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EVALUATION OF PEROXYGENS FOR THE AMELIORATION OF RIVER POLLUTION

ON BEHALF OF THE ENVIRONMENT AGENCY, THAMES REGION

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EXECUTIVE SUMMARY

The purpose of this study is to assess the use of peroxygens, including hydrogen peroxide, as a possible method of ameliorating river pollution. The assessment is based on a review of published data and operational experience gained through a number of trials carried out by various regions of the Environment Agency and former National Rivers Authority. The use of peroxygens has been assessed, firstly, in the context of their possible use to deal with the effects of pollution incidents in freshwater rivers, and secondly, for the amelioration of the effects of storm sewage discharges to the Tidal Thames. The assessment has considered the potential of peroxygens as a means of increasing river dissolved oxygen levels and has also assessed any relevant logistical, financial, toxicological and Health & Safety implications associated with their use.

Numerous trials conducted by Thames Region and other regions of the Environment Agency and the former National Rivers Authority, have demonstrated that hydrogen peroxide is an effective, reliable and safe method of increasing dissolved oxygen in rivers suffering from the effects of polluting discharges, without any apparent adverse effects. Hydrogen peroxide as an aqueous solution of either 35 or 50 % strength is the most appropriate method of dealing with the majority of situations, although the solid material sodium carbonate peroxyhydrate (PCS) can have advantages in certain applications. The trials have demonstrated that hydrogen peroxide can be used to deal effectively with the effects of storm sewage discharges to the Tidal Thames as well as the effects of pollution incidents in freshwater rivers.

The trials carried out by Thames Region to investigate the potential of hydrogen peroxide to counteract the effects of storm sewage discharges to the Tidal Thames have demonstrated that the 20 tonne capacity storage and dosing system located at Kew STW is of sufficient capacity and at a suitable location to provide extra protection for the river. This system should be viewed as a valuable supplement to the protection afforded by the mobile oxygenation vessel, the Thames Bubbler which is currently used as the primary means of preventing extensive fish mortalities following intense summer storms which occur several times each year.

The trials conducted by Thames Region and several other regions have demonstrated that hydrogen peroxide is a safe and convenient method of increasing dissolved oxygen levels in rivers and streams following pollution incidents. The equipment and materials needed are readily available and easily transportable to remote locations.

QUALITY ASSURANCE

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1.0 INTRODUCTION

1.1 STUDY OBJECTIVES

The purpose of this study is to assess the use of peroxygens, including hydrogen peroxide, as a possible method of ameliorating river pollution. The assessment is based on a review of published data and operational experience gained through a number of trials carried out by various regions of the Environment Agency and former National Rivers Authority. The use of peroxygens has been assessed, firstly, in the context of their possible use to deal with the effects of pollution incidents in freshwater rivers, and secondly, for the amelioration of the effects of storm sewage discharges to the Tidal Thames. The assessment has considered the potential of peroxygens as a means of increasing river dissolved oxygen levels and has also assessed any relevant logistical, financial, toxicological and Health & Safety implications associated with their use.

1.2 PHYSICAL / CHEMICAL PROPERTIES

Peroxygens is the generic term applied to a family of compounds which contain the 'O-O' group. The family includes; hydrogen peroxide, sodium carbonate peroxyhydrate, peracetic acid, calcium peroxide, organic peroxides and Caro's acid. Peroxygen species are powerful oxidising agents capable of oxidising many of the most commonly occurring pollutants, for example, compounds containing C, N or S. The 'active oxygen' content of peroxygens can also be utilised as a source of oxygen(1).

1.2.1 HYDROGEN PEROXIDE

Hydrogen peroxide occurs naturally in the environment and is produced in surface water by a photochemical process involving organic matter and dissolved oxygen, with a typical value for the hydrogen peroxide content of uncontaminated river water of 10^{-6}M(2). Micro-organisms, particularly algae, play a major role in the formation of hydrogen peroxide in natural waters. Concentrations in surface water generally contain less than 100 µg/l and are influenced by precipitation as rainfall contains relatively high concentrations of hydrogen peroxide (cloud droplets can contain up to 8,000 µg/l)(3).

Hydrogen peroxide is a clear colourless liquid which is readily miscible with water. In the presence of a suitable catalyst, for example transition metals or enzymes such as catalase, hydrogen peroxide rapidly decomposes to produce water and oxygen, thus:

$$2\ H_2O_2 \text{ ----> } 2\ H_20 + 0_2$$

Commercially available hydrogen peroxide is generally supplied as a solution of either 35% or 50% strength. Some of the physical properties of these solutions is shown in Table 1.

Table 1: Properties of aqueous hydrogen peroxide

Concentration, w/w %	**35**	**50**
Specific gravity, g/ml at 20°C	1.133	1.196
Freezing point, °C	-33	-52
Boiling point, °C	108	114
Viscosity, cp at 20°C	1.11	1.17
Available oxygen, wt %	16.5	23.5

Hydrogen peroxide solutions may contain low concentrations of impurities which are present in the raw materials used in the manufacturing process. Solvay Interox Limited has supplied environmental data for 35% hydrogen peroxide (Specification 411) as shown in Table 2.(4)

Table 2: Typical analysis of 35% hydrogen peroxide

Metal	**Cu**	**Cr**	**Ni**	**Zn**	**Pb**	**Hg**	**Cd**	**Fe**	**Sn**	**V**
Conc. (µg/l)	< 50	< 100	< 200	< 10	< 1	< 1	< 1	< 200	< 10	< 10

Hydrogen peroxide may contain trace quantities of phosphates. The phosphate concentration can range from 100 - 500 mg/l, with a typical concentration of 150 mg/l. According to Solvay Interox, they are not aware nor can they envisage the presence of any other Red List chemicals (apart from mercury and cadmium as shown in Table 2), in the product at any significant concentration.

Stabilisers are usually added to commercially available hydrogen peroxide to slow down the disproportionation to an acceptable level. Stabilisers employed include: EDTA, phosphates and tin salts. Hydrogen peroxide is normally supplied in a very slightly acid condition (pH 5) to further reduce the rate of decomposition.

The precise nature of the stabilisers employed is commercially sensitive and consequently Solvay Interox Limited have been unable to supply detailed information concerning their nature and composition. However, they have confirmed that the stabilisers used in the hydrogen peroxide solutions supplied to the Environment Agency are phosphate based.

The reactive nature of hydrogen peroxide in the presence of catalysts means that care needs to be taken in the selection of suitable materials for the storage and use of the material. For example, passivated aluminium or stainless steel can be used but anodised aluminium must not. Plastics such as PTFE, polythene and unplasticised PVC are also suitable for solutions less than 50%, provided mineral fillers and plasticisers are absent. Polyethylene should contain antioxidents and UV stabilisers.

Under recommended storage conditions at ambient temperature, hydrogen peroxide is very stable and typically loses 1% of its hydrogen peroxide in a 12 month period (i.e. product delivered on 1st January 1997 containing 35% w/w hydrogen peroxide would contain 34.65% w/w on 31st December 1997). This can be compared with liquid oxygen which requires storage under cryogenic conditions to minimise losses by evaporation to acceptable levels.

1.2.2 SODIUM CARBONATE PEROXYHYDRATE

Sodium carbonate peroxyhydrate (PCS) is a source of hydrogen peroxide chemically bound to a solid substrate which dissolves in water to release hydrogen peroxide in an alkaline solution. It decomposes to yield oxygen, sodium carbonate and water. It is available in 25 kg bags and is particularly useful in situations where storage or transport of liquid hydrogen peroxide might prove problematic. The maximum theoretical yield of available oxygen is 13%. The relatively high cost of PCS compared with aqueous hydrogen peroxide solutions coupled with the lower available oxygen yield per unit weight, make PCS significantly more expensive.

1.2.3 PERACETIC ACID

Peracetic acid (PAA) is the active ingredient of a peroxygen used for the disinfection of coastal sewage effluent discharges, which is marketed by Solvay Interox under the Registered Trademark of Oxymaster™. It is an equilibrium mixture of acetic acid and hydrogen peroxide, and combines the active oxygen characteristics of a peroxide within an acetic acid molecule. The peracid species is believed to be primarily responsible for disinfection. The ultimate decomposition products are water, oxygen and acetic acid.

Extensive trials have been carried out to investigate the environmental impact of PAA for the disinfection of coastal sewage effluent discharges. An investigation into the environmental impact on subtidal marine benthos during PAA dosing trials at Southend on Sea concluded that no major changes had taken place(4) However, further inspection of the data from this trial concluded that this could not be substantiated. Also information gained from other trials, which observed that there was some change in macrofaunal communities at times co-incident with the summer disinfection season, and correlated to some extent, with the proximity of the discharge.(5)

1.3 COSTS.

In the UK, peroxygens are manufactured by Solvay Interox Limited, Warrington, Cheshire, who can supply bulk quantities of hydrogen peroxide by road tanker. Smaller quantities of hydrogen peroxide can be supplied in either I m^3 IBC containers or 30 kg drums, by a distributor such as Ellis & Everrard, who operate an extensive network of regional distribution centres. PCS is usually supplied in 25 kg bags. The corresponding amounts of available oxygen afforded by these methods is shown in Table 3.

Table 3: Oxygen yields of peroxygen

Description	Quantity	Theoretical yield (% oxygen)	Yield of oxygen
50% hydrogen peroxide (bulk)	Bulk	23.5	240 kg / tonne
35% hydrogen peroxide	30 kg drum	16.5	5 kg / 30 kg drum
PCS	25 kg sack	13.5	3.4 kg / 25 kg sack

The cost is somewhat dependent on the quantity and form of material ordered, but for the purposes of this study all financial assessments are based on the unit cost indicators as shown in Table 4.

Table 4: Relative cost of peroxygens

Material description	Unit cost (£ / tonne)	Cost of available oxygen (£ / tonne)
35% Hydrogen peroxide, 30 kg drums (£20/drum)	666	4,036
50% Hydrogen peroxide in bulk	400	1,702
PCS in 25 kg sacks (13.5% available oxygen)	800	5.926

The relatively high cost of hydrogen peroxide has generally tended to preclude against its use in situations where alternative sources of oxygenation can be used or where other forms of treatment available. However, it is felt that the high cost can be justified in certain situations where speed of response, ease of application and immediate impact are paramount.

1.4 APPLICATIONS

Hydrogen peroxide has many industrial and commercial applications, including use as a disinfectant, deodorant, antiseptic and as a bleaching agent for natural fibres. Historically, in the water industry, hydrogen peroxide has been extensively used to control odour problems in sewers associated with the evolution of hydrogen sulphide caused by septicity.

An examination of published literature has revealed that, apart from investigations carried out by the Environment Agency and former National Rivers Authority, there appears to be very little information concerning the use of hydrogen peroxide for the amelioration of river pollution incidents or storm sewage discharges. The use of direct hydrogen peroxide injection to problematic storm overflows to the River Lippe has however been reported.(7)

There is however, a wealth of information concerning the use of hydrogen peroxide in other environmental applications, including:

- The successful treatment of tip leachates to counteract odour and pollution problems caused by sulphides.(8 - 10)
- The use of hydrogen peroxide in waste water treatment plants has been studied extensively. It has been used as a supplementary oxygen source to eliminate bulking in activated sludge plants, to reduce sulphide odours and to increase BOD removal efficiency.(11 - 15)
- Numerous studies to assess the use of hydrogen peroxide as an algicide.(16 - 23)
- Hydrogen peroxide has also been studied for use in the of remediation of contaminated land and groundwater.(24 - 27)
- Hydrogen peroxide at concentrations of up to 1,500 mg/l have been used to treat fish affected by sea lice at salmon farms in the Kyles of Bute and Loch Riddon, in trials reported by the Clyde River Purification Board in 1993.(28)

In addition, according to Solvay Interox Limited, hydrogen peroxide and PCS have been used with encouraging results to counteract dissolved oxygen problems associated with the effects of contaminated silt within the dock system of the Salford Quays development.

1.5 HEALTH & SAFETY

Hydrogen peroxide is a strong oxidising agent and improper storage, application or handling could create hazardous conditions. However, provided appropriate precautions are taken, for example the use of suitable personal protective equipment, there appears to be no reason why it cannot be used in pollution amelioration situations.

The Health and Safety Officer of the Environment Agency, Thames Region, has undertaken a detailed assessment of the use of hydrogen peroxide for the amelioration of river pollution and has produced Health and Safety Instructions and a Risk Assessment as shown in Appendix 1.

Material Safety Data Sheets for hydrogen peroxide and PCS (sodium carbonate peroxyhydrate) are shown in Appendices 2 and 3.

There are no British or European standards relating to the requirements of hydrogen peroxide storage tanks. However, Solvay Interox have produced guidance on the design and construction of such facilities in the form of a document, 'Hydrogen Peroxide and Handling Systems Design Manual.' According to Solvay Interox, there are around 200 bulk storage installations handling 35% hydrogen peroxide. They are not aware of any fires caused by or at hydrogen peroxide bulk storage tanks. Hydrogen peroxide itself is non flammable and acts only as a source of oxygen. Incidents involving hydrogen peroxide are rare and are usually caused by contamination of the product with other incompatible materials.

A detailed review of toxicity data for hydrogen peroxide is contained in the Joint Assessment of Commodity Chemicals No. 22.(29) The assessment concluded that the acute oral toxicity of hydrogen peroxide in experimental animals varies with the strength of its solution, the lethal dose varying from 75 to 2,000 mg/kg body weight. In human beings, death has resulted from ingestion of unknown quantities of 30 - 40% solutions. Toxic effects were generally related to the corrosive action on the gastrointestinal tract and the generation of large volumes of oxygen. There was complete recovery within 2 - 3 weeks even in near fatal cases.

The assessment also concluded that dermal toxicity is low. Hydrogen peroxide solutions of less than 35% are not classified as irritant to rabbit skin; solutions of 50% and higher are corrosive. Effects on the mucosa of the gingiva and tongues of dogs were found after direct contact with a 1% solution, whilst in human beings mouth washes with up to 3% neutralised hydrogen peroxide did not cause mucosal irritation. Intestinal / clinical use of 1 - 3% solutions in contact with the intestinal mucosa induced colitus and inflammation.

Hydrogen peroxide solutions of 10% or more cause irreversible damage to the eye, including blindness. However, in human beings 1 - 3% solutions have been used for eye treatment without serious injury.

1.6 AQUATIC TOXICOLOGY

An assessment of available toxicological data for hydrogen peroxide in the aquatic environment has been undertaken by the Environment Agency, Thames Region, Ecotoxicity and Chemistry Section, as shown in Table 5.(30)

The assessment, concluded that the available data indicates that hydrogen peroxide is of moderate to low toxicity to freshwater organisms. The most sensitive organisms appeared to be algae and crustacea.

Table 5: **Aquatic toxicity of hydrogen peroxide to freshwater organisms**

Species	Test conditions	Effect concentration (mg/l)	Reference
ALGAE			
Anabaena sp.	24 hr EC (reduced chlorophyll to 20%)	9.86	Stratford et al, 1982
Ankistrodesmus sp.	Threshold toxicity	6.2 - 10.2	Stratford et al, 1982
Raphidiopsis sp.	Threshold toxicity	3.4	Stratford et al, 1982
Microcystis	Threshold toxicity	1.7	Stratford et al, 1982
INVERTEBRATES			
Gammarus sp.	96hr LC50	4.42	Stratford et al, 1982
Physa ap.	96hr LC50	17.68	Stratford et al, 1982
Daphnia magna	24hr EC50	7.7	Bringmann & Kuhn, 1982
	EC0	3.8	
Daphnia pulex	48hr LC50	2.4	Shutleff, 1989
	NOEC	1.0	Gannon & Gannon, 1975
	5 mins immobilisation	4.2	
Dragonfly niaids	NOEC	170	Morse et al, 1976
Stationyd fly	NOEC	217.6	Kay et al, 1982
FISH			
Fingerling Trout	48hr no effect observed	40	Eden et al, 1952
Catfish	96hr LC50	37.4	Stratford et al, 1982
	96hr LC0	9.86	
Carp	48hr LC50	42	DOSE
Golden Orfe	24hr LC50	35	Degussa, 1977
Fathead Minnow	96hr LC50	16.4	Shurleff, 1989
	NOEC	5	
Guppy	No effect	34	Quimby, 1981

Key: NOEC No observable effect concentration.

LC50 Concentration at which 50% of the test population died within a specified exposure period.

EC50 Concentration at which an effect was observed on 50% of the test population within a specified exposure period.

2.0 TIDAL THAMES

2.1 STORM SEWAGE DISCHARGES

Following improvements to the major sewage treatment works discharging to the Tidal Thames during the mid nineteen seventies the quality of the river is now generally very good. The Quality Objective for the uppermost tidal reaches of the river between Teddington and Battersea (21 km) requires , *inter alia*, that the 80 percentile dissolved oxygen should be greater than 40% saturation, with a 95 percentile of greater than 10% and a minimum of 5%. The middle section of the river between Battersea and Mucking (60 km) has a similar objective except that the 80 percentile dissolved oxygen is 30%. The Tidal Thames in the London area now supports a healthy and diverse fish population, including the passage of migratory fish. However, the quality of the river can be seriously affected by intense summer storms which cause large quantities of storm sewage to be discharged to the river through numerous storm overflows from the Greater London trunk sewer network. Discharges of storm sewage can result in the rapid formation of a dissolved oxygen sag in the upper tidal reaches of the river. For example, after heavy storms on 10 August 1994, river dissolved oxygen in the Chelsea area fell from around 70% saturation to below 5% in less than 72 hours, as demonstrated by the daily dissolved oxygen plots from the AQMS system shown in Appendix 4.

Dissolved oxygen levels can fall to below 10% saturation within 24 hours of a storm and extensive fish mortalities throughout the Central London area would result without remedial action being taken. The location at which the dissolved oxygen sag develops is variable, depending on a number of factors including tidal conditions at the time of the storm and the direction of movement of the weather pattern. Once formed the sag oscillates with a range of 12 kilometres as a result of tidal action, whilst at the same time moving seaward by several kilometres per day in the upper reaches of the river due to the flushing effects of upland freshwater flow. The magnitude and rate of development of the sag are also highly variable depending on several factors including river water temperature, pre-storm dissolved oxygen levels, algal activity, upland freshwater flows and the volume and strength of storm sewage discharged.

Extensive investigations carried out by Thames Water Authority during the late 1970s(31) and early 1980s(32) concluded that, at that time, the most appropriate means of ameliorating the effects of these discharges was by oxygenation of the river using oxygen to maintain dissolved oxygen levels above 10% saturation and thus prevent fish mortalities. The highly variable nature of the development and movement of the sag, coupled with the lack of sufficient numbers of suitable sites in the densely populated Central London area, precluded against a shore based installation and therefore a mobile system was proposed. Safety considerations and logistical difficulties associated with the storage and movement of liquid oxygen resulted in the development of a system based on the Pressure Swing Adsorption principle, in which

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ENVIRONMENT AGENCY

Title

Tidal Thames

Hydrogen peroxide trials - survey area

Drawn
Date
Notes

Scale

Drawing Number

Figure 1

oxygen is obtained by preferential adsorption of nitrogen from air, using a zeolite molecular sieve. Water is abstracted from the river and the 95% pure oxygen from the PSA plant is injected into the water in a Vitox venturi system and then returned to the river through a series of nozzles which assist with the rapid dissolution of the oxygen. Following extensive experience gained with a barge mounted prototype system capable of producing 10 tonnes of oxygen per day, a purpose built self propelled vessel, the Thames Bubbler, with a capacity of 30 tonnes of oxygen per day was acquired in 1989 (Plate 1). The vessel is currently owned and operated by Thames Water plc. Its deployment and use is covered by an operating agreement with the Environment Agency under the provisions of the Water Resources Act.

Using river water quality information provided by an extensive network of telemetered automatic quality monitoring stations (AQMS's), on occasions supplemented by dissolved oxygen information supplied from boat surveys, the vessel follows the sag as it oscillates with the tide, injecting oxygen at the point of minimum dissolved oxygen. Despite extensive measures to minimise the size of the vessel to enable it to navigate freely in the upper reaches of the river, the existence of shallow water conditions at low tide and the presence of a number of low bridges in the area of operation, notably Hammersmith Bridge (Plate 2), means that it is not always possible to maintain the vessel on station within the sag and consequently there are occasions when oxygen additions to the affected area of the river are reduced. These navigational restrictions are particularly pronounced in the upper reaches of the river in the Putney to Kew areas.

Information gained from examining the effects of storms over many years has revealed that many of those with the greatest potential adverse effect on the river are characterised by the rapid development of a major sag in the Kew area. Any reduction in the amount of oxygen injected into this sag as a result of navigational or operational restrictions could prove disastrous and consequently consideration has been given to additional amelioration measures which could be used to supplement the effect of the Thames Bubbler.

2.2 HYDROGEN PEROXIDE TRIALS

Within Thames Region of the Environment Agency, the first experience of using peroxygens was gained when PCS was used to good effect to ameliorate the effects of an unsatisfactory discharge from Slough Sewage Treatment Works(33). Dissolved oxygen levels in the Roundmoor Ditch, approximately 1 kilometre downstream of the dosing point were found to rise from 27% to 48% after the addition of 75 kg of PCS. In the light of the encouraging results obtained during this operation, a decision was taken to further investigate whether peroxygens could be used in other situations, including dealing with the effects of storm sewage discharges to the Tidal Thames.

Since 1994, Thames Region have carried out a number of trials to investigate the feasibility of using hydrogen peroxide to increase dissolved oxygen levels in the Tidal Thames. Initially, the trials were carried out at Mogden STW but later trials were held at Kew STW, which was in a more suitable location to deal with the effects of dissolved oxygen sags which form after major discharges of storm sewage from outfalls in the West London area, as shown in Figure 1. The trials have been intended to investigate the following aspects:

- To assess the duration and rate of dosing to determine to what extent dissolved oxygen concentrations in the river can be increased and for how long any increase can be observed.
- To assess mobilisation and logistical procedures to determine whether the hydrogen peroxide can be effectively introduced into the affected part of the river.
- To assess the fate of residual hydrogen peroxide in the river and the consequence of any associated possible aquatic toxicity implications.
- To investigate any practical difficulties associated with the storage and dosing of hydrogen peroxide, including compliance with relevant Health & Safety requirements.

2.2.1 14 SEPTEMBER 1994 TRIAL

Methodology

The first trial was carried out on 14 September 1994(34), when approximately 13.0 tonnes of 50% hydrogen peroxide, with a theoretical total yield of available oxygen of 3.0 tonnes, was added at Mogden sewage treatment works, Isleworth (Dry Weather Flow 4.86 cumecs), approximately 24 kilometres upstream of London Bridge. During this trial, hydrogen peroxide was dosed directly into the final effluent carrier from a road tanker which had delivered the material to the works. The final effluent conduit runs underground for approximately one kilometre before discharging to the River Thames through a series of submerged outlets at Isleworth Ait. The dosing was carried out in two stages, each lasting approximately 1.5 hours with a dosing rate of approximately 4 tonnes per hour. The first addition was made approximately 3 hours after local high water when the tide was ebbing. The second addition was made around local low water during slack tide conditions.

Monitoring

Dissolved oxygen measurements were determined immediately downstream of the outfall to the river. Further information was obtained from the AQMS's at Kew and Hammersmith.

Results

Dissolved oxygen saturation increased from around 75% to 143% immediately downstream of outfall with an increase of around 20 to 25% detected at the AQMS's at Kew and Hammersmith, approximately 3 and 11 kilometres downstream of the dosing point respectively. This almost instantaneous increase in dissolved oxygen in the river as a result of the hydrogen peroxide addition was considered to be significant. Consequently, additional trials were planned to further investigate the feasibility of using hydrogen peroxide to counteract the effects of major storms.

2.2.2 18 JULY 1995 TRIAL

Methodology

A second trial was carried out on 18 July 1995(35), when 16.9 tonnes of 50% hydrogen peroxide, with a theoretical total yield of available oxygen of 4.0 tonnes, was added at Kew sewage treatment works (Dry Weather Flow 0.23 cumecs), approximately 20 kilometres upstream of London Bridge. The location of Kew works approximately 4 kilometres downstream of Mogden was considered to be more suitable for dealing with the effects of storm sewage inputs because it discharges to the river in the area where major storm sags are known to develop. The works discharges to the Tideway by way of a submerged outfall which is located close to the south bank of the river.

The hydrogen peroxide was introduced into the final effluent chamber from a purpose built 20 tonne storage tank and dosing facility which had been constructed at the works (Plate 3). Two additions of hydrogen peroxide were made at a rate of approximately 7 tonnes per hour. The first addition was of approximately 9.9 tonnes was made over a period of 1 hour 25 minutes on an ebb tide. The second addition of approximately 7 tonnes was made over a period of 1 hour, approximately 8.5 hours later as the same body of water passed back past the dosing point on the next flood tide.

Monitoring

Dissolved oxygen and hydrogen peroxide concentrations were determined by making transects across the river in a boat in an attempt to track the plume and build up a profile of dissolved oxygen enhancement and residual hydrogen peroxide concentrations. As before additional information concerning dissolved oxygen levels in the river was obtained from the network of AQMS's. A number of samples were taken for a range of chemical analysis to determine whether there were any detectable changes in other river parameters. In addition, aquatic toxicity was assessed using an ECLOX meter which assesses aquatic toxicity due to inhibition of enzymatic reactions.

Results

The trial demonstrated that initially the hydrogen peroxide did not mix well but tended to remain close to the south bank of the river. However, subsequent tidal action resulted in the dispersion of the plume across the river and consequently dosing at Kew was considered to be a suitable method of introducing hydrogen peroxide into that section of the river. An approximate increase of 15% in dissolved oxygen saturation was observed in the river which was considered to be significant.

A previous assessment of toxicological data relating to hydrogen peroxide, resulted in a self imposed target of a maximum of 20 mg/l for residual hydrogen peroxide in the river. Measurements detected a maximum of 19.7 mg/l close to the outfall approximately 40 minutes after dosing started. However, concentrations rapidly fell as the plume became dispersed as a result of tidal action.

The results of the ECLOX tests indicated that aquatic toxicity was lower in areas where hydrogen peroxide concentration was highest.

Chemical analysis of river water samples taken before and after dosing revealed no significant detectable changes and therefore it was concluded that the dosing had little effect on nitrogenous or carbonaceous matter present in the river.

2.2.3 11 OCTOBER 1995 TRIAL

Methodology

A third trial was carried out on 11 October 1995(36), when 12.8 tonnes of hydrogen peroxide, with a theoretical total yield of 3.0 tonnes of available oxygen, were added at Kew sewage treatment works. Three additions of hydrogen peroxide were made on this occasion, each of approximately one hour duration. The dosing times chosen, were intended to enable each of the additions to be made into the same body of water as it oscillated past the dosing point as a result of tidal movement. The first addition was made at 14.32 to 15.32 towards the end of a flood tide. The second addition was made at 18.00 to 19.00 as the same body of water passed back past the dosing point on the ebb tide with a final addition being made at 02.55 to 04.40 as the body of water passed the dosing point for a third time on the next flood tide. The purpose of making three additions to the same body of water was intended to maximise the amount of hydrogen peroxide added to a specific part of the river whilst at the same time minimising the possibility of increasing residual hydrogen peroxide concentrations to an undesirable level.

Monitoring

Dissolved oxygen and hydrogen peroxide concentrations were obtained by making transects across the river in a boat in an attempt to track the plume and build up a profile of dissolved oxygen enhancement and residual hydrogen peroxide concentrations. As before, additional information concerning dissolved oxygen was obtained from the network of AQMS's, and an assessment of aquatic toxicity was made using an ECLOX meter.

In addition, a survey of macrpinvertebrates was carried out using a standard FBA three minute kick sampling technique at four strategic locations along the southern foreshore within the study area before and after dosing to assess whether there had been any detectable adverse effects on the macroinvertebrate population.

Results

The trial once again demonstrated a significant elevation in river dissolved oxygen levels following dosing. It confirmed that it was possible to introduce hydrogen peroxide to the river in a controlled manner and that it was possible to dose a specific section of the river at the correct rate and time, enabling multiple additions of hydrogen peroxide to be made to the affected section of the river as it oscillated past the dosing point as a result of tidal action.

Although one sample taken from the immediate vicinity of the outfall during the dosing period slightly exceeded the self imposed 20 mg/l limit for residual hydrogen peroxide, measurements demonstrated that concentrations rapidly fell as the plume became more dispersed as a result of tidal action.

The limited 'kick sample' survey showed that the macroinvertebrate species present and their abundances were very similar both before and after dosing suggesting that the was little effect from the dosing of hydrogen peroxide at any of the four sites monitored. However, the survey was regarded as insufficiently detailed for firm conclusions to be made. Resources would therefore need to be made available for a more comprehensive survey during any further trials. The ECLOX measurements suggested that the toxicity of the water was decreased in the area of highest hydrogen peroxide concentration.

2.2.4 11 SEPTEMBER 1996 TRIAL

Methodology

A fourth trial was carried out on 11 September 1996, when 7.0 tonnes of 50% hydrogen peroxide, with a theoretical total yield of 1.6 tonnes of available oxygen, were added at Kew sewage treatment works. Interpretation of results from previous trials had been somewhat complicated as a result of the multiple additions of hydrogen peroxide. For this trial it was therefore decided to make only a single addition of hydrogen peroxide at a rate of 7 tonnes per hour, which previous trials had demonstrated was the optimum rate to maximise the oxygen input to the river without causing undesirable concentrations of residual hydrogen peroxide. Dosing was carried out from 01.25 to 02.25 during the final stages of the flood tide. Daily gauged mean flow recorded at Kingston (u/s Teddington Weir) was 4.2 cumecs on 11 September 1996, dropping to 3.7 cumecs on 12 and 13 September 1996.

Monitoring

One of the primary aims of this trial was to investigate, more thoroughly, the dispersion and fate of residual hydrogen peroxide in the river. Depth samples were therefore obtained to determine whether any significant degree of stratification was evident within the water column.

Monitoring of residual hydrogen peroxide was also carried out over an extended period to assess the rate of decay and residence time within the river.

A more thorough survey of macroinvertebrates in the study area before and after dosing was intended to have been undertaken by Environment Agency biologists(37). Unfortunately, however, due to operational difficulties the surveys were incomplete. No post-dosing mid-channel dredge samples were obtained and only 4 of the originally intended 10 foreshore sampling sites were assessed post-dosing, significantly restricting the value of the investigation.

To assess any affect of hydrogen peroxide on algae, an extensive survey of algae throughout the river before and after dosing was proposed. Unfortunately, due to resource constraints, no pre-dosing samples at all were obtained, and no samples were obtained from above Kew, which significantly restricted the value of the investigation. However, fifteen post-dosing river water samples were obtained from the routine river monitoring sites between Purfleet (approximately 43 kilometres downstream of the dosing point) and Kew.

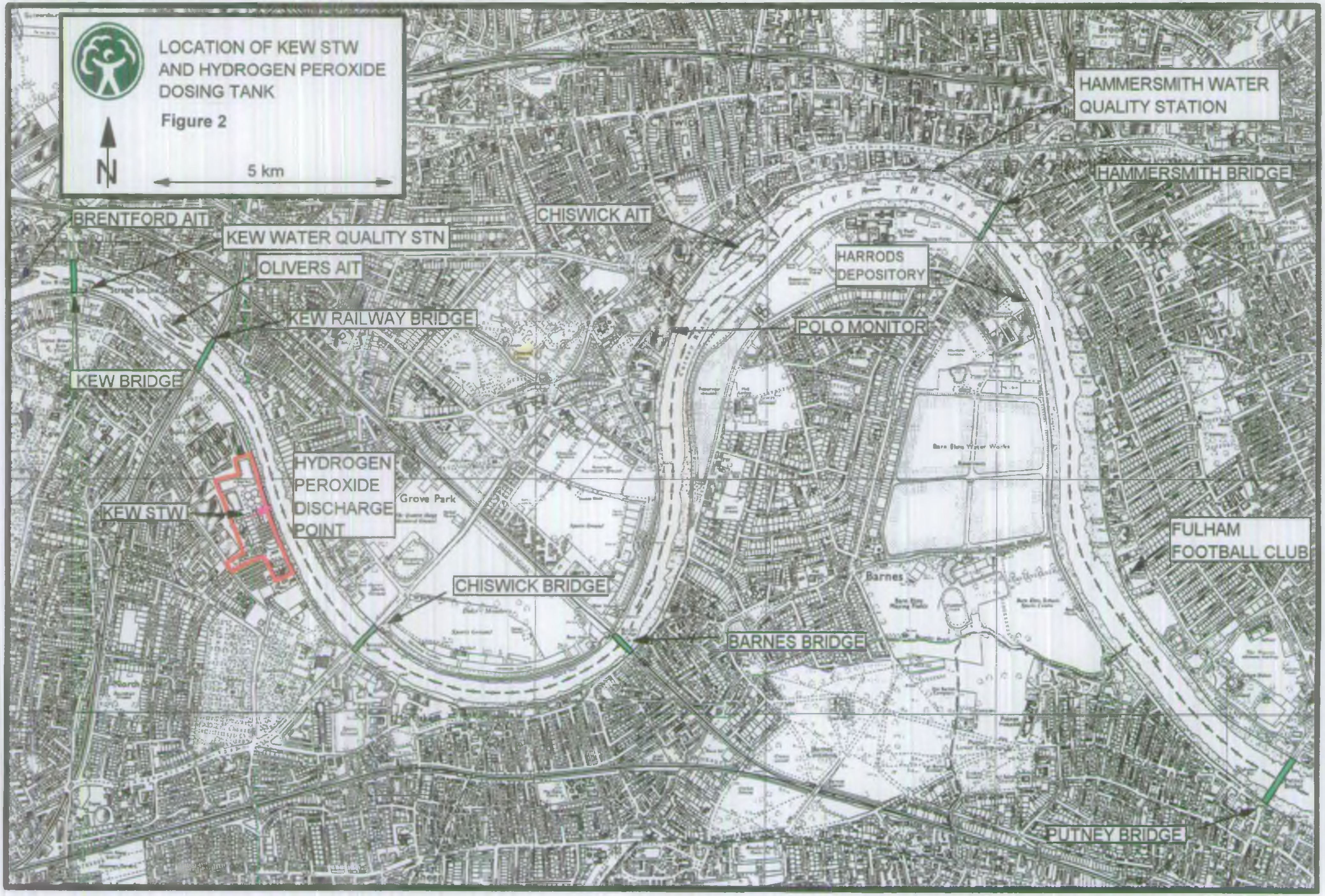
Samples were taken of Kew final effluent before and after dosing for GC/MS analysis by Thames Water plc, to determine whether there had been any detectable changes in the chemical composition of the effluent as a result of the addition of hydrogen peroxide.

Results

Monitoring of dissolved oxygen and hydrogen peroxide concentration demonstrated that the plume initially moved upstream with the flood tide, keeping close to the south bank as far as Brentford Ait, approximately 3 kilometres upstream of the dosing point (Figure 2). After high water, as the tide began to ebb, the plume rapidly became dispersed across the total width of the river.

Dissolved oxygen

Dissolved oxygen profiles obtained from the AQMS's at Kew, Hammersmith and Putney, for the tide immediately preceding dosing (No. 38 Flood) and the following two tides (No. 39 Ebb and No. 40 Flood) are shown in Figure 3. The effect of dosing is characterised by the presence of a distinct peak detected by all three AQMS's during tide No. 39 Ebb, representing an increase of approximately 10% saturation at 16 kilometres above London Bridge. The peak is again evident during tide No. 40 Flood, approximately 8 - 10 hours after dosing. Dissolved oxygen enhancement has reduced to approximately 7% as a result of dispersion and has moved downstream to approximately 12 kilometres above London Bridge as a consequence of net seaward movement.



LOCATION OF KEW STW AND HYDROGEN PEROXIDE DOSING TANK

Figure 2

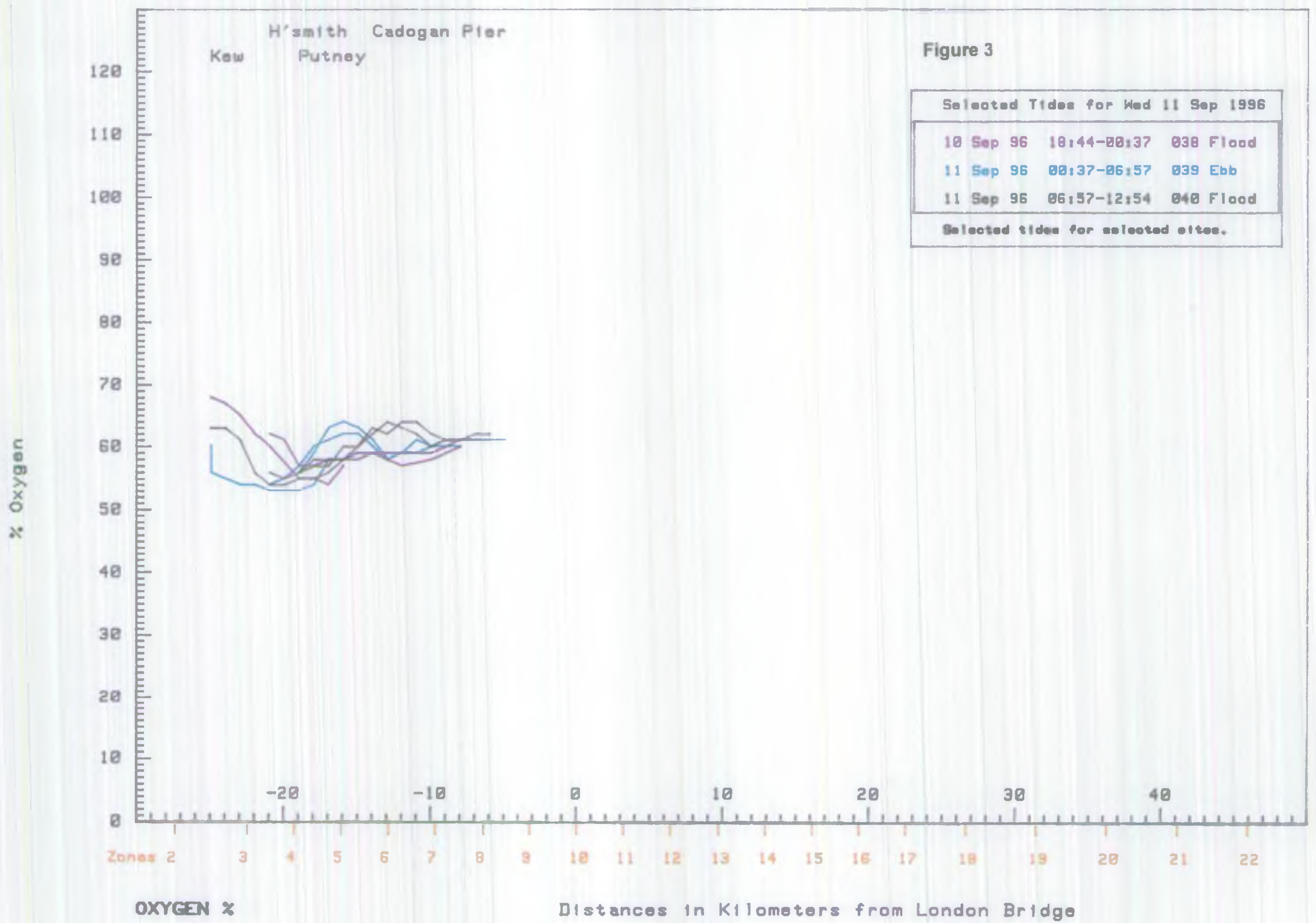


Figure 3
H'smith
Cadogan Pier
Kew
Putney
Selected Tides for Wed 11 Sep 1996
10 Sep 96 18:44-00:37 038 Flood
11 Sep 96 00:37-06:57 039 Ebb
11 Sep 96 06:57-12:54 040 Flood
Selected tides for selected sites.
% Oxygen
120
110
100
90
80
70
60
50
40
30
20
10
0
-20
-10
0
10
20
30
40
Zones 2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
OXYGEN %
Distances in Kilometers from London Bridge

It is particularly interesting to note that the dissolved oxygen enhancement was recorded by all three AQMS's. Kew and Putney AQMS's are located close to the south bank of the river but Hammersmith AQMS is located close to the north bank. Therefore it can be seen that the plume has completely dispersed across the whole width of the river after only one tide.

Residual Hydrogen Peroxide

Detailed results of residual hydrogen peroxide after dosing are shown in Appendix 5 and summarised in Tables 6 and 7.

Depth samples were taken at a number of locations within the plume to assess whether any significant degree of stratification of residual hydrogen peroxide was evident, as shown in Table 6.

Table 6: **Maximum recorded concentration of hydrogen peroxide concentration at various depths**

Location	Time	Depth				
		0 m	1 m	2 m	3 m	4 m
Discharge point	01.48	18.8	18.0	18.4	-	18.0
Kew Railway Bridge	02.44	13.0	-	8.9	-	7.7
20 m u/s Kew Railway Bridge	03.24	1.2	1.1	-	-	0.5

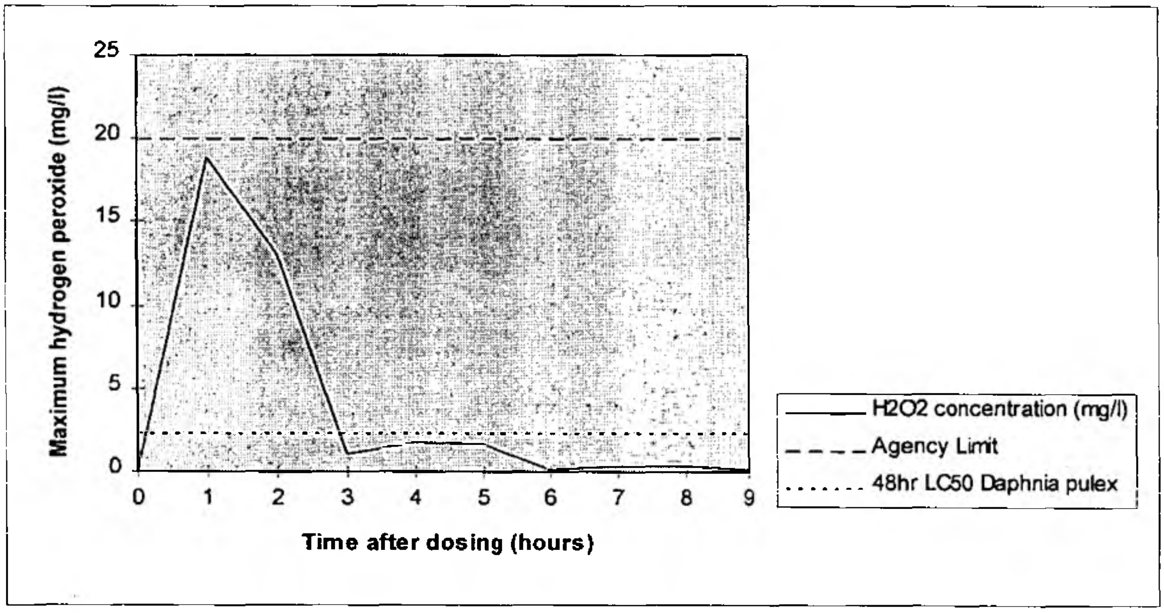
Inspection of the results in Table 6, demonstrates that there was no appreciable degree of stratification of hydrogen peroxide within the water column in the immediate vicinity of the discharge point but that as the plume moved away from the outfall some stratification was evident, with higher concentrations recorded in the near-surface layers. However, it is not thought that the degree of stratification observed could be considered significant in the context of oxygen transfer efficiency. The presence of higher concentrations in the near-surface layers means that any future surface sampling to determine residual hydrogen peroxide concentration will be likely to represent worst case conditions.

To investigate the fate of residual hydrogen peroxide in the river as the plume became more dispersed, the plume was tracked over an extended period. The approximate location of the body of water which had received the hydrogen peroxide addition is shown in Figure 4 as it moves first upstream then downstream due to the effects of tidal movement. Details of maximum recorded hydrogen peroxide concentration in the river as a function of position relative to the dosing point and from the time elapsed since the commencement of dosing are summarised in Table 7 and presented graphically in Figure 5.

Table 7: **Maximum recorded concentration of residual hydrogen peroxide**

Time after dosing commenced (Hours)	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Maximum recorded hydrogen peroxide concentration (mg/l)	0.0	18.8	13.0	1.2	1.8	1.6	0.1	0.4	0.4	0.1
Approximate distance upstream (+) or downstream (-) of the plume from the dosing point (kms)	0	0	+1	+2	-2	-7	-10	-13	-15	-15

Figure 5: **Maximum recorded concentration of residual hydrogen peroxide**



Inspection of Figure 5 and the results in Table 7, demonstrates that residual hydrogen peroxide in the river attained a maximum concentration of 18.8 mg/l in the immediate vicinity of the outfall immediately after dosing. However as a result of degradation and dispersion the concentration fell rapidly. Two hours after dosing had finished the maximum concentration recorded had fallen to below 2 mg/l, and after five hours was below 0.5 mg/l.

Aquatic toxicity

The macroinvertebrate survey found an apparent significant reduction in the BMWP score at the 4 survey sites in the study area. The greatest reduction in the BMWP score was recorded at the Kew Bridge site, approximately 1 kilometre upstream of the dosing point. A much smaller reduction was observed at the survey site immediately upstream of the dosing point which would have been subject to the highest concentration of hydrogen peroxide. Similar reductions in BMWP score were also recorded at the downstream sampling points which would have been subject to even lower concentrations of hydrogen peroxide, because dosing

Approximate location of the peroxide dosed area

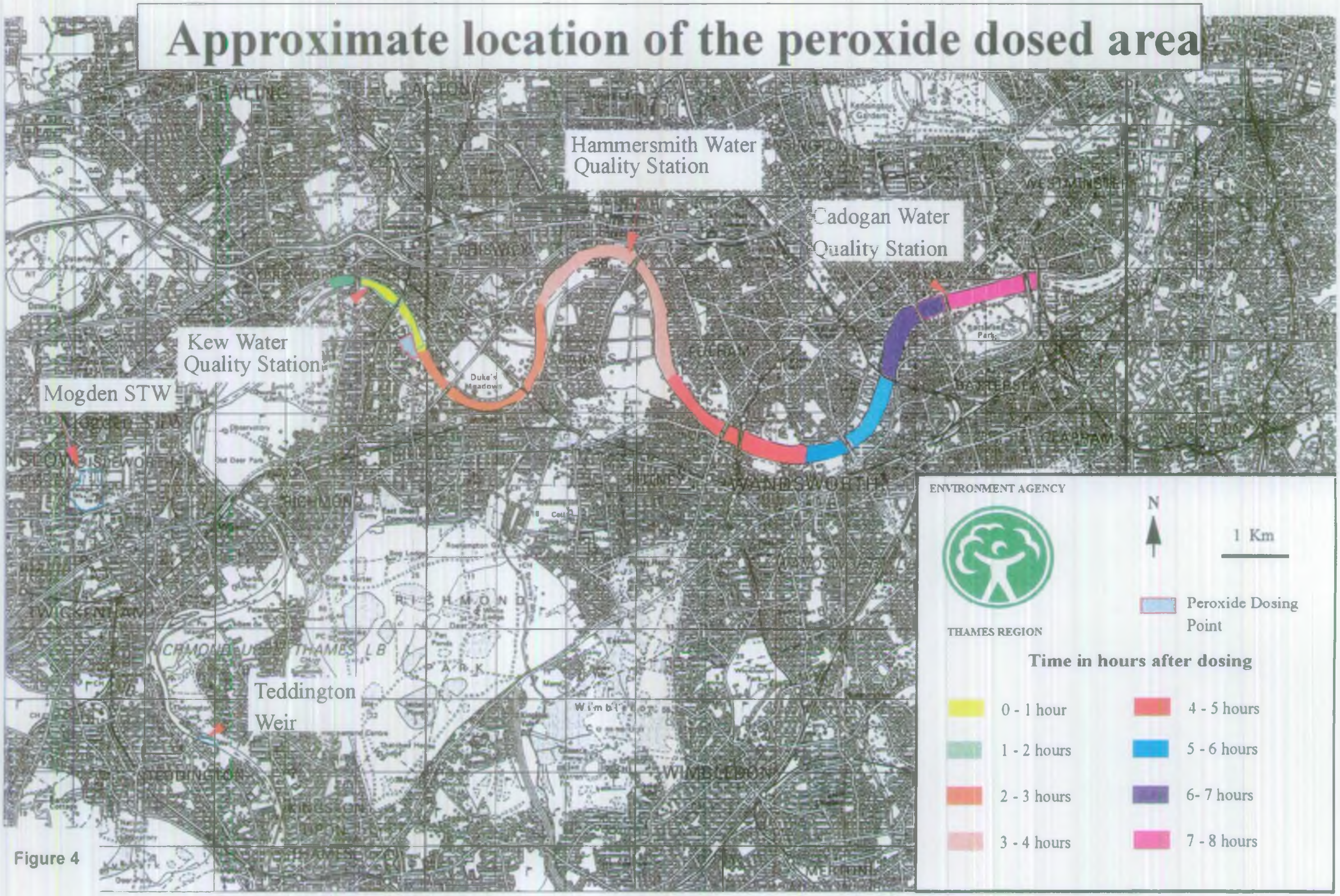


Figure 4

had only occurred during the flood tide. The absence of data relating to control sites or mid-channel dredge sites make it impossible to accurately assess the effects of hydrogen peroxide dosing. However, the distribution of the reduction in the BMWP score suggests that it was more likely to be as a result of some other unidentified problem rather than the hydrogen peroxide dosing operation, although further investigation is required to confirm this fact.

Analysis of samples taken during the algal study concluded that, compared with previous algal surveys of the Tidal Thames, the cell count and algal diversity was typical. There was no record of change or damage to algal cells. However, the absence of data relating to conditions pre-dosing makes it difficult to draw any firm conclusions concerning the effect of hydrogen peroxide dosing on algae and further investigation is therefore required to study this aspect.

GC/MS analysis of samples of Kew final effluent taken before and after dosing did not detect any changes in the chemical composition of the effluent.

2.3 DISCUSSION

2.3.1 OPERATIONAL ASPECTS

Since its acquisition in 1989, the mobile oxygenation vessel operated by Thames Water, the Thames Bubbler, has proved to be an effective and relatively reliable method of preventing widespread fish mortalities in the Tidal Thames as a result of discharges of storm sewage. However, the inherent reliability concerns associated with a complex piece of machinery coupled with navigational restrictions which exist for the Thames Bubbler in the upper reaches of the Tideway as a result of low bridges and limited draft, make the provision of additional oxygen enhancement capacity in this extremely vulnerable section of the river, a particularly attractive and valuable asset.

The four hydrogen peroxide dosing trials carried out at Mogden and Kew Sewage Treatment Works since 1994 have demonstrated that hydrogen peroxide dosing is an effective method of counteracting the decrease in dissolved oxygen which occurs in the upper reaches of the Tidal Thames on a number of occasions each year due to effects of storm discharges to the river. The use of hydrogen peroxide dosing can therefore be considered to represent a reliable and cost effective method of supplementing the protection afforded to the river by the use of the Thames Bubbler.

The highly dynamic state of the river following major storms and the large number of variables which influence the development of dissolved oxygen sags following discharges of storm sewage, make it extremely difficult to predict the rate of development and magnitude of a sag. Past experience has shown that there is often a delay of several hours after the initial identification of a sag before the affected part of the river is next visible to the monitoring station network to enable a further assessment of conditions to be made. Under unfavourable tidal conditions, it can take up to 8 hours for the Thames Bubbler to reach the affected area of the river from its moorings at Crossness (approximately 40 kilometres downstream), from the time mobilisation instructions are given. Consequently, in order to provide sufficient levels of protection to the river, it is sometimes necessary to mobilise the Thames Bubbler before sufficient river quality information is available to accurately predict whether its use will actually be required to prevent fish mortalities. Once mobilised, it is normally necessary to maintain operations for at least 24 hours before sufficient information is available to enable the operation to be stood down. The cost of mobilisation is high (Approximately £3,300 per day) and consequently the ability to be able to delay mobilisation during these marginal events would be useful.

The nature and location of the hydrogen peroxide dosing system at Kew means that almost instantaneous decisions can be taken to instigate dosing operations. This enables the development of a sag to be monitored for a longer period during the initial post storm period to determine whether remedial action will be required to prevent the possibility of fish mortalities. The mere existence of a hydrogen peroxide dosing capability at Kew would therefore significantly reduce the number of unnecessary mobilisations of the Thames Bubbler with associated significant cost savings. Even if dosing is actually undertaken, the cost of this operation (approximately £2,800 for a 7 tonne addition of hydrogen peroxide) is comparable with the minimum mobilisation cost of the Thames Bubbler.

The efficiency of the Thames Bubbler is seriously compromised in the upper reaches of the river. The maximum theoretical oxygenation capacity of the Thames Bubbler is 30 tonnes per day. No detailed trials have been undertaken to accurately assess the amount of oxygen actually dissolved in the river, however trials carried out to assess the performance of the prototype unit coupled with observations made during operational conditions concluded that, for operational purposes, it was reasonable to assume that an approximate dissolution efficiency of 75% was achievable. It is also recognised that to be effective, it is necessary for the Thames Bubbler to operate precisely at the point of minimum dissolved oxygen. The well defined nature of storm sags means that it is necessary to be able to maintain the unit in an area of water no greater than 1 kilometre in length which is continuously oscillating with the tide. In practice, restrictions to navigation and other factors, means that it is unlikely that this is achievable for more than 50% of the time of operation. Taking these factors into account, the effective oxygenation capability of the Thames Bubbler in the upper reaches of the river, is more likely to be of the order of 11 tonnes per day.

Given the current velocity within the river in the Kew area, it is likely that dosing will be limited to approximately I hour on each tide to ensure that the hydrogen peroxide is added to the river at the precise location where it is most needed. The existence of two ebb and two flood tides each day means that, at a maximum dosing rate of 7 tonnes per hour, a total of 28 tonnes of hydrogen peroxide with a theoretical yield of available oxygen of 7 tonnes is possible. The maximum oxygen input afforded by hydrogen peroxide dosing at Kew, can therefore be seen to be significant in comparison with the operation of the Thames Bubbler under unfavourable conditions in the upper reaches of the river.

The 20 tonne capacity pilot trial hydrogen peroxide storage and dosing plant which was installed at Kew Sewage Treatment Works in 1994 at an approximate cost of £50,000, has been found to be in a suitable location and of sufficient capacity for the effective treatment of the major dissolved oxygen sags which frequently develop in the Kew area. The site is secure and there is easy access to the dosing system for replenishment of the storage tank by road delivery tankers. Consideration should be given to undertaking any modifications necessary to plant and operational procedures to include this system in any Tidal Thames river quality management strategies.

The method of dosing into the final effluent chamber appears to provide sufficient turbulence and dispersion to ensure that the hydrogen peroxide is adequately mixed within the river as a result of tidal action, thereby providing oxygen to the section of river which requires it and also minimising the potential for elevated concentrations of residual hydrogen peroxide in the river.

The present 20 tonne capacity of the storage tank means that the tank would require replenishment after two additions, and it is therefore important to ensure that additional supplies of hydrogen peroxide can be delivered to the site within a 12 hour notice period.

The method of mobilisation of the hydrogen peroxide dosing system appears to work reliably and effectively. It relies on Environment Agency personnel making an assessment of relevant information to determine whether unsatisfactory conditions are likely to develop. This assessment includes consideration of many factors, including: river water quality data obtained from the network of automatic quality monitoring stations (AQMS's); data supplied by Thames Water plc regarding the duration of pumping and quantity of storm sewage discharged from pumping stations; and an assessment of relevant climatic related factors for example, fresh water flows and pre-storm river conditions. Predicted tidal movement data is then used to calculate when the affected body of water will be in the vicinity of the Kew sewage treatment works hydrogen peroxide dosing facility. Telephone instructions are given to the works operational staff regarding necessary dosing rates and duration. This system appears to work effectively and the trials have demonstrated that this procedure can reliably and consistently introduce hydrogen peroxide into the section of river which most needs it.

Although the unit cost of hydrogen peroxide is relatively high, the cost of the storage and dosing system is modest in comparison with alternative remediation strategies. Therefore, overall hydrogen peroxide dosing can be considered to represent a cost effective and reliable system for dealing with storm sewage sags and preventing widespread fish mortalities in the upper reaches of the river.

In order to comply with the provisions of the relevant pollution control legislation, there may be a requirement to issue a discharge consent for Kew STW which specifically refers to the addition of hydrogen peroxide. Further consideration should be given to the legislative and administrative implications of hydrogen peroxide dosing into existing consented discharges.

The net seaward movement of the sag as a result of freshwater flows means that it is unlikely to remain within an area where additions of hydrogen peroxide from Kew would be effective for longer than two complete tidal cycles. Therefore, it would be advantageous to provide additional hydrogen peroxide dosing facilities at other locations, downstream of the Kew facility. This would enable further treatment of a major sag if it was found to be necessary as it moved downstream out of the zone of influence afforded by the Kew system.

A potential location for a second hydrogen peroxide dosing facility has been identified at Hammersmith. The site is a potable water pumping station operated by Thames Water plc as part of the London Ring Main scheme. The location of the site, adjacent to the river in an area which would enable further additions of hydrogen peroxide to be made to the river as a dissolved oxygen sag moves downstream as a result of freshwater flows, away from the influence of the Kew facility. It has been suggested that hydrogen peroxide would be dosed into potable water abstracted from the Ring Main before being discharged to the river. It is estimated that approximately 1,300 m^3/hour of water would be required to achieve similar dilution characteristics to those existing at Kew. The use of significant quantities of potable water may be considered to be wasteful of a scarce resource at certain times of the year and therefore consideration could be given to the utilisation of groundwater from the chalk and basal sands aquifer which exists beneath the site. Groundwater levels in this aquifer are currently at approximately 50 m below ordnance datum but are rising as a result of reduced abstractions and there are concerns about the possible adverse effect on building foundations and underground tunnels in the London area if this rise continues. Another advantage of using groundwater instead of potable water is that water obtained from the ring main contains low concentrations of chlorine which would react with the hydrogen peroxide reducing the amount available for oxygen enhancement in the river. The use of groundwater from this source can therefore be seen to preserve other water resources and represent a positive benefit in controlling the local rise in groundwater levels. It may be possible to utilise a redundant well or alternatively construct a new purpose built borehole, although further work is needed to ensure that autocatalytic decomposition of hydrogen peroxide does not occur due to the presence of elevated iron concentrations in the groundwater.

2.3.2 AQUATIC TOXICITY

Concerns have been expressed relating to the possible adverse aquatic toxicity effects of residual concentrations of hydrogen peroxide. The trials have demonstrated that, at a dosing rate of 7 tonnes per hour, concentrations of hydrogen peroxide in the river do not exceed 20 mg/l. Furthermore, this concentration is only attained in the vicinity of the dosing point and is of relatively short lived duration. Concentrations of hydrogen peroxide in the river were found to fall to below 2 mg/l within 3 hours of completion of the dosing operation and below 0.5 mg/l within 6 hours. The possible adverse aquatic toxicity effects are not therefore thought to be significant in view of the rapid reduction of residual hydrogen peroxide concentration as a result of decomposition and dispersion. In addition, it must be remembered that the trials have been conducted in predominantly dry weather conditions when river water quality is relatively good. During storm conditions, more rapid decomposition of peroxide, and hence lower residual concentrations, are to be expected due to the effects of increased solids and organic matter present in the river at these times.

An assessment of the aquatic toxicity of hydrogen peroxide has been undertaken by the Environment Agency(38), based on available published data. The assessment concluded that hydrogen peroxide is of low toxicity to aquatic organisms with algae and crustacea being the most sensitive. *Daphnia pulex* was found to be the most sensitive species, for which data was available, with a 48 hour LC 50 of 2.4 mg/l. The most sensitive species likely to be present in the upper reaches of the Tidal Thames, which is predominantly freshwater, was Gammarus sp with a 96 hour LC 50 of 4.42 mg/l. The trials have demonstrated that hydrogen peroxide in the river exceed these concentrations only in the vicinity of the outfall during and immediately after dosing. In view of the rapid reduction in hydrogen peroxide concentrations as a result of degradation and dispersion it seems unlikely that there will be any adverse effect on even these most sensitive organisms. However, in view of the limited available data relating to the toxicity of hydrogen peroxide to aquatic species present in the upper reaches of the Tidal Thames and the limited relevance of 48 and 96 hour LC 50s when considering exposure periods of only 2 to 3 hours, it might be advisable to consider undertaking a series of Direct Toxicity Assessments to further investigate this aspect. The assessments should pay particular attention to the short term effects of hydrogen peroxide below 20 mg/l which dispersion studies have found to be representative of conditions in the river during dosing and also to ensure that the assessments are relevant to species common to the upper reaches of the Tidal Thames.

It should be remembered that concentrations of hydrogen peroxide of up to 1500 mg/l have been used to control sea lice at fish farms in the Kyles of Bute and Loch Riddon. A series of chemistry and plankton studies on the surrounding waters did not detect any adverse effects on either the fish or local plankton populations(28).

It has been suggested that the use of hydrogen peroxide should be viewed with caution because of the apparent concerns surrounding the use of it's close relative, peracetic acid (PAA) for disinfection of coastal sewage discharges. However, although this study has not considered fully any possible relationship between the use of hydrogen peroxide and PAA it seems unreasonable to make any direct comparisons. Hydrogen peroxide dosing is being proposed for infrequent use of limited duration to deal with specific pollution events compared with the continuous long term use of PAA to deal with problems, for which there are other available solutions.

Laboratory studies carried out by Thames Water plc using GC / MS to investigate the effect of hydrogen peroxide dosing on Kew final effluent have indicated that, at the concentrations of peroxide achieved during the dosing trials, no significant changes in the composition of the effluent had occurred. Furthermore, the study suggested that below hydrogen peroxide concentrations of 2,000 mg/l no degradation of COD took place demonstrating that at these concentrations the hydrogen peroxide was acting primarily as an oxygen source rather than as an oxidising agent. At Kew works, storm water arising from any overflow from the storm tanks is discharged to the river by way of a separate outfall. Hydrogen peroxide can therefore only ever be dosed into treated final effluent, and consequently it is unlikely that conditions significantly different from those existing during the trials will be experienced during times of storm.

The absence of significant amounts of COD degradation during dosing conditions tend to suggest that there would be no particular advantage in direct hydrogen peroxide dosing of the storm sewage discharges themselves. Moreover, the location of the storm discharges and the limitation that the time and duration of dosing is restricted to the period during which they are discharging makes this option unsuitable for ameliorating the effects of a dissolved oxygen sag which has formed in the river.

2.3.3 HEALTH & SAFETY

Hydrogen peroxide is a strong oxidising agent and can cause burns to the skin and eyes if handled incorrectly. However, the material has widespread use throughout commerce and industry, and provided appropriate Health & Safety precautions are observed during its use, there is no reason to suspect that use of hydrogen peroxide would be any more hazardous than that associated with the use of many other chemicals used extensively throughout the Water Industry. Detailed Health & Safety Instructions and a Risk Assessment have been prepared by the Environment Agency, Thames Region, which should be observed at all times when hydrogen peroxide is used.

Concerns have also been expressed relating to the possible safety implications of discharging hydrogen peroxide to an area of the river which has extensive recreational use for boating and sculling. Determination of residual hydrogen peroxide has demonstrated that the maximum concentration found in the river does not exceed 20 mg/l (0.002 %) and is confined to the immediate vicinity of the outfall during dosing. The infrequent use of hydrogen peroxide and limited extent of the plume means that the probability of a member of the public becoming totally immersed in the plume is extremely low. Even if this were to occur, in view of the extremely low concentrations of hydrogen peroxide, it seems unlikely that any significant pathological damage would result over that associated with exposure and possible ingestion of almost neat treated sewage effluent which exists in the vicinity of the outfall. Mouth washes and eye washes containing up to 3% hydrogen peroxide (30,000 mg/litre) have been used without significant injury to eyes or causing mucosal irritation.

3.0 FRESHWATER RIVERS

3.1 BACKGROUND

Fish mortalities are frequently caused by a rapid fall in river dissolved oxygen levels following unconsented discharges of agricultural, industrial or sewage effluent. Many of these discharges are of high organic strength and are readily biodegradable in the river resulting in the rapid reduction of dissolved oxygen levels which could lead to extensive fish mortalities if appropriate remedial action was not taken.

A characteristic of this type of incident is that they usually occur without prior warning and often, the first manifestation of a problem is the presence of distressed, dying or dead fish. Consequently there is a requirement to be able to bring about a rapid increase in dissolved oxygen within the river if further extensive fish mortalities are to be prevented. Another problem often encountered is that the incidents frequently occur at inconvenient times and at locations were there is limited access for personnel and equipment. Therefore, any method employed to deal with these problems has to be readily available at short notice, safe, portable, capable of being operated by a minimum number of staff and expedient in increasing river dissolved oxygen levels.

Historically, many methods have been employed by river protection personnel to ameliorate the effects of this type of discharge and thus prevent extensive fish mortalities, including deployment of aerators and direct oxygenation using liquid oxygen or gaseous oxygen from cylinders. Recently, hydrogen peroxide as a solution or in a solid form as sodium carbonate peroxyhydrate (PCS), have been recognised as possible alternative methods of dealing with this type of incident. Consequently, a number of trials have been undertaken to assess the viability of these methods under operational conditions, by various Regions within the Environment Agency, including: Thames, South West, Midlands, Welsh and North East. In addition the Clyde River Purification Board have studied the effects of hydrogen peroxide during its use to control sea lice at a salmon farm.

This assessment has considered in detail a number of trials undertaken within Thames Region and has also reviewed the experience gained from trials carried out by other regions, to determine whether hydrogen peroxide and PCS can be considered to be a suitable method of increasing river dissolved oxygen levels and thus prevent fish mortalities.

3.2 THAMES REGION TRIALS

3.2.1 SITE SELECTION

The River Mole in the Kinnersley Manor area was selected as an appropriate location to carry out trials to investigate the use of hydrogen peroxide and PCS in freshwater rivers. This location was chosen because there was a history of problems associated with low dissolved oxygen as a result of the impact of two major treated sewage effluent discharges from Horley STW (0.75 cumecs) and Crawley STW (0.38 cumecs), located approximately 5 and 9 kilometres upstream of Kinnersley Manor respectively, as shown in Location Plan, Figure 8. As a result of these problems, a number of studies had previously been carried out of the river in this locality and thus there was a considerable body of knowledge concerning this section of river. In addition, the presence of an automatic quality monitoring station (AQMS) at Kinnersley Manor was able to provide additional river water quality data to supplement data derived from portable instruments. Also, the area was away from major roads and thoroughfares with sufficient riverside space for safe and easy access to the river to permit installation of equipment and monitoring systems.

The presence of a strong diurnal variation in river water quality parameters as a result of the dominant effects of the two sewage treatment works was identified as a potential complicating factor in the interpretation of results. However, it was felt that the other positive aspects of this location outweighed the possible difficulties of data interpretation associated with these diurnal water quality variations.

3.2.2 20 JUNE 1995 TRIAL

Methodology

During this trial hydrogen peroxide was added to the final effluent of two sewage treatment works discharging to the River Mole.(39) Thirty three 30 kg drums of 35% hydrogen peroxide were added to Horley STW (Dry Weather Flow 0.75 cumecs) and twenty nine drums at Crawley STW (Dry Weather Flow 0.38 cumecs). At each location, hydrogen peroxide was dosed at a rate of approximately one drum every 15 minutes (0.12 tonnes per hour). Dosing started at 22.15 on 20 June and finished at 06.15 on 21 June. A total of 1,860 kg of hydrogen peroxide with a theoretical yield of available oxygen of 307 kg (cost £1,240).

Monitoring

Grant water quality instruments were used to determine dissolved oxygen levels at several locations downstream of the dosing points as shown in Table 8.

Table 8: Location of dissolved oxygen monitoring points.

Location	Distance downstream from Crawley STW (kilometres)	Distance downstream from Horley STW (kilometres)
Horley Weir	4	-
Wick Farm	6	2
Kinnersley Manor	9	5
Sidlow Bridge	10.5	6.5
Bures Manor	12.5	8.5

Residual concentrations of hydrogen peroxide were determined approximately 50 metres downstream of each dosing point.

A survey of macroinvertebrates before and after dosing was undertaken by Environment Agency biologists.(41) Three sites were examined, one upstream and two downstream of the dosing point at Horley STW.

Results

Significant increases in dissolved oxygen were observed at all the locations monitored as the plug of oxygen enriched water moved downstream.

Measurements of residual hydrogen peroxide showed that concentrations ranged from 8.2 to 19.7 mg/l with readings typically around 16 - 19 mg/l.

The macroinvertebrate survey concluded that the biological quality of the River Mole both above and below Horley STW was poor. The results of the surveys carried out in connection with the dosing operation corresponded well with historical data for the area, with BMWP scores mostly below 50. The results for before and after dosing showed very similar faunal communities with no significant differences. No dead invertebrates were found at the sites sampled after hydrogen peroxide dosing and no oxidation effects were observed on the macrophytes in the river below the dosing point. The survey concluded that the results indicated that there was no acute impact on the macroinvertebrate fauna of the River Mole. Although the study could not rule out the possibility of more long term chronic effects, these effects were felt to be unlikely, given the way hydrogen peroxide residuals act as oxidising agents.

3.2.3 21 JULY 1996 TRIAL

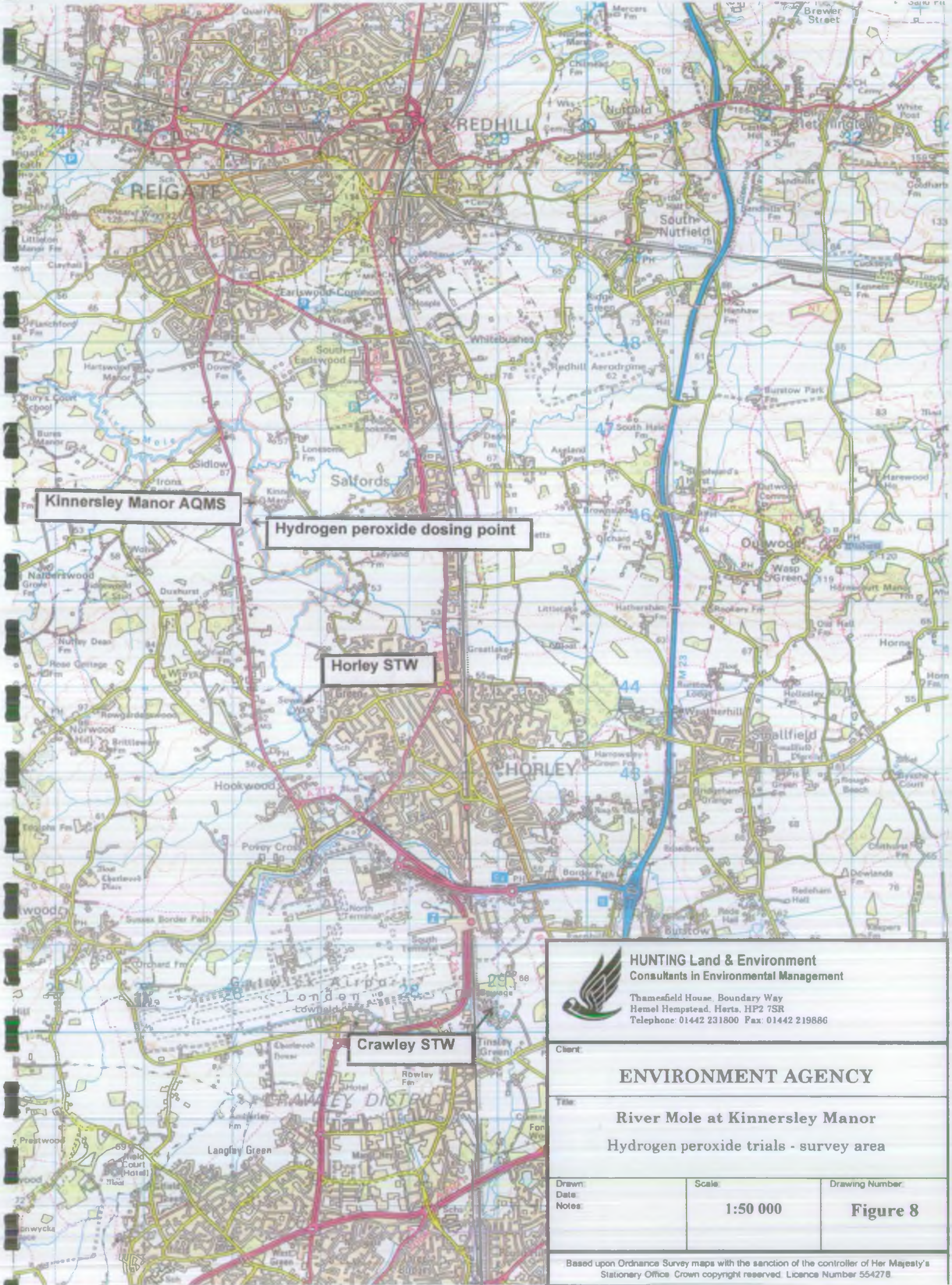
Methodology

During this trial, hydrogen peroxide and PCS was added directly to the River Mole at three locations, Long Bridge, Wick Farm and Kinnersley Manor.(40) 20 bags of PCS were added at Wick Farm between 00.25 and 05.00. 18 bags of PCS were added at Wick Farm between 23.15 and 03.05, followed by 5 drums (30 kg) of 35% hydrogen peroxide. 10 bags of PCS were added at Kinnersley Manor between 05.20 and 06.30.

A total of 950 kg of PCS (38 sacks) with a theoretical yield of available oxygen of 128 kg was added (cost £760), and 150 kg of hydrogen peroxide (5 drums) oxygen yield 25 kg (cost £100).

Monitoring

Dissolved oxygen and pH measurements were obtained from the Kinnersley Manor AQMS which is located approximately 6 kilometres downstream of the Long Bridge dosing point and 3 kilometres downstream of the Wick Farm dosing point. The AQMS is located upstream of



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Client:

ENVIRONMENT AGENCY

Title:

River Mole at Kinnersley Manor

Hydrogen peroxide trials - survey area

Drawn: Date: Notes:	Scale:	Drawing Number:
	1:50 000	**Figure 8**

the Kinnersley Manor dosing point, therefore any effect associated with this operation was not recorded.

Results

The AQMS detected a rise in dissolved oxygen saturation of approximately 10% and an increase in pH from around 7.0 to around 8.0 which lasted for approximately 12 hours.

3.2.4 18 SEPTEMBER 1996 TRIAL

The previous trials had demonstrated that it was possible to dose the River Mole at a variety of locations using both hydrogen peroxide and PCS. Providing basic safety precautions were observed, the operation could be carried out easily and without incident.

The purpose of this trial was to compare a variety of techniques under controlled conditions to assess the relative merits and disbenefits of each option, including:

- An assessment of any potential logistical difficulties and Health & Safety implications associated with the use of hydrogen peroxide and PCS at remote sites.
- Determination of the possible enhancement in river dissolved oxygen levels and the rate of response in the river which could be achieved using readily available equipment and techniques
- To assess the relative merits and disbenefits associated with the use of a variety of traditional methods of pollution amelioration and hydrogen peroxide or PCS dosing techniques
- To investigate the rate of dispersion and decomposition of hydrogen peroxide to assess any possible adverse aquatic toxicity implications

The dissolved oxygen enhancement techniques assessed during this trial were as follows:

- Atmospheric aeration using 'Tornado' turbo aerators (1 HP and 2 HP) which are commonly used by Thames Region Fisheries staff (Plate 4). These units need to be placed in the river at a suitable location and tethered to anchoring points on the river banks. River water is drawn through the aerators and is subjected to intimate mixing with air to achieve a high degree of oxygen transfer from the atmosphere.
- Injection of oxygen from cylinders utilising a Godiva fire pump and Vitox venturi system which had been used for many years by Thames Region (Plate 5). The unit is operated from the river bank, drawing water from the river and injecting it with oxygen supplied by cylinders, and returning the oxygenated water to the river. High oxygen transfer efficiencies are achieved by the use of the Vitox venturi system.

- Manual hydrogen peroxide dosing from 30 kg drums using the 1 HP Tornado aerator to assist with dispersion and agitation (Plate 6). The drums are laid on their side and a suitable plastic pipe is connected to the drain tap which directs hydrogen peroxide to the desired point in the river.
- Hydrogen peroxide dosing using a venturi based system, developed and used effectively for several years by South West Region (Plate 7). A 2 inch portable centrifugal pump is used to draw river water through a venturi fitted to the outlet of the pump. Hydrogen peroxide is drawn into the venturi from 30 kg drums of 35% solution located close to the pump. Operational experience has demonstrated that the most effective method of returning the dosed water back to the river is in the form of a jet which can be easily directed to the desired point in the river and provides adequate levels of agitation to ensure rapid dispersion within the river. Dosing rates can be closely controlled by adjustment of the dosing valve and pump speed.
- Dosing with Sodium Carbonate Peroxyhydrate (PCS), in which hydrogen peroxide is available, chemically bonded to a solid substrate which decomposes in the presence of water. During the trial, PCS bags were emptied into the river from a small boat moored centre stream. Bags were added at a rate of approximately one bag every 15 minutes.

Each of the remediation techniques was operated for a set period of time with a rest period between each, in an attempt to create a series of pulses in the river which could be monitored. The mean daily gauged flow at Kinnersley Manor on 18 September 1996 was 0.421 cumecs, with a minimum flow of 0.302 cumecs at 12.00 and maximum flow of 0.497 cumecs at 18.45.

Monitoring

Several dissolved oxygen monitoring instruments were located at strategic positions upstream and downstream of the test site to determine any changes in dissolved oxygen as a result of the trials. The locations of the meters is shown in Table 9.

Table 9: Location of dissolved oxygen meters

Location	Type	Position relative to test site (metres downstream)
u/s test site	Hydrolab	-20
u/s test site	Grant	-10
80 m d/s test site	Hydrolab	+80
Kinnersley Manor	Grant	+400
80 m d/s Kinnersley	Hydrolab	+480
Foot bridge d/s Kinnersley	Grant	+800
80 m u/s Sidlow Bridge	Grant	+1,720
Sidlow Bridge	Grant	+1,800

Details concerning the description and duration of the various dosing operations are shown in Table 10.

Table 10: Description and duration of dosing operations

Operation	Start time	Finish time
Tornado aerators (1 HP and 2 HP)	06.00	06.15
Hydrogen peroxide dosing with 2 x 30 kg drums of 35% solution, using 1 HP Tornado aerator to aid dispersion	06.15	06.49
Tornado aerators (1 HP and 2 HP)	09.49	10.23
Hydrogen peroxide dosing of 2 x 30 kg drums of 35% using venturi system	10.54	11.24
Hydrogen peroxide dosing with 2 x 30 kg drums of 35% solution, using 1 HP Tornado aerator to aid dispersion	12.25	12.58
Hydrogen peroxide dosing of 2 x 30 kg drums of 35% using venturi system	14.00	14.20
Oxygen dosing using Vitox venturi system (1 x 10 kg O_2 cylinder)	15.15	15.33
PCS dosing from boat using 3 x 25 kg bags	16.10	16.40
PCS dosing using 14 x 30 kg hessian bags placed on river bed	17.30	-

Results

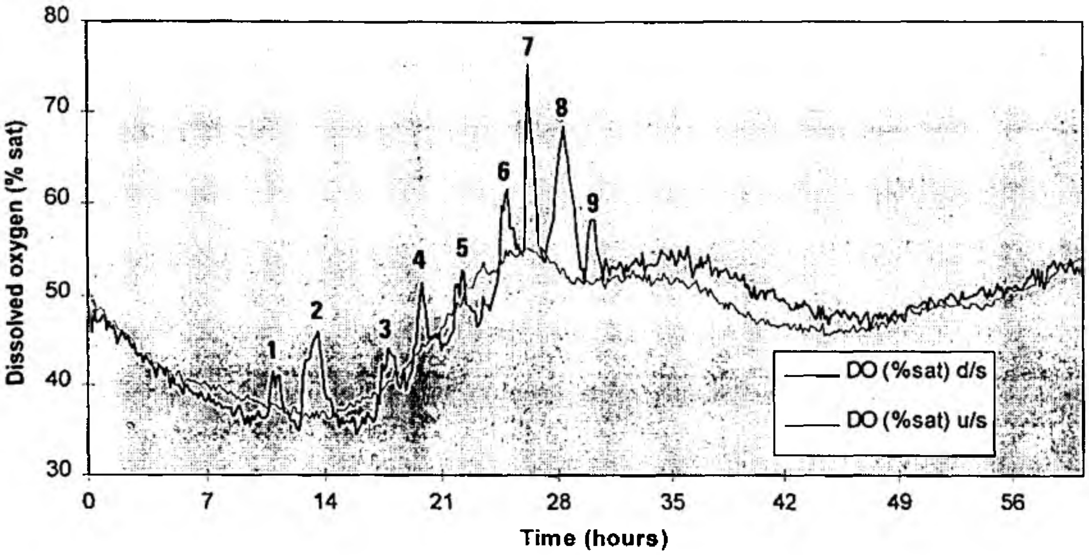
The trial was started early in the morning to coincide with the period when lowest dissolved oxygen levels are known to exist in the rivers as a consequence of diurnal variation.

Dissolved oxygen

Dissolved oxygen profiles obtained from the monitoring instruments are shown in Figures 9 and 10 and at Appendix 6.

The profiles from the meters paced upstream and 80 metres downstream of the dosing site are shown superimposed in Figure 11 to demonstrate the immediate effect of dosing operations.

Figure 11: **Dissolved oxygen profiles for monitoring points upstream and downstream of the dosing point.**



Key

Reference	Operation
1	Tornado aerators (1 HP and 2 HP)
2	Hydrogen peroxide dosing with 2 x 30 kg drums of 35% solution, using 1 HP Tornado aerator to aid dispersion
3	Tornado aerators (1 HP and 2 HP)
4	Hydrogen peroxide dosing of 2 x 30 kg drums of 35% using venturi system
5	Hydrogen peroxide dosing with 2 x 30 kg drums of 35% solution, using 1 HP Tornado aerator to aid dispersion
6	Hydrogen peroxide dosing of 2 x 30 kg drums of 35% using venturi system
7	Oxygen dosing using Vitox venturi system (1 x 10 kg O_2 cylinder)
8	PCS dosing from boat using 3 x 25 kg bags
9	PCS dosing using 14 x 30 kg hessian bags placed on river bed

Inspection of the profile for the monitoring point upstream of the dosing point (Figure 11) demonstrates that dissolved oxygen was approximately 37% saturation between 06.00 and 09.00 but started to rise rapidly after that time to reach a maximum of 55% at 15.00.

The profiles from all the monitoring points downstream of the dosing site clearly demonstrate the existence of enhanced dissolved oxygen levels as a result of the dosing operations. The monitoring points at 80 m d/s of the dosing point and Kinnersley Manor (400 m d/s) show clearly defined peaks which can be attributed to each of the various dosing operations. However, as the pulses move further downstream they become more dispersed causing the peaks to become less well defined making it difficult to differentiate between individual dosing

River Mole Location Map

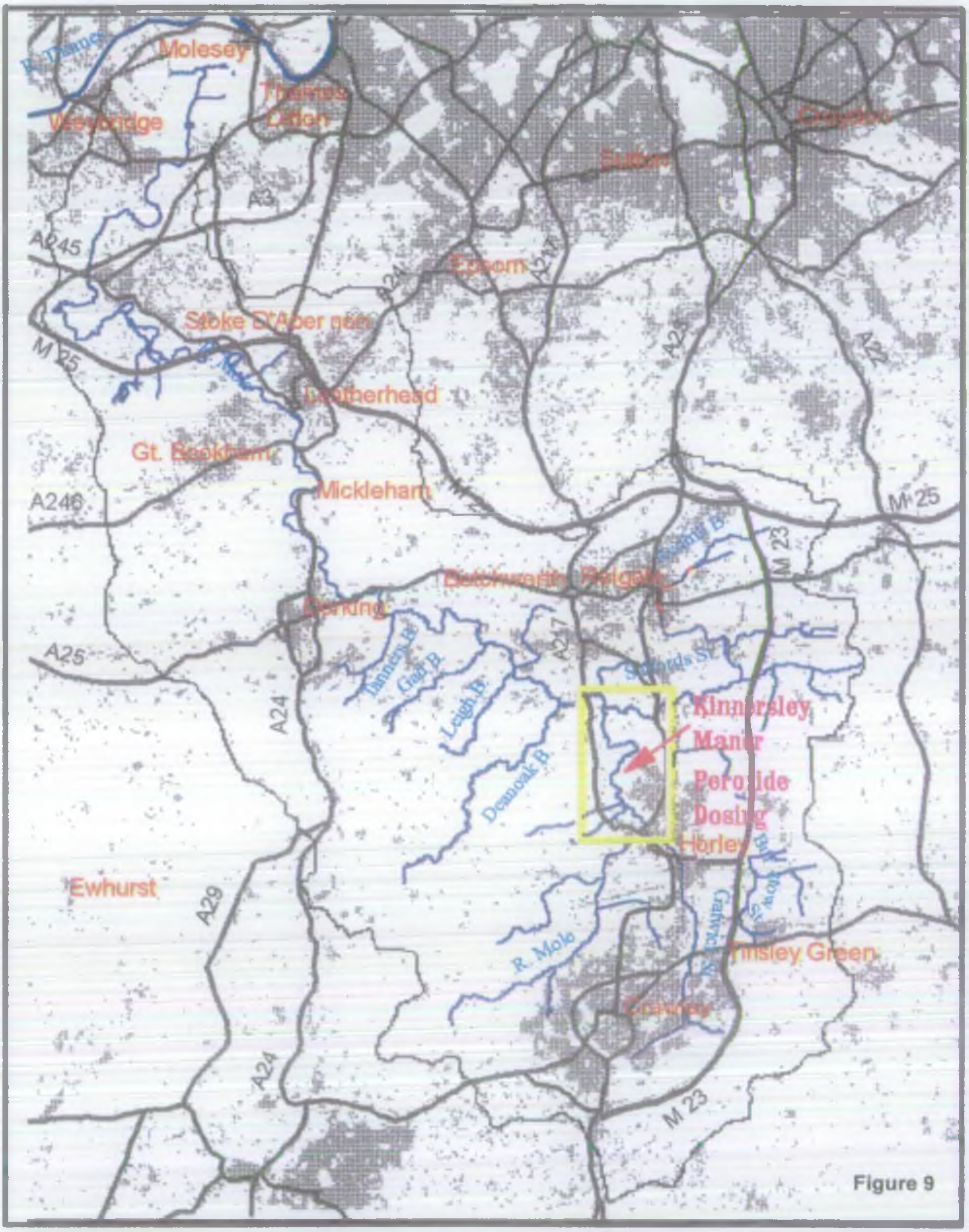


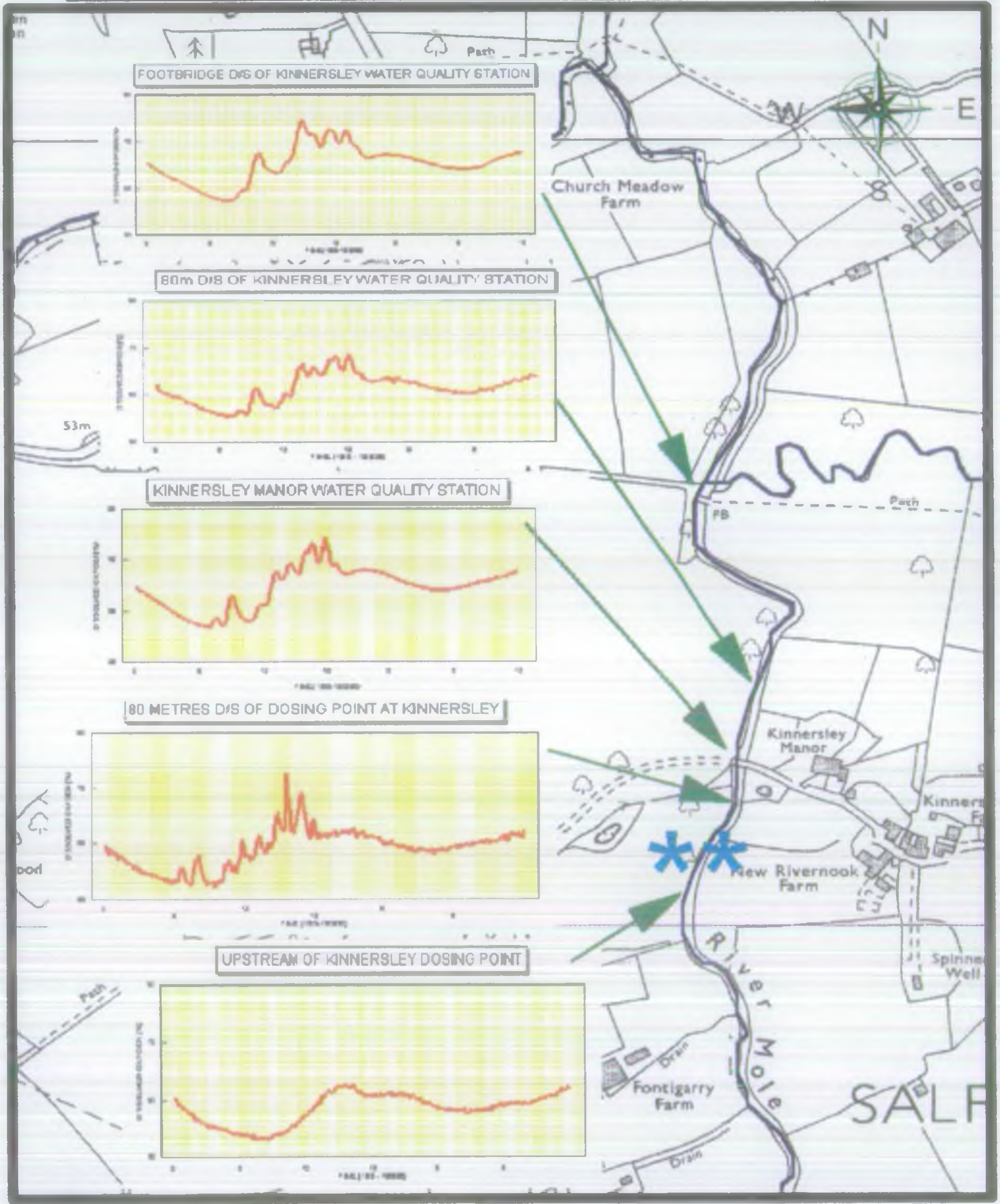
Figure 9

Environment Agency

Key

- Urban Area
- Peroxide Dosing Area Kinnersley Manor
- Main river (open channel and culvert)
- Main Road
- Railway

KINNERSLEY MANOR DISSOLVED OXYGEN (%)



ENVIRONMENT AGENCY

Figure 10

** - DOSING / AERATION POINT

operations. Unfortunately, the desire to carry out as many different dosing operations as possible within a single day has resulted in insufficient rest periods between pulses to make accurate determinations of the dissolved oxygen increase associated with each dosing operation. It seems likely that towards the end of the trial there was a significant amount interference caused by the flushing out of residual quantities of hydrogen peroxide trapped in weeds etc. However, best estimates of river dissolved oxygen increase at the monitoring points located at 80 and 400 metres downstream of the dosing point are shown in Table 11.

Table 11: Dissolved oxygen increase from various dosing operations at 80 and 400 metres downstream.

Dosing operation	Maximum theoretical yield of available oxygen (kg)	Dissolved oxygen increase at 80 m d/s (% saturation)	Dissolved oxygen increase at 400 m d/s (% saturation)
Tornado aerators 1st trial)	-	5	3
35% hydrogen peroxide from drums 1st trial)	10	10	12
Tornado aerators (2nd trial)	-	5	6
35% hydrogen peroxide using venturi (1st trial)	10	10	19
35% hydrogen peroxide from drums (2nd trial)	10	8	6
35% hydrogen peroxide using venturi (2nd trial)	10	12	9
Oxygen dosing using Vitox system	10	21	8
Direct PCS dosing	10	14	9
PCS in hessian sacks	57	4	4

Inspection of the results in Table 11 indicates shows that all the methods were capable of causing a rise in river dissolved oxygen ranging from 3% to 21% saturation. The systems using hydrogen peroxide and direct dosing of PCS generally resulted in an increase of around 10% which was evident almost immediately and persisted for some distance downstream.

The venturi based hydrogen peroxide dosing system achieved slightly higher increases in river dissolved oxygen compared with direct dosing from drums.

The effect of PCS dosing from hessian sacks placed on the river bed is slightly more difficult to discern. However, it appears that a rise of around 4% saturation was achieved which persisted for up to 12 hours after installation of the sacks.

Only four individual peaks were evident at the Sidlow Bridge monitoring point (approximately 1.8 kilometres downstream of the dosing point). Although it is impossible to discern individual peaks, an overall increase of up to approximately 20% saturation was evident. In view of the predominance of hydrogen peroxide dosing techniques employed, it seems reasonable to assume that this increase can be largely attributed to the overall combined effects of hydrogen peroxide dosing.

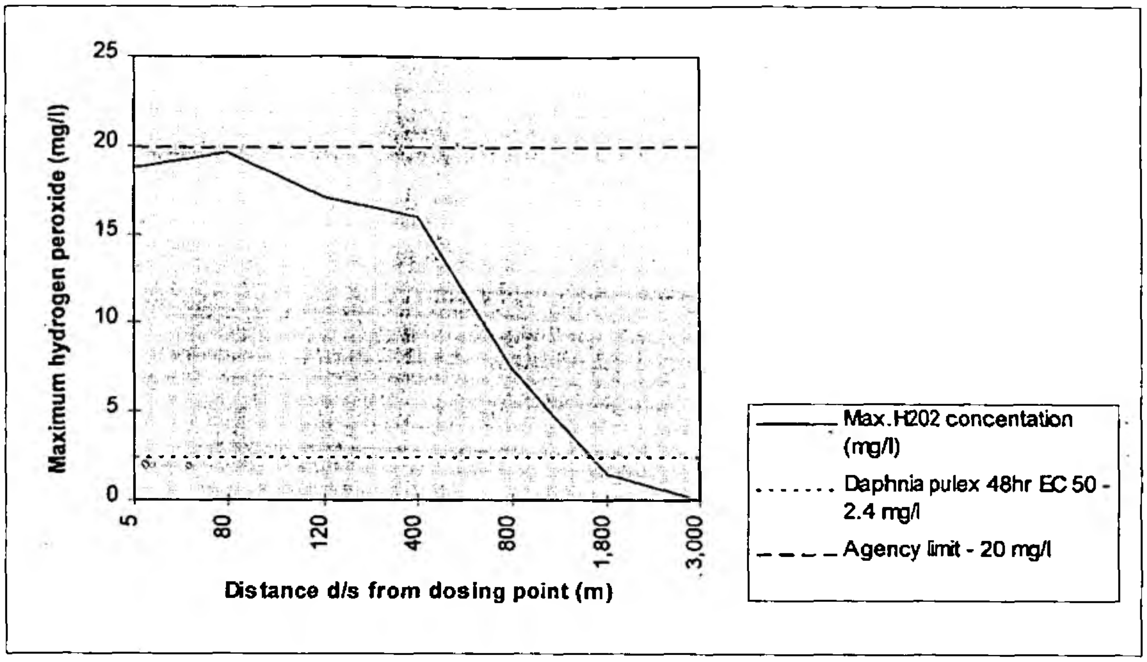
Residual hydrogen peroxide

Measurements of residual hydrogen peroxide concentration were made at various locations downstream of the dosing site as the pulse of treated river water from the first hydrogen peroxide dosing operation moved down river. Detailed results of the monitoring are shown in Appendix 7, with a summary of the results shown in Table 12 and presented graphically in Figure 12.

Table 12: Maximum recorded hydrogen peroxide at various locations downstream of dosing site.

Location	Distance downstream of dosing site (metres)	Maximum recorded hydrogen peroxide concentration (mg/l)
5 metres d/s dosing site	5	19.2
80 metres d/s dosing site	80	19.6
120 metres d/s dosing site	120	17.1
Kinnersley Manor	400	16.0
Footbridge d/s Kinnersley Manor	800	7.4
Sidlow Bridge	1,800	1.5
Bures Manor	3,000	>0.1

Figure 12: **Maximum recorded hydrogen peroxide concentration at various distances downstream of the dosing point**



Inspection of the results in Table 12 and Figure 12, reveals that the maximum concentration of hydrogen peroxide occurred 80 metres downstream of the dosing point, but concentrations fell as the pulse moved down river. Maximum concentrations had dropped to below 2 mg/l by the time the pulse had reached Sidlow Bridge approximately 12 hours after dosing.

pH

No detectable effect on river was observed after dosing with hydrogen peroxide solution. However, significant increases in pH were observed at all points after direct dosing with PCS as summarised in Table 13.

Table 13: **pH at various locations downstream of dosing site after PCS dosing.**

Location	Distance downstream of dosing site (metres)	Maximum recorded pH
u/s dosing site	-	7.3
80 metres d/s dosing site	80	8.9
Kinnersley Manor	400	8.4
Footbridge d/s Kinnersley Manor	800	8.1
Sidlow Bridge	1,800	

Inspection of results in Table 13 shows that an increase of pH from 7.3 to 8.9 was observed at the point 80 metres downstream of the dosing site after direct dosing with PCS but that pH dropped steadily as the plume moved downstream.

A small increase in pH to 7.7 was observed after PCS contained in hessian bags were first placed in the river but levels quickly fell to approximately 0.2 above background which is not considered to be significant.

3.3 DISCUSSION

3.3.1 HYDROGEN PEROXIDE

The various trials have demonstrated that it is possible to add hydrogen peroxide to the river safely under operational circumstances. Significant increases in dissolved oxygen were observed to occur almost instantaneously, thereby providing a ready source of oxygen in pollution incident situations.

Of the techniques employed during the survey, the most attractive appears to be the venturi-based hydrogen peroxide dosing system developed by South West Region. The system appears to have a number of possible benefits over other methods, including:

- Fine control of dosing rate can be achieved by adjustment of the pump speed and dosing control tap. Control of dosing rate is difficult when using gravity feed techniques because the rate tends to decrease as the drum empties.
- Good levels of dispersion of hydrogen peroxide in the receiving watercourse is achieved without the need for additional agitation. This is especially important in slow flowing rivers or ponds. Direct dosing from drums might often require additional agitation in slow flowing streams.
- The system is easily portable in the back of a small estate car and is not excessively heavy if it needs to be carried to the dosing site It can be used in difficult situations where direct access to the river is impossible, for example where there are steep banks. The jet of water from the dosing system can be easily adjusted to direct the flow to the centre of the river or to avoid excessive plant growth close to the bank. Unless there is a suitable bridge available from which to add the hydrogen peroxide, direct dosing from drums will often require access to the river to install the delivery pipe in a suitable location.
- The venturi system draws hydrogen peroxide direct from drums standing on the ground in an upright position . Potentially hazardous operations which might occur during tipping drums on their side or lifting onto platforms is therefore minimised. A risk exists that spillages of hydrogen peroxide could occur during direct dosing from the drum, if either the delivery hose or drum tap were to become dislodged.
- Once set-up the venturi system requires very little attention, releasing staff for other duties within the immediate vicinity of the dosing site.

There are however a number of possible disadvantages associated with the venturi system, which although are not considered to be serious, nevertheless should be recognised, including:

- One potential disadvantage, is that the system relies on the mechanical reliability of the pump and possible difficulties in priming the unit if it is required to draw water from an excessively high head. The equipment needed to revert from the venturi system to a gravity dosing system is minimal and therefore if there are problems with the pumping operation, gravity dosing could always be used as a fall-back option.
- Another potential disadvantage is that extreme caution should be observed during refuelling operations in the presence of hydrogen peroxide because of the fire hazard associated with the use of petrol.
- Although reasonably quiet, there may be occasions when noise levels may become obtrusive if operated for long periods during unsocial hours in residential neighbourhoods. In these cases it may be necessary to revert to gravity dosing techniques.

Experience of using the 1 m^3 IBC containers has demonstrated that they can be somewhat difficult to handle. They require the use of a rough terrain fork-lift truck to manoeuvre them into position and it has been found difficult to accurately control dosing rate. Consequently it is felt that their use would more likely be restricted to situations were large quantities of hydrogen peroxide are required at convenient secure installations, rather than to deal with pollution incidents at remote locations. However, North East Region of the Environment Agency have purchased a trailer for transporting the containers and have sent some of their personnel on a Hazchem training course.

3.3.2 PCS

PCS is significantly more expensive in terms of oxygen yield per unit cost than other forms of hydrogen peroxide. Hydrogen peroxide solutions are therefore likely to represent a more cost effective means of dosing in the majority of situations. There are however certain advantages associated with the use of PCS which may outweigh the cost disadvantage in certain situations, including:

- PCS can be stored for extended periods at strategic locations close to known problem areas, and can therefore be deployed rapidly in response to an incident without the need to collect hydrogen peroxide solution from a central storage location.
- PCS can be added directly to the river without the need for additional equipment, provided there is adequate access to the river, for example, a convenient bridge.
- Trials of PCS in hessian sacks placed on the river bed, suggest that the material decomposes slowly resulting in a continuous supply of oxygen to the river over an extended period. This could be particularly advantageous to deal with long term

incidents. PCS could be placed at several strategic locations of affected river to achieve coverage of longer stretches of river than might be effectively treated from a single dosing point.

- When PCS decomposes in the river, an increase in pH occurs which could result in an increase in the concentration of unionised ammonia. Therefore care would need to taken to ensure that aquatic toxicity does not result as a consequence of elevated unionised ammonia concentrations.
- One potential disadvantage of PCS over other hydrogen peroxide dosing techniques is the relatively high staff resource requirement. In order to achieve a steady rate of dosing it is necessary for personnel to be continuously employed to empty the sacks into the river at a controlled rate. Therefore sufficient personnel dedicated to this task must be available throughout the dosing period which could prove onerous in many situations.

3.3.3 COSTS

The trials have demonstrated that for a river of a similar magnitude and with comparable flow characteristics to the River Mole, a dosing rate of approximately 4 drums of 35% hydrogen peroxide solution or 6 bags of PCS per hour would be able to increase dissolved oxygen levels by approximately 10%, which would provide suitable conditions to prevent widespread fish mortalities. Continuous dosing would be required to maintain dissolved oxygen levels at a satisfactory level. Dosing for a 12 hour period at this rate would cost £960 for hydrogen peroxide solution and £1,440 for PCS.

3.3.4 AQUATIC TOXICITY

From the available aquatic toxicology data, the most sensitive species is *Daphnia pulex*, with a 48hr LC50 of 2.4 mg/l. At a dosing rate of approximately 120 kg per hour in the River Mole, the maximum concentration of residual hydrogen peroxide in the river reached 19.6 mg/l. Concentrations dropped as the time and distance from the dosing point increased, falling to less than 2 mg/l, approximately 2 kilometres (12 hours) after dosing. Bearing in mind that hydrogen peroxide would only be used in emergency situations when serious damage to river organisms would have been likely to have occurred anyway, any small additional effect as a result of dosing is unlikely to be significant.

3.3.5 HEALTH & SAFETY

Appropriate health & Safety were employed throughout the trial. Hydrogen peroxide containers were stored on plastic sheet to prevent any spillages reaching dry grass and possibly causing a potential fire hazard as shown in Plate 8. The area was cordoned off to prevent unauthorised access. All personnel handling hydrogen peroxide wore gloves, overalls and eye protection. Eye wash bottles were kept in the immediate vicinity of the hydrogen peroxide dosing area and a large aspirator of water was provided for drenching.

All dosing operations were carried out without incident and it was concluded that provided basic Health & safety precautions were followed, hydrogen peroxide could be used safely in remote locations for the amelioration of river pollution.

3.4 TRIALS IN OTHER REGIONS

3.4.1 SOUTH WEST REGION

Hydrogen peroxide was used to restore dissolved oxygen levels in the River Tamar after an incident in which approximately 25,000 gallons (113 m^3) of stored farmyard slurry was accidentally released into the river on 19 June 1991. Following the use of hydrogen peroxide to boost dissolved oxygen levels, an investigation was undertaken to assess the impact of the operation on the macroinvertebrate community.(42)

Two survey sites were identified, one upstream and one downstream of the hydrogen peroxide dosing point. The investigation found that there were differences in invertebrate distributions between the two sites, with eight invertebrate families present in the upstream site but absent in the downstream site. Seven of these families, however, were present in low statistically non-significant numbers and therefore their absence could not be attributed solely to the effects of hydrogen peroxide without further investigation. However, the caseless caddis larvae *Hydropsyche siltalai*, which was present in large numbers (52) was totally absent at the downstream site, suggesting that there may have been some impact as a result of hydrogen peroxide dosing. The investigation considered that it may have been possible that the hydrogen peroxide had oxidised the food nets, removing the animal's protection from the current, and thereby increasing their acceptability to drift. However, the report concluded that the operation was likely to have minimal ecological impact on the ecosystem as lost invertebrates would have been rapidly replaced by the process of invertebrate drift from upstream.

South West Region have used hydrogen peroxide on numerous other occasions, and thus have built up a wealth of practical experience. Various invertebrate studies carried out on these occasions have shown no detrimental effects from its use and hydrogen peroxide has therefore been proposed as a method preferable to other techniques for the following reasons;

- It is portable and can be deployed in any location
- It can increase dissolved oxygen from zero to 100% saturation almost instantaneously
- It can be added without noise

There have been occasions however, when hydrogen peroxide has not increased dissolved oxygen, for example in ponds with a summer dissolved oxygen problem, where there is a limited amount of suspended solid matter. Even when hydrogen peroxide has not decomposed, its addition has been found to be beneficial, presumably because it was dissociating on the gills of the fish. In some cases, distressed fish had been observed swimming towards the source of hydrogen peroxide addition.

Operational experience within the Region has led to the development of a venturi system based on a portable, petrol engined, two inch centrifugal pump. The advantage of this method over manual addition is considered to be the ability to control the dosing rate more accurately and also to provide better dispersion of the hydrogen peroxide in the river.

3.4.2 WELSH REGION

Extensive fish mortalities occurred in the lower reaches of the River Loughor, downstream of Garnswlt STW during July 1995, primarily as a result of low dissolved oxygen levels. The low dissolved oxygen was attributed to a high biomass of algae downstream of the works. A series of remedial actions were proposed to protect remaining fish stocks, including direct aeration of the river and dosing of Garnswlt STW final effluent with hydrogen peroxide. A report detailing the results of the remediation actions taken, drew a number of conclusions from the operation.(43)

Direct aeration of the river, using aerators, was not successful in maintaining levels above the EC freshwater Fish Directive of 5 mg/l for migratory salmonids. The aerators were able to reduce the extent of the sags and their duration in the immediate vicinity of the aerators but were incapable of extending the effect downstream.

Approximately 1 tonne of hydrogen peroxide was introduced into the final effluent between 18.00 and 07.30 at a rate of 90 litres/hour. Dosing on subsequent occasions was carried out at a reduced rate of 17 litres/hour.

Hydrogen peroxide dosing of the final effluent was successful in maintaining dissolved oxygen levels well above the 5 mg/l level during the treatment period for a distance of at least 600 metres. However, dissolved oxygen levels dropped to 3.55 mg/l within 2 hours of cessation of dosing. No appreciable elevation of dissolved oxygen was detected at monitoring sites 2.3 and 3.1 kilometres downstream. The report indicated that there were concerns about increasing the dosing rate in view of possible further damage to the fish population, although it does not appear that any measurements of residual hydrogen peroxide concentrations were made to determine whether this was a likely possibility. The report does not provide any information to suggest that an assessment of aquatic toxicity had been undertaken.

3.4.3 MIDLANDS REGION

Extensive fish mortalities occurred in the River Tame during the summer months of 1995 as a result of contaminated run-off following localised thunderstorms over the Birmingham area. A trial was therefore conducted in March 1996 to assess whether hydrogen peroxide would be suitable to prevent further mortalities in the future.[(44)] The trial utilised direct dosing of 5 tonnes of hydrogen peroxide from 1 tonne IBC containers to 3 points in the vicinity of the Lea Marston treatment lake facility on the River Tame. The dosing rate used was 1 tonne in 8 minutes (approximately 7.5 tonnes per hour). Extensive Health & Safety precautions were employed, including the preparation of a safe system of work and construction of containment bunds using plastic sheeting.

The trial demonstrated that dissolved oxygen levels were increased from 75% to 86% at Kingsbury (1 kilometre downstream of the dosing site); from 62% to 66& at Hopwas (18 kilometres downstream) and from 57% to 59% at Alrewas (32 kilometres downstream). The duration of the elevated dissolved oxygen level was approximately 3 hours. No assessment of residual hydrogen peroxide or aquatic toxicology was made.

The investigation concluded that 45 tonnes of hydrogen peroxide would be required to oxygenate the River Tame and suggested that further trials should be undertaken to further investigate the optimum dosing interval and rate. It also recommended that further consideration should be given to the provision of alternative valves on the storage tanks to enable more accurate control of the dosing rate.

3.4.4 NORTH EAST REGION

A trial was undertaken in July 1996, to investigate the use of hydrogen peroxide to counteract the effects of low dissolved oxygen in the River Browney downstream of Lanchester STW.[(45)] Dissolved oxygen levels in the river 1.2 kilometres downstream were increased from approximately 100% saturation to over 700% saturation. No information was provided concerning the amount or dosing rate of hydrogen peroxide used in this trial. Consequently, apart from the obvious large increase in river dissolved oxygen levels which was observed, it is difficult to make any further detailed assessment of this trial.

3.4.5 CLYDE RIVER PURIFICATION BOARD

A detailed investigation of the effects on plankton, of hydrogen peroxide used to treat sea lice at salmon farms in the Kyles of Bute and Loch Riddon, has been carried out by the Clyde River Purification Board in 1993.[(28)]

A total of 28 tonnes of hydrogen peroxide was used during three applications to achieve concentrations within the fish tanks of 1,500 mg/l. The study concluded that impacts observed to the plankton were limited to the immediate vicinity of hydrogen peroxide release, both temporally and spatially. Also that hydrogen peroxide in coastal seawater dispersed rapidly on release, giving negligible quantities in only a short time.

4.0 CONCLUSIONS

Numerous trials conducted by Thames Region and other regions of the Environment Agency and the former National Rivers Authority, have demonstrated that hydrogen peroxide is an effective, reliable and safe method of increasing dissolved oxygen in rivers suffering from the effects of polluting discharges, without any apparent adverse effects. Hydrogen peroxide as an aqueous solution of either 35 or 50 % strength is the most appropriate method of dealing with the majority of situations, although the solid material PCS can have disadvantages in certain applications.

The trials have demonstrated that hydrogen peroxide can be used to deal effectively with the effects of storm sewage discharges to the Tidal Thames as well as the effects of pollution incidents in freshwater rivers and streams.

4.1 STORM SEWAGE DISCHARGES TO THE TIDAL THAMES

The trials carried out by Thames Region to investigate the potential of hydrogen peroxide to counteract the effects of storm sewage discharges to the Tidal Thames have demonstrated that the 20 tonne capacity storage and dosing system located at Kew STW is of sufficient capacity and at a suitable location to provide extra protection for the river. This system should be viewed as a valuable supplement to the protection afforded by the mobile oxygenation vessel, the Thames Bubbler which is currently used as the primary means of preventing extensive fish mortalities following intense summer storms which occur several times each year.

The nature of hydrogen peroxide dosing means that it is possible to make almost instantaneous decisions concerning the need to dose, which means that is possible to delay dosing or mobilisation of the Thames Bubbler until sufficient information is available to be able to accurately assess the potential for the development of conditions likely to result in fish mortalities following major storms. This is likely to result in significant cost savings due to a reduction in unnecessary Thames Bubbler mobilisations or dosing operations.

Hydrogen peroxide dosing acts as a valuable additional source of dissolved oxygen to the river, especially in the upper reaches of the river in the Putney to Kew area, where restraints to navigation can result in severe restrictions to the effective oxygenation capacity of the Thames Bubbler, which can reduce its oxygenation capacity from a theoretical maximum of 30 tonnes oxygen per day to approximately 11 tonnes per day under extreme conditions. This reduction in oxygenation potential could result in insufficient protection of the river during the most serious events. Under these conditions, supplementary oxygen addition capability could prove invaluable.

Hydrogen peroxide dosing represents an alternative source of dissolved oxygen for the river, in the event of unavailability of the Thames Bubbler, due to mechanical failure or other incident, which due to the inherent reliability concerns associated with a complex piece of mechanical plant, must be considered to be a real possibility. The hydrogen peroxide dosing system is relatively simple with few mechanical components which could fail. Operational experience gained from the existing prototype system at Kew has demonstrated that the mobilisation and operational procedures are straightforward, effective and reliable, thereby minimising the possibility of unavailability due to system malfunction or operational failure.

The hydrogen peroxide dosing system enables oxygen to be supplied precisely into the part of the river which needs it most. The addition of 7 tonnes of 50% hydrogen peroxide from Kew STW has been shown to increase river dissolved oxygen by approximately 7%, which could represent a significant increase during post storm conditions.

The cost of one 7 tonne addition of hydrogen peroxide is approximately £2,800 which compares favourably with operating costs for the Thames Bubbler of approximately £3,300 per day. In addition, the capital costs of hydrogen peroxide dosing systems are considerably less than those associated with mobile oxygenation systems. The existing Thames Bubbler was acquired in 1989 at a cost of approximately £3.5 million and a second similar unit is currently under construction at an estimated budget cost of approximately £6 million. These costs can be compared with an estimated budget cost of £100,000 for the construction of a hydrogen peroxide dosing facility on a site owned and operated by Thames Water plc.

If necessary, it would be possible to introduce a maximum of 28 tonnes of hydrogen peroxide over a 24 hour period, to the affected section of river, at a cost of £11,400. This amount of hydrogen peroxide has a maximum theoretical oxygen capacity of 6.4 tonnes which although less than that achieved by the Thames Bubbler, nonetheless has a beneficial impact on the river, when viewed in the context of the 11 tonnes per day oxygenation capacity likely to be achievable by the Thames Bubbler under unfavourable conditions.

Hydrogen peroxide is of low toxicity to aquatic organisms, with *Daphnia pulex* being the most sensitive species with an LC 50 of 2.4 mg/l. Measurements of residual hydrogen peroxide in the river during and after dosing have demonstrated that concentrations attain a maximum of less than 20 mg/l in the immediate vicinity of the outfall but fall rapidly to below 2.0 mg/l two hours after dosing is stopped. In view of the short duration and limited extent of residual hydrogen peroxide concentrations greater than 2.0 mg/l, it seems unlikely that there will be any significant effect on aquatic organisms. Furthermore, the clinical use of hydrogen peroxide solutions of up to 3% (30,000 mg/l) as mouth washes and eye rinses without adverse effect, suggest that it is highly improbable that any serious injury could occur in the unlikely event that a member of the public were to become immersed in the hydrogen peroxide plume, even in the immediate vicinity of the outfall.

Surveys carried out to assess the effect of hydrogen peroxide dosing on macroinvertebrate and algal populations have not demonstrated any definite adverse effect, although it may be

Surveys carried out to assess the effect of hydrogen peroxide dosing on macroinvertebrate and algal populations have not demonstrated any definite adverse effect, although it may be advisable to carry out further investigations to confirm this. Consideration should be given to carrying out additional surveys, including: surveys of algae during the spring diatom bloom, additional macroinvertebrate foreshore surveys and direct toxicity assessments.

No detectable changes in the nature or composition of the final effluent at Kew STW have been found by GC/MS analysis of samples taken before and after hydrogen peroxide dosing.

A second potential hydrogen peroxide dosing site has been identified at Hammersmith, which would extend the area of the river which could be protected and also increases the amount of hydrogen peroxide which could be added. Mains water from the Thames Water, London Ring Main or groundwater from the underlying chalk aquifer have been identified as suitable carriers to enable the hydrogen peroxide to be introduced into the river.

4.2 POLLUTION INCIDENTS IN FRESHWATER RIVERS

Trials conducted by Thames Region and several other regions have demonstrated that hydrogen peroxide is a safe and convenient method of increasing dissolved oxygen levels in rivers and streams following pollution incidents. The equipment and materials needed are readily available and easily transportable to remote locations.

Extensive trials in the River Mole have demonstrated that river dissolved oxygen levels can be increased by approximately 10% by dosing at a rate of 120 kg/hour. The effect on dissolved oxygen levels is almost instantaneous and the effects could be observed at monitoring points nearly 2 kilometres downstream of the dosing point.

Direct dosing of 35% hydrogen peroxide solution from 30 kg drums using a plastic pipe to direct the hydrogen peroxide to the desired point in the river can be easily employed without the need for additional equipment. However, a venturi dosing system developed by ~~South West Region~~ Launceston Nerve Centre Patent Pending is thought to provide additional benefits over the manual dosing method, in terms of ease of application and provision of turbulent conditions to aid dispersion in the river.

PCS which is a solid form of hydrogen peroxide, although more costly than hydrogen peroxide solutions, has several advantages which make its use desirable in certain situations. It can be stored almost indefinitely at relatively remote locations and can be carried in private cars or vans, making it particularly valuable when dealing with incidents out of hours at remote locations.

Hydrogen peroxide is of low toxicity to aquatic organisms. Surveys carried out after dosing operations in both Thames and South West Regions have not detected any significant adverse effects on macroinvertebrate communities. Measurements of residual hydrogen peroxide in the River Mole have demonstrated that at a dosing rate of approximately 120 kg/hour, concentrations did not exceed 20 mg/l immediately downstream of the dosing site river affected and relatively short duration of elevated hydrogen peroxide concentrations, it seems unlikely that any significant adverse effect would be experienced by aquatic organisms. Furthermore, it must be remembered that any aquatic organisms would already be likely to be seriously affected by the effects of pollution for which hydrogen peroxide dosing had been employed.

Hydrogen peroxide contains stabilisers in small (or trace) quantities to reduce decomposition during storage. According to Solvay Interox Limited, the stabilisers used in material supplied to Thames Region are phosphate based. Solvay Interox Limited have also confirmed that they are not aware, nor can they envisage, the presence of any Red List chemicals in the product at any significant concentration.

Hydrogen peroxide is a strong oxidising agent and improper storage, application or handling could create hazardous conditions and will cause burns if it comes into contact with the skin and eyes. However, the trials have demonstrated that hydrogen peroxide can be used without incident at remote locations, provided basic Health & Safety precautions are employed, for example, the use of protective clothing, including: gloves, face mask. Drums of hydrogen peroxide must not be carried in cars or vans, and only six 30 kg drums can be carried at any one time in a trailer.

REFERENCES

1 Peroxygens in water disinfection. Fraser J.A.L., and Shacklady R.J. Presented at SCI Disinfection of Water Conference. 1992.

2 The role of hydrogen peroxide in natural aquatic media. Shtamm E.V., Purmal' A.P. and Skurlatov Y.I. Russian Chemical Reviews, 60 (11), 1228-1248, 1991.

3 Joint assessment of commodity chemicals No. 22. Hydrogen peroxide. CAS No. 7722-84-1. ECETOC. January 1993

4 Southend on Sea ecological survey, an assessment of the environmental impact of 'Oxymaster' - disinfected sewage effluent on subtidal marine benthos. Joslin P.A. and Gould D.J. Acer Environmental Report MAN 8500 002R, May 1991

5 Efficacy and environmental effects of peracetic acid as a sewage disinfectant. Consultants in Environmental science. NRA Project Report 231/B. December 1991.

6 Environmental Data, 35% hydrogen peroxide (Specification 411). Solvay Interox. REV. 3. 9/1995.

7 Wasserstoffperoxid gegen Fischsterben in der Lippe. Spering F. Wasser / Abwasser. 129 (9), 587-591, 1988.

8 Tip leachate treatment using hydrogen peroxide. Fraser J.A.L. and Sims A.F.E. Proc I.W.P.C. Conf. September 1982.

9 Operational experience using H_2O_2 in landfill leachate treatment. Fraser J.A.L and Tytler N.B. Effluent and water Treatment Journal. April 1983.

10 Municipal wastewater sulfide control with H_2O_2. Interox Case History, 1990.

11 Mechanical aeration versus hydrogen peroxide in stabilization pond treatment. Iwugo K.O. Effluent and Water Treatment Journal, January 1981.

12 Bio-oxygen stabilisation using hydrogen peroxide. Chin C., Hicks G. and Geisler C.A. J.W.P.C.F., 45 (2), 283-291, 1973.

13 Wastewater hydrogen peroxide treatment shows multiple benefits. Anon. Public Works, February 1979.

14 Hydrogen peroxide as a supplemental oxygen source. Cole C.A., Ochs L.D. and Funnel F.C. J.W.P.C.F., 46 (11), 2579-2592, 1974.

15 Hydrogen peroxide for waste water treatment. Kibbel W.H. Public Woks, January 1976.

16 Hydrogen peroxide as an algicide in sewage lagoons. Ouzts J.C., Ouzts J.D. and Quimby P.C. J. of Mississippi Academy of Sciences. 34, 39-43, 1989.

17 Preliminary investigation of hydrogen peroxide as a potential herbicide for aquatic weeds. Quimby P.C. J. Aquatic Plant Management, 19, 53-55, 1981.

18 Photo-enhancement of hydrogen peroxide toxicity to submerged vascular plants and algae. Kay S.H., Quimby P.C. and Ouzts J.D. J. Aquat. Plant Management, 22, 25-34, 1984.

19 Preliminary studies on the potential of hydrogen peroxide as an algicide on filametous species. 7th Symposium on Aquatic Weeds, 1986.

20 Hydrogen peroxide as a potential algicide for Oscillatoria Rubescens D.C. Barroin G. and Feuillade M. Water Research, 20 (5), 619-623, 1986

21 Biological consequences of treating a lake with hydrogen peroxide on the plankton biocenosis. Balvay G. Water Research, 15, 691-696, 1981.

22 Control of Coontail with hydrogen peroxide and copper. Kay S.H., Quimby P.C. and Ouzts J.D. J. Aquatic Plant management, 21, 38-40, 1983.

23 Susceptibility of Aedes Aegypt to various levels of hydrogen peroxide. Kay S.H., Quimby P.C. and Ouzts J.D. Mosquito News, June 1991.

24 Biotreatment techniques get chemical help. Elizardo K. Pollution Engineering, November 1993.

25 Groundwater Treatment with zero air emissions. Cheuvront D.A., Giggy C.L., Loven C.G. and Swett G.H. Proc of Petroleum Hydrocarbons and Organic Chemicals in Groundwater Conference, Houston, Texas, November 1988.

26 Hydrogen peroxide for physiochemical degrading petroleum contaminated soils. Watts R.J. Remediation, Autumn 1992.

27 Use of hydrogen peroxide as an oxygen source for in situ biodegredation. Aggarwall et al. J. of Hazardous Materials, 27, 301-314, 1991.

28 A summary of chemistry and plankton studies on the waters surrounding the Kyles of Bute and Loch Riddon salmon farms, during sea lice treatments with hydrogen peroxide. Ross D.J. Clyde River Purification Board. Technical Report. August 1993.

29 Joint assessment of commodity chemicals No. 22. Hydrogen peroxide. CAS No. 7722-84-1. ECETOC. January 1993

30 Hydrogen peroxide, Aquatic toxicity. Ecotoxicity & Chemistry Section. Environment Agency, Thames Region. Technical Note. June 1995.

31 Scheme for remedying the effects of storm sewage discharges to the Tidal Thames. Wood L.B., Borrows P.F., Whiteland. M.R. Progress in Water Technology 12(3), 93-107, 1980.

32 Recent developments in oxygenation of the Tidal Thames, Lloyd P.J., Whiteland M.R. J. Inst. of Water and Environmental Management. 3, 1990.

33 Dosing of Slough STW final effluent with sodium carbonate peroxyhydrate (PCS) on Monday 27th February 1995. Goldie A.R. NRA, Thames Region. Technical Report. March 1995.

34 The addition of hydrogen peroxide to Mogden STW final effluent 14 September 1994. Goldie A.R. NRA, Thames Region. Technical Report. October 1994.

35 Dosing of Kew STW final effluent with hydrogen peroxide (50%) on Thursday the 18th July 1995. Goldie A.R. NRA, Thames Region. Technical Report. November 1995.

36 Dosing of Kew STW final effluent with hydrogen peroxide (50%) on Wednesday 11th October 1995. Goldie A.R. NRA, Thames Region. Technical Report. January 1996.

37 An assessment of the Thames Estuary macroinvertebrate and algal communities with reference to hydrogen peroxide dosing from Kew STW. Dale C. Environment Agency, Thames Region. Technical Note. October 1996.

38 Aquatic toxicity of hydrogen peroxide. Wilkinson H. Environment Agency, Thames Region. Internal Memorandum, ETAS/ENQ. May 1996.

39 River Mole hydrogen peroxide dosing on 20-21/6/96. Goldie A.R. Environment Agency, Thames Region. Technical Note. July 1996.

40 Dosing of the River Mole on the 21-22 July 1996. Goldie A.R. Environment Agency, Thames Region. Technical Note. August 1996.

41 Mole at Horley STW, Biological Investigation. Tubb A. Environment Agency, Thames Region. Biology Laboratory Report, 03AT96.BLR. July 1996.

42 Report to assess the ecological impact of hydrogen peroxide, North Tamerton Bridge, 26 June 1991. Painter D. and Brown L., NRA South West Region. Technical Report. July 1991.

43 An investigation into the cause of fish mortalities during the summer of 1995, and assessment of the effectiveness of remedial activities undertaken. Jenkins M.J. and Evans D.M. NRA, Welsh Region. Technical Report PL/EAW/95/5a.

44 Hydrogen peroxide dosing trials, Lea Marston, 18 & 19 March 1996. Stone J. and Freakley D. Environment Agency, Midlands Region. Technical Report. April 1996.

45 River Browney contingency plan, hydrogen peroxide trial, Wednesday 5 June 1996. Brooker S., Environment Agency, North East Region. Technical Note. June 1996

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PLATES

Plate 1: Thames Bubbler

Plate 2: Hammersmith Bridge

Plate 3: Hydrogen peroxide dosing facility at Kew STW

Plate 4: Tornado turbo-aerators in the River Mole at Kinnersley Manor

Plate 5: Godiva fire pump for BOC 'Vitox' oxygenation system

Plate 6: 30 kg hydrogen peroxide drums

Plate 7: Venturi based hydrogen peroxide dosing system

Plate 8: Hydrogen peroxide storage area

APPENDIX 1

Health & Safety Instructions and Risk Assessment for using Hydrogen Peroxide

HEALTH AND SAFETY INSTRUCTIONS FOR USING HYDROGEN PEROXIDE

1. Introduction

1.1 Liquid Hydrogen Peroxide and its powdered form Sodium Carbonate Peroxyhydrate is a powerful oxidising agent. When added to water it readily decomposes to produce water and oxygen. The latter is utilised by the Environment Agency to re-oxygenate water bodies.

1.2 The following health and safety guidance is produced to assist users comply with the safe use, handling, storage and transport of these products.

2. The Products

2.1 NAME: Hydrogen Peroxide 35%

SYNONYMS: Hydrogen Peroxide Solution

DESCRIPTION: Colourless liquid

CAS NO.: 7722-84-1

HAZARDS: Corrosive to skin, eyes and mucus membranes. Not combustible but will contribute to the combustion of other materials. May cause violent , sometimes explosive reactions.

FIRST AID:

- Inhalation - Remove from exposure, rest, keep warm and seek medical attention
- Skin - Drench with plenty of water. Remove contaminated clothing. If large areas of skin are damaged seek medical attention.
- Eyes - Irrigate thoroughly for at least 10 minutes. Obtain immediate medical attention.
- Ingestion - Wash out mouth with water, Do not induce vomiting. Seek medical attention.

MATERIALS TO AVOID: Acids, alkalies, metals, organic materials, flammable substances.

2.2	NAME	Sodium carbonate peroxyhydrate
	SYNONYMS:	PCS
	DESCRIPTION:	White, crystalline powder
	CAS NO.:	15630-89-4
	HAZARDS:	Irritating to mucus membranes, eyes and skin. Not combustible but will contribute to the combustion of other materials.
	FIRST AID:	As 2.1 above
	MATERIALS TO AVOID:	As 2.1 above

3. Storage

3.1 Hydrogen Peroxide

In a cool well ventilated place in original containers.
Away from combustible and flammable materials.
Away from materials to be avoided (section 2.1).
Away from PCS.
In storage vessels of aluminium, 304L or 316L stainless steel or HDPE.

3.2 PCS

In a cool dry area, protected from direct sunlight.
In original containers (paper and PE coating).
Away from combustible or flammable materials and heat sources.
Away from Hydrogen Peroxide.

4. Transport

4.1 Hydrogen Peroxide

On open backed vehicles, trailers or boats. In an upright position and restrained. Observe storage and materials to avoid requirements.
In enclosed vehicles with an airtight bulkhead between load and driver.

4.2 PCS

On open backed vehicles, trailers and boats. Packages to be restrained and protected from direct sunlight and rain. Sheeting may be required. In enclosed vehicles, packages must be restrained. Observe storage and materials to avoid requirements.

4.3 LOAD AND PACKAGE SIZES

The total load carried on or in any vehicle or vehicle/trailer combination must not exceed 500kg or litres. No individual package size must exceed 200kg or litres.

4.4 FIRE EXTINGUISHERS

Fire extinguishers for tackling vehicle/boat fires must be provided.

5. Personal Protective Equipment

5.1 Hand - PVC gloves

Eyes - Chemical resistant anti dust goggles (BS2092-1 (or 2) CD)

Skin - Overalls and gloves, preferably of PVC

Suggest disposable overall Microguard 3000 coverall or Microguard 3000 jacket and trousers. ARCO Catalogue P170.

Respiratory - Type 3M 8715 disposable dust/fume respirator. ARCO Catalogue P72.

5.2 Kits containing gloves, goggles and respiratory equipment must be available and dedicated for hydrogen peroxide and PCS use. These kits will also contain other equipment such as hoses, connectors, signs, labels etc.

6. Additional Safety Equipment

6.1 Where hydrogen peroxide or PCS is stored, transported and used at least 3 x 300ml saline eye wash bottles must be provided and readily accessible.

6.2 Where hydrogen peroxide is stored in bulk containers an emergency shower facility must be provided in addition to saline eye wash bottles.

6.3 Where saline and emergency showers are provided, adequate arrangements must be in place to prevent "freezing" during cold weather.

6.4 At all locations where hydrogen peroxide or PCS is stored, used or transported a first aid kit must be available in addition to the saline eye wash. Site use of hydrogen peroxide and PCS will require all persons to have attended an emergency aid or Appointed Persons course.

7. Site Use

7.1 Procedures for site use will seek to prevent spillage, splashing or dust emission from the use of hydrogen peroxide or PCS. Personal protective equipment will be used at all times, as detailed in section 5.

7.2 The site use of hydrogen peroxide or PCS is not suitable for lone worker categorisation.

7.3 Adequate arrangements must be made to use and store hydrogen peroxide, PCS and ancillary equipment in a way which limits the risk to other employees and members of the public. Barriers and warning signs will be in place on site and in storage areas.

7.4 All pumping plant, hoses, venturis etc. will be thoroughly flushed through with water to remove all traces of hydrogen peroxide prior to leaving site.

7.5 Do not return partially empty containers to base. Use the contents of a container once opened.

7.6 Empty packages are a source of hazard until they have been effectively cleaned. They must be handled and stored accordingly. Rinse PCS sacks prior to disposal but **DO NOT** rinse hydrogen peroxide containers, as these will be returned to the supplier for cleaning.

7.7 The site must not be left unattended during use of hydrogen peroxide or PCS.

8. Safety Signs

8.1 The following safety signs will be displayed. All sign references refer to Network Signs or Stock Signs catalogues.

8.2 On site and in storage

NO SMOKING OR NAKED LIGHTS	White on red with pictogram (Ref 2 1017 KD)
ORGANIC PEROXIDE	Black on yellow/white with pictogram (Ref 1 1707 MK)

8.3 On site

CAUTION DO NOT ENTER	Barrier tape 75mm x 250m Black on yellow (Ref 66230)

ENVIRONMENT AGENCY DO NOT ENTER THIS AREA IN AN EMERGENCY CONTACT: 0800-807060 OR 0181-3105500	Bespoke sign, ideally white on blue, but may be designed and encapsulated in house.
ENVIRONMENT AGENCY SAFETY GOGGLES, GLOVES AND OVERALLS MUST BE WORN IN THIS AREA AT ALL TIMES	Bespoke sign, ideally white on blue, but may be designed and encapsulated in house.

9. SMOKING

9.1 At all times during use, storage, handling and transport, strict **NO SMOKING** requirements will apply.

RISK ASSESSMENT

The Use of Hydrogen Peroxide to Re-Oxygenate Water Bodies

Liquid hydrogen peroxide and its powdered form (sodium carbonate peroxyhydrate) is a powerful oxidising agent. When added to water it readily decomposes to produce water and oxygen. The latter is used by the Environment Agency to re-oxygenate water bodies. It requires care during use, handling, transport and storage. The risk assessment should be read in conjunction with the written safe systems of work and the suppliers Health and Safety Data Sheet.

HAZARD	CONTROL MEASURES	FURTHER INFO.
1. Lack of information, instruction, training and supervision.	All those using, storing or transporting the substances must be in possession of the written Regional Safe System of Work, the suppliers H & S Data sheets and the Risk Assessment All those currently using, storing or transporting the substances must attend an awareness training session or be under the control and direct supervision of a person who has attended an awareness training session.	
2. Personal injury or ill health through exposure to the substances.	Use the personal protective equipment specified in the Safe System of Work, which includes protection for the body, hands, eyes, feet and respiratory system.	
3. Dangers to the public from site use of the substances.	Follow the written instructions in the Safe System of Work. Controls will involve suitable site location to avoid public access (where possible). Supervision of site. Barriers and signs.	

4. Hazards of storage.	Storage will be in accordance with the Safe System of Work and manufacturers H & S Data Sheets. Storage areas will be adequately signed, secure and under the control of a competent person. Adequate PPE will be provided or available to those needing to access storage areas or loading /unloading the substances. Steps must be taken to ensure non contamination of other goods in storage, particularly from the granular form. Storage areas will be organised so as to avoid physical damage to the packages and the presence of non compatible substances.	
5. Hazards of transportation.	Vehicles used for transportation will ensure the adequate level of separation between load and driver. Drivers will have attended an awareness session. During transport no smoking will be allowed. Appropriate documents including the Safe System of Work, H & S data Sheets, Risk Assessment will be carried by the driver	

6. Contaminated from other plant and equipment used in the dosing process. 7. Contamination from packaging.	All plant and equipment used in the closing process (eg. pumps, pipework, hoses etc) shall be adequately flushed through or otherwise decontaminated prior to transport and/or storage. For the purposes of H & S, empty packages will be treated as full. Plastic drums <u>will not</u> be cleaned or flushed out but returned to storage with the caps in place. The outside of the drum may be flushed with water. Empty drums will be returned to the supplier. Sacks will be emptied of all residue and rinsed out. They must be transported back to the storage location where they will be disposed of in accordance with the Safe System of Work. No packaging of any description will be burnt.	

APPENDIX 2

Material Safety Data Sheet - Hydrogen Peroxide

SOLVAY

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HYDROGEN PEROXIDE (20 % <= Conc. < 60 %)

Material Safety Data Sheet
Date prepared 27.03.1995

References: FDS/S0584/P161/GB00010/12.04.1995/GB/en

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Identification of the substance or the preparation

Product name

- HYDROGEN PEROXIDE (20 % <= Conc. < 60 %)

  Formula: H_2O_2
  Molecular Weight: 34.02
  CAS Number: 7722-84-1
  EEC Number: 008-003-00-9
  EINECS Number: 231-765-0

2. COMPOSITION/INFORMATION ON INGREDIENTS

- Hydrogen peroxide
  Concentration : between 20 to 60 %
  CAS Number: 7722-84-1
  Symbols: O, C
  Phrases R: 8, 34

3. HAZARDS IDENTIFICATION

- Toxicity effects principally related to its corrosive properties.
- Non-combustible, but may contribute to the combustion of other substances and causes violent and sometimes explosive reactions.

4. FIRST-AID MEASURES

General recommendations

- Personal protective equipment for rescuers (see section 8).
- In case of product splashing into the eyes and face, treat eyes first.
- Do not dry soiled clothing near an open flame or incandescent heat source.
- Submerge soiled clothing in a basin of water.

Effects

General effects

- Corrosive to mucous membrane, eyes and skin.
- The seriousness of the lesions and the prognosis of intoxication depend directly on the concentration and duration of exposure.

Inhalation

- Slight nose and throat irritation.
- Cough.
- In case of repeated or prolonged exposure: risk of sore throat, nose bleeds, chronic bronchitis.
- Risk degree 2: moderate consequences in all circumstances - first aid sufficient - general precautions in all circumstances.

Eyes contact

- Severe eye irritation, watering, redness and swelling of the eyelids.
- Risk of serious or permanent eye lesions.
- Risk degree 4: serious consequences in all circumstances - medical assistance essential - special precautions in all cases

Skin contact

- Irritation and temporary whitening at contact area.
- Risk of burns.
- Risk degree 3: serious consequences under certain conditions - medical assistance necessary - systematic general precautions and specialist according to circumstances.

Ingestion

- Paleness and cyanosis of the face.
- Severe irritation, burns, perforation of the gastrointestinal tract accompanied by shock.
- Excessive fluid in the mouth and nose, with risk of suffocation.
- Risk of throat oedema and suffocation.
- Bloating of stomach, belching.
- Nausea and vomiting (bloody).
- Cough and difficulty breathing.
- Risk of chemical pneumonitis and pulmonary oedema.
- Risk degree 4: serious consequences in all circumstances - medical assistance essential - special precautions in all cases

First aid

Inhalation

- Remove the subject from the contaminated area.
- Consult with a physician in case of respiratory symptoms.

Eyes contact

- Flush eyes as soon as possible with running water for 15 minutes, while keeping the eyelids wide open.
- Consult with an ophthalmologist immediately in all cases.
- In the case of difficulty of opening the lids, administer an analgesic eye wash (oxybuprocaine).

Skin contact

- Remove shoes, socks and contaminated clothing, under the shower if necessary; wash the affected skin with running water.
- Avoid loss of body heat (cover), provide clean clothing.
- Consult with a physician in all cases.

Ingestion

General recommendations

- Consult with a physician immediately in all cases.
- Take to hospital.

If the subject is completely conscious:

- Rinse mouth and administer fresh water.
- Do not induce vomiting.

If the subject is unconscious:

- Loosen collar and tight clothing, lay the victim on his/her left side.
- Pulmonary resuscitation and administer oxygen if necessary.
- Keep warm (blanket).

Medical treatment

General recommendations

- None

Inhalation

- None

Eyes contact

- On the advice of the ophthalmologist.

Skin contact

- Usual treatment for burns.

Ingestion

- Oxygen therapy via intra-tracheal intubation.
- If necessary, tracheotomy.
- Placement of gastric catheter to release stomach gases.
- Avoid gastric washing (risk of perforation).
- In case of intense pain: inject an I.M. morphomimetic analgesic drug (piritramide) before taking to hospital.
- Prevention or treatment for shock and pulmonary oedema.
- Urgent digestive endoscopy with aspiration of the product.
- Treatment of gastrointestinal tract burns and resulting effects.

5. FIRE-FIGHTING MEASURES

Common extinguishing methods

- Large quantities of water, water spray.

Inappropriate extinguishing methods

- No restriction.

Specific hazards

- Oxidising agent, may cause spontaneous ignition with combustible materials.
- Oxygen released on exothermic decomposition may support combustion in case of surrounding fire.
- Contact with organic products may cause fires or fierce explosions.

Protective measures in case of intervention

- Evacuate all non-essential personnel.
- Wear self contained breathing apparatus when in close proximity or in confined spaces.
- When in close proximity or intervention wear acid resistant suit.
- Intervention only by capable personnel who are trained and aware of the hazards of the product.
- After intervention proceed to clean the equipment (take a shower, remove clothing carefully, clean and check).

Other precautions

- If safe to do so, remove the exposed containers, or cool with large quantities of water.
- Keep at a safe distance in a protected location sheltered from splashes.
- Approach down wind.
- Never approach containers which have been exposed to fire, without cooling them sufficiently.

6. ACCIDENTAL RELEASE MEASURES

Precautions

- If safe to do so, without exposing the personnel, try to stop the spillage.
- In case of leak, isolate the area.
- Respect the protection measures given in section 5.
- Respect the protection measures given in section 8.
- Avoid materials and products which are incompatible with the product (see section 10).

Cleanup methods

- If possible, dam large quantities of liquid with sand or earth.
- Dilute with large quantities of water.
- Do not add chemical products.
- For disposal methods, refer to section 13.
- In order to avoid the risk of contamination, the recovered product must not be returned to the original tank/container.

Precautions for protection of the environment

- Small quantities can be discharged into the sewer with large quantities of water.
- Immediately notify the appropriate authorities in case of important discharge.

7. HANDLING AND STORAGE

Handling

- Never return product to container.
- Use only containers which are compatible with the substance.
- Operate in a well-ventilated area.
- Lockout piping circuits and equipment before any operation.
- Keep away from sources of ignition and heat.
- Keep away from reactive substances.
- Containers and equipment used to handle the product should be used exclusively for that product.
- Prevent all contact with organic materials.

Storage

- Containment bund for the packages and transfer installation.
- In a ventilated, cool area.
- Keep away from heat sources.
- Keep in original packaging, closed.
- Keep in container fitted with vent/safety vent.
- Keep away from reactive substances.
- Keep away from combustible substances.
- For bulk storage, consult the producer.
- Regularly check the state and temperature of the containers.

Other precautions

- Warn personnel of the dangers of the product.
- Respect the protective measures given in section 8.
- Do not confine the product in the circuit, between closed valves, or in a container without a vent.

Packaging

- Aluminum 99.5 %
- Stainless steel 304 L and 316 L.
- HDPE

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls

- Local ventilation.
- Install apparatus with respect to the limit values.
- Respect the measures given in section 7.

Authorized limit values **EH40/94**

- Hydrogen peroxide
  LTEL 1 ppm, 1.5 mg/m^{-3}
  STEL 2 ppm, 3 mg/m^{-3}

Respiratory protection

- Face mask with type NO cartridge in case of emissions.
- Self-contained breathing apparatus in medium confinement/insufficient oxygen/in case of large uncontrolled emissions/in all circumstances when the mask and cartridge do not give adequate protection.
- Use only respiratory protection that conforms to international/ national standards.

Hand protection

- Protective gloves - chemical resistant:
- Recommended materials: PVC, neoprene, rubber

Eye protection

- Wear protective goggles for all industrial operations.
- Chemical proof goggles/face shield, if risk of splashing.

Skin protection

- Overalls
- Apron/boots of PVC, neoprene, rubber if risk of splashing.

Other precautions

- Shower and eye wash stations.
- Consult your industrial hygienist or safety manager for the selection of personal protective equipment suitable for the working conditions.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance: liquid
Color/Colour: colorless/colourless
Odor/Odour: slightly pungent.

Change of state

- Freezing point:
  -33°C
  Test Substance :
  Hydrogen peroxide 35 %
- Freezing point:
  -52°C
  Test Substance :
  Hydrogen peroxide 50 %
- Boiling point/range (1013 mbars):
  108°C
  Test Substance :
  Hydrogen peroxide 35 %
- Boiling point/range (1013 mbars):
  115°C
  Test Substance :
  Hydrogen peroxide 50 %

Flash point

- Non-flammable

Flammability

- Non-flammable

Auto-flammability

- Non-flammable

Vapor/vapour pressure

- 12 mbar
  temperature 20°C
  Remark:
  Total pressure (H_2O_2 + H_2O)
  Test Substance :
  Hydrogen peroxide 50 %
- 72 mbar
  temperature 50°C
  Remark:
  Total pressure (H_2O_2 + H_2O)
  Test Substance :
  Hydrogen peroxide 50 %
- 1 mbar
  temperature 30°C
  Remark:
  Partial pressure (H_2O_2)

Test Substance :
Hydrogen peroxide 50 %

Density
- Specific gravity (D 20/4)
  1.1
  Test Substance :
  Hydrogen peroxide 27,5 %
- Specific gravity (D 20/4)
  1.2
  Test Substance :
  Hydrogen peroxide 50 %

Vapor/vapour density (air=1)
- 1
  Test Substance :
  Hydrogen peroxide 50 %

Solubility
- Soluble in
- Water
- Miscible in all proportions
- Soluble in
- Polar organic solvents

pH
- 1 to 4
  Remark:
  Apparent pH

Partition coefficient P (n-octanol/water)
- No data

Viscosity
- Viscosity
  1101 mPa.s
  temperature 20°C
  Test Substance :
  Hydrogen peroxide 27,5 %
- 1170 mPa.s
  temperature 20°C
  Test Substance :
  Hydrogen peroxide 50 %

Decomposition temperature
- >= 60°C
  Remark:
  Self-accelerated decomposition temperature with oxygen release.

Danger of explosion

- Remark:
  With flammable liquids.
- Remark:
  With certain materials (see section 10).
- Remark:
  In case of rapid decomposition if inadequately vented
- Remark:
  In case of heating if inadequately vented.

Oxidizing properties

- Oxidizer

Surface tension

- 74 mN/m
  Remark:
  (20°C)
  Test Substance :
  Hydrogen peroxide 27,5 %
- 75.6 mN/m
  Remark:
  (20°C)
  Test Substance :
  Hydrogen peroxide 50 %

10.STABILITY AND REACTIVITY

Stability

- Stable under normal conditions of use with slow gas release.

Conditions to avoid

- Heat/Sources of heat

Materials to avoid

- Acids
- Bases
- Metals
- Salts of metals
- Reducing agents
- Organic materials.
- Flammable substances

Hazardous decomposition products

- Oxygen

Other information

- Decomposition releases steam/heat.

11. TOXICOLOGICAL INFORMATION

Acute toxicity

- Oral route, LD 50, rat, 841 mg/kg.
  Test Substance :
  Hydrogen peroxide 60 %.
- Oral route, LD 50, rat, 1232 mg/kg.
  Test Substance :
  Hydrogen peroxide 35 %.
- Dermal route, LD 50, rabbit, > 2000 mg/kg.
  Test Substance :
  Hydrogen peroxide 35 %.
- Inhalation, LC 50, 4 hour(s), rat, 2000 mg/kg.

Irritation

- Rabbit, corrosive (eyes).
  Test Substance :
  Hydrogen peroxide (70 %).
- Rabbit, Irritant (skin).
  Test Substance :
  Hydrogen peroxide < 50 %.
- Rabbit, corrosive (skin), 1 hour(s).
  Test Substance :
  Hydrogen peroxide >= 50 %.

Sensitization

- Rat, Non sensitizing.

Chronic toxicity

- In vitro, without metabolic activation, mutagenic effect.
- In vivo, No genotoxic effect.
- Oral route, prolonged administration (> 6 months), mouse, Target organ: duodenum, carcinogenic effect.
- Dermal route, prolonged administration (> 6 months), mouse, no carcinogenic effect.
- Oral route, prolonged administration (> 6 months), rat, no carcinogenic effect.
- Oral route, prolonged administration (> 6 months), rat, gastro-intestinal.
  Test Substance :
  Hydrogen peroxide (70 %).
- Oral route, prolonged administration (> 6 months), mouse, gastro-intestinal.
- Oral route, Effect on reproduction/insufficient data.
- Inhalation, irritating effect.
  (LOAEL: 7 ppm).

Comments

- Toxic effect linked with corrosive properties
- The carcinogenic effect found in animals is not demonstrated in human

12.ECOLOGICAL INFORMATION

Acute ecotoxicity

- Fishes, Pimephales promelas, LC 50, 96 hour(s), 16.4 mg/l.
- Fishes, Pimephales promelas, NOEC, 96 hour(s), 5 mg/l.
- Crustaceans, Daphnia pulex, EC 50, 48 hour(s), 2.4 mg/l.
- Crustaceans, Daphnia pulex, NOEC, 48 hour(s), 1 mg/l.
- Algae, various species, EC 50, between 72 to 96 hour(s), between 3.7 to 160 mg/l.
  Conditions: fresh water.
- Algae, Nitzchia closterium, EC 50, between 72 to 96 hour(s), 0.85 mg/l.
  Conditions: salt water.

Chronic ecotoxicity

- Result: no data.

Mobility

- Air, Henry's law constant (H) = 1 mPa.m3/mol.
  Result: non-significant volatility.
  Conditions: 20°C.
- Air, condensation on contact with water droplets..
  Result: rain washout.
- Water.
  Result: non-significant evaporation.
- Soil/sediments.
  Result: non-significant evaporation and adsorption.

Abiotic degradation

- Air, indirect photo-oxidation, t 1/2 between 10 to 20 hour(s).
  Conditions: sensitizer: OH radical.
- Water, oxidation/reduction, t 1/2 between 2.5 day(s), 10000 ppm.
  Conditions: mineral and enzymatic catalysis/fresh water.
- Water, oxidation/reduction, t 1/2 between 20 day(s), 100 ppm.
  Conditions: mineral and enzymatic catalysis/fresh water.
- Water, oxidation/reduction, t 1/2 between 60 hour(s).
  Conditions: mineral and enzymatic catalysis/salt water.
- Soil, oxidation/reduction, t 1/2 between 15 hour(s).
  Conditions: mineral catalysis.

Biotic degradation

- Aerobic, t 1/2 < 1 minute(s).
  Result: rapid and considerable biodegradation.
  Conditions: biological treatment sludge.
- Aerobic, t 1/2 between 0.3 to 2 day(s).
  Result: rapid and considerable biodegradation.
  Conditions: fresh water.
- Anaerobic.
  Result: not applicable.
- Effects on biological treatment plants, > 200 mg/l.
  Result: inhibitory action.

Potential for bioaccumulation

- Result: non-bioaccumulable (enzymatic metabolism).

Comments

- Toxic for aquatic organisms.
- Nevertheless, hazard for the environment is limited due to product properties:
- . no bioaccumulation.
- . considerable abiotic and biotic degradability.
- . no toxicity of degradation products (H20 and O2).

13.DISPOSAL CONSIDERATIONS

Waste treatment

- Comply with local and national regulations.
- Small quantities.
- Dilute until 0.1 % with water.
- After this treatment, the product can be discharged into the sewer.
- Large quantities:
- Contact the producer.

Packaging treatment

- Rinse the empty containers with plenty of water and treat the effluent in the same way as waste.
- Do not rinse the dedicated containers.
- The empty and clean containers are to be recycled or disposed of in conformity with local regulations.

14.TRANSPORT INFORMATION

UN Number: 2014

IATA Class: 5.1
Subsidiary risk: CORROSIVE
Packing group: II
Hazard label: OXIDIZER + CORROSIVE

IMDG Class: 5.1
Subsidiary risk: CORROSIVE
Packing group: II
Hazard label: OXIDIZING AGENT + CORROSIVE
Placard: 2014

ADR Class: 5.1,1° b
Subsidiary risk: 8
Packing group: II
Hazard label: 5.1 + 8
Placard: 58/2014

RID Class: 5.1,1° b
Subsidiary risk: 8
Packing group: II
Hazard label: 5.1 + 8
Placard: 58/2014

- IATA: forbidden over 40 %

15.REGULATORY INFORMATION

EEC Labelling

- According to Annex I of Dir. 67/548/EEC (12th APT: Dir. 93/72/EEC).
  The concentration must be indicated on the label
  Symbols:
  C Corrosive
  Phrases R:

34	Causes burns.

Phrases S:

3	Keep in a cool place.
(1/2)	(Keep locked up and out of the reach of children.)
28	After contact with skin, wash immediately with plenty of water.
36/39	Wear suitable protective clothing and eye/face protection.
45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

- Labelling "Dangerous for the environment": not classified (see section 12).

16.OTHER INFORMATION

Reason for update

- Update: sections 4 - 7 - 8 - 9 - 13 - 14 - 16

The information given corresponds to the current state of our knowledge and experience of the product, and is not exhaustive. This applies to product which conforms to the specification, unless otherwise stated. In the case of combinations and mixtures one must make sure that no new dangers can arise. In any case, the user is not exempt from observing all legal, administrative and regulatory procedures relating to the product, personal hygiene, and protection of human welfare and the environment.

APPENDIX 3

Material Safety Data Sheet - PCS

Ellis & Everard
CHEMICALS MARKETING & DISTRIBUTIO

SAFETY DATA SHEET

1. Identification of the substance/preparation and company/undertaking.

NAME Sodium Carbonate Peroxyhydrate S.D.S. No. S112

Synonyms Oxyper * PCS * Sodium Percarbonate

Supplied by:
Ellis & Everard
46 Peckover Street
BRADFORD
West Yorkshire
BD1 5BD

Tel: 01274 377000
Fax: 01274 737058
Emergency No: 01274 377070

2. Composition/information on ingredients.

Contains:

Chemical	% Conc	Classification	Exposure	CAS	EINECS
Sodium Carbonate Peroxyhydrate	>88%	O,Xn;R8-22-36/38		15630-89-4	239-707-6

3. Hazards identification.

Toxicity is principally related to its irritant effects. Does not present a significant hazard to the environment. Oxidizing agent, may contribute to the combustion of other materials.

4. First Aid measures.

Exposure Route	Symptom	Treatment
Inhalation	Slight nose and throat irritation.	Remove from exposure, rest and keep warm. In severe cases, or if recovery is not rapid or complete seek medical attention.
Skin Contact	Slight irritation.	Drench the skin with plenty of water. Remove contaminated clothing and wash before reuse. If large areas of the skin is damaged or if irritation persists seek medical attention.
Eye Contact	Severe irritation, watering, reddening.	Irrigate thoroughly with water for at least 10 minutes. Obtain medical attention.
Ingestion	Severe irritation of mouth and throat. Bloating of stomach, belching, nausea, vomiting and diarrhoea.	Wash out mouth with water. Do not induce vomiting. If patient is conscious, give water to drink. If patient feels unwell seek medical attention.

---

5. Fire Fighting measures.

Suitable Extinguishers Water

Hazardous Combustion Products Decomposes evolving oxygen which may contribute to fire.

Special Equipment for Fire Fighting Self contained breathing apparatus.

---

6. Accidental Release measures.

Safety Precautions Wear appropriate PPE - See section 8

Environmental Precautions Avoid raising dust. Inform authorities of significant discharge to drains and watercourses.

Clean up Procedure Collect the material and place in clean, dry, vented, labelled containers. Isolate in a safe place and hold for waste disposal.

---

7. Handling & Storage.

Handling **Ventilation** Good general ventilation.

Prohibited procedures & equipment Never return product to container.

Recommended procedures & equipment Use dedicated equipment. Keep dry.

Storage **Temperature range** <40°C
Humidity range Dry

Keep away from See section 10

Suitable storage Media Stainless steel. Polyethylene, PE coated paper, glass, passivated Aluminium.

---

8. Exposure Controls/personal protection.

Exposure Limits 10 mg/m^3 inhalable dust, 8hr TWA; 5 mg/m^3 respirable dust, 8 hr TWA **Type** EH 40 guidance

Monitoring Method

Protective Measures

Respiratory: Type approved RPE for dusts. (P2)
Hand: PVC, neoprene or rubber gloves.
Eye: Safety glasses.
Skin: Overalls.

Hygiene Measures Always wash thoroughly after handling chemicals.

9. Physical & Chemical Properties.

Appearance	White crystalline powder.
pH	10.4 - 10.6 (1% solution)
Flammability	Not flammable, but will increase flammability of other materials.
Oxidizing Properties	Oxidizing agent
Bulk density	900 - 1100 Kg/m^3
Solubility in water	150 g/l @ 20°C, 175 g/l @ 30°C
Decomposition Temperature	SADT with oxygen release above 50°C

10. Stability & Reactivity.

Stability Stable under normal conditions.

Conditions to avoid Heat or heat sources; Moisture.

Materials to avoid Water, acids, alkalis, heavy metal salts, reducing agents, organic materials, flammable materials.

11. Toxicological Information.

Effects

Irritating to eyes and mucous membranes.

LD_{LO}

LD_{50} 1034 mg/Kg **oral-rat** >2000 mg/Kg **skin-rabbit**

12. Ecological Information.

Environmental Effects

Mobility Soluble in water
Degradability Significant hydroysis in water, forms Sodium Carbonate, Carbonic acid and Hydrogen Peroxide.
Bioaccumulative potential Not bioaccumulable
Aquatic Toxicity Toxic to aquatic organisms. Never the less, danger to the environment is limited as a result of absence of bioaccumulation and its degradability.

13. Disposal considerations.

Substance	Via an authorized waste disposal contractor to an approved waste disposal site, observing all local and national regulations.
Container	As substance.

14. Transport Information.

Not regulated for road transport.

15. Regulatory Information.

Supply label details	Ref. CHIP 2
Label Name	Sodium Carbonate Peroxyhydrate
Symbols	Oxidizing and Harmful
Risk Phrases	8 - 22 - 36/38 Contact with combustible material may cause fire. Harmful if swallowed. Irritating to eyes and skin.
Safety Phrases	3 - 17 - 24/25 - 26 Keep in a cool place. Keep away from combustible material. Avoid contact with skin and eyes. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
E.E.C. No	

Use of this material may be governed by the following regulations:-

Users are advised to consult these regulations for further information.

The information contained in this data sheet does not constitute an assessment of workplace risks.

16. Other Information.

This material is usually used for:

It must not be used for:

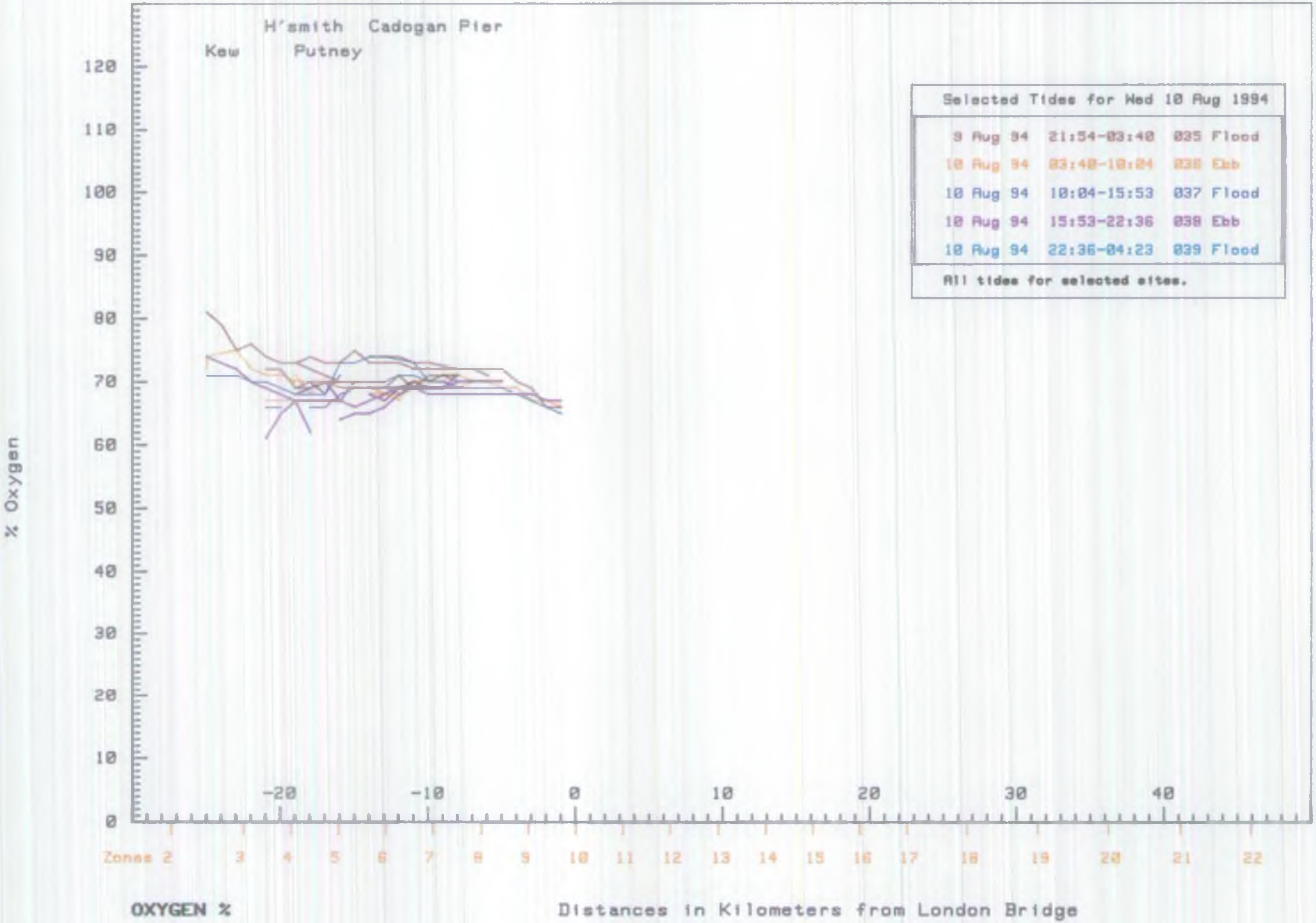
Further details may be available upon request from your local Ellis & Everard distribution site.

Legal Disclaimer:
The above information is based on the present state of our knowledge of the product at the time of publication. It is given in good faith, no warranty is implied with respect to the quality or the specification of the product. The user must satisfy himself that the product is entirely suitable for his purpose.

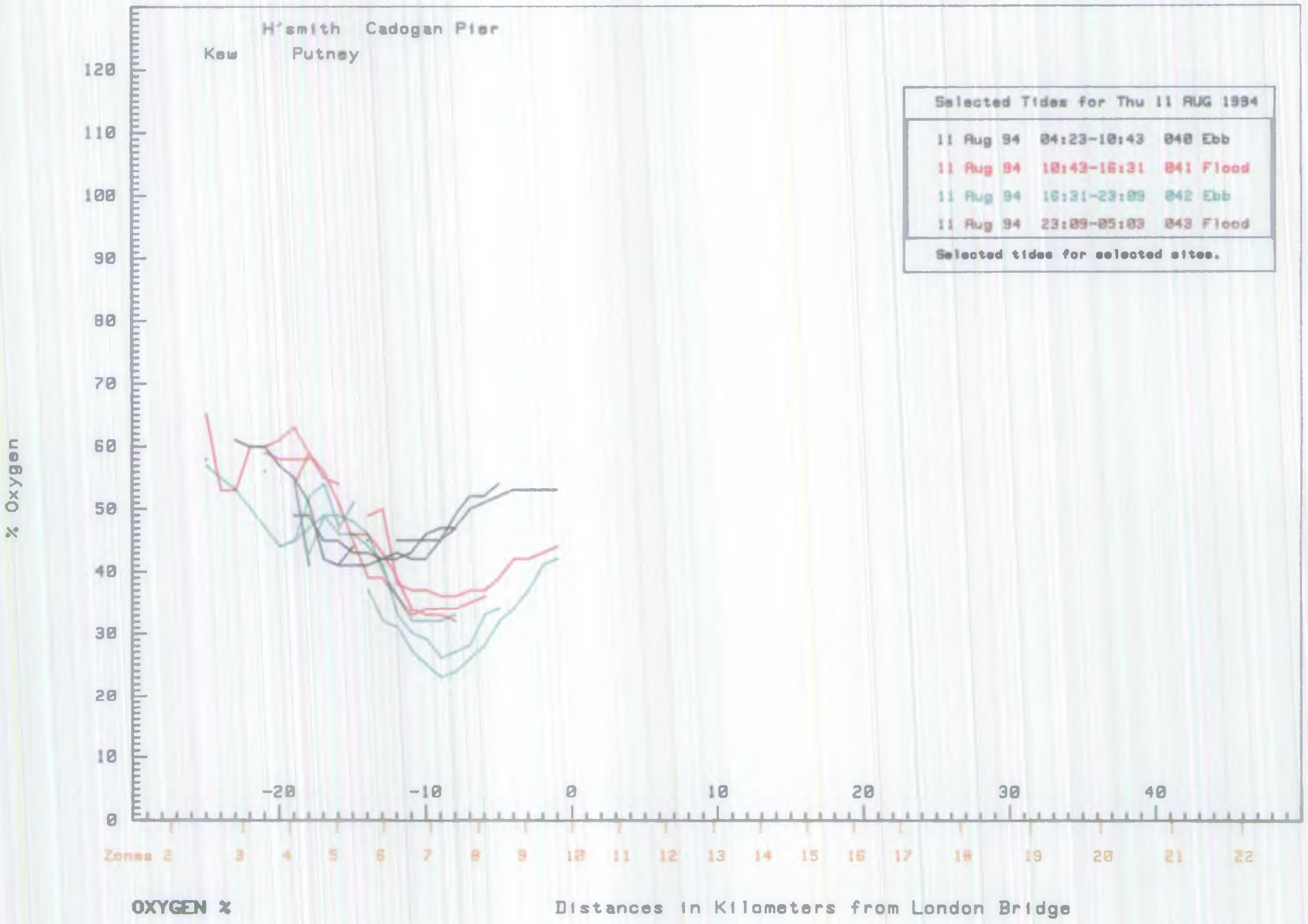
Revision No	**1**	**Dated**	**April 1995**
Replaces S.D.S.		**Dated**	**Jan 1991**

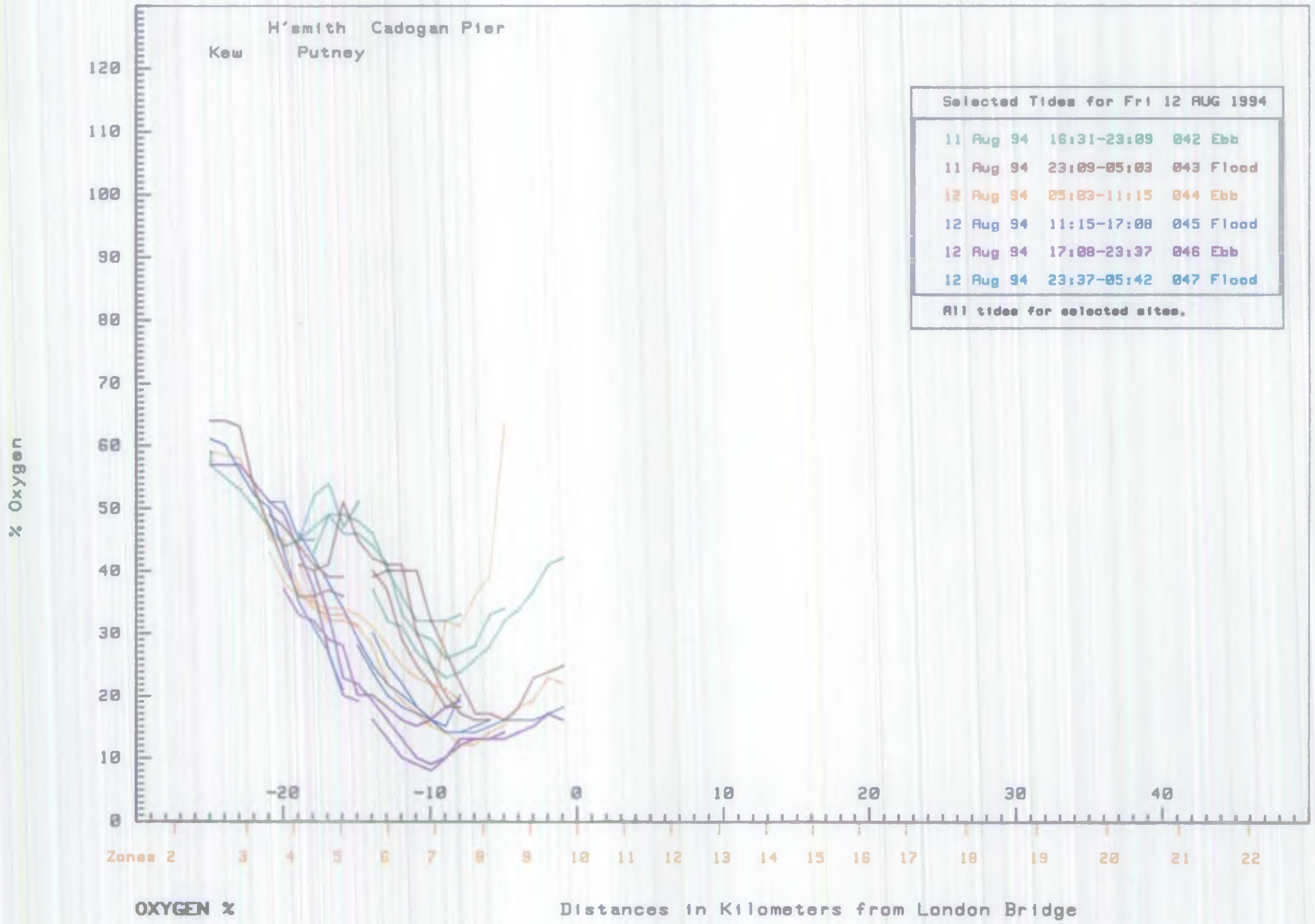
APPENDIX 4

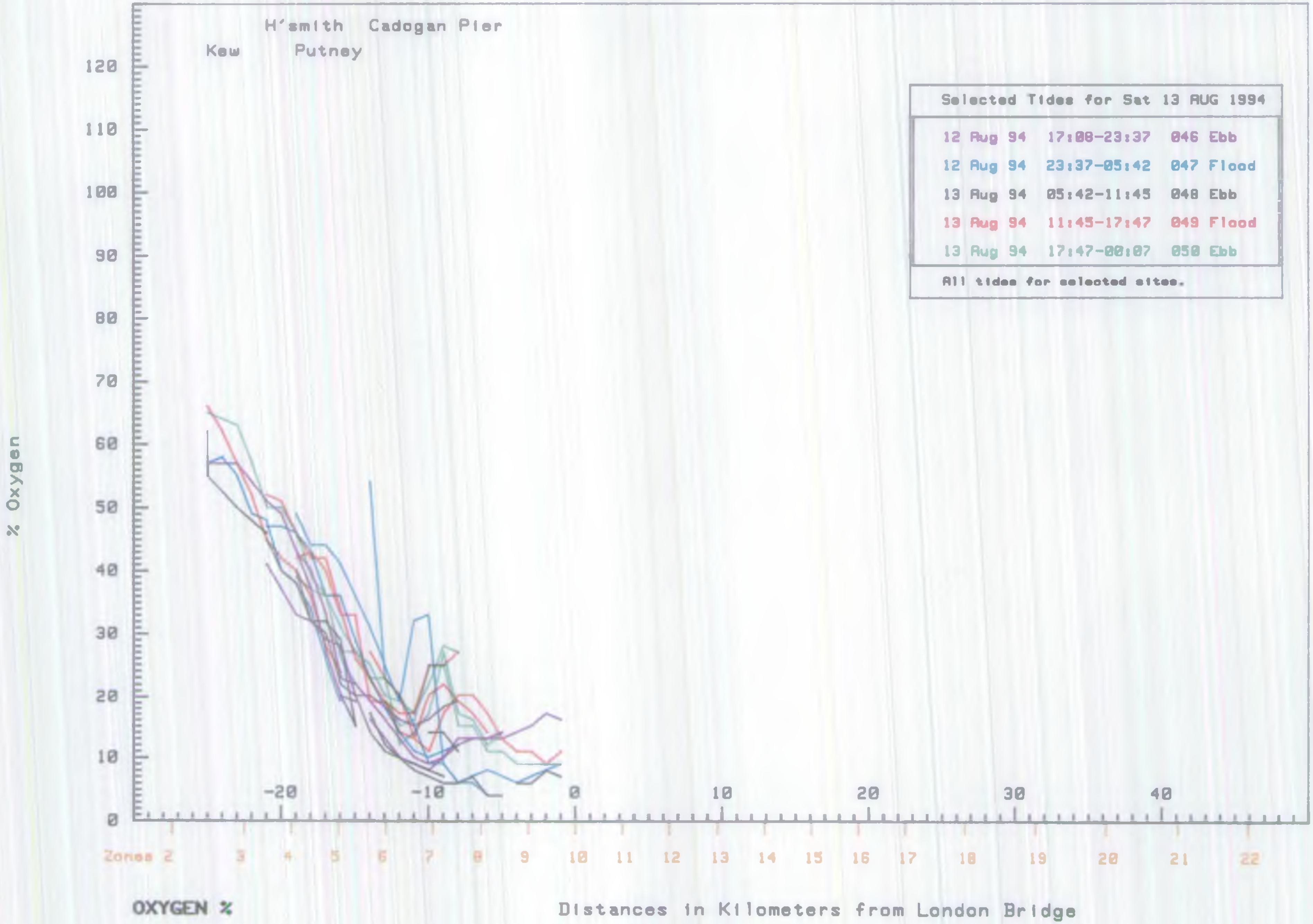
River Thames 'post storm' dissolved oxygen profiles


H'smith
Cadogan Pier
Kew
Putney
Selected Tides for Wed 10 Aug 1994
9 Aug 94 21:54-03:40 035 Flood
10 Aug 94 03:40-10:04 036 Ebb
10 Aug 94 10:04-15:53 037 Flood
10 Aug 94 15:53-22:36 038 Ebb
10 Aug 94 22:36-04:23 039 Flood
All tides for selected sites.
% Oxygen
120
110
100
90
80
70
60
50
40
30
20
10
0
-20
-10
0
10
20
30
40
Zones 2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
Distances in Kilometers from London Bridge

OXYGEN %


H'smith
Cadogan Pier
Kew
Putney
Selected Tides for Thu 11 AUG 1994
11 Aug 94 04:23-10:43 040 Ebb
11 Aug 94 10:43-16:31 041 Flood
11 Aug 94 16:31-23:09 042 Ebb
11 Aug 94 23:09-05:03 043 Flood
Selected tides for selected sites.
% Oxygen
0
10
20
30
40
50
60
70
80
90
100
110
120
-20
-10
0
10
20
30
40
Zones 2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
OXYGEN %
Distances in Kilometers from London Bridge

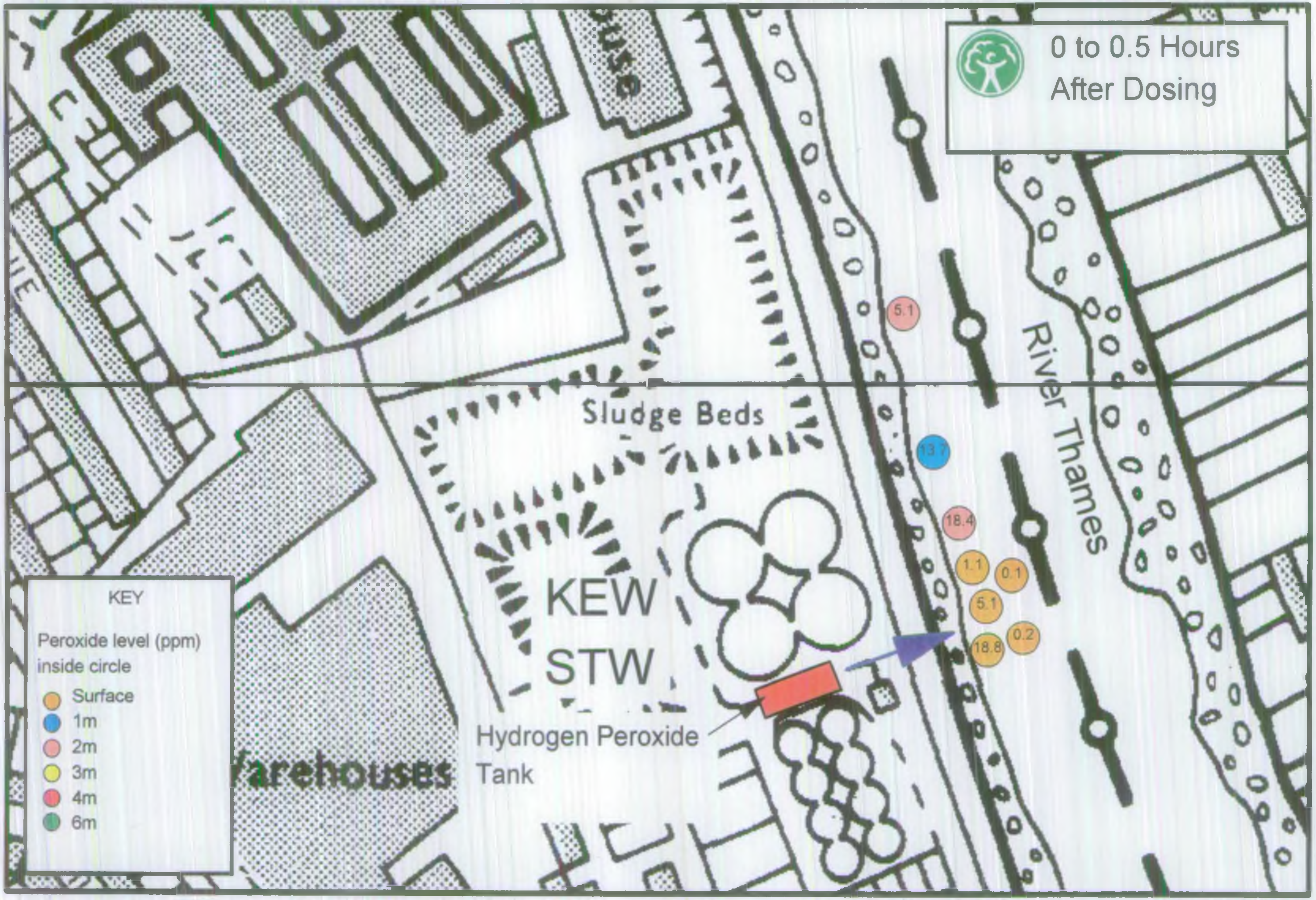

H'smith
Cadogan Pier
Kew
Putney
Selected Tides for Fri 12 AUG 1994
11 Aug 94 16:31-23:09 042 Ebb
11 Aug 94 23:09-05:03 043 Flood
12 Aug 94 05:03-11:15 044 Ebb
12 Aug 94 11:15-17:08 045 Flood
12 Aug 94 17:08-23:37 046 Ebb
12 Aug 94 23:37-05:42 047 Flood
All tides for selected sites.
% Oxygen
120
110
100
90
80
70
60
50
40
30
20
10
0
-20
-10
0
10
20
30
40
Zones 2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
OXYGEN %
Distances in Kilometers from London Bridge

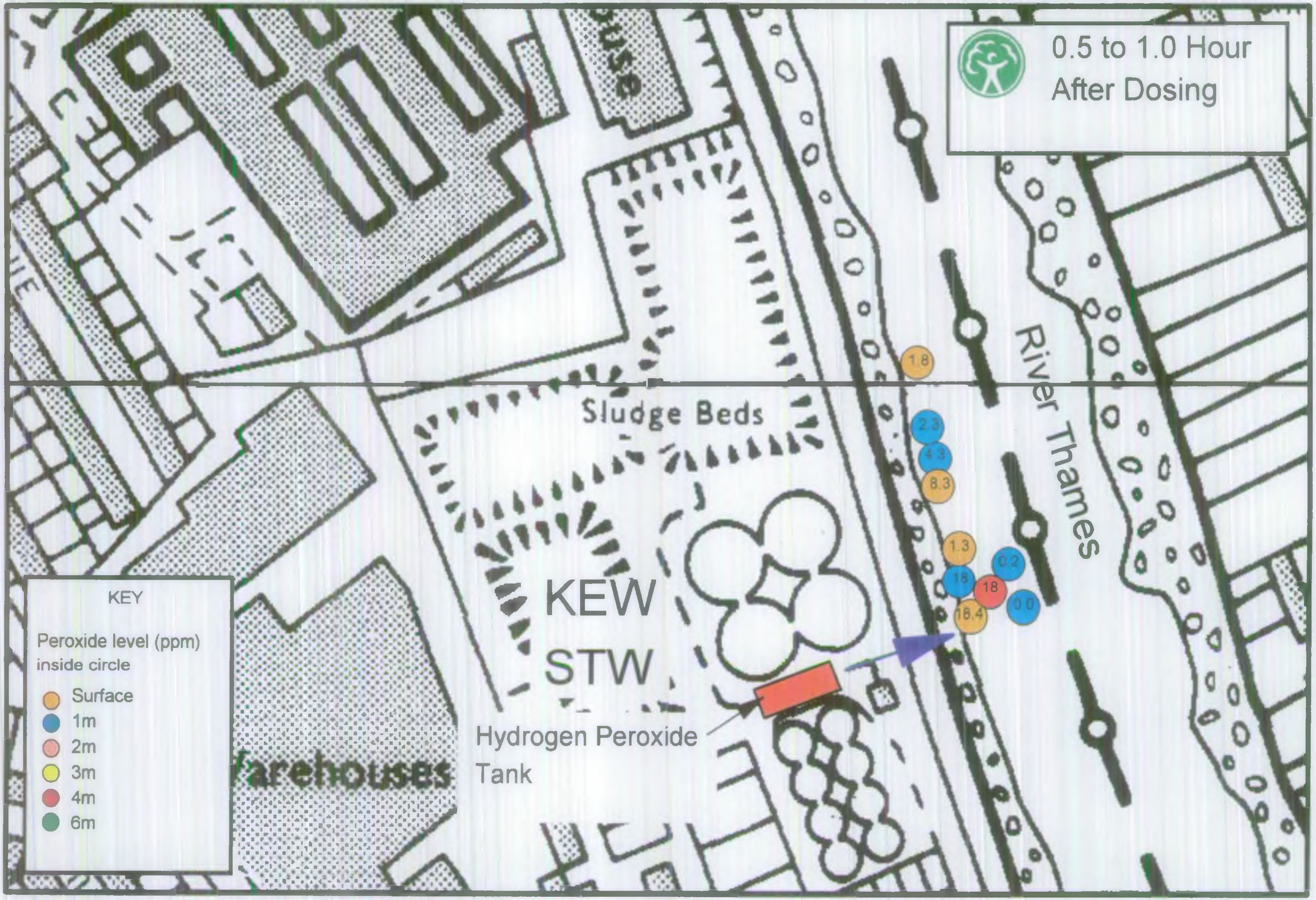

H'smith
Cadogan Pier
Kew
Putney
Selected Tides for Sat 13 AUG 1994
12 Aug 94 17:08-23:37 046 Ebb
12 Aug 94 23:37-05:42 047 Flood
13 Aug 94 05:42-11:45 048 Ebb
13 Aug 94 11:45-17:47 049 Flood
13 Aug 94 17:47-00:07 050 Ebb
All tides for selected sites.
% Oxygen
120
110
100
90
80
70
60
50
40
30
20
10
0
-20
-10
0
10
20
30
40
Zones 2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
OXYGEN %
Distances in Kilometers from London Bridge

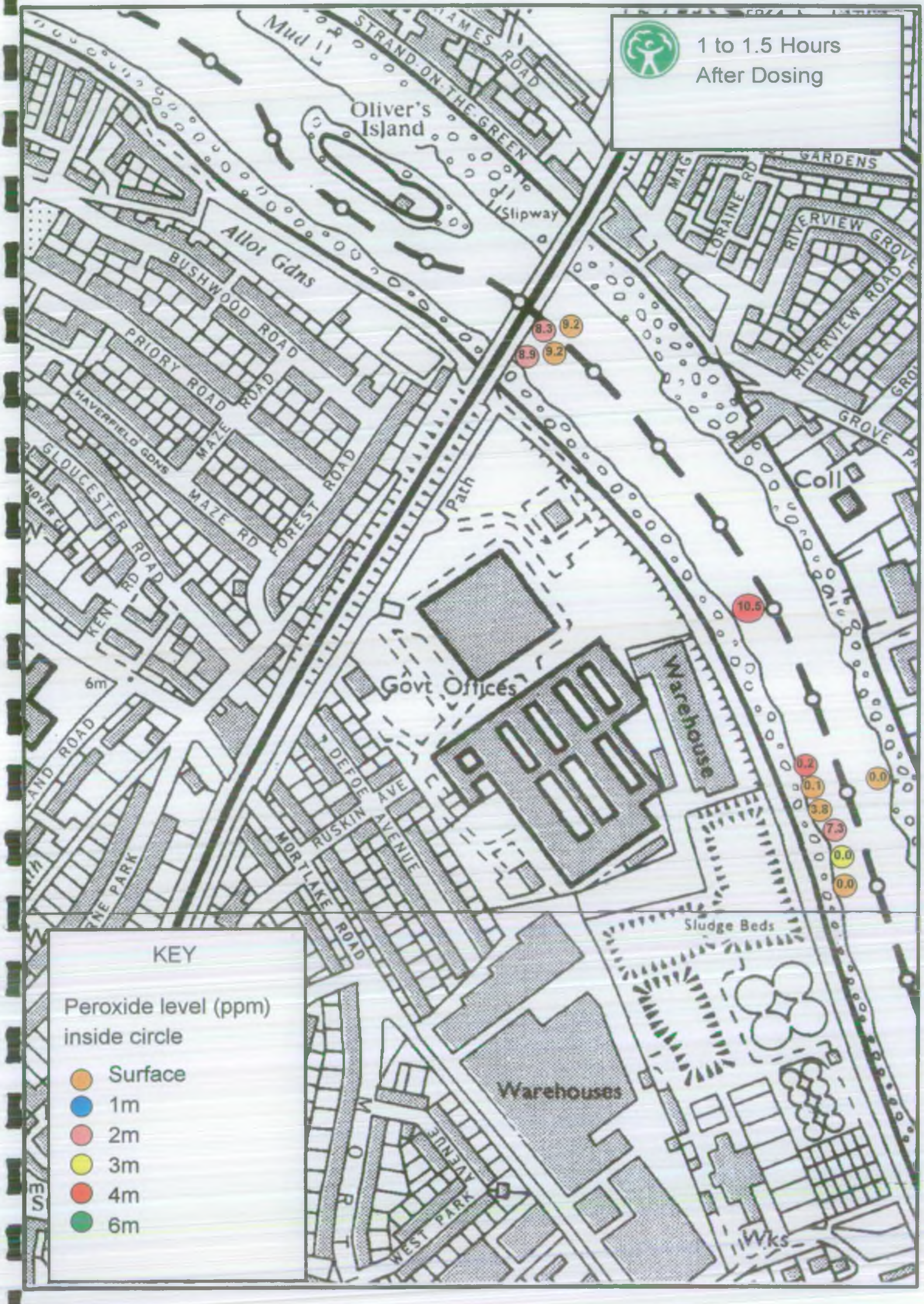
APPENDIX 5

Kew Trial - 11 September 1996

Residual hydrogen peroxide concentrations


0 to 0.5 Hours
After Dosing
ouse
Sludge Beds
KEW
STW
River Thames
Hydrogen Peroxide
Tank
Warehouses
5.1
13.7
18.4
1.1
0.1
5.1
18.8
0.2
KEY
Peroxide level (ppm)
inside circle
Surface
1m
2m
3m
4m
6m

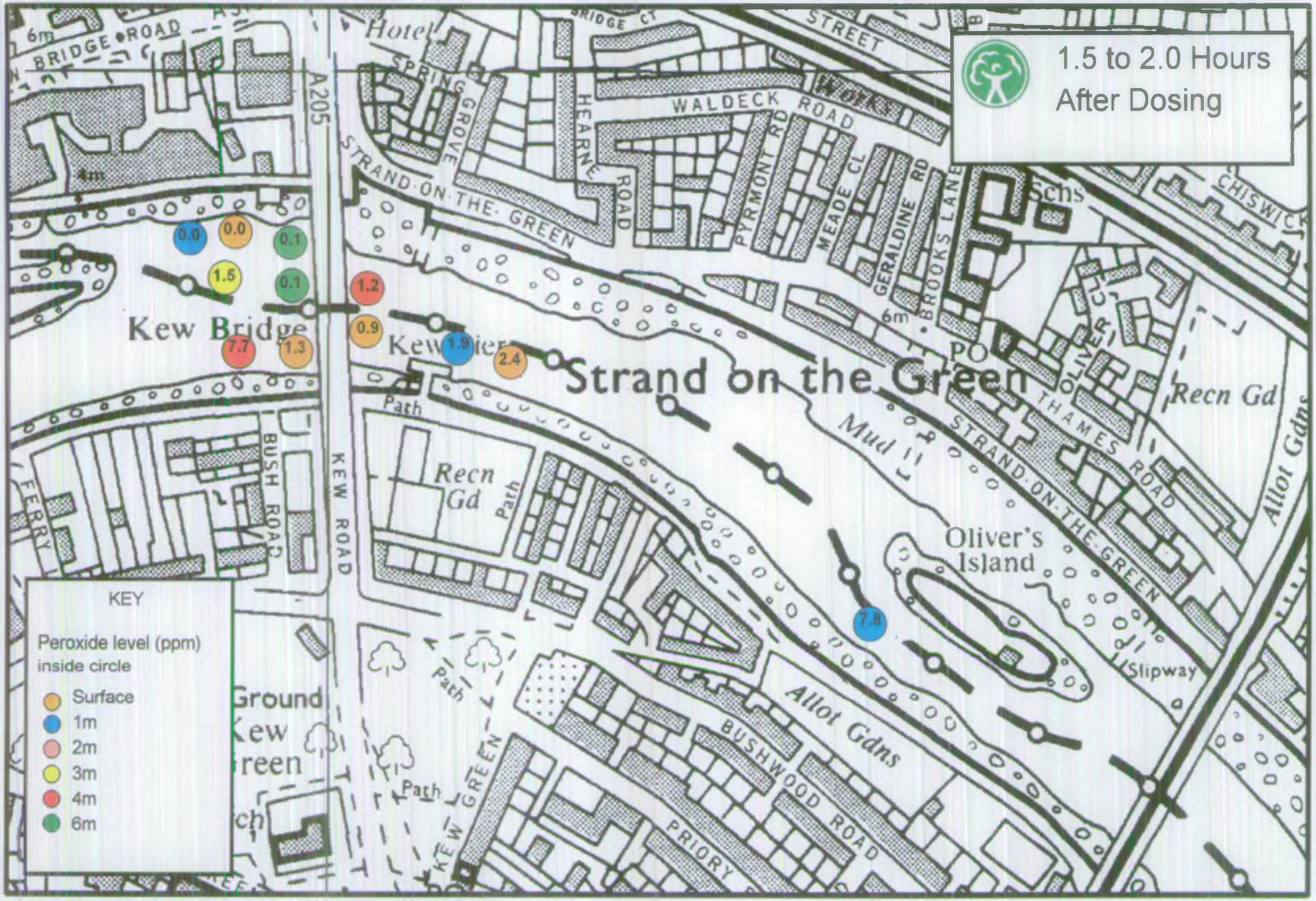

0.5 to 1.0 Hour
After Dosing
Sludge Beds
River Thames
KEW
STW
Hydrogen Peroxide
Tank
Warehouses
1.8
2.3
4.3
8.3
1.3
0.2
18
18
0.0
18.4
KEY
Peroxide level (ppm)
inside circle
Surface
1m
2m
3m
4m
6m



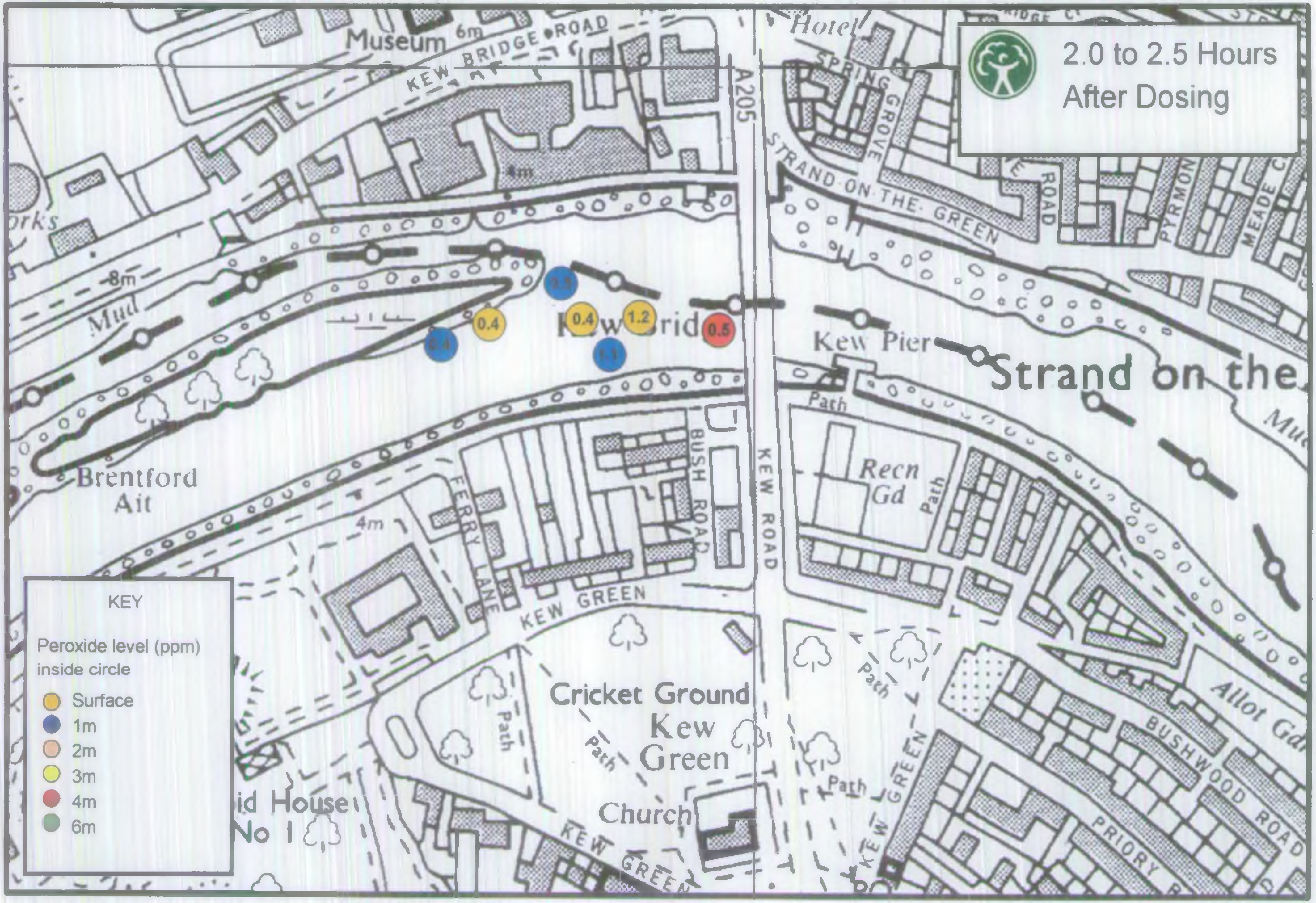
1 to 1.5 Hours After Dosing

KEY

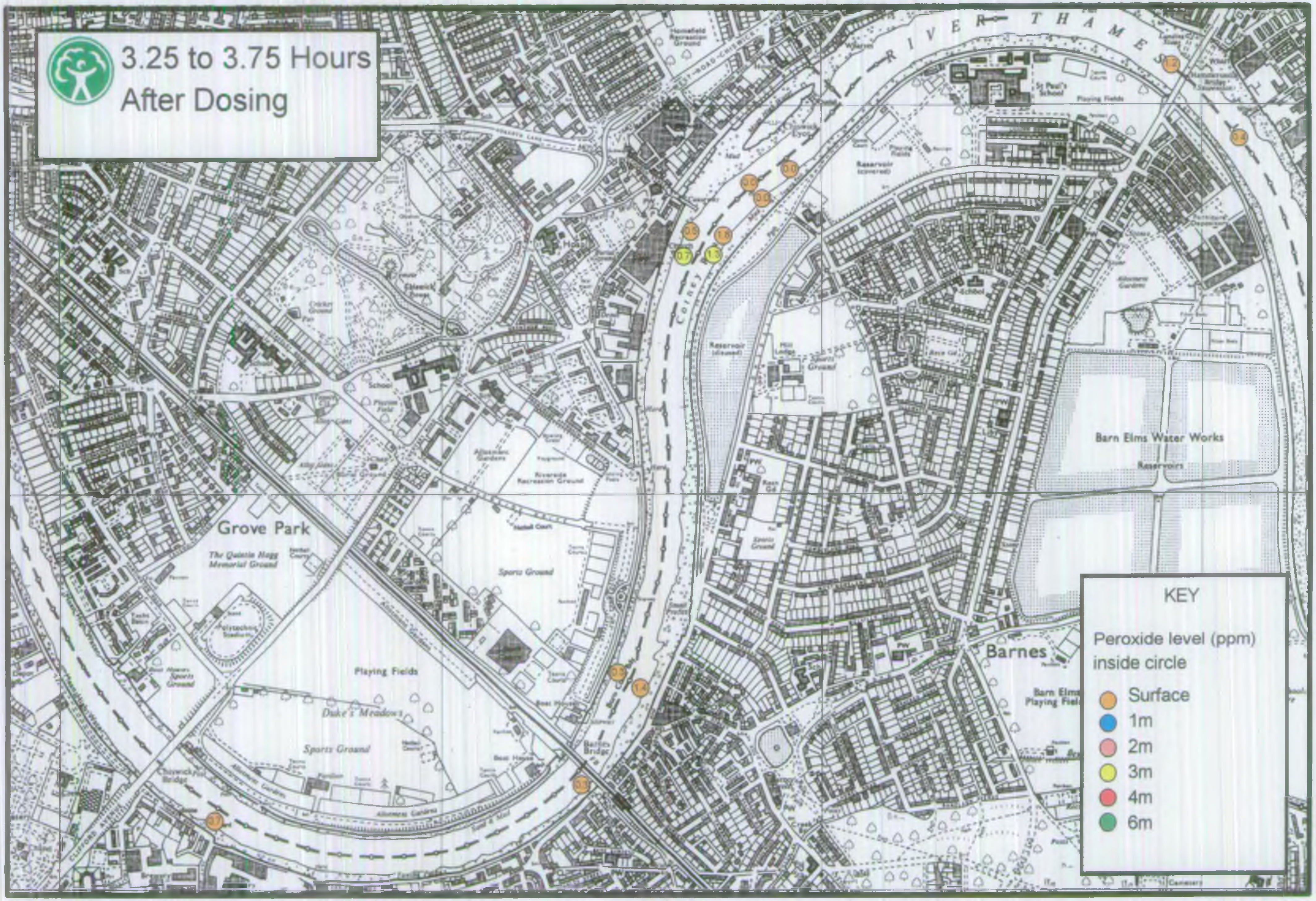
Peroxide level (ppm) inside circle



1.5 to 2.0 Hours After Dosing



2.0 to 2.5 Hours After Dosing



3.25 to 3.75 Hours After Dosing

KEY

Peroxide level (ppm) inside circle

- ● Surface
- ● 1m
- ● 2m
- ● 3m
- ● 4m
- ● 6m


3 -75 to 4-75 hours
After Dosing
Hammersmith Cemetery
Chapel
The Queen's Club
Normand Park
Recreation Ground
Playground
Chapel
Cemetery
Water Works
Queen Elizabeth Walk (Path)
Barn Elms Schools Sports Centre
Boat House
Fulham Football Ground
Fulham
School
The Warren Allotment Gardens
Fulham Palace
Putney Hospital
Putney Common
All Saints Church
Putney Pier
Putney Bridge
Mud
Mean High Water
0.5
0.1
0.8
0.8
0.6
1.0
0.2
0.7
0.0
1.6
0.8
1.4

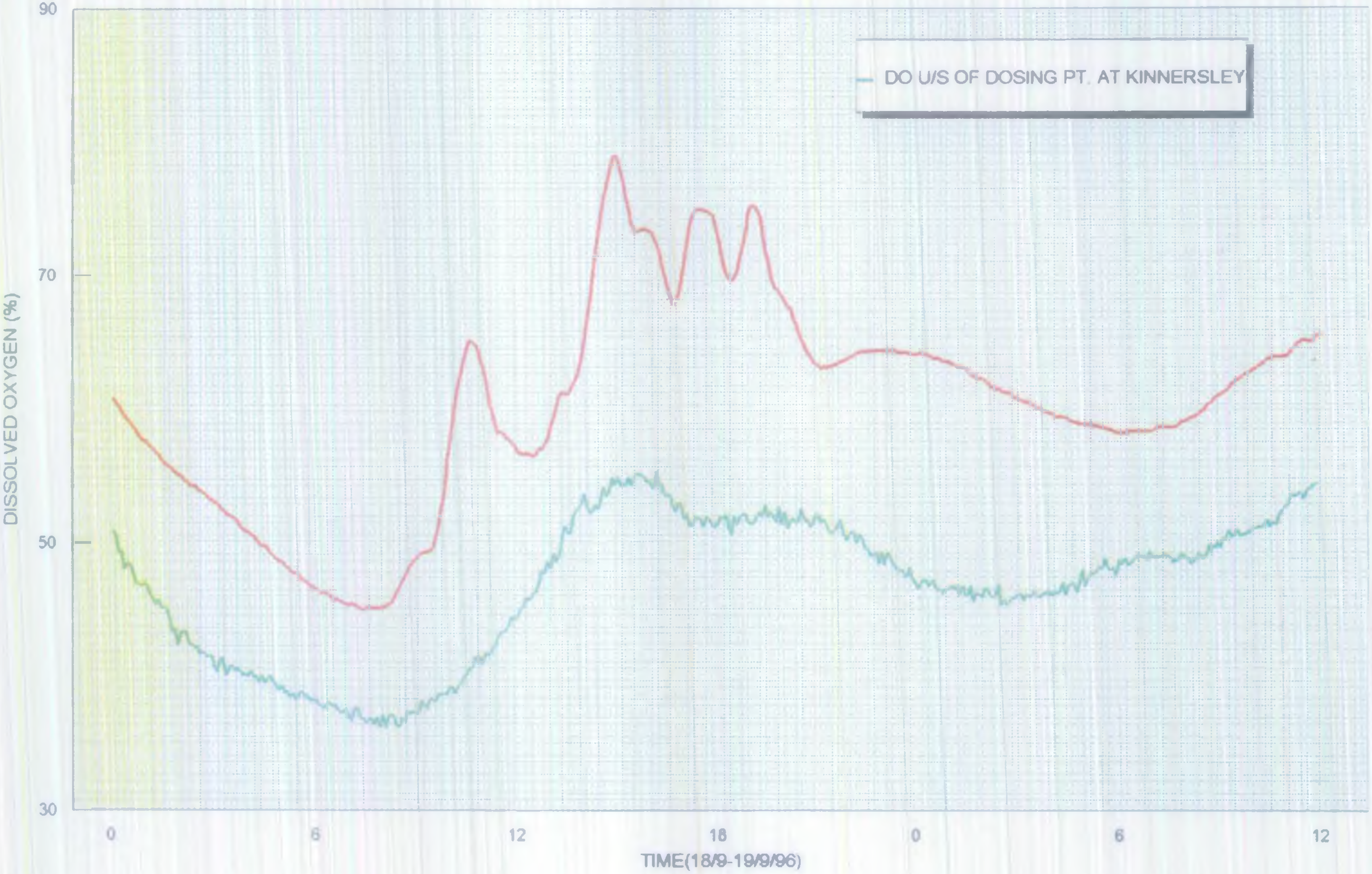
APPENDIX 6

River Mole Trial - 18 September 1996

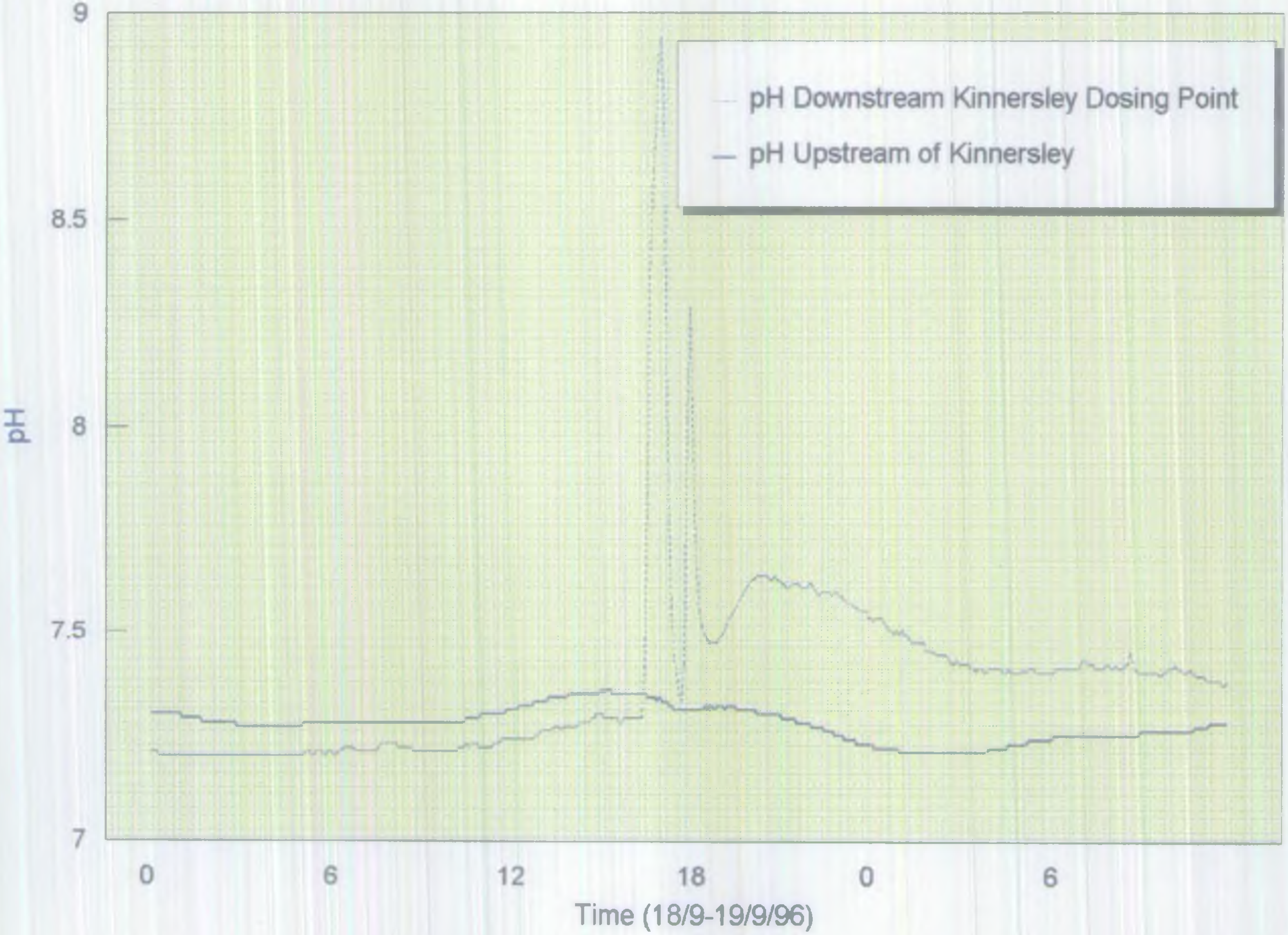
Dissolved oxygen profiles

U/S AND 80m D/S OF KINNERSLEY WATER QUALITY STATION

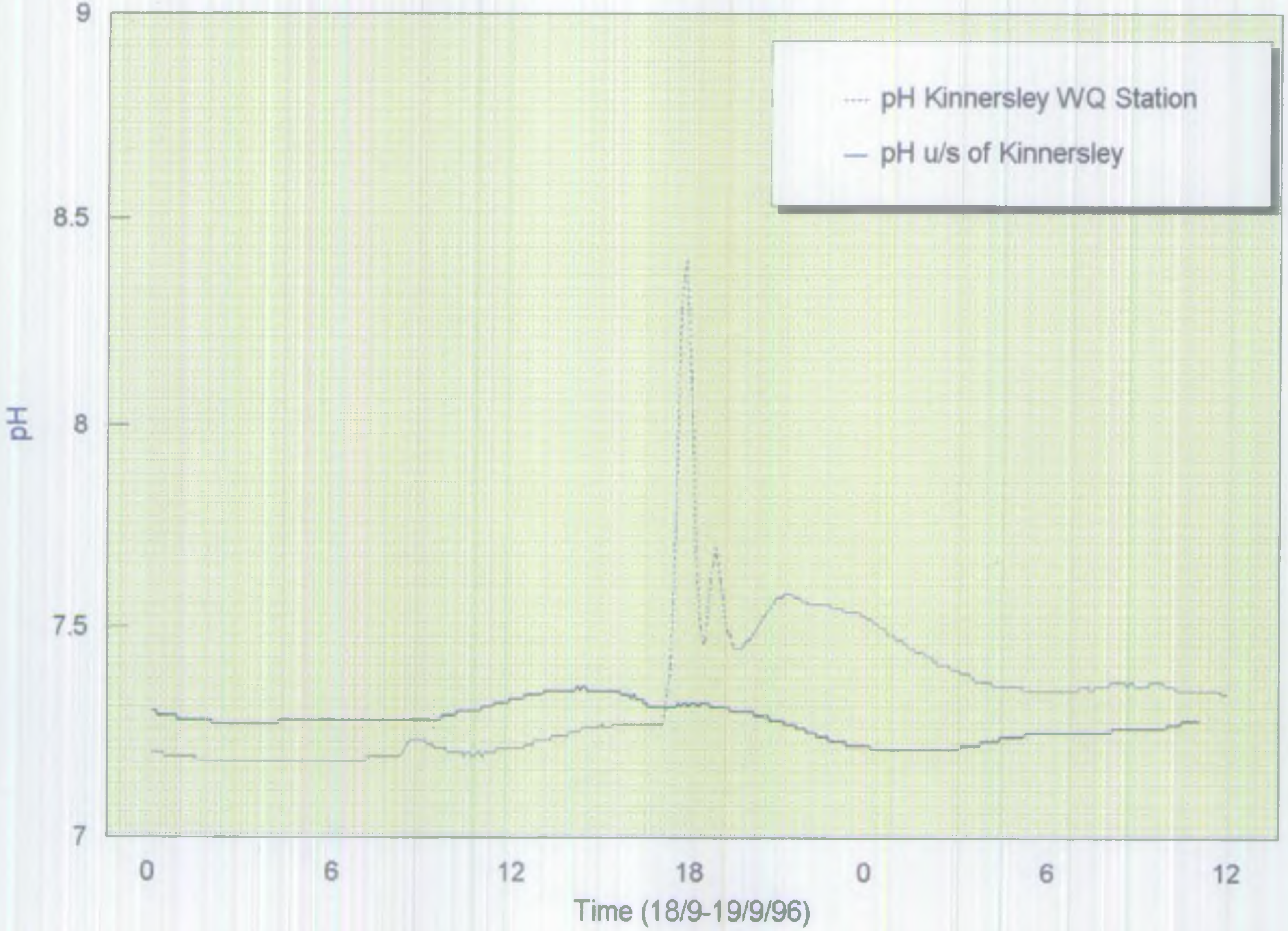
U/S OF DOSING PT. AND FOOTBRIDGE D/S OF KINNERSLEY WATER QUALITY STA.



80m DOWNSTREAM OF KINNERSLEY DOSING POINT



UPSTREAM AND AT KINNERSLEY WQ STATION



U/S AND 80m D/S OF KINNERSLEY WATER QUALITY STATION

U/S AND AT KINNERSLEY FOOTBRIDGE

APPENDIX 7

River Mole Trial 18 September 1996. Hydrogen peroxide concentrations at various locations.

Time	5m d/s	80m d/s	120m d/s	Kinnersley Manor	Footbridge	Sidlow	Bures
11.03	0.3						
11.32		12.8					
11.40				0.1			
11.44	3.0						
11.49		19.6					
12.00				0.7			
12.10		9.1					
12.15			17.1	0.5			
12.43	18.8						
12.46		1.8		12.7			
12.50				13.0			
12.54			4.3	15.0			
13.00				16.0			
13.05				13.7			
13.10				13.2			
13.15				11.6		>0.1	
13.20				9.2			
13.35					>0.1		
13.40				3.3			
14.00	0.3						
14.17	8.7						
14.25	11.8						
14.31		3.0			6.6		
14.38		11.8			7.0		
14.46			1.0				
14.50		14.3			6.8		
15.00					7.4		
15.10	0.3				6.1		
15.20					5.3		
15.25	0.3						
16.14	0.6						
16.20				4.8			
16.28	15.4						

Time	5m d/s	80m d/s	120m d/s	Kinnersley Manor	Footbridge	Sidlow	Bures
15.30						0.3	
16.50	16.5						
17.05		11.4		0.6			
17.08			8.4				
17.15						0.6	
17.35						1.0	
17.40				9.4			
17.50				11.7			
18.00						1.5	
18.05				6.5			
18.30				2.4			
18.45						1.3	
18.54		2.0					
19.15						1.2	
19.06		3.4					
18/09/96							
10.15	0.6						
10.26		2.0					
10.36				1.2			
11.00					1.6		
11.08						0.6	
11.54							>0.1
14.00				1.0			
17.03	>0.1						
17.11		0.1					
17.33						0.3	

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Hunting Technical Services is registered to ISO 9001, Certificate Number 95/5605. Registered through SGS Yarsley International Certification Services Limited (Registration Number 005).

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