## Cranfield University

#### School of Water Sciences

#### PhD Thesis

Academic years 1999-2002

Peter James Hogben

Inlet monitoring of a potable water supply using a sensor array

Supervisor: Dr Richard Stuetz

October 2003

This thesis is submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

© Cranfield University 2003. All rights reserved. No part of this publication may be reproduced without the written permission of the copyright owner.

#### **Abstract**

Monitoring for pollutants in potable water is an area of interest and concern for water supply companies. Supply of sub-standard water can draw complaints from public and industrial consumers. Water and water tainted with pollutants were used to assess the application of a non-specific chemical sensor array (eNose) to monitor for changes in the headspace generated from a flow-cell by means of statistically designed experiments. 2-chlorophenol and diesel were used to further assess trends in headspace generation during trials where different combinations of sampling parameters were applied. Field trials were carried out at a drinking water abstraction facility. The trials were conducted in accordance with the most suitable methodology determined during initial studies under laboratory conditions.

The headspace is generated by bubbling nitrogen through the flow-cell containing a water sample. The liquid sample is flushed and regenerated after each sensor acquisition cycle. The resultant headspace sample is transferred to the sensor array module where the resistance of the conducting polymer sensors is monitored as they are exposed to each respective headspace sample. The change in each sensor resistance after 60 seconds of exposure is used to represent the headspace character. Subsequent acquisitions are added to a data set and then presented graphically. Sudden changes in the sensor resistance plots represent changes in water quality.

The results showed that the developed apparatus and sampling methodology can determine the presence or absence of pollution in a water matrix. Laboratory analysis showed that detection levels for 2-chlorophenol and diesel were both <5 ppm in the mixed stream. Future developments should focus on increasing the sensitivity of the system by concentrating the pollutants in either the liquid or gas phase or by modifying the sampling protocol to enable sensor recognition at lower concentration levels. The sensor array could act as a screening technique to support quantitative and characterising analytical equipment at the abstraction point. Establishing a pollution alarm limit, within the bounds

of acceptable system variation, would enable conventional analytical techniques to remain on standby until activated by a statistically significant change in water quality. Once established continued testing would enable alarm levels to be incorporated into a contaminant database for additional pollutant compounds and combinations of known taste and odour causing compounds.

### Acknowledgements

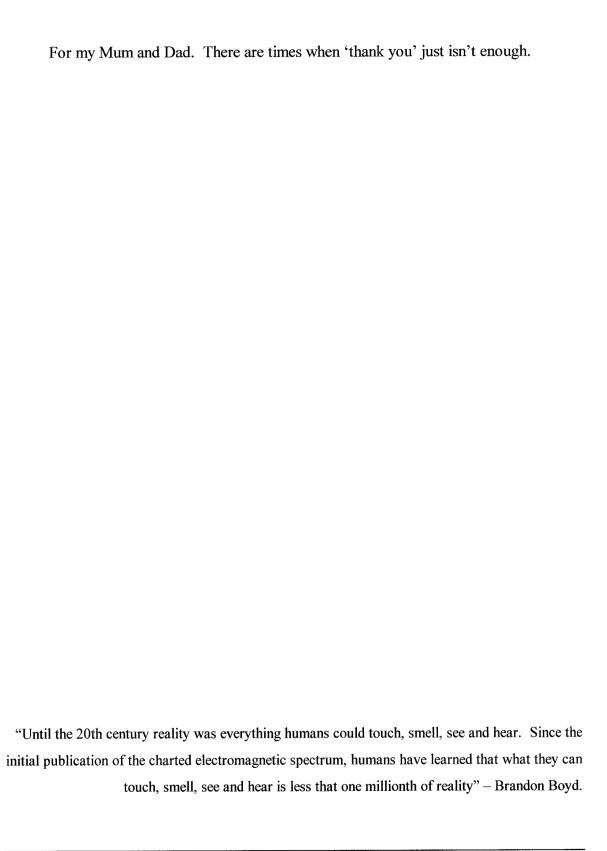
I would like to thank both EPSRC and Severn Trent Water Ltd. for their financial assistance during my research project and Marconi Applied Technologies for their technical support. Special thanks to Brian Drage and Mike Purvis from Severn Trent Water Ltd. and Gurjit Kang, Pat Casey, Neil Collins and Andrew Pike from Marconi Applied Technologies.

I would like to show gratitude to my supervisor, Dr Richard Stuetz, whose enthusiasm, guidance and knowledge are boundless and Dr Bruce Jefferson for his help and advice during the final months.

There are many individuals and good friends that have made my time within the 'institution' a memorable experience, to name you all would be like a bad speech at the Oscars! Thanks all the same ©.

Finally I would like to thank my family. Thank you for believing in me.

#### Dedication



## Table of Contents

Abstract		i-ii
Acknowledgements		iii
Dedication		iv
Table of cont	ents	v
List of tables		X
List of figure	S	xvii
List of abbrev	viation	xxvi
Publications a	and conferences	xxviii
1.	Introduction	1
2.	Literature Review	4
2.1	Introduction	4
2.2	Water quality standards	4
2.2.1	Abstraction	5
2.2.2	Water intended for human consumption	5
2.3	Taste and odour episodes	6
2.3.1	Olfactometry	10
2.3.1.1	Flavour profile analysis	10
2.3.1.2	Threshold odour number	12
2.3.1.2.1	Olfactometry assessment	13
2.4	Techniques applied for water monitoring	15
2.4.1	Technical analysis	15
2.4.1.1	Chromatography	15
2.4.1.1.1	Sample preparation	16
2.4.1.1.2	Sample detection	16
2.4.1.2	Infrared spectroscopy	20

Aims and Objectives	62
	59
	55
Instrumentation	51
Overview of less common gas sensors	49
Acoustic wave sensors	47
Metal oxide sensors	44
•	39
Sensor types	37
Sensor array system	37
Sensor arrays	37
· ·	36
What makes a good monitoring system?	35
Conclusion 'Why is there the need for abstraction monitoring?'	34
Case 4: River Trent	33
Case 3: Danube River Basin	32
Case 2: Rhine Basin	29
Case 1: Ruhr Basin	28
	28
	26
-	25
•	25
	24
	23
-	22
·	22
Parametric analysis	21
	Case 2: Rhine Basin Case 3: Danube River Basin Case 4: River Trent Conclusion 'Why is there the need for abstraction monitoring?' What makes a good monitoring system? Emerging technology Sensor arrays Sensor array system Sensor types Conducting polymer Metal oxide sensors Acoustic wave sensors Overview of less common gas sensors

4.	Materials and methods	63
4.1	Introduction	63
4.2	Laboratory based development	63
4.2.1	Sensor array	63
4.2.1.1	Sensor acquisition	63
4.2.2.	Headspace generation	64
4.2.3	Sample preparation	66
4.2.4	Data mining	66
4.2.5	Experimental design	68
4.2.6	Pollutant introduction	68
4.3	Field based development	68
4.3.1	Sensor array	69
4.3.2	System set up	70
4.3.3	Pollutant introduction	72
4.4	Data analysis	72
4.4.1	Graphical representation	72
4.4.2	Statistical analysis	72
4.4.3	Experimental design	73
4.4.3.1	Main effects	73
4.4.3.2	Variable interactions	74
4.4.3.2.1	Significance	76
5.	Results	77
5.1	Experimental development	77
5.1.1	Initial labortory testing	77
5.1.2	Reducing RH and gas flow effects	86
5.1.3	Selecting a suitable sampling window	88
5.1.4	Identification of pollution	89
5.1.5	Sample temperature blending	92
5.2	Laboratory based assessment	93
J. L	Euroratory oused assessment	73

5.2.1	Test matrix	93
5.2.2	Trends in matrix data when each parameter is made the subject	100
	for viewing	
5.2.2.1	Sample concentration – temperature by flow	102
5.2.2.2	Sample concentration – flow by concentration	111
5.2.2.3	Sparge gas flow rate – temperature by concentration	118
5.2.2.4	Sparge gas flow rate – concentration by temperature	124
5.2.2.5	Sample temperature – flow by concentration	131
5.2.2.6	Sample temperature – concentration by flow	135
5.3	Field based assessment	140
5.3.1	Background river monitoring	140
5.3.2	Field spiking	142
5.3.3	On-line sampling modification	143
5.4	Data analysis	144
5.4.1	Principal component analysis of 2-chlorophenol and diesel	144
	peaks	
5.4.2	Statistical analysis of testing matrix – effects on sensor response	149
5.4.2.1	$\Delta$ Sensor response (RH)	150
5.4.2.2	$\Delta$ Sensor response (501, 2-CP)	156
5.4.2.3	$\Delta$ Sensor response (502, diesel)	160
5.4.3	Statistical analysis of laboratory based spiking experiments	164
6.	Discussion	169
6.1	System development	169
6.2	Laboratory based assessment	169
6.2.1	Addressing levels of detection	170
6.3	Field based assessment	172
6.3.1	Monitoring frequency	172
6.3.2	Detection levels	173
6.3.3	Preconcentration	174

6.4	Data analysis	178
6.4.1	Parametric compensation	178
6.4.2	Addition of sensor response values	186
6.5	Potential for real time analysis	186
6.5.1	Application of statistical significance test	197
7.	Conclusions	198
8.	Future work and prospects	200
	References	202

## List of Tables

Chapter Two - Literature Review		
2.3.1	Chemicals causing off-flavours and odours in drinking water	7
2.3.2	Tabulated drinking water taste and odour wheel	8
2.3.1.2.1	Comparison between OTC values for the two most commonly	14
	reported off tastes/odours in drinking water	
2.4.1.1.1	Applications of GC for water monitoring	18
2.4.1.1.2	Applications of LC for water monitoring.	19
2.5.1	Comparison of the key variables for online monitoring techniques	27
2.6.2.1	Methods for, and detection levels of the contaminants in the Rhine	31
	Basin Program	
2.6.4.1	On-line instrumentation used on the River Trent	33
2.8.2.1.1	Advantages and disadvantages of using conducting polymer	44
	sensors.	
2.8.2.2.1	Advantages and disadvantages of metal oxide sensors.	47
2.8.2.3.1	Advantages and disadvantages of acoustic wave gas sensors	49
2.8.3.1.1	Sensor array manufactures and available models	53
2.8.3.1.1	Applications of sensor array systems	56
2.8.3.1.2	Environmental/consumer related applications of sensor arrays	57
2.8.4.1	Common statistical techniques used for the analysis of sensor array	59
	data.	
Chapter Four	- Materials and Methods	
4.2.5.1	Experimental design matrix	73
4.4.3.2.1	Contrast pattern matrix	75
111101211	Community Patronia marini	, ,

Chapter Five	e - Results	
5.1.1.1	Experimental design matrix and results for 8 RH experiments on	80
	DI-water using the flow-cell apparatus	
5.1.1.2	Average contribution and average effect of temperature, gas flow	80
	rate and sparger porosity on RH levels, Day 1	
5.1.1.3	Average contribution and average effect of temperature, gas flow	81
	rate and sparger porosity on RH levels, Day 2	
5.1.1.4	Average contribution and average effect of temperature, gas flow	81
	rate and sparger porosity on RH levels, Day 3	
5.1.1.5	Ranked average effects of temperature, gas flow rate and sparger	81
	porosity's (relative to RH)	
5.1.1.6	Contrast pattern matrix generated for the 8 RH experiments	82
5.1.1.7	Main effect coefficients and interaction coefficients generated for	83
	the 3x8 RH experiments on DI-water	
5.1.1.8	The significance of the averaged main effect generated for the	83
	three days of the 3x8 RH experiments on DI-water	
5.2.1.1	Responding sensors from initial testing matrix.	94
5.2.2.1	2-chlorophenol testing matrix	101
5.2.2.2	Diesel testing matrix	101
5.2.2.1.1	Parameter comparisons and their effect on sensor and RH	102
	response. Concentration held at 5ppm. Sample temperature at	
	15°C Vs flows of 50, 100 and 200 ml/min	
5.2.2.1.2	Parameter comparisons and their effect on sensor and RH	103
	response. Concentration held at 10ppm. Sample temperature at	
	15°C Vs flows of 50, 100 and 200 ml/min	
5.2.2.1.3	Parameter comparisons and their effect on sensor and RH	103
	response. Concentration held at 20ppm. Sample temperature at	
	15°C Vs flows of 50, 100 and 200 ml/min	

5.2.2.1.4	Parameter comparisons and their effect on sensor and RH	104
	response. Concentration held at 5ppm. Sample temperature at	
	30°C Vs flows of 50, 100 and 200 ml/min	
5.2.2.1.5	Parameter comparisons and their effect on sensor and RH	104
	response. Concentration held at 10ppm. Sample temperature at	
	30°C Vs flows of 50, 100 and 200 ml/min	
5.2.2.1.6	Parameter comparisons and their effect on sensor and RH	105
	response. Concentration held at 20ppm. Sample temperature at	
	30°C Vs flows of 50, 100 and 200 ml/min	
5.2.2.2.1	Parameter comparisons and their effect on sensor and RH	112
	response. 2-chlorophenol at 5ppm. Flows of 50, 100 and 200	
	ml/min Vs sample temperatures of 15°C and 30°C	
5.2.2.2.2	Parameter comparisons and their effect on sensor and RH	112
	response. 2-chlorophenol at 10ppm. Flows of 50, 100 and 200	
	ml/min Vs sample temperatures of 15°C and 30°C	
5.2.2.2.3	Parameter comparisons and their effect on sensor and RH	113
	response. 2-chlorophenol at 20ppm. Flows of 50, 100 and 200	
	ml/min Vs sample temperatures of 15°C and 30°C	
5.2.2.2.4	Parameter comparisons and their effect on sensor and RH	114
	response. Diesel at 5ppm. Flows of 50, 100 and 200 ml/min Vs	
	sample temperatures of 15°C and 30°C	
5.2.2.2.5	Parameter comparisons and their effect on sensor and RH	115
	response. Diesel at 10ppm. Flows of 50, 100 and 200 ml/min Vs	
	sample temperatures of 15°C and 30°C	
5.2.2.2.6	Parameter comparisons and their effect on sensor and RH	118
	response. Diesel at 20ppm. Flows of 50, 100 and 200 ml/min Vs	
	sample temperatures of 15°C and 30°C	

5.2.2.3.1	Parameter comparisons and their effect on sensor and RH	119
	response. 2-chlorophenol at flows of 50 ml/min. Sample	
	temperatures of 15°C and 30°C Vs sample concentrations of 5, 10	
	and 20 ppm	
5.2.2.3.2	Parameter comparisons and their effect on sensor and RH	119
	response. 2-chlorophenol at flows of 100 ml/min. Sample	
	temperatures of 15°C and 30°C Vs sample concentrations of 5, 10	
	and 20 ppm	
5.2.2.3.3	Parameter comparisons and their effect on sensor and RH	120
	response. 2-chlorophenol at flows of 200 ml/min. Sample	
	temperatures of 15°C and 30°C Vs sample concentrations of 5, 10	
	and 20 ppm	
5.2.2.3.4	Parameter comparisons and their effect on sensor and RH	122
	response. Diesel at flows of 50 ml/min. Sample temperatures of	
	15°C and 30°C Vs sample concentrations of 5, 10 and 20 ppm	
5.2.2.3.5	Parameter comparisons and their effect on sensor and RH	123
	response. Diesel at flows of 100 ml/min. Sample temperatures of	
	15°C and 30°C Vs sample concentrations of 5, 10 and 20 ppm	
5.2.2.3.6	Parameter comparisons and their effect on sensor and RH	124
	response. Diesel at flows of 200 ml/min. Sample temperatures of	
	15°C and 30°C Vs sample concentrations of 5, 10 and 20 ppm	
5.2.2.4.1	Parameter comparisons and their effect on sensor and RH	124
	response. 2-chlorophenol at flows of 50 ml/min. Sample	
	concentrations of 5, 10 and 20 ppm Vs sample temperatures of	
	15°C and 30°C	
5.2.2.4.2	Parameter comparisons and their effect on sensor and RH	125
	response. 2-chlorophenol at flows of 100 ml/min. Sample	
	concentrations of 5, 10 and 20 ppm Vs sample temperatures of	
	15°C and 30°C	

5.2.2.4.3	Parameter comparisons and their effect on sensor and RH	128
	response. 2-chlorophenol at flows of 200 ml/min. Sample	
	concentrations of 5, 10 and 20 ppm Vs sample temperatures of	
	15°C and 30°C	
5.2.2.4.4	Parameter comparisons and their effect on sensor and RH	128
	response. Diesel at flows of 50 ml/min. Sample concentrations of	
	5, 10 and 20 ppm Vs sample temperatures of 15°C and 30°C	
5.2.2.4.5	Parameter comparisons and their effect on sensor and RH	129
	response. Diesel at flows of 100 ml/min. Sample concentrations of	
	5, 10 and 20 ppm Vs sample temperatures of 15°C and 30°C	
5.2.2.4.6	Parameter comparisons and their effect on sensor and RH	130
	response. Diesel at flows of 200 ml/min. Sample concentrations of	
	5, 10 and 20 ppm Vs sample temperatures of 15°C and 30°C	
5.2.2.5.1	Parameter comparisons and their effect on sensor and RH	131
	response. 2-chlorophenol 15°C. Sparge flows at 50, 100 and 200	
	ml/min Vs sample concentrations of 5, 10 and 20 ppm	
5.2.2.5.2	Parameter comparisons and their effect on sensor and RH	134
	response. 2-chlorophenol at 30°C. Sparge flows at 50, 100 and	
	200 ml/min Vs sample concentrations of 5, 10 and 20 ppm	
5.2.2.5.3	Parameter comparisons and their effect on sensor and RH	135
	response. Diesel at 15°C. Sparge flows at 50, 100 and 200 ml/min	
	Vs sample concentrations of 5, 10 and 20 ppm	
5.2.2.5.4	Parameter comparisons and their effect on sensor and RH	135
	response. Diesel at 30°C. Sparge flows at 0, 100 and 200 ml/min	
	Vs sample concentrations of 5, 10 and 20 ppm	
5.2.2.6.1	Parameter comparisons and their effect on sensor and RH	136
	response. 2-chlorophenol at 15°C. Sample concentrations of 5, 10	
	and 20 ppm Vs sparge flows of 50, 100 and 200 ml/min	

5.2.2.6.2	Parameter comparisons and their effect on sensor and RH	136
	response. 2-chlorophenol at 30°C. Sample concentrations of 5, 10	
	and 20 ppm Vs sparge flows of 50, 100 and 200 ml/min	
5.2.2.6.3	Parameter comparisons and their effect on sensor and RH	137
	response. Diesel at 15°C. Sample concentrations of 5, 10 and 20	
	ppm Vs sparge flows of 50, 100 and 200 ml/min	
5.2.2.6.4	Parameter comparisons and their effect on sensor and RH	137
	response. Diesel at 30°C. Sample concentrations of 5, 10 and 20	
	ppm Vs sparge flows of 50, 100 and 200 ml/min	
5.4.1.1	Variance Table for PCA of sensors 501, 502, 503 + 504 from plot	146
	5.4.1.1	
5.4.1.2	Variance Table for PCA of sensors 501, 502, 503 + 504 from plot	148
	5.4.1.4	
5.4.2.1.1	Experimental design matrix including variable values	150
5.4.2.1.2	RH responses from experimental design (two separate runs,	150
	A and B)	
5.4.2.1.3	Average contribution and effect of temperature, flow rate and	151
	concentration on RH levels, run A (2-chlorophenol)	
5.4.2.1.4	Average contribution and effect of temperature, flow rate and	151
	concentration on RH levels, run B (diesel)	
5.4.2.1.5	Ranked average effects of sample temperature, gas flow rate and	152
	concentration (relative to RH)	
5.4.2.1.6	Contrast pattern matrix generated for runs A and B	152
5.4.2.1.7	Main effect coefficients and interaction coefficients generated for	153
	runs A and B worked from Table 5.4.2.1.6	
5.4.2.1.8	Significance of the coefficient values – Run A, from Table	153
	5.4.2.1.7	
5.4.2.1.9	Significance of the coefficient values – Run B, from Table	154
	5.4.2.1.7	

5.4.2.1.10	Significance of the coefficient values – average of Run A and Run	154
	B, from Table 5.4.2.1.7	
5.4.2.1.11	Coefficients for corresponding variables used in the prediction	155
	equation	
5.4.2.1.12	Δ Sensor RH. Response predictions	156
5.4.2.2.1	Experimental design matrix including variable values	157
5.4.2.2.2	Average contribution and effect of temperature, flow rate and	157
	concentration on $\Delta$ sensor response (501, 2-CP) Differences are in	
	order of ranked effect	
5.4.2.2.3	Contrast pattern matrix generated for the $\Delta$ sensor response (501	158
	2-CP)	
5.4.2.2.4	Main effect coefficients and interaction coefficients generated for	159
	the $\Delta$ sensor response (501, 2-CP)	
5.4.2.2.5	Δ Sensor 501. Response predictions	160
5.4.2.3.1	Experimental design matrix including variable values	161
5.4.2.3.2	Average contribution and effect of temperature, flow rate and	161
	concentration	
5.4.2.3.3	Contrast pattern matrix generated for the $\Delta$ sensor response (502)	162
	Diesel)	
5.4.2.3.4	Main effect coefficients and interaction coefficients generated	162
	for the $\Delta$ sensor response (502, diesel)	
5.4.2.3.5	$\Delta$ Sensor 502. Response predictions Vs actual results	164
5.4.3.1	Statistical data for sensors 501, 502, 503 and 504 for sampling	165
	periods prior to 2-chlorophenol spiking at sample temperatures of	
	15 °C	
5.4.3.2	Statistical data for sensors 501, 502, 503 and 504 for sampling	166
	periods prior to 2-chlorophenol spiking at sample temperatures of	
	30 °C	
5.4.3.3	Statistical data for sensors 501, 502, 503 and 504 for sampling	167
	periods prior to diesel spiking at sample temperatures of 15 °C	

5.4.3.4	Statistical data for sensors 501, 502, 503 and 504 for sampling periods prior to diesel spiking at sample temperatures of 30 °C	168
Chapter Si	x - Discussion	
6.3.3.1	Advantages and disadvantages of methods used for either concentrating or isolating organic compounds from water	176

# List of Figures

Chapter Two – Literature Review			
		tan adam ayan ayan dalar 1969 <del>) 1 - 1</del>	
2.3.1	Photograph of a smell bell	9	
2.4.2.1.	A turbidimetric device	22	
2.4.3.1.1	Illustration of the mussel test	23	
2.4.3.2.1	Application of a fish test, their behavior is monitored as they are	24	
	subjected to known concentrations of pollutants		
2.4.3.3.1	Dynamic daphnia test	25	
2.8.1.1	Key components of a sensor array	37	
2.8.2.1	Photograph of the four most common sensors (metal oxide,	39	
	conducting polymers, surface acoustic wave and quartz crystal		
	microbalances (BAWs)) used in commercial sensor array systems		
2.8.2.1.1	Photograph of a conducting polymer sensor	40	
2.8.2.1.2	Single monomer units (A) Analine, (B) Pyrrole and (C) Thiophene	40	
2.8.2.1.3	Polymerised pyrrole structure	41	
2.8.2.1.4	Representation of bond breakage and formation caused by electron	42	
	passage through the compound during conduction		
2.8.2.1.5	Response profile from an array of conducting polymer sensors	43	
2.8.2.2.1	Photograph of a metal oxide sensor	45	
2.8.2.2.2	Dopant effects on metal oxide sensor response characteristics	46	
2.8.2.3.1	Photograph of a BAW sensor	48	
2.8.3.1.1	Principal components of a sensor array system	51	
2.8.3.1.2	Photograph of BH114 sensor array system	54	
2.8.3.1.3	Photograph of eNOSE 5000 instrument with autosampler	54	
2.8.3.1.4	Photograph of ProSAT on-line process monitoring system	55	
2.8.3.1.5	Photograph of Cyranose 320 portable sensor array monitor	55	

2.8.4.1	PCA plot showing the separation between a 2-chlorophenol	60
2.0.4.1	spiking event within a water matrix	00
2042	•	61
2.8.4.2	Three-layer feed forward network	01
Cl 4 F		
Chapter Four	- Materials ans Methods	····
4.2.2.1	The sampling system for experimentation, consisting of a sample	65
	vessel, flow-cell chamber, sensor array module and a PC for data	
	analysis/collection/control	
4.2.2.2	The Flow-cell	65
4.2.2.1.1	A response pattern generated by a chemical sensor array showing	67
	the sensor response (%) change verses time and the point at which	
	data is mined to produce the representative pattern profile	
4.2.2.1.2	Graphical representation of the sensor responses, RH and system	67
	temperature over a period of 900 runs (105 hours continuous	
	analysis)	
4.3.1.1	Photograph of ProSAT on-line process monitoring system	69
4.3.2.1	Photograph of the ProSAT and Flow-cell at the River Trent	71
	monitoring station	
4.3.2.1	Schematic of the ProSAT and Flow-cell at the River Trent	71
	monitoring station	
Chapter Five	- Results	
5.1.1.1	Plot of sensor responses showing instabilities in preliminary studies	78
5.1.1.2	Modified laboratory set up including heated transfer line and	79
	temperature regulated sensor array	
5.1.1.3	Statistical design plots showing areas of increased stability in RH	85
	generation	

5.1.1.4	Plot of sensor responses and RH showing improved system	85
	stability due to the implementation of a statistical design	
5.1.2.1	Plot of diurnal drift in sensor and RH Profiles over a 4 day	86
	sampling period	
5.1.2.2	Plot of relative humidity and gas flows for an 85 hour sampling	87
	period showing fluctuations in response profiles	
5.1.2.3	Plot of relative humidity and gas flows for an 85 hour sampling	88
	period showing reduced fluctuation in profile variation	
5.1.3.1	Disjointed data sets showing the problems associated with cross-	89
	comparison of data that has not been collected concurrently	
5.1.4.1	Sensor 501 between runs 200-500 using DI water as matrix. 10	90
	ppm 2CP spike at sample number run396. Blank DI spike at	
	sample number run316	
5.1.4.2	Plot of four sensors and RH between runs 1-100. 10 ppm	91
	2-chlorophenol injection at run 55	
5.1.4.3	Plot of four sensors between runs 225-324. 10 ppm	91
	2-chlorophenol injection at run 273	
5.1.5.1	Sensor 401 and RH between runs 561-750. Blank spike introduced	92
	between sample numbers run613-623. 1 ppm 2-chlorophenol spike	
	introduced between sample numbers run670-700	
5.2.1.1	Sensor 501 between runs 201-399. 100ml/min sparge rate. 5 ppm	95
	2-chorophenol spike between sample numbers 238-256	
5.2.1.2	Sensor 501 between runs 1-101. 200ml/min sparge rate10 ppm	95
	2-chorophenol spike between sample numbers 47-69	
5.2.1.3	Sensor 501 between runs 201-300. 200ml/min sparge rate. 20 ppm	96
	2-MIB spike between sample numbers 251-284	
5.2.1.4	Sensor 502 between runs 201-300. 200ml/min sparge rate. 10 ppm	97
	2-MIB spike between sample numbers 251-284	
5.2.1.5	Sensor 501 between runs 201-300. 200ml/min sparge rate. 20 ppm	98
	diesel spike between sample numbers 240-260	

5.2.1.6	Sensor 504 between runs 201-300. 200ml/min sparge rate. 20 ppm	98
	diesel spike between sample numbers 240-260	
5.2.1.7	Sensor 601 between runs 251-350 200ml/min sparge rate. 20 ppm	99
	1,2-propandiol spike between sample numbers 282-293	
5.2.2.1.1	Sensor 501 between runs 1-101. 200 ml/min sparge flow rate. 10	105
	ppm 2-chorophenol spike between runs 47-69. Liquid samples at	
	30°C	
5.2.2.1.2	Sensor 501 between runs 51-150. 100 ml/min sparge flow rate 10	106
	ppm 2-chlorophenol spike between runs 111-129. Liquid samples	
	at 30°C	
5.2.2.1.3	Sensor 501 between runs 251-350. 100 ml/min sparge flow rate.	107
	20 ppm 2-chlorophenol spike between runs 307-335. Liquid	
	samples at 30°C	
5.2.2.1.4	Sensor 501 between runs 250-350. 200 ml/min sparge flow rate.	107
	20 ppm 2-chlorophenol spike between runs 284-312. Liquid	
	samples at 30°C	
5.2.2.1.5	Sensor 501 between runs 201-300. 200 ml/min sparge flow rate.	108
	20 ppm diesel spike between runs 240-260. Liquid samples at	
	30°C	
5.2.2.1.6	Sensor 501 between runs 201-300. 100 ml/min sparge flow rate.	108
	20 ppm diesel spike between runs 239-263. Liquid samples at	
	30°C	
5.2.2.1.7	Sensor 501 between runs 201-300. 200 ml/min sparge flow rate.	109
	20 ppm diesel spike between runs 240-260. Liquid samples at	
	30°C	
5.2.2.1.8	Sensor 502 between runs 201-300. 200 ml/min sparge rate.	110
	20 ppm diesel spike between sample numbers 240-260. Liquid	
	samples at 30°C.	

5.2.2.1.9	Sensor 503 between runs 201-300. 200 ml/min sparge rate.	110
	20 ppm diesel spike between sample numbers 240-260. Liquid	
	temperatures at 30°C	
5.2.2.1.10	Sensor 504 between runs 201-300. 200 ml/min sparge flow rate.	111
	20 ppm diesel spike between sample numbers 240-260. Liquid	
	temperatures at 30°C	
5.2.2.2.1	Sensor 501 between runs 1-151. 50 ml/min sparge flow rate. 20	113
	ppm 2-chlorophenol spike between runs 81-126. Liquid samples at	
	15°C	
5.2.2.2.2	Sensor 501 between runs 1-101. 50 ml/min sparge flow rate. 20	114
	ppm 2-chlorophenol spike between runs 74-96. Liquid samples at	
	30°C	
5.2.2.2.3	Sensor 501 between runs 1-130. 100 ml/min sparge flow rate. 10	116
	ppm diesel spike between runs 87-119. Liquid samples at 30 °C	
5.2.2.2.4	Sensor 502 between runs 1-130. 100 ml/min sparge flow rate. 10	116
	ppm diesel spike between runs 87-119. Liquid samples at 30 °C	
5.2.2.2.5	Sensor 503 between runs 1-130. 100 ml/min sparge flow rate. 10	117
	ppm diesel spike between runs 87-119. Liquid samples at 30 °C	
5.2.2.2.6	Sensor 504 between runs 1-130. 100 ml/min sparge flow rate. 10	117
	ppm diesel spike between runs 87-119. Liquid samples at 30 °C	
5.2.2.3.1	Sensor 501 between runs 250-350. 200ml/min sparge flow rate. 20	121
	ppm 2-chorophenol spike between sample numbers 284-312.	
	Liquid samples at 30 °C	
5.2.2.3.2	Sensor 501 between runs 1-101. 200ml/min sparge flow rate. 10	121
	ppm 2-chorophenol spike between sample numbers 47-69. Liquid	
	samples at 30 °C	
5.2.2.3.3	Sensor 501 between runs 201-399. 200ml/min sparge gas flow	122
	rate. 5 ppm 2-chorophenol spike between sample numbers 238-	
	256. Liquid samples at 30°C	

5.2.2.4.1	Sensor 501 between runs 21-120. 100 ml/min sparge flow rate. 10	126
	ppm 2-chlorophenol spike between runs 77-92. Liquid samples at	
	15°C	
5.2.2.4.2	Sensor 501 between runs 51-150. 100 ml/min sparge flow rate. 10	126
	ppm 2-chlorophenol spike between runs 111-129. Liquid samples	
	at 30°C	
5.2.2.4.3	Sensor 501 between runs 251-350. 100 ml/min sparge flow rate.	127
	20 ppm 2-chlorophenol spike between runs 287-301. Liquid	
	samples at 15°C	
5.2.2.4.4	Sensor 501 between runs 251-350. 100 ml/min sparge flow rate.	127
	20 ppm 2-chlorophenol spike between runs 307-335. Liquid	
	samples at 30°C	
5.2.2.4.5	Sensor 501 between runs 201-300. 100 ml/min sparge flow rate.	129
	20 ppm diesel spike between runs 250-269. Liquid samples at	
	15°C	
5.2.2.4.6	Sensor 501 between runs 201-300. 100 ml/min sparge flow rate.	130
	20 ppm diesel spike between runs 239-263. Liquid samples at	
	30°C	
5.2.2.5.1	Sensor 501 between runs 51-200. 200 ml/min sparge flow rate. 5	132
	ppm 2-chlorophenol spike between runs 75-90. Liquid samples at	
	15 °C	
5.2.2.5.2	Sensor 501 between runs 1-150. 200 ml/min sparge flow rate. 10	132
	ppm 2-chlorophenol spike between runs 30-45. Liquid samples at	
	15 °C	
5.2.2.5.3	Sensor 501 between runs 1-150. 200 ml/min sparge flow rate. 20	132
	ppm 2-chlorophenol spike between runs 29-42. Liquid samples at	
	15 °C	
5.2.2.6.1	Sensor 502 between runs 1-120. 50 ml/min sparge flow rate. 10	138
	ppm diesel spike between runs 20-37. Liquid samples at 15 °C	

5.2.2.6.2	Sensor 502 between runs 1-100. 100 ml/min sparge flow rate. 10	138
	ppm diesel spike between runs 61-78. Liquid samples at 15 °C	
5.2.2.6.3	Sensor 502 between runs 1-120. 200 ml/min sparge flow rate. 10	139
	ppm diesel spike between runs 50-64. Liquid samples at 15 °C	
5.3.1.1	River Trent temperature profile over a 24 hour period (June 1 <sup>st</sup>	141
	2001)	
5.3.1.2	River Trent temperature profile over a 48 hour period (June 1st	141
	and 2 <sup>nd</sup> 2001)	
5.3.2.1	Sensor 1 (501) between 15.17 p.m. (15-5-02) and 13.09 p.m.	142
	(17-5-02). 20 ppm 2-chlorophenol spike introduced between runs	
	85-90	
5.3.3.1	Schematic of proposed on-line sampling modification	143
5.4.1.1	Sensor 501 between runs 0-483. 20 ppm 2-CP spike between runs	145
	284-314. 200ml/min sparge rate. Liquid temperatures at 30°C	
5.4.1.2 2	PCA analysis of a 20ppm 2-chlorophenol spike. Component 1 by	146
	component 2	
5.4.1.3	PCA analysis of a 20ppm 2-chlorophenol spike. Component 2 by	147
	component 3	
5.4.1.4	Sensor 501 between runs 0-400. 20 ppm diesel spike between runs	148
	240-260. 100ml/min sparge rate 30°C	
5.4.1.5	PCA analysis of a 20ppm diesel spike. Component 1 by	149
	component 2	
Chapter Six	z – Discussion	
6.12.2.1	Schematic for proposed preconcentrator	177
6.4.2.1	Sensor 501 between runs 0-483. 200 ml/min sparge rate.	179
	20 ppm 2-CP spike between runs 284-314. Liquid temperatures at	
	30°C	

6.4.1.2	Sensor 501Vs RH between runs 0-483. 200 ml/min sparge flow	180
	rate. 20 ppm 2-CP spike between runs 284-314. Sample	
	temperatures at 30°C	
6.4.1.3	Sensor 501 normalised with respect to RH between runs 0-483.	180
	200 ml/min sparge rate. 20 ppm 2-CP spike between runs 284-	
	314. Liquid temperatures at 30°C	
6.4.1.4	Sensor 1 (501) between 15.17 pm (15-5-02) and 13.09 pm	181
	(17-5-02). 20 ppm 2CP spike introduced between runs 85-90.	
	ProSAT @ River Trent Monitoring Station	
6.4.1.5	Sensor 1 verses RH. 20 ppm 2CP spike introduced between runs	182
	85-90. ProSAT @ River Trent Monitoring Station	
6.4.1.6	Sensor 501Vs RH between runs 0-483.5 ppm 2-CP spike between	183
	runs 284-314.	
6.4.1.7	Sensor 501Vs RH between runs 0-483. 200 ml/min sparge flow	183
	rate. 20 ppm 2-CP spike between runs 284-314. Sample	
	temperatures at 30°C	
6.4.1.8	Sensors 501, 502, 503 and 504 Vs RH between runs 0-483. 200	184
	ml/min sparge flow rate.20 ppm 2-CP spike between runs 284-	
	314. Sample temperatures at 30°C	
6.4.1.9	Sensor 501 between runs 0-400. 200 ml/min sparge flow.	185
	20 ppm diesel spike between runs 240-260. Liquid temperatures at	
	30°C	
6.4.1.10	Sensor 501vs RH between runs 0-400. 200 ml/min sparge flow.	185
	20 ppm diesel spike between runs 240-260. Liquid temperatures at	
	30°C	
6.5.1	20ppm 2-chlorophenol spike within a data set of 500 sample	188
	acquisitions	
6.5.2	Statistical significance test using ten previous data point values to	188
	calculate the average and SD values for a 20ppm 2CP spike	

6.5.3	Statistical significance test using twenty previous data point values	189
	to calculate the average and SD values for a 20ppm 2CP spike	
6.5.4	Statistical significance test using thirty previous data point values	189
	to calculate the average and SD values for a 20ppm 2CP spike	
6.5.5	Statistical significance test using fifty previous data point values to	190
	calculate the average and SD values for a 20ppm 2CP spike	
6.5.6	20ppm diesel spike within a data set of 400 sample acquisitions	191
6.5.7	Statistical significance test using ten previous data point values to	191
	calculate the average and SD values for a 20ppm diesel spike	
6.5.8	5ppm 2-chlorophenol spike within a data set of 1000 sample	192
	acquisitions	
6.5.9	Statistical significance test using ten previous data point values to	193
	calculate the average and SD values for a 5ppm 2CP spike	
6.5.10	5ppm diesel spike within a data set of 300 sample acquisitions	194
6.5.11	Statistical significance test using ten previous data point values to	194
	calculate the average and SD values for a 5ppm diesel spike	
6.5.12	Sensor 501 during a 20 ppm 2CP spike introduced between runs	195
	85-90. Using the ProSAT at the River Trent Monitoring Station	
6.5.13	Statistical significance test using ten previous data point values to	196
	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	
6.5.14	Statistical significance test using twenty previous data point values	196
	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	
6.5.15	Statistical significance test using thirty previous data point values	197
	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.	

### List of Abbreviations

2-CP	2-chlorophenol	FET	Field effect transistor
2-MIB	2-methylisoborneol	FID	Flame ionisation detector
Ag	Silver	FPA	Flavour profile analysis
ANN	Artificial neural network	FTIR	Fourier transform Infrared spectrometry
BAW	Bulk acoustic wave	GAC	Granular activated carbon
CA	Cluster analysis	GC	Gas chromatograph
CCA	Canonical correlation analysis	In <sub>2</sub> O <sub>3</sub>	Indium oxide
CLSA	Closed loop stripping analysis	IR	Infra red
CO	Carbon monoxide	KG	Kilograms
$CO_2$	Carbon dioxide	KI	Potassium iodide
CP	Conducting polymer	Km	Kilometres
DAD	Diode array detection	LC	Liquid chromatography
DAEWS	Danube accident emergency warning system	LLE	Liquid-liquid extraction
ΔR	Change in sensor resistance	MDA	Multiple discriminant analysis
DI	De ionised water	Ml/min	Millilitres per minute
DM	Deutschemark	MOS	Metal oxide sensor
EA	Environment Agency	MOSFET	Metal oxide sensor field effect transistor
ECD	Electron capture detector	MS	Mass spectrometry
EtOH	Ethanol	MTBE	Methyl tert butyl ether
EU	European Union	$N_2$	Nitrogen
Fe	Iron	NOEC	No observed effect concentration

NTU	Nephelometric turbidity unit	SAW	Surface acoustic wave
OES	Optical emission spectrometry	SD	Standard deviation
Os	Osmium	SE	Standard error
OTC	Odour threshold concentration	SnO <sub>2</sub>	Tin oxide
PC	Personal computer	SPE	Solid phase extraction
PCA	Principal component analysis	SPMD	Semi permeable membrane device
Pd	Palladium	SPME	Solid phase micro extraction
pН	Potential hydrogen	TCD	Thermal conductivity detector
PIAC	Principal international alert centre	TCP	Trichlorophenol
PID	Photo-ionisation detector	TFN	Threshold flavour number
PPB	Parts per billion	TID	Thermonic ionisation detector
PPM	Parts per million	$TiO_2$	Titanium dioxide
Pt	Platinum	TOC	Total organic carbom
QCM	Quartz crystal microbalance	TON	Threshold odour number
R	Resistance	UV	Ultra violet
RH	Relative humidity	Vs	Versus
RO	Reverse osmosis	$WO_3$	Tungsten oxide
RPM	Revolutions per minute	Z	Statistical significance
SAMOS	System for the automated measurement of organic micropollutants in surface water	ZnO	Zinc oxide

#### **Publications and Conferences**

Bourgeois W., Hogben P., Pike A., and Stuetz R.M. (2003) Development of a sensor array based measurement system for continuous monitoring of water and wastewater. Sensors and Actuators B 88 (3), 312-319.

Hogben P., Drage B. Stuetz R.M. (2002) Monitoring for pollutants in a source of drinking water. Third IWA UK Young Researchers Conference, University of Nottingham

Bourgeois W., Hogben P., Stuetz R.M., Gaugler M. and Pike A. (2001) Headspace monitoring of water and wastewater using a sensor array. Proceedings AWWA 19<sup>th</sup> Convention, Canberra, CD-Rom 8pp.

Hogben P., Stuetz R.M., and Drage B. (2001) Use of a chemical sensor array and an online flow-cell for monitoring water quality. Proceedings AWWA Water Quality Technology Conference, Nashville, CD-Rom

Hogben P., Drage B. and Stuetz R.M. (2001) Development of an on-line sensor array system for monitoring pollutants in potable water. Eighth International Symposium on Olfaction and the Electronic Nose (ISOEN8). Washington D.C.

Hogben P., Drage B. and Stuetz R.M. (2001) Development of an on-line intake protection sensor array system for monitoring pollutants in a potable water source. IWA Second Young Researchers Event, Cranfield University.