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INVESTIGATION INTO
DENITRIFICATION UNDERGROUND

Interim Thirty Three Month Report

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Study conducted for

ANGLIAN WATER

by

DEPARTMENT OF GEOLOGICAL SCIENCES

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SUMMARY

Further experimentation with methanol has shown that denitrification can develop under both methanol-limited and nitrate-limited conditions. Denitrification was sustained even when an equivalent 24 hour dose of methanol was given over 4 hours per day. However, the process was not self-sustaining once the supply of methanol was discontinued. The major disadvantage with the method is the development of biomass within the sand and gravel matrix which eventually blocked the upper section of the columns in both experiments. Furthermore, a distinct cloudiness and odour developed in the water leaving the nitrate-limited experiment. After injection of methanol ceased, a 50% decline in the heads measured along both columns was noticed.

Continued experimentation with straw, aimed at optimising the denitrifying capacity of the bio-reactor by increasing the amount of straw used, did not lead to a significant improvement in the technique. In the absence of an increased volume of sand and limestone support material, the result of this experiment was to strongly discolour the reactor effluent. An aeration stage between the straw reactor and filter column initially increased the oxygen content of the final water, but did not lead to an improvement in the overall colour of the water.

A small-scale experiment into blocking continues at present. A short column filled with a uniform grade sand has been subjected to denitrification and is now being prepared for microscopic inspection. The major difficulty with this work is the preparation of thin sections from saturated, unconsolidated material.

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1. INTRODUCTION

The last interim report (University of Birmingham, February 1988) identified the need to further investigation into denitrification with the following experiments:

- (1) Gravel column experiments - dose with methanol to initiate denitrification under both methanol-limited (80% nitrate removal) and nitrate-limited (100% nitrate removal) conditions, and to monitor for blocking of the sand and gravel;
- (2) Bio-reactor experiments - pack the straw reactor with as much straw as possible and, with a change of reactor material every 20 days, attempt to increase the denitrification capacity of this treatment process;
- (3) Blocking experiments - investigate the blocking process by both taking head measurements on the gravel packed columns, and by direct experimentation with a small-scale model of a well injection point.

Experiments (1) and (2) have been completed and experiment (3) is currently in progress. The results to date are contained in this report.

Several unknowns existed at the start of the above experiments and included the following:

- (1) Will there be a gradual decrease in the nitrite concentration with increasing time in the methanol-limited experiment?
- (2) Will the sand and gravel columns block over an extended period of operation?
- (3) If methanol is pumped directly into the base of the columns will blocking rapidly develop at the point of injection?

- (4) The performance of a bio-reactor when packed densely with straw.
- (5) The effect of aerating the reactor outflow (before filtration) upon final water quality and nitrate concentration.

Therefore, the aims of this report are to:

- (a) Present and interpret the results from the column and bio-reactor experiments;
- (b) Detail the further laboratory work discussed at the last Project Meeting held on 15th June 1988.

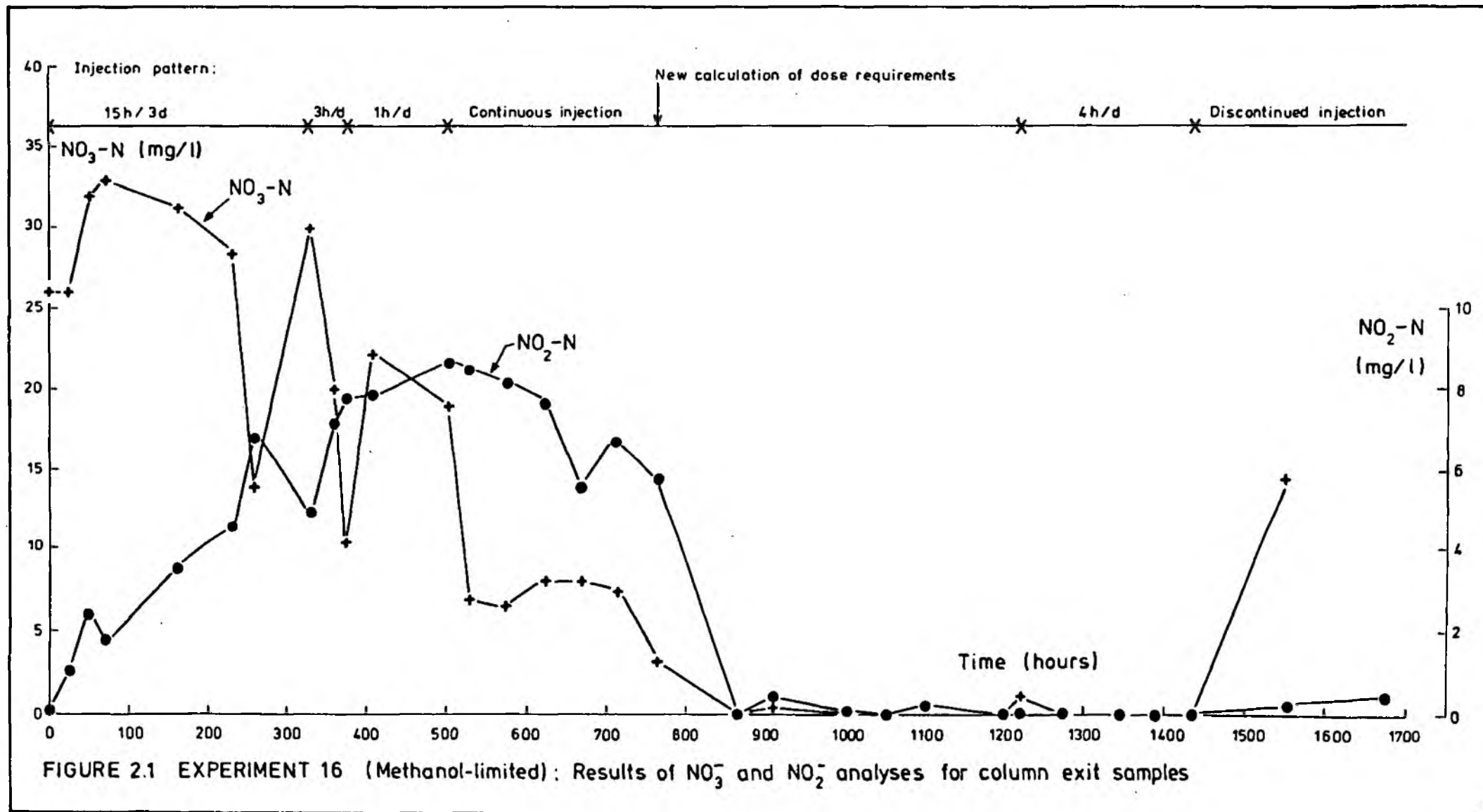
2. RESULTS FROM COLUMN EXPERIMENTS

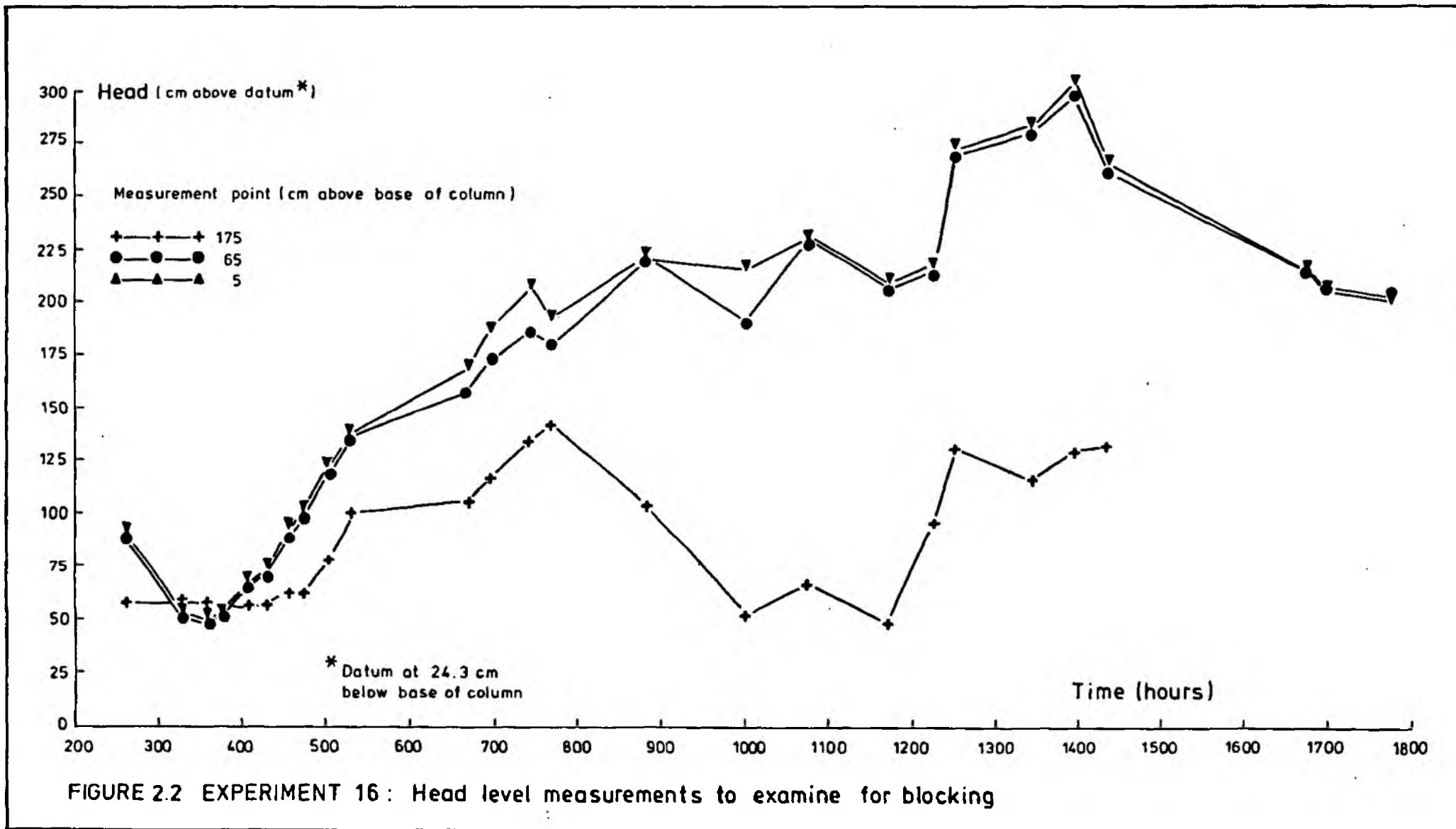
2.1 Results from Experiment 16

The object of this experiment was to use methanol as an organic carbon substrate to assist denitrification, and to perform the experiment methanol-limited (80% removal of nitrate). Zero oxygen conditions were maintained artificially. The experiment was continued until blocking with biological material developed. Details of the experiment are contained in Table 1.1 of Appendix 1. The experimental results are presented in the latter table and also in Figure 2.1. The head measurements recorded to investigate blocking are given in Table 2.1 of Appendix 2 and also in Figure 2.2.

The results are summarised below:

- (1) Initially, a variable reduction in nitrate concentration resulted when injecting enough methanol, during 15 hours, to cover a 3 day period of treatment (15 h/3d). A similar response was noticed for an injection period of 3 and 1 h/d. By 400 h the nitrite concentration had increased to 8.7 mg N/l.
- (2) Continuous injection of methanol (at a rate equal to about 27% of the total flow) initiated a decline in both nitrate and nitrite. A further improvement in the calculation of the required chemical dose led to complete denitrification by 865 h.
- (3) Once denitrification was established, the injection period was reduced (after 1220 h) to 4 h/d with no effect on denitrification rate.
- (4) After injection of methanol ceased (after 1440 h) the nitrate concentration recovered to 14.8 mg N/l (66% of raw water content) and the nitrite concentration increased to 0.47 mg N/l.





- (5) Results of head measurements at 3 points along the column showed that blocking gradually developed. The head difference between the top and lower halves of the column remained constant until the start of denitrification (800 h). In the bottom half of the column, an increase in head of 250 cm was observed after 1400 h. A decrease in the measured heads in the lower half of the column was observed once methanol injection had ceased (1440 h).
- (6) Complete blocking of the upper measurement port (located 175 cm above the base of the column) occurred after 1650 h. At this time, an accumulation of biological material (black in colour) had collected at the top of the column.
- (7) Neither deterioration in colour nor detection of odour in the water leaving the column were detected throughout the experiment.
- (8) After 1840 h, and with no methanol injection, the measured D.O. was still zero, but the pH and E.C. had declined to 7.02 and 555 $\mu\text{S}/\text{cm}$; more representative of the initial raw water (6.58 and 350 $\mu\text{S}/\text{cm}$).

2.2 Results from Experiment 17

In operation this experiment was identical to Experiment 16. The only difference was to run the experiment nitrate-limited (100% removal of nitrate). Again, zero oxygen conditions were maintained artificially and the experiment continued until blocking developed. Details of the experiment are contained in Table 1.2 of Appendix 1. The experimental results are presented in the latter table and also in Figure 2.3. The head level measurements recorded to investigate blocking are given in Table 2.1 of Appendix 2 and also in Figure 2.4.

The results are summarised below:

- (1) Denitrification was quickly established within 330 h at an injection rate of 15 h/3d, but was thereafter disrupted by a change in injection rate to 3 and 1 h/d. Denitrification was re-established during the period of continuous injection between 504 and 1440 h).
- (2) After the injection of methanol was stopped, the nitrate and nitrite concentrations increased to 13.7 mg N/l (61% of the raw water value) and 0.39 mg N/l, respectively.
- (3) Head measurements collected along the column showed a similar response to the results of Experiment 16. After 1250 h an increase in head of 200 cm was observed, and was maintained until the time when methanol injection was stopped (1440 h). After 1700 h the heads in the lower half of the column had dropped by 100 cm. The top measurement port also became completely blocked with a dense biomass by 1670 h.
- (4) With greater time, and as denitrification continued at the expense of increasing heads, a noticeable musty odour and cloudiness developed in the water leaving the column. This commenced at 1200 h and continued until methanol injection ceased.
- (5) After 1840 h the measured D.O. was still zero, and the pH and E.C. had declined to 7.05 and 540 uS/cm.

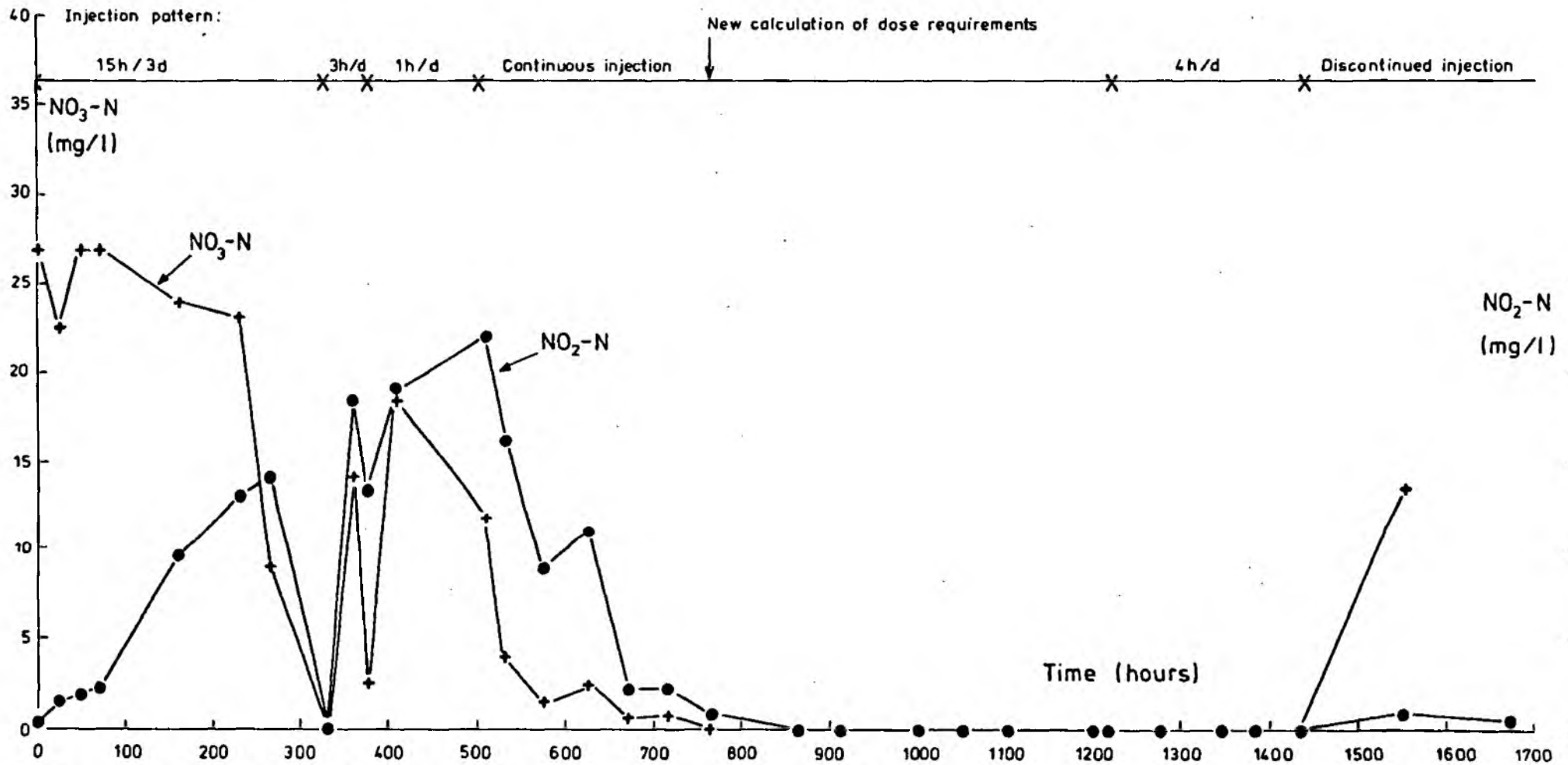


FIGURE 2.3 EXPERIMENT 17 (Nitrate-limited) ; Results of NO₃⁻ and NO₂⁻ analyses for column exit samples

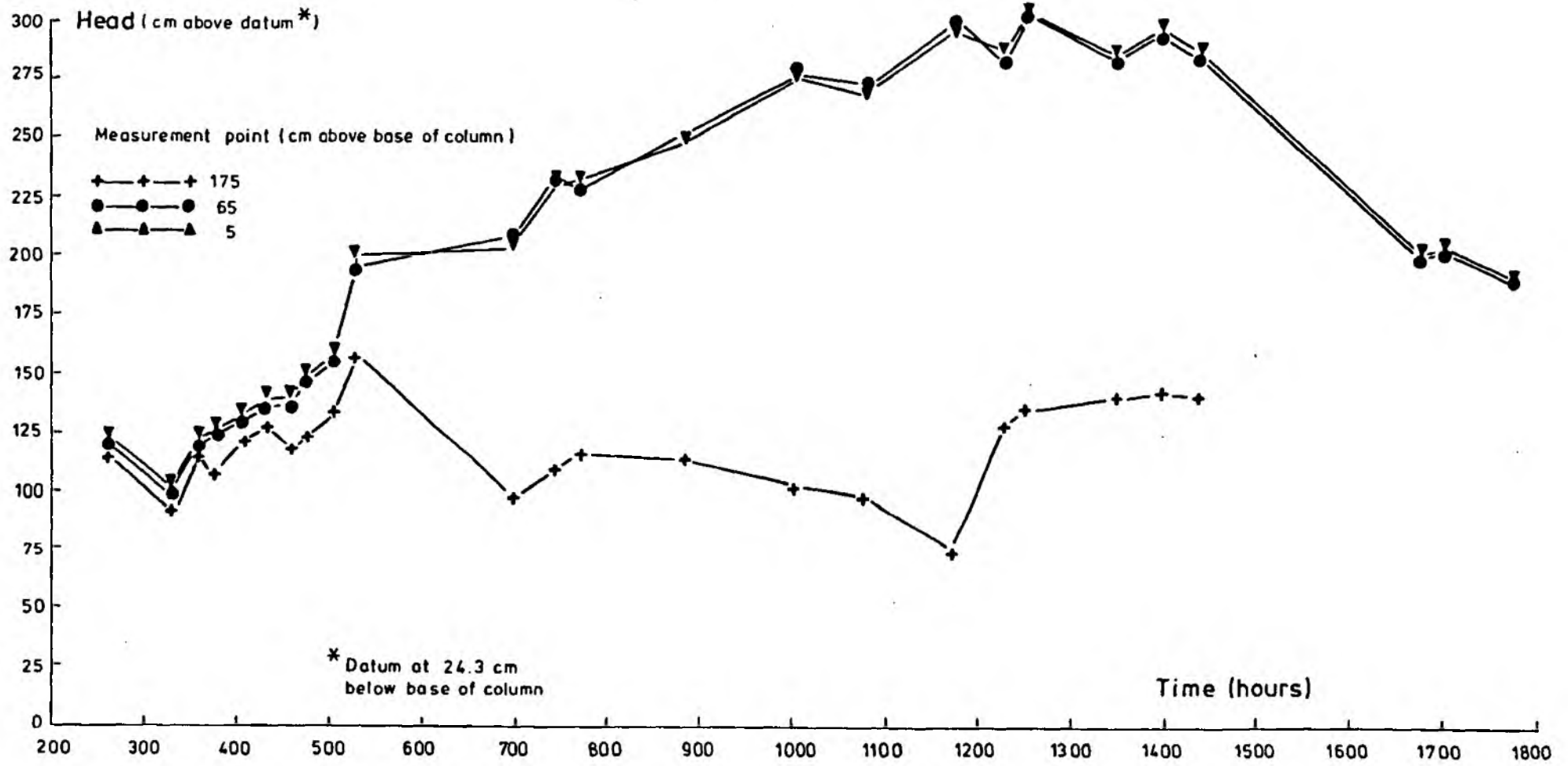


FIGURE 2.4 EXPERIMENT 17: Head level measurements to examine for blocking

2.3 Small-scale investigation into blocking

The objectives of this work are to: observe the development of biomass within a sand and gravel matrix; and to investigate the dependence of blocking upon retention time, and the location and density of biomass growth.

To observe blocking at a microscopic level presents considerable practical difficulties. The most difficult problem to overcome is the preparation of thin sections from saturated, unconsolidated material. Two approaches are reported in the literature. The first, given by Bullock *et al.* (undated) and Murphy (1986), requires acetone-drying and impregnation of the sample with a polyester resin. The method is complicated and lengthy, requiring 3 to 6 weeks for complete impregnation of the sample. The second method, given by Greene-Kelly *et al.* (1970), does not require any initial preparation of the sample, and uses a polyethylene glycol for impregnation and setting of the sample.

For this work, the commercially available Carbowax 6000 (average molecular weight of 6000) was chosen. This polyethylene glycol has a melting point of 60 to 63°C and a solubility in water of about 50% (w/w at 20°C). At room temperature Carbowax 6000 forms a white, soft to hard, waxy crystalline solid. Disadvantages with using this wax are its softness and low melting point which provide problems during thin section manufacture. Since the wax is soluble in water, special mineral oils of low viscosity, such as Shell Fusus A or Castrol Honilo, are used in cutting and grinding of sections.

Given this background, a small column was built (with a diameter of 51 mm and a length of 196 mm) and filled with a uniform, clean sand with an average diameter of 1.4 mm. Next, water containing 22.6 mg N/l was pumped

through the column with a retention time of 5 hours (equivalent to a flow rate of 0.4 ml min^{-1}). The nutrients methanol and phosphate, and the oxygen reducing agent sodium metabisulphite were added to the raw water in order to promote denitrification. After continuing the experiment for 21 days, the saturated sand, together with the column were immersed in liquid Carbowax at a temperature of 70°C for 22 hours. The vessel containing the wax was then allowed to cool slowly at room temperature. Rapid cooling is not advised since this may lead to distortion and a central cavity forming within the sample.

At present this experiment continues, with the next stage being the cutting and mounting of a thin section prior to microscopic inspection.

3. RESULTS FROM BIO-REACTOR EXPERIMENTS

3.1 Results from bio-reactor experiment 10

The aims of this experiment were to extend the denitrification capacity of the bio-reactor by increasing the amount of straw used and to investigate the filter column for any blocking that may result from running the experiment over an extended period. To enable continuous removal of nitrate, each bio-reactor (on the basis of earlier experiments) was replaced no later than 20 days after being brought on-line. Another aim of the experiment was to test if aeration of the reactor effluent before entry to the filter column would result in an improvement in the final water quality. Aeration of the reactor outflow was achieved with the use of a small air stone. Details of the experiment (until the end of the life of the third bio-reactor) are given in Table 1.3 of Appendix 1. The experimental results are presented in the latter table and also in Figure 3.1.

The results are summarised below:

- (1) Three reactors have so far been used and have all behaved differently. The ability of each to sustain denitrification has been variable and nitrate concentrations have fluctuated. At this stage, a reduction in nitrate concentration by 35 to 55% is generally possible.
- (2) The result of using a dense pack of straw, with no proportional increase in sand and limestone, is to strongly discolour the reactor effluent and to generate a very distinct odour. This condition persists for the first 2 to 3 days of operation, whereupon the colour and odour decline markedly.

- (3) Concentrations of nitrite in the reactor effluent also fluctuate, with values as high as 1.65 and 2.31 mg N/l being recorded in bio-reactors 2 and 3, respectively. Nitrite concentrations decrease as the straw becomes degraded.
- (4) Nitrate concentrations measured on water leaving the filter column were zero throughout, and confirm that denitrification continues in the sand and gravel column at the long retention time imposed.
- (5) Aeration of the water between the reactor and filter column had the desirable effect of maintaining a residual oxygen content (0.5 to 1.3 mg/l) and a moderately high redox potential (365 to 390 mV) in the final water. In terms of aesthetic quality, the water still retained a slight colour, but was odourless.

4. CONCLUSIONS AND FURTHER WORK PROPOSALS

4.1 Conclusions from column experiments

Column experiments 16 and 17 have provided results that will require further investigation. At the start of experimentation it was found that denitrification commenced more quickly under a nitrate-limited condition than under a methanol-limited condition. With continuous injection of methanol near to the base of the column, denitrification was established and maintained in both experiments. It is important to realise that complete nitrate removal occurred in the methanol-limited case where less than the theoretical amount of methanol was injected. Except for a small increase in nitrate and nitrite concentrations (<1.07 and <0.03 mg N/l, respectively) in Ex. 16, denitrification was also maintained in both experiments when a periodic methanol dose of 4 hours per day was imposed. After injection of methanol ceased, the nitrate and nitrite concentrations increased suggesting that the bacteria cannot sustain denitrification in the absence of an organic feed.

The evidence for blocking of the columns with biological material is clear, given the large increase in head of between 200 and 250 cm in the lower half of each column. This may have been caused by the development of biomass at the top of each column. After methanol injection ceased, denitrification stopped and a black material was observed to accumulate at the top of each column suggestive of dead biomass. The blocking and accumulation of debris in Ex. 17 imparted an odour and cloudy suspension to the final water. Such quality problems were not encountered in the methanol-limited experiment. Again it is concluded that it is desirable to use less than the theoretical quantity of methanol for denitrification.

4.2 Conclusions from bio-reactor experiment

It is concluded that packing more straw into the reactor does not have a beneficial effect on either the capacity of the reactor to remove nitrate, or on the treated water quality. The effect of having an aeration stage between the straw reactor and the filter column is only marginal in the long term. Initially, aeration had the desirable effect of maintaining a residual oxygen content ($< 1.3 \text{ mg/l}$) in the final water, but no improvement in colour resulted. With greater time (beyond 40 days), and as the filter column becomes presumably contaminated with organic debris from the reactor, the declining redox potential within the column suggests that the additional oxygen is reduced.

4.3 Further work proposals

The following proposals were discussed at the last Project Meeting held at the University of Birmingham on 15th June 1988. The next two sections summarise the results of this meeting. A detailed breakdown of the experiments to be conducted, and a timetable for their execution are given in Table 4.1.

4.3.1 Gravel column experiments

Further work is required to investigate the nature of blocking within the gravel packed columns, and to resolve the location and density of biomass development. Factors affecting the generation of organic matter may include: velocity of flow; organic feed concentration and source; initial oxygen and nitrate concentrations; and pore space distribution (porosity).

A number of experiments are planned to study the problem and include:

- (1) Starting denitrification with a continuous methanol dose, and then decreasing the dose rate until a residual 10 mg N/l remains in the final water;
- (2) Repeating an earlier experiment (Ex. 16), but with ethanol as the organic substrate. Since ethanol is expected to degrade more slowly than methanol (due to its larger molecule), then denitrification may be spread over a greater volume of gravel material;
- (3) Starting denitrification with a continuous methanol dose, and then to pulse the methanol dose in order to allow for a clean-up period between injections;

- (4) Starting denitrification with methanol and, with continuous injection, cyclically vary the flow rate in order to disperse the denitrifying bacteria further along the gravel column;
- (5) Starting denitrification with methanol, but then (with no organic feed) to commence dosing with sulphur dioxide (to remove the oxygen content of the raw water) and phosphate. If a retention time of 10 days is also imposed at this stage, then it may be possible to repeat the results of an earlier experiment (Ex. 12), but with the added advantage of having first seeded the gravel column with denitrifying bacteria.

4.3.2 Straw bio-reactor experiments

The main disadvantage with the straw reactor approach is the limited time for which useful denitrification occurs. Since straw is slow to degrade, it may be advantageous to allow for a rest period in which further breakdown of the cellulose fraction of the straw can occur.

To investigate this possibility, bio-reactor experiment 10 is still in progress and, at the time of writing this report, is into a fifth straw reactor stage. However, the fourth reactor has been sealed-up and is intended for re-use after a one month rest period. Furthermore, the gravel material in the filter column has not been replaced and so it should be possible to continue monitoring its long-term performance.

REFERENCES

- Bullock, P., Murphy, C.P. and Biswell, K.J., undated. The preparation of thin sections of soils and unconsolidated sediments. Unpubl. Report, Soil Survey of England and Wales, Rothamstead Experimental Station, Harpenden, Herts., 8 pp.
- Greene-Kelly, R., Chapman, S. and Pettifer, K. 1970. The preparation of thin sections of soils using polyethylene glycols. In: D.A. Osmond and P. Bullock (Eds.), Technical Monograph No. 2: Micromorphological techniques and applications. Soil Survey of England and Wales, Harpenden, pp. 15-24.
- Murphy, C.P., 1986. Thin section preparation of soils and sediments. A.B. Academic Publishers, Berkhamstead, 149 pp.
- University of Birmingham, 1988. Investigation into denitrification underground. Interim Twenty Nine Month Report, February 1988, 38 pp.

APPENDICES

1. Analytical Chemical Data

Table 1.1 Results from column experiment 16

Table 1.2 Results from column experiment 17

Table 1.3 Results from bio-reactor experiment 10

2. Head level measurements to investigate blocking

Table 2.1 Head level measurements for column experiments 16 and 17

APPENDIX 1 Analytical Chemical Data

Table 1.1 Results from column experiment 16

EXPERIMENT 16 (METHANOL-LIMITED EXPERIMENT)

Experiment using methanol to stimulate an 80% reduction in the nitrate content of water dosed to 125 mg N/l

Column retention time = 10 hours approx.

Methanol dose = 56.5 mg per litre of water treated

Phosphate dose = 1 mg P/l

Sodium metabisulphite dose = 118.8 mg/l (enough to remove 20 mg/l O₂)

Raw water supply from Wildmoor PS, N. Worcs and amended to 125 mg N/l

Time since pump on (hrs)	Sample number (from column exit)	pH	D.O. (mg/l)	Temp (°C)	E.C. (µScm ⁻¹)	Eh (mV)	NO ₃ -N (mg/l)	NO ₂ -N (mg/l)	Notes (see below)
0	N39						26.1	0.10	1
24	N41						26.1	1.07	
48	N43						32.0	2.36	
72	N45	6.90	0	15.4	640	350	32.9	1.80	
162	N51						31.4	3.52	
233	N53						28.3	4.55	
260	N55	7.30	0	16.7	730	310	14.1	6.84	
332	N57						29.9	4.97	2
359	N61						20.2	7.12	
377	N63						10.5	7.76	3
408	N65						22.1	7.84	
504	N67						19.0	8.68	4
529	N69						6.9	8.52	
577	N71						6.6	8.20	
624	N75						8.2	7.72	
670	N77						8.2	5.56	
696	-	7.60	0	16.8	765	320	-	-	5
714	N79						7.4	6.71	
764	N81						3.3	5.80	6
865	N83						0	0	
912	N85	7.58	0	18.0	750	335	0.4	0.32	
1002	N89						0	0.03	
1051	N91						0	0	
1103	N95						0	0.26	

Table 1.1 Continued

Time since pump on (hrs)	Sample number (from column exit)	pH	D.O. (mg/l)	Temp (°C)	E.C. (μScm^{-1})	Eh (mv)	NO ₃ -N (mg/l)	NO ₂ -N (mg/l)	Notes (see below)
1200	N97						0	0	
1218	N99						1.07	0.03	7
1274	N101						0	0	
1344	N103						0	0	
1387	N105						0	0	
1435	N109	7.35	0	20.1	795	220	0	0	8
1556	N110						14.8	0.25	
1675	N112							0.47	
1842	N114	7.02	0	20.6	555	530			9

NOTES:

- 1 Injection period = 15 hours. Dose equivalent to 72 hours.
- 2 Injection period = 3 hours. Dose equivalent to 24 hours.
- 3 Injection period = 1 hour. Dose equivalent to 24 hours.
- 4 Continuous injection at approximately 1.1 ml min^{-1} (= 27% of total flow).
- 5 Measurements on raw water from Wildmoor PS:
pH = 6.58 Temp = 14.2°C EC = 350 μScm^{-1} .
- 6 Improved calculation of dosage requirements on basis of measured pumping rates.
- 7 Injection period = 4 hours. Dose equivalent to 24 hours.
- 8 Dosing of methanol and Na₂S₂O₅ discontinued.
- 9 Experiment stopped at 1896 h.

Table 1.2 Results from column experiment 17

EXPERIMENT 17 (NITRATE-LIMITED EXPERIMENT)

Experiment using methanol to completely reduce the nitrate content of water dosed to 100 mg N/l

Column retention time = 10 hours approx.

Methanol, phosphate and sodium metabisulphite dose as for Ex 16

Raw water supply from Wildmoor PS, N. Worcs. and amended to 100 mg N/l

Time since pump on (hrs)	Sample number (from column exit)	pH	D.O. (mg/l)	Temp (°C)	E.C. (μScm^{-1})	Eh (mV)	NO ₃ -N (mg/l)	NO ₂ -N (mg/l)	Notes (see below)
0	N40						26.8	0.14	1
24	N42						22.7	0.60	
28	N44						26.9	0.80	
68	N46	7.00	0	14.9	585	365	26.9	0.88	
162	N50						23.9	3.84	
233	N52						23.0	5.32	
265	N54	7.35	0	17.2	715	285	9.2	5.72	
332	N56						0	0	2
359	N60						14.3	7.40	
377	N62						2.7	5.44	3
408	N64						18.5	7.56	
504	N68						12.0	8.88	4
529	N70						4.1	6.52	
577	N72						1.6	3.64	
624	N74						2.4	4.38	
670	N76						0.6	0.88	
714	N78	7.62	0	15.9	690	316	0.7	0.91	
764	N82						0	0.35	5
865	N84						0.14	0	
912	N87						0	0	
1002	N88						0.14	0	
1051	N92						0	0	
1103	N94						0	0	
1200	N96						0	0	6
1218	N98						0	0	7

Table 1.2 Continued

Time since pump on (hrs)	Sample number from column exit)	pH	D.O. (mg/l)	Temp (°C)	E.C. (μScm^{-1})	Eh (mV)	NO ₃ -N (mg/l)	NO ₂ -N (mg/l)	Notes (see below)
1274	N102						0	0	
1344	N104						0	0	
1387	N106						0	0	
1435	N108	7.50	0	19.0	780	275	0	0	8
1556	N111						13.7	0.39	9
1675	N113							0.19	
1842	N115	7.05	0	19.0	540	445			10

NOTES:

- 1 Injection period = 15 hours. Dose equivalent to 72 hours.
- 2 Injection period = 3 hours. Dose equivalent to 24 hours.
- 3 Injection period = 1 hour. Dose equivalent to 24 hours.
- 4 Continuous injection at approximately 1.1 ml min^{-1} (= 27% of total flow).
- 5 Improved calculation of dosage requirements on basis of measured pumping rates.
- 6 Detection of odourous compounds in final water.
- 7 Injection period = 4 hours. Dose equivalent to 24 hours.
- 8 Dosing of methanol and Na₂S₂O₅ discontinued.
- 9 No evidence of odourous compounds in final water.
- 10 Experiment stopped at 1896 h.

Table 1.3 Results from bio-reactor experiment 10

BIO-REACTOR EXPERIMENT 10

Experiment to examine the efficiency of a gravel packed column in filtering the effluent leaving successive straw packed reactors. Aeration stage between reactor and column.

Nature of bio-reactor packing material: Limestone, sand and straw.

Reactor retention time = 5 hours. 94% of effluent allowed to go to waste.

Filter column retention time = 50 hours.

Raw water supply from Wildmoor PS, N. Worcs. and amended to 100 mg N/l.

Phosphate dose = 1 mg P/l

Time since pump on (hrs)	Sample number	Reactor samples		Filter column samples		Notes (see below)
		TON as N (mg/l)	NO ₂ as N (mg/l)	TON as N (mg/l)	NO ₂ as N (mg/l)	
BIO-REACTOR 1						
96	W29	15.5	0.35			
145	W31			0	0	1
146	W30	16.3	0.45			
171	W32	13.6	0.44			
217	W33			0	0.02	
237	W34	23.9	0.59			
264	W35			0	0	
284	W36	26.7	0.05			
312	W37			0	0	2
335	W38	5.4	0			
BIO-REACTOR 2						
414	w39			0	0	
456	W40	22.7	1.65			
460	W41			0	0	
482	W42	20.2	1.06			
551	W43			0	0	
571	W44	8.9	0.17			
575	W45			0	0	
595	W46	16.9	0.15			
626	W47			0	0	

Table 1.3 Continued

Time since pump on (hrs)	Sample number	Reactor samples		Filter column samples		Notes (see below)
		TON as N (mg/l)	NO ₂ as N (mg/l)	TON as N (mg/l)	NO ₂ as N (mg/l)	
BIO-REACTOR 2 cont.						
646	W48	5.4	0			
672	W49	9.3	0.04			
725	W50			0	0.06	
BIO-REACTOR 3						
798	W51			0	0.05	
818	W52	12.3	2.31			
894	W53			0	0	
914	W54	13.9	0.25			
939	W55			0	0	
956	W56	11.9	1.09			
985	W57			0	0	3
1005	W58	12.1	0			4
1105	W59			0	0	
1224	W60				0	5

NOTES:

- Pump controlling flow through the filter column was switched on 20 hours after the start of the experiment. Thus, add 20 hours to the times for the filter column samples to give equivalent time-scale for the reactor samples.
- Measurements at 312 h at exit from filter column:
pH = 7.20 DO = 1.30 mg/l Temp = 16.0°C EC = 525 μScm^{-1} Eh = 390 mV
- Measurements at 985 h at exit from filter column:
pH = 7.50 DO = 0.50 mg/l Temp = 17.2°C EC = 492 μScm^{-1} Eh = 365 mV
- After 1008 h the bio-reactor was taken off-line. The filter column was therefore supplied with reactor effluent collected during the previous 24 h. Bio-reactor 4 brought on-line at 1296 h.
- Experiment still in progress

APPENDIX 2 Head level measurements to investigate blocking

Table 2.1 Head level measurements for column experiments 16 and 17

Time since pump on (hrs)	Ex 16 ¹			Ex 17 ²		
	Measurement point ³			Measurement point		
	175 (cm above base of column)	65	5	175 (cm above base of column)	65	5
260	56.3	89.6	90.6	114.1	120.3	121.6
329	56.5	51.2	52.7	92.3	99.3	100.8
358	56.0	48.3	49.6	115.0	120.4	121.8
376	55.5	52.1	53.4	107.2	124.2	125.5
407	55.5	64.6	65.9	121.2	130.4	131.8
432	55.8	71.4	72.6	126.5	136.4	137.8
457	61.5	91.0	92.7	118.3	136.8	138.6
475	61.9	98.7	100.5	123.2	147.4	149.1
505	77.3	119.6	123.4	133.0	156.2	158.3
528	99.8	134.9	136.4	158.2	195.4	198.3
668	105.4	158.2	168.0	-	-	-
697	115.8	172.8	185.7	98.0	208.2	205.0
744	134.0	186.4	205.6	107.8	232.2	229.6
768	141.1	200.1	210.5	115.9	229.3	232.1
884	104.0	219.6	220.4	112.6	-	248.1
1001	52.0	190.3	214.0	103.4	276.0	274.0
1077	66.3	228.1	228.6	98.9	272.3	268.9
1168	40.8	206.6	207.4	74.0	299.0	294.8
1225	95.4	212.8	215.8	128.0	282.7	286.1
1249	129.6	267.8	272.3	135.0	304.4	307.3
1346	115.0	278.5	301.5	139.8	282.9	285.0
1393	127.9	296.8	302.2	143.1	294.4	296.3
1436	131.0	261.2	263.9	141.0	284.9	286.6
1674	- ⁴	215.0	214.7	- ⁴	199.1	200.4
1698	-	206.3	204.1	-	202.3	202.5
1775	-	202.2	201.2	-	188.6	190.1

NOTES:

- 1 Column experiment with a methanol-limited condition
- 2 Column experiment with a nitrate-limited condition
- 3 Measurement datum at 24.3 cm below base of column
- 4 Measurement port blocked