Presented at 4th CIWEM (Chartered Institute of Water and Environmental Management) Annual Conference held 12-14 September 2006, Newcastle.

N-Tox® - Early warning of nitrification toxicity for activated sludge treatment

Callister, S.[1], Stephensona, T.[2], Butler, M.[2] and Cartmell, E.[2]

[1]Water Innovate and [2]Cranfield University

ABSTRACT

N-Tox® is a new technique for evaluating the nitrification efficiency in industrial or municipal activated sludge systems, using direct measurement of nitrous oxide (N_20) as an indicator of nitrification failure. Research using pilot-scale activated sludge plants treating real settled wastewater has demonstrated that detection of increased N_2O concentration in the aeration tanks by N-Tox® is able to provide early warning of nitrification failure. The N-Tox® monitor relies on non-invasive gas-phase detection which avoids sampling of activated sludge and eliminates associated probe fouling problems and maintenance issues. Nitrification failure detection by N-Tox® is rapid, giving plant operators the time to take remedial action before possible release of ammonia.

Recently presented data has shown the effectiveness of N-Tox® in providing early warning of nitrification inhibition following loss of aeration and ammonia overloading events. New data is now presented to demonstrate the effectiveness of N-Tox® in providing early warning of nitrification failure for a number of well-known toxic chemicals. These include the organic compound phenol, the nitrification suppressant allylthiourea (ATU) and the inorganic fungicide and herbicide, sodium azide. N-Tox® was able to detect nitrification failure when the first step of nitrification was inhibited, resulting in a rise in effluent ammonia, and when the second step was inhibited, resulting in a rise in effluent nitrite. The pattern of N_2O emission indicated the failure mode: a sharp peak indicated ammonia breakthrough whereas a sustained increase in N_2O indicated nitrite formation. The N-Tox® device can also be used to quantify emissions of N_2O, a powerful greenhouse gas, from wastewater treatment plant

KEY WORDS

N_2O, Nitrous Oxide, Nitrification, Inhibition, Toxicity, Monitor, Greenhouse Gas

INTRODUCTION

As regulations on effluent quality get increasingly stringent, many industrial and municipal wastewater treatment plants are now required to remove nitrogen through nitrification and denitrification. It has been reported that nitrous oxide (N_2O), a greenhouse gas 310 times more powerful than carbon dioxide, could be produced during both nitrification and denitrification in activated sludge and released into the atmosphere (Colliver and Stephenson, 2000). It has been suggested that N_2O is released into the atmosphere during nitrification as a by-product (Zheng *et al*., 1994) and in denitrification as an intermediate (Wicht, 1996).

Nitrification, the oxidation of ammonia to nitrite and nitrate, is a sensitive process undertaken by nitrifying bacteria which can be inhibited by high ammonia concentrations and chemical pollutants, which reduces the efficiency of the process or causes the treatment system to break down entirely. It is not easy to predict when the nitrification process will be inhibited, but it results in ammonia leaking into the effluent, which in turn often causes a breach of the ammonia discharge consent. Previous research has shown that when the nitrification process fails, N_2O gas is emitted (Burgess *et al*., 2002a). Research on pilot-scale activated sludge plants showed the initial detection of increased N_2O concentration above the aeration tank, followed by a lag time of almost one hydraulic retention time (HRT) (7 h in this case) before the appearance of NH_3 in the effluent, as a result of high NH_3 shock loading. It is this lag time that can be used as an early warning and forms the basis of the patented N-Tox®. The rate of N_2O production can be linked to oxygen depletion and higher than normal 'shock' loadings of ammonia arriving at the treatment plant (Burgess *et al*., 2002b). When oxygen is depleted, nitrification fails and N_2O is produced.

The current papers reports on pilot-scale research using real settled sewage to test the efficacy of N-Tox® when activated sludge is subjected to a range of toxic shocks, including addition of chemicals inhibitory to nitrifying bacteria. Monitoring of anoxic and aerobic zones at a full-scale activated sludge plant is also reported.

MATERIALS AND METHODS

Pilot-Scale Activated Sludge Plant

The pilot plant was designed to model a full-scale system in terms of volume-geometric, kinematic, chemical, biological and thermal similarity. The pilot plant consisted of two lanes, each comprising a 300 l aeration tank and a 100 l clarifier (Figure 1). Each aeration tank was initially filled with 150 l wastewater and 150 l activated sludge taken from the return activated sludge (RAS) channel of a municipal wastewater treatment works (Cotton Valley Wastewater Treatment

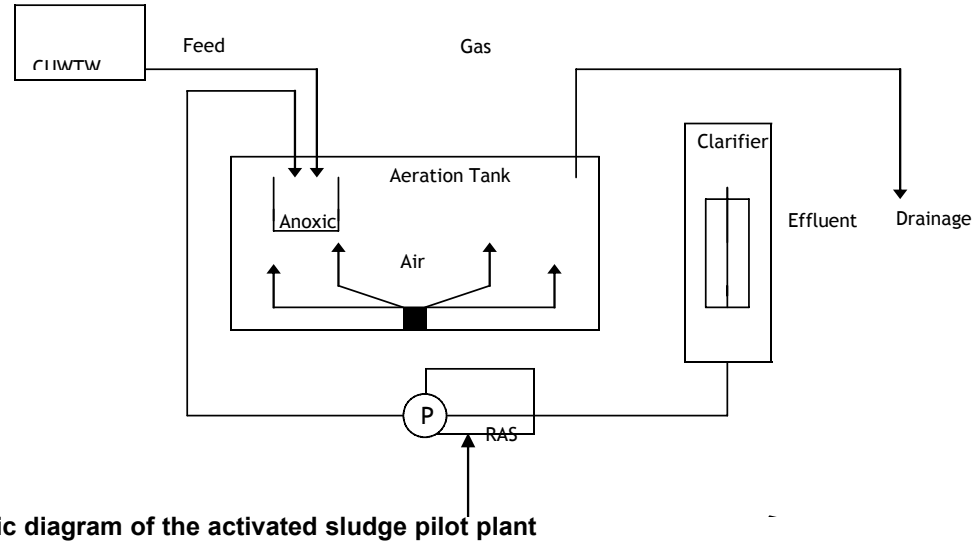

Figure 1: Schematic diagram of the activated sludge pilot plant

Works, Anglian Water). The hydraulic retention time (HRT) was approximately 8h.

The feed was settled sewage, which was supplied from Cranfield University Wastewater Treatment Works. The feed, RAS and wasted activated sludge (WAS) were pumped by a peristaltic pump (Watson and Marlow, 505U). The aeration tank and clarifier both had lids to minimise evaporation and solids were brushed off the side of the aeration tank and clarifier daily. Measurements for mixed liquor suspended solids (MLSS), influent/effluent COD, NH_3, nitrite (NO_2), nitrate (NO_3) and N_2O were made at regular intervals.

Shock load experiments were conducted on the test unit of the activated sludge pilot-plant. Prior to the shock loads, the activated sludge plant was operated for at least 2 sludge ages with stable process performance parameters as would be expected for a full-scale system. During the O_2 starvation experiment the air was turned off for 1 h and then turned back on after this period. An ammonia shock load was achieved by spiking the test pilot plant lane with 7.25 g of NH_3Cl, dissolved in 1 l of distilled H_2O. Phenol, allythiourea and sodium azide shock loads were also undertaken.

During all the experiments; influent/effluent (both activated sludge lanes) COD, NH_3, NO_2, NO_3, MLSS and N_2O gas was taken at the beginning of shock load experiments, with the effluent (test-rig) NH_3, NO_2, NO_3 and N_2O gas being taken periodically throughout the experiment.

Full Scale Trial

N-Tox® was used to monitor N_2O on a full-scale municipal activated sludge plant (Butler *et al*., 2005). A detailed study was carried out at Finham wastewater treatment works, UK.

The effluent treatment system at Finham incorporates a single stage nitrification process, with both chemical oxygen demand (COD) and ammonia removal taking place in a single biological process with a total volume of 4500 m^3. Aeration lanes are 30 m long, the first 5 m portion relating to the anoxic zone (see Figure 2). The activated sludge lanes have a total HRT of 12 h corresponding to a daily average influent flow of 110,000 m^3/24hours. The anoxic component of the HRT is 2 h.

One of the activated sludge lanes was fitted with a prototype of the N_2O off-gas monitoring system. A sampling system was designed to produce a lane profile of N_2O levels to detect the production of off-gas and monitor potential toxic shock upsets. Each sampling point was analysed for 24 h and then either moved across the lane or down the lane by 5 m. A floating hood, suspended over the mixed liquor and connected to sample line tubing, directed gases to a gas

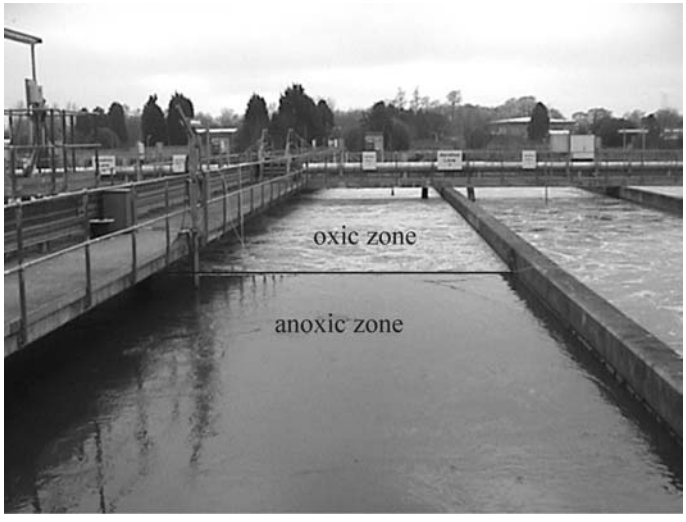

Figure 2: Activated sludge aeration lane at Finham

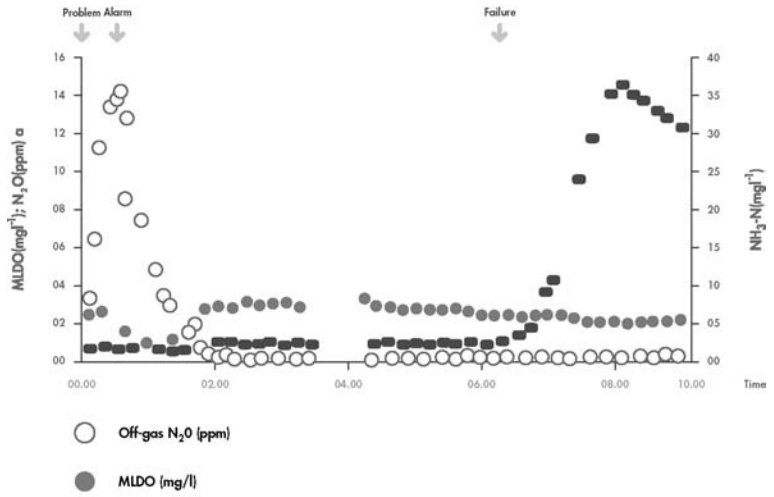

Figure 3: Loss of aeration event

analyser that measured N_2O in the range 0-1000 mg/l.

The gas analyser remained separated from the activated sludge at all times, drawing the off gas via a small pump inside the gas analyser, from the headspace via additional tubing. This avoided problems such as corrosion and sensor fouling.

The influent and effluent chemical oxygen demand (COD), ammonia (NH_3), NO_2, NO_3 and pH levels were measured daily, as were levels of mixed liquor suspended solids (MLSS), online pH, temperature and dissolved oxygen.

Analytical Methods

A gas analyser (VIA 510, Horiba, Japan) accurately measured N_2O gas in the range of 0-200 mg/l, and was calibrated from compressed air (zero gas, BOC Group Plc, UK) and 160 mg/l N_2O, with a detection limit of 0.1 mg/l. The gas analyser remained separated from the activated sludge at all times, drawing the off gas (by a small pump inside the gas analyser) from the headspace via Perfluoroalkoxy tubing (PFA), which avoided operational problems that are normally associated with sensor fouling and corrosion.

Measurements of the influent/effluent COD, NH_3, NO_2, NO_3 (Hach vial methods, Camlab and Merck vial methods, Vwr International adapted from Standard Methods, APHA, 1998) and mixed liquor suspended solids concentration were measured using standard methods (APHA, 1998).

RESULTS

Loss of Aeration

A simulated short aeration failure resulted in Mixed liquor dissolved oxygen concntrations falling and a peak in N_2O was detected by N-Tox in the off gases above the activated sludge tank (Figure 3). The delay between the increased level of N_2O being detected and the appearance of ammonia in the effluent means that operators can get the duration of one HRT cycle as advance warning of nitrification failure.

Ammonia Shock Loads

An ammonia shock load of 2.44g NH_3-N (dosed as 7.25g of NH_3Cl dissolved in 1.0l H_20) was dosed directly into the aeration tank, a dose calculated to exert an instantaneous oxygen demand of 3.5 mg/l. As can be seen in Figure 4, N-Tox® detected an immediate increase in N_2O levels, thus providing early warning of nitrification failure several hours before ammonia appeared in final effluent.

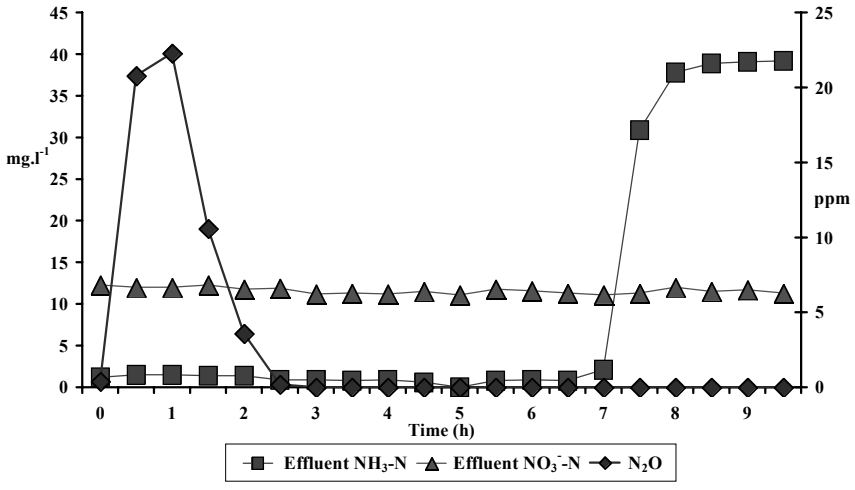

Figure 4: Ammonia Shock Loads

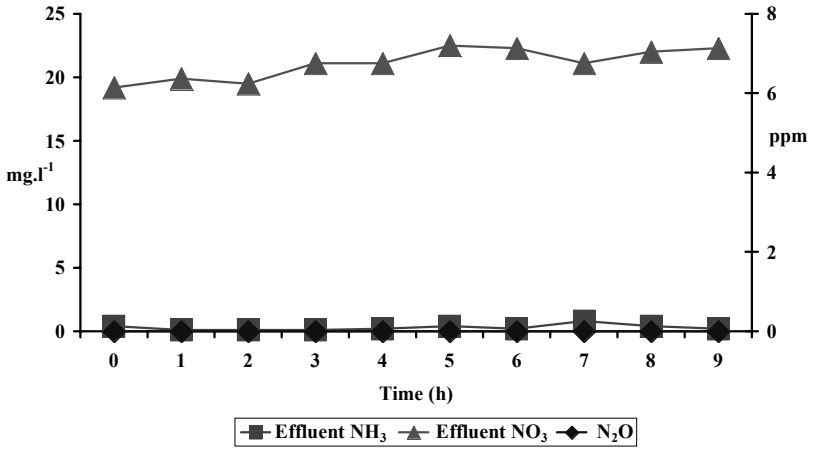

Figure 5: 75% inhibitory phenol shock load at MLSS of 3270 mg/l

Phenol Shock Loads

An anticipated 75% inhibitory shock load of phenol (C_6H_5OH), equivalent to a concentration in the aeration basin of 5.6 mg/l, was applied at a mixed liquor suspended solids (MLSS) concentration of 3370 mg/l. However, this had no impact on nitrification, as indicated by no change in effluent ammonia and nitrate. As would be expected, N-Tox® showed that no N_2O was detected (Figure 5). When the same phenol shock load was applied at a MLSS concentration of 1340 mg/l, N-Tox® detected an increase in N_2O 2-3 hours after the shock load (Figure 6). After 5 h, effluent ammonia concentrations began to rise, reaching > 2.0 mg/l after 9 h. Therefore N-Tox® was able to give early warning of nitrification failure.

A shock load with an aeration basin concentration of 28 mg/l phenol, which is approximately 4 times the minimum concentration reported to induce complete nitrification inhibition, was applied to the pilot-plant. As expected, nitrification failure was observed. This caused a steady climb in N_2O, rather than a brief peak in concentration (Figure 7). This was indicative of only a brief increase in effluent ammonia concentration but a steady increase in effluent nitrite. Again, N-Tox® provided early warning of the increase in effluent nitrite, normally absent during nitrification and a carcinogen precursor.

Allylthiorurea Shock Loads

Allylthiorurea (ATU) is a well-known inhibitor of nitrification that is used to suppress ammonia oxidation in the standard 5-day biochemical oxygen demand (BOD_5) test. The compound blocks the ammonia to hydroxylamine (NH_2OH) step of nitrification. An anticipated 75% inhibitory shock load of ATU, equivalent to a concentration in the aeration basin of 76 µg/l, was applied at a mixed liquor suspended solids (MLSS) concentration of 3390 mg/l. This had no impact on nitrification, as indicated by no change in effluent ammonia and nitrate. As expected, N-Tox® showed that no N_2O was detected (Figure 8).

When a x10 higher concentration of ATU - 760 µg/l - was applied to the aeration basin of an activated sludge plant, inhibition of nitrification occurred. This is not unexpected, being a concentration of ATU 7.5x the minimum concentration to cause complete inhibition. Detection of N_2O occurred several hours (>5 h) before ammonia appeared in the effluent. Again, N-Tox® gave early warning of nitrification failure with the sharp peak in N_2O indicative of increased effluent ammonia (Figure 9).

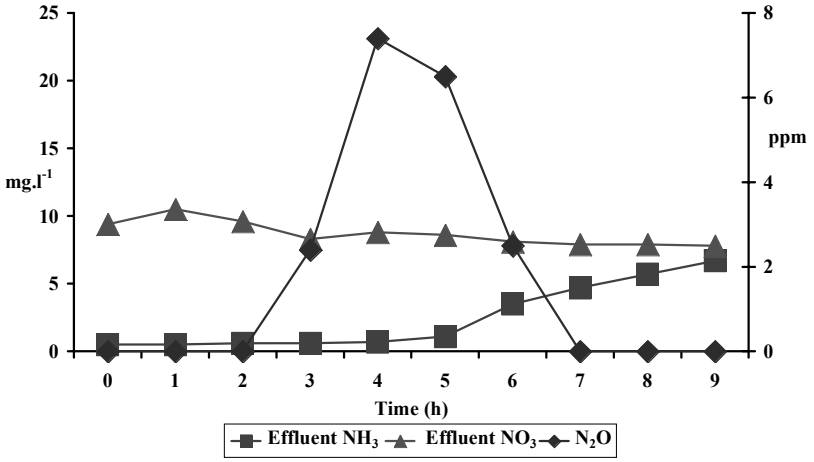

Figure 6: 75% inhibitory phenol shock load at MLSS of 1340 mg/l

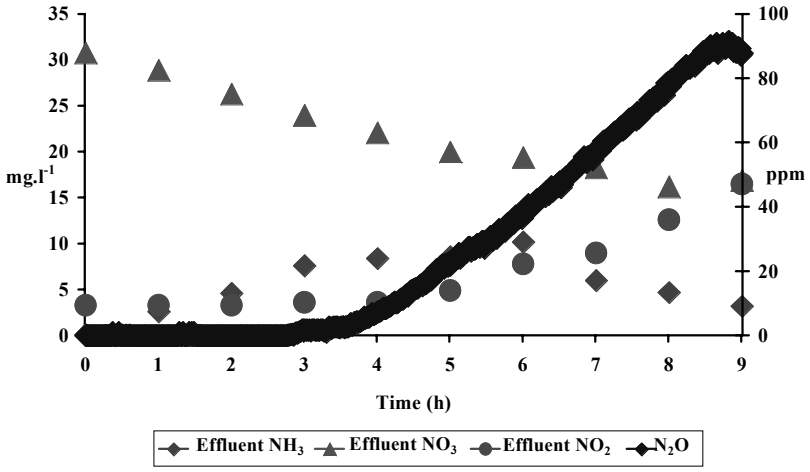

Figure 7: Phenol shock load almost 4x minimum inhibitory concentration

Sodium Azide Shock Loads

Sodium Azide (NaN_3) is a well-known inorganic fungicide and herbicide that can also be lethal to bacteria. An anticipated 75% inhibitory shock load of sodium azide, equivalent to a concentration in the aeration basin of 23 mg/l, was applied at a mixed liquor suspended solids (MLSS) concentration of 4260 mg/l. However, this unexpectedly caused nitrification inhibition with nitrite detected in the effluent 6 hours after the shock load (Figure 10). N-Tox® showed an almost instantaneous rise in N_2O to provide early warning of the nitrification failure. The N_2O concentration remained high, indicative of the increased effluent nitrite as opposed to ammonia.

Full-Scale Trial

The removal rates for the monitored activated sludge lane can be seen in Table 2. There were no toxic shock loadings during the monitoring period. The samples taken for effluent NH_3 showed a range of 0.1-1.2 mg/l. If there had been a shock load, this would have caused a noticeable increase in the effluent NH_3 concentration.

N_2O off-gas measurements were averaged at each 5 m interval, and results from three monitoring points (left, middle and right side of aeration lane) were averaged at each interval down the lane for the corresponding 24 hour period. The lane profile (see Figure 12) shows an initial increase in the average N_2O concentrations followed by a decrease as the sampling system moved down the lane.

At 0 m, a rise in the average N_2O off-gas peaked at 7.2 mg/l (7 h), followed by a decrease and then a second increase at 20 hours. At 5 m, average N_2O concentrations declined and were found to be less than 0.9 mg/l up to 46 hours into the trial, with low levels maintained throughout the rest of the experiment apart from a 2.1 mg/l peak (84 h), a peak of 1.8 mg/l (107 h), and a minor increase to 0.9 mg/l (138 h).

The results suggest that the initial increase of N_2O concentration was a consequence of the denitrification process. As stated earlier, N_2O is an obligate intermediate in this process. When the monitoring system was moved down the activated sludge lane it recorded a decrease in the N_2O off-gas level, but only to background emission levels.

The pilot scale experiments at Cranfield had used high ammonia loadings of 2.44 g/l NH_3-N combined with oxygen deprivation to yield a maximum N_2O concentration of 18.7 mg/l as a result of nitrification failure. A second experiment with an increased shock load (7.32 g/l NH_3-N) produced a significantly higher maximum concentration of N_2O off-gas, but even the lower peak at 18.7 mg/l N_2O was well in excess of the background levels monitored at Finham.

These pilot scale experiments had shown an initial increase

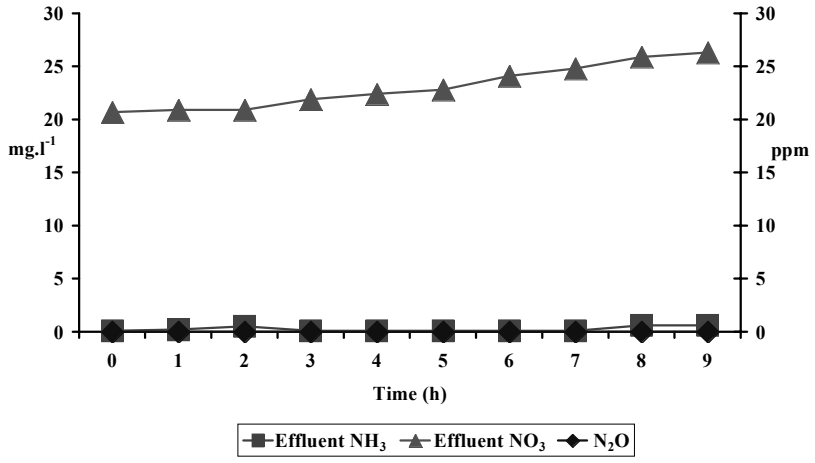

Figure 8: Allylthiourea (ATU) shock load at 75% of reported minimum inhibitory concentration

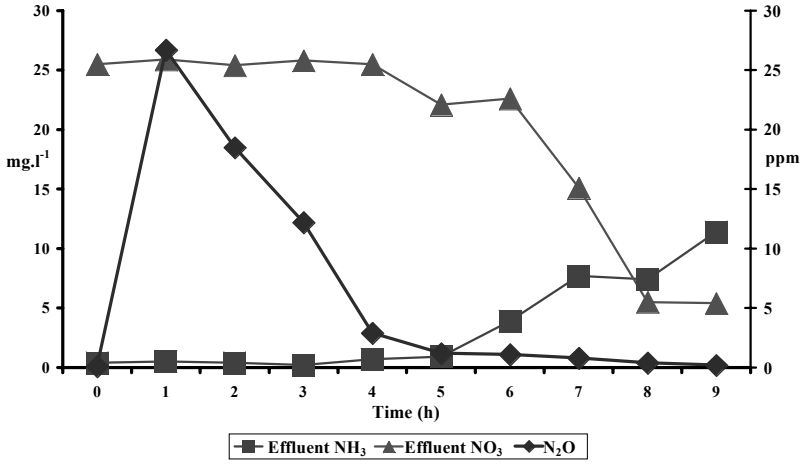

Figure 9: Allylthiourea (ATU) shock load at x7.5 of reported minimum inhibitory concentration

in the N_2O concentration followed by a time lag before a sharp increase of NH3 in the effluent. It is this period, before NH3 appears in the effluent, which is used to indicate failure of the nitrification process, thus providing an early warning for plant managers and operators.

The monitoring of N_2O at Finham produced small variability in the N_2O background emissions of 0 - 2 mg/l. Hence, a N_2O peak would be measured in the event of a toxic shock load to the activated sludge plant.

If a toxic shock was to occur at Finham, then the N_2O peak would have been expected from the activated sludge lane followed by a time lag of approximately one HRT (10 h) of NH_3 in the effluent. Hence, staff at Finham would have up to 10 hours to take remedial action to rectify the problem and prevent ammonia discharge.

DISCUSSION

The key markets for this non-invasive technology are municipal sewage and industrial effluent treatment. Many treatment works are consented for NH_3 at < 5 mg/l. Like Finham, these plants rely on bacteria to remove ammonia by converting it to nitrate, and the use of the technique to measure N_2O peaks could provide valuable time to attend to process problems.

N_2O peak warning is even more critical in activated sludge plants treating some industrial effluents, such as landfill leachate or pharmaceutical wastewaters, because their high ammonia levels make the consequences of nitrification failure much more serious.

The technology is also used to quantify N_2O greenhouse gas emissions from wastewater treatment plants - an area of increasing concern for plant operators and regulators, as the global warming potential of N_2O is almost 300 times that of CO_2. According to the US Environmental Protection Agency, wastewater treatment accounts for up to 4 % of N_2O emissions and tightening of nitrogen discharge consents means more nitrification and denitrification will be needed. The new monitoring technique can help plant operators control processes effectively to significantly reduce a predicted increase in N_2O emissions.

A N_2O monitor based on the research carried out by Cranfield has been developed and patented by Water Innovate Ltd. under the name N-Tox®. The design comprises an integral sample pump, gas conditioning device, non-dispersive IR gas analyser, auto-calibration system and data logging unit, housed within an IP65 enclosure. The instrument transmits 4-20 mA in proportion to N_2O level and has various configurable alarms for setting plant failure warnings.

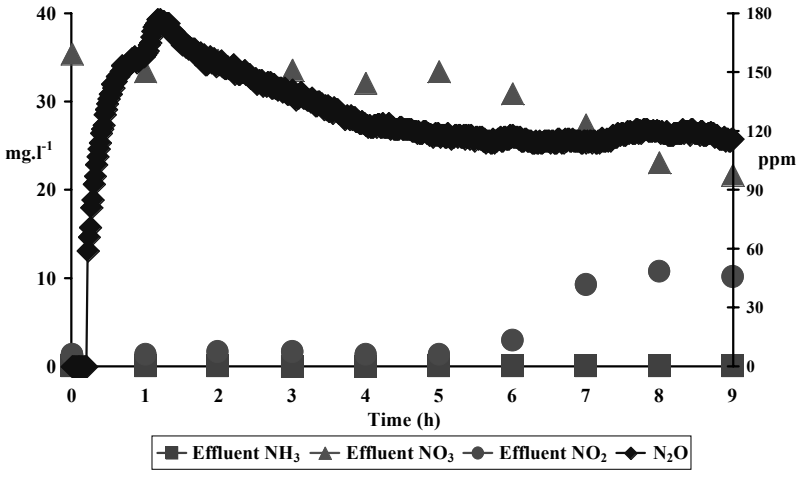

Figure 10: Sodium azide shock load at 75 % of reported minimum inhibitory concentration

Table 2: Operating performance parameters at Finham

MLSS	Influent		Effluent	
mg/l	mg/l	mg/l	mg/l	mg/l
2034 – 2879	35.2 – 78.5	571.5 – 687.5	0.1 – 1.2	37 – 67

ACKNOWLEDGEMENTS

The authors acknowledge the co-operation and support of the staff at Severn Trent Water, in particular Les Stokes. View expressed in this paper represent those of the authors alone. Mark Butler's PhD was supported by a UK Engineering and Physical Sciences Research Council industrial CASE studentship with Severn Trent Water.

REFERENCES

American Public Health Association (1998) *Standard Methods for the Examination of Water and Wastewater*. (1998). 20th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Burgess, J E, Colliver, B B, Stuetz, R M, and Stephenson, T (2002a) Dinitrogen oxide production by a mixed culture of nitrifying bacteria during ammonia shock load and aeration failure. *J. Ind. Microbiol. Biotechnol*., **29**, 309–313.

Burgess, J E, Stuetz, R M, Morton, S, and Stephenson, T (2002b) Dinitrogen oxide detection for process failure early warning systems. *Water Sci. Technol*., **45** (4), 247–254.

Butler, M D, Cartmell, E, Stokes, L, and Stephenson, T (2005) Non-invasive monitoring for early warning of nitrification failure. Proceedings of WEFTEC 2005, Water Environment Federation, Alexandria, USA. 14pp.

Colliver, B.B. and Stephenson, T. (2000). Production of nitrogen oxide and dinitrogen oxide by autotrophic nitrifiers. *Biotechnol. Adv*., **18**, 219–232.

Wicht, H. (1996). A model for predicting nitrous oxide production during denitrification in activated sludge. *Water Sci. Technol*. **34** (5/6), 99–106.

Zheng H., Hanaki K. and Matsuo T. (1994). Production of nitrous oxide gas during nitrification of wastewater. *Water Sci. Technol*. **30** (6), 133–141.

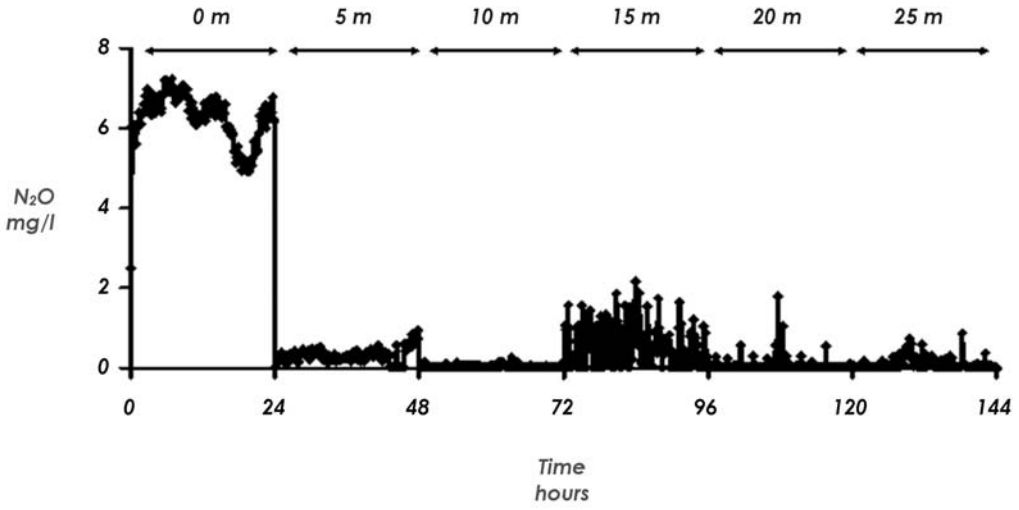

Figure 11: N_2O aeration lane profile results at Finham