5.4 Statistical significance test using thirty previous data point values to calculate the average and SD values for a 20ppm 2CP spike.

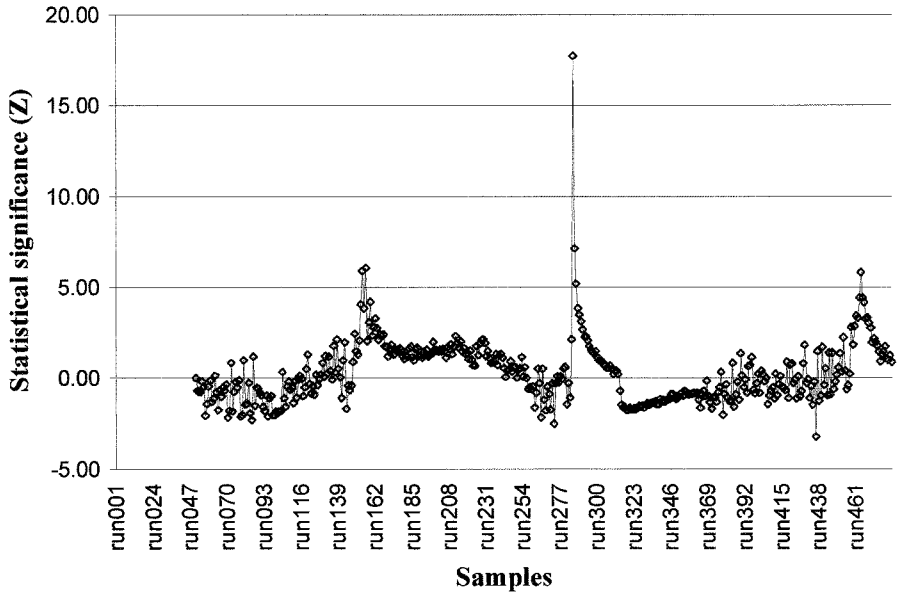


Figure 6.5.5 Statistical significance test using fifty previous data point values to calculate the average and SD values for a 20ppm 2CP spike.

Figure 6.5.6 shows a typical 20ppm diesel spike within a data set of 400 sample acquisitions. The statistical significance test was applied resulting in the plot presented in Figure 6.5.7. The change in statistical significance for the Diesel pollution is instantly recognisable.

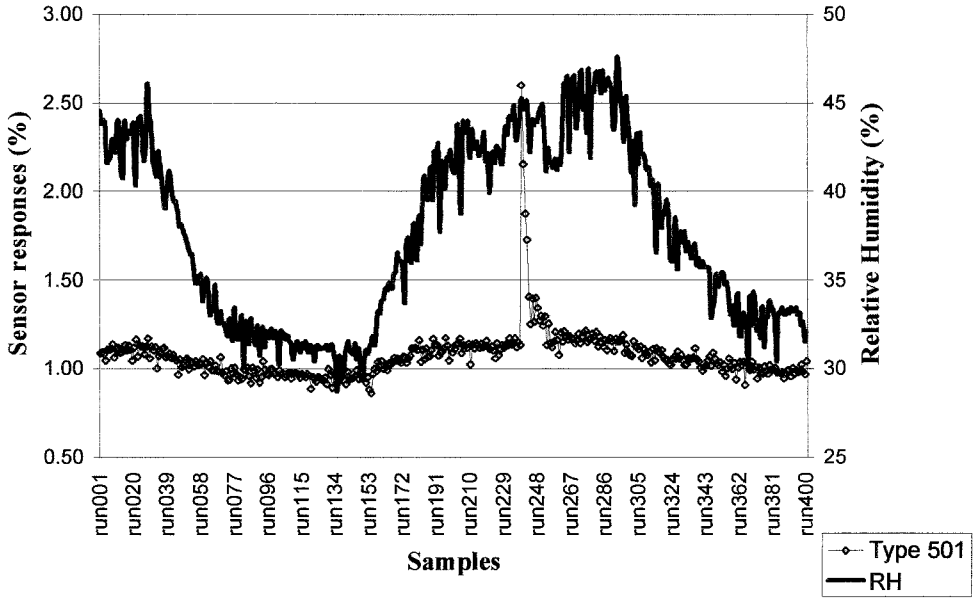


Figure 6.5.6 20ppm diesel spike within a data set of 400 sample acquisitions

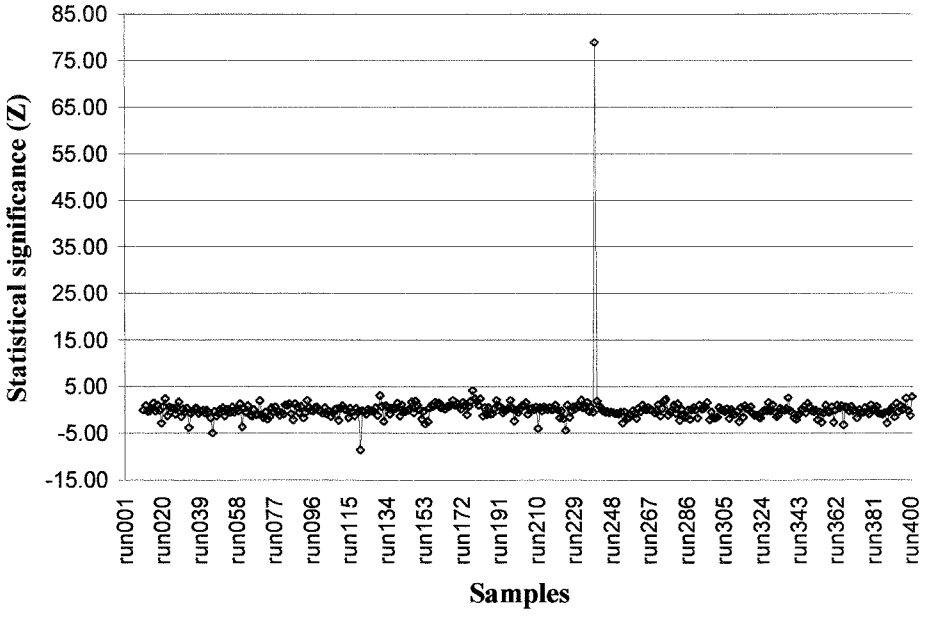


Figure 6.5.7 Statistical significance test using ten previous data point values to calculate the average and SD values for a 20ppm diesel spike.

Both the previous statistical significance application examples have used data taken from 20 ppm spiked data sets. To set a limit level for a pollution alarm the significance test must be able to ascertain lower levels of pollution. Figure 6.5.8 shows a period of 1000

data points into which a 5 ppm 2-chlorophenol spike was introduced. The resultant statistical significance calculation yielded Figure 6.5.9. The presence and absence of the pollution, although less significant than for the 20 ppm test are still clear. A statistical significance of greater than +4 can be attached to a 5 ppm 2-chlorophenol spike. If it was so desired a negative value could be incorporated into the alarm indicating the passing of the pollution episode and therefore ceasing the operational status of the supporting analytical procedures.

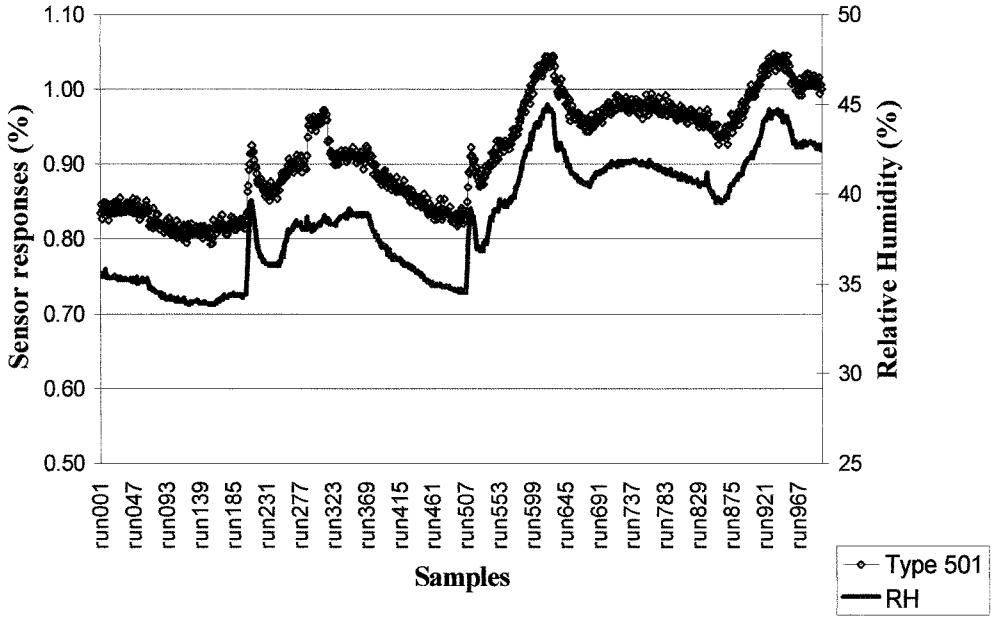


Figure 6.5.8 5ppm 2-chlorophenol spike within a data set of 1000 sample acquisitions

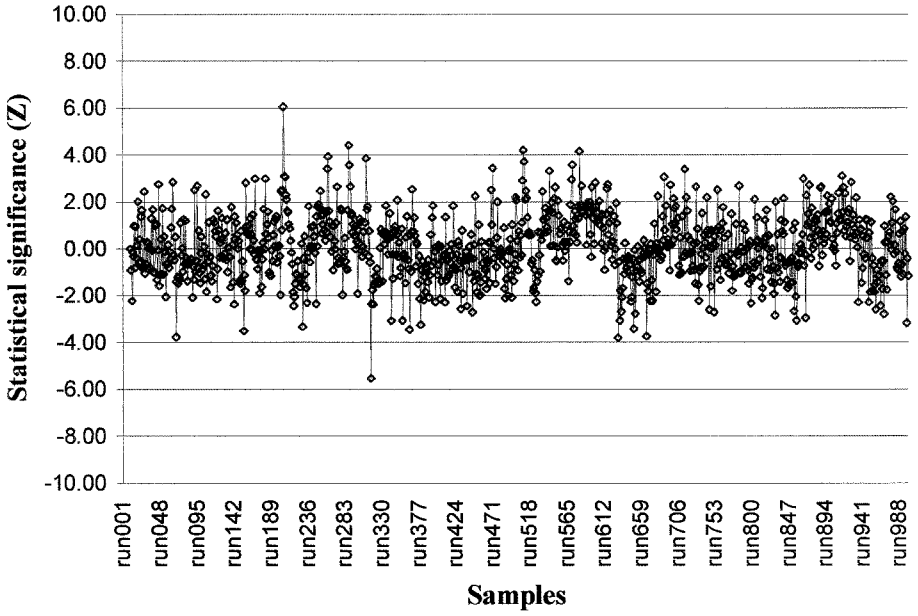


Figure 6.5.9 Statistical significance test using ten previous data point values to calculate the average and SD values for a 5ppm 2CP spike.

Figure 6.5.10 shows a 5ppm diesel spike within a data set of 300 sample acquisitions. The statistical significance test was applied resulting in the plot presented in Figure 6.5.11. The change in statistical significance for the diesel pollution is recognisable, however fluctuations have a greater effect at lower concentrations and at the latter end of the set negative significance is noted. A statistical significance of greater than +5 can be attached to this 5 ppm spike. The inclusion of a negative value would be impossible in a noisy environment.

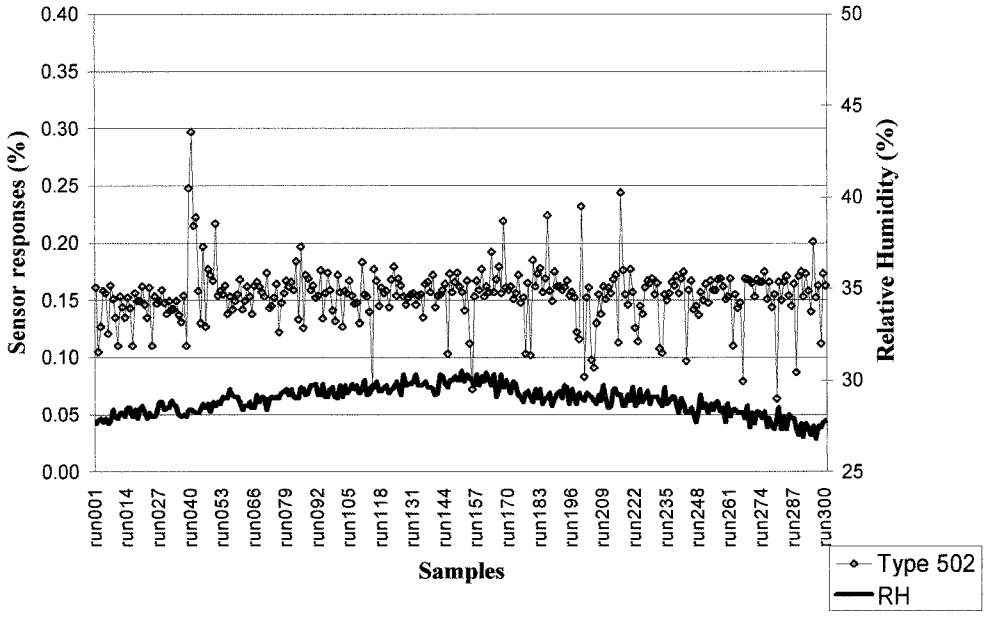


Figure 6.5.10 5ppm diesel spike within a data set of 300 sample acquisitions

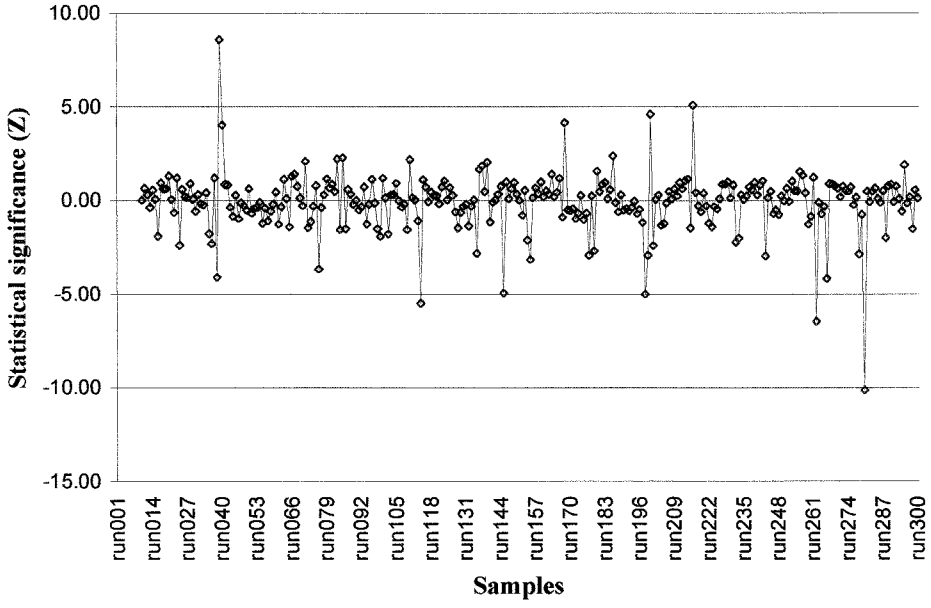


Figure 6.5.11 Statistical significance test using ten previous data point values to calculate the average and SD values for a 5ppm diesel spike.

Application of the statistical significance test to first generation field data (Figure 6.5.12) shows very little in the way of statistical change even when Z is calculated using the standard deviation and average of the previous 10, 20 or thirty data points, Figures 6.5.13, 6.5.14 and 6.5.14, respectively. The limited levels of detection, system fluctuations and undesirable blending properties mask visual pollutant identification. This test should be reapplied once the field application is stable and operating without undesirable system fluctuation.

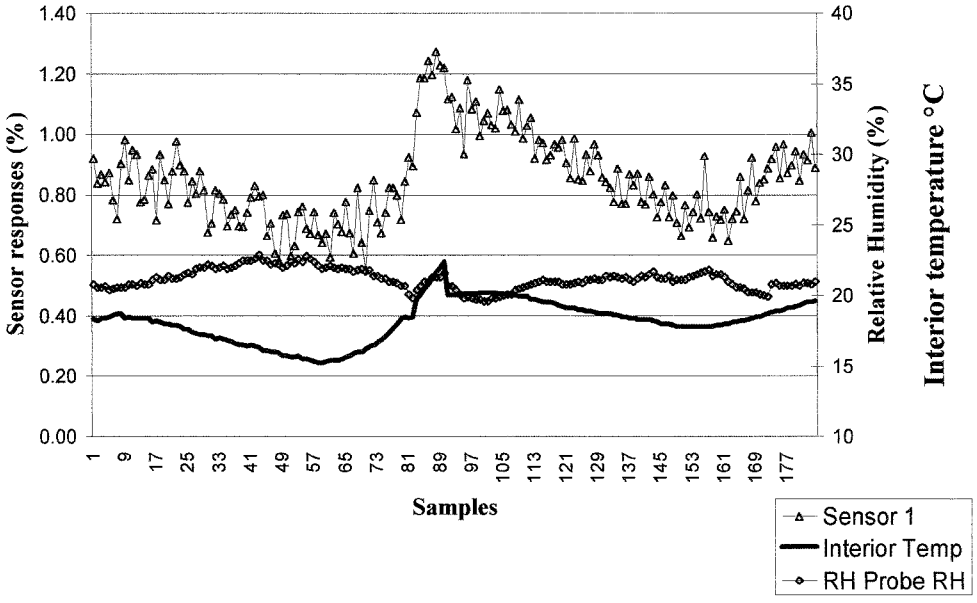


Figure 6.5.12 Sensor 501 during a 20 ppm 2CP spike introduced between runs 85-90. Using the ProSAT at the River Trent Monitoring Station.

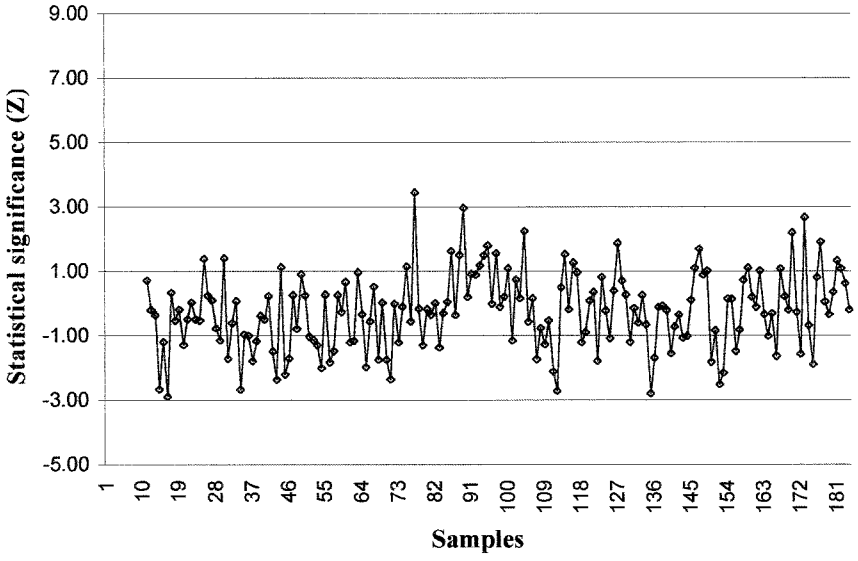


Figure 6.5.13 Statistical significance test using ten previous data point values to calculate the average and SD values for Sensor 501 during a 20 ppm 2CP spike introduced between runs 85-90. Using the ProSAT at the River Trent Monitoring Station.

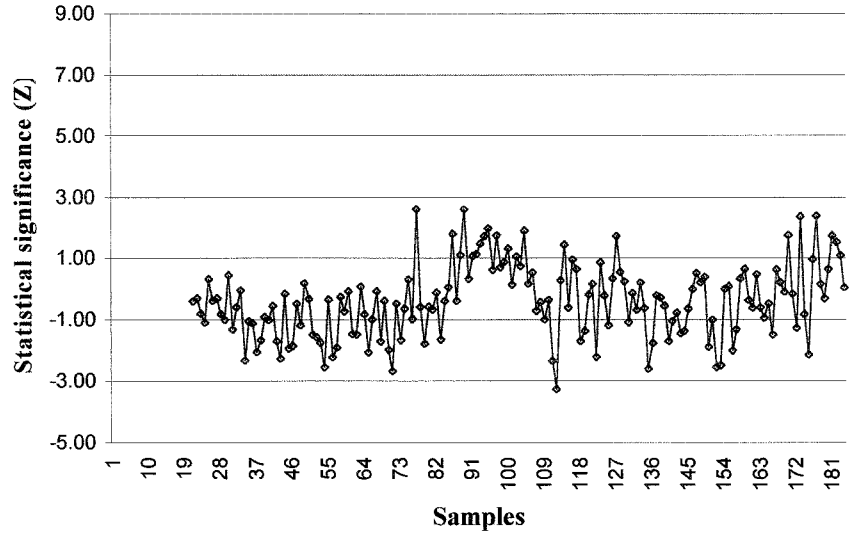


Figure 6.5.14 Statistical significance test using twenty previous data point values to calculate the average and SD values for Sensor 501 during a 20 ppm 2CP spike introduced between runs 85-90. Using the ProSAT at the River Trent Monitoring Station.

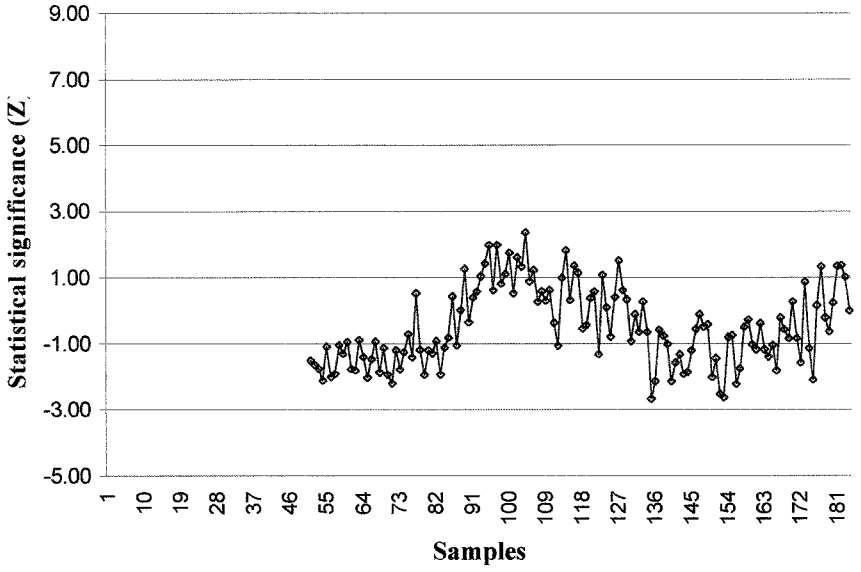


Figure 6.5.15 Statistical significance test using thirty previous data point values to calculate the average and SD values for Sensor 501 during a 20 ppm 2CP spike introduced between runs 85-90. Using the ProSAT at the River Trent Monitoring Station.

### 6.5.1. Application of statistical significance test

Application of the statistical significance test in the form of Time-Series analysis would be ideal for a process monitoring application. The sensor resistance value at 59 seconds would be graphically visualised on screen. Each point would be added to the screen as the sensor profile is mined. The screen would have a maximum of 200 points upon it at all times, as each additional point is added the least current ($200^{th}$) point is displaced to a master data file.

However a minor drawback to this proposal is that our current data handling system does not support a real-time data analysis due to the configuration of the sampling programming. Data are continually added to an open dataset and if an attempt is made to abstract data while the set is building the system crashes forcing the data collection to be aborted. The programming requires modification to enable 'data picking' during analysis.