DEVELOPMENT OF OPERATIONAL AND POLICY GUIDANCE ON THE USE OF HYDROGEN PEROXIDE

Apem Ltd

R&D Technical Report P191

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Development of Operational and Policy Guidance on the use of Hydrogen Peroxide

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Statement of Use
This report is intended to give guidance on the safe and effective use of hydrogen peroxide to ameliorate pollution events which impact upon oxygen levels. The information within this document is for use by Environment Agency staff .

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1.1 Hydrogen Peroxide – What is it?

Hydrogen peroxide is a clear, colourless, weakly acidic liquid which is miscible with water. It is a powerful oxidising agent which, in the presence of catalysts, rapidly decomposes to water and oxygen. It is therefore a valuable tool to remediate against certain pollution events.

1.2 When Should it be Used?

Peroxide appears to be most effective in waterways which normally have oxygen concentrations high enough to sustain a fish population but suffer a one-off pollution incident, such as a spill of organic material or an ingress of storm sewage. In these circumstances, peroxide can increase oxygen concentrations and may accelerate degradation of the pollutant(s), increasing faunal survival and minimising the environmental damage.

Peroxide is less cost effective when the low oxygen or pollution problem is more long-term, such as where a combination of low summer flows, high temperatures and an effluent discharge cause oxygen levels to fall over a prolonged period of time. Aeration and/or injection of liquid oxygen are likely to be more appropriate remediation techniques in such circumstances.

Figures 1 to 3 illustrate the logical decision process which should be followed to determine whether peroxide is the most appropriate remediation technique to use following a low oxygen event and, if it is, the most effective way in which it can be applied. Based on current knowledge and experience, these guidelines describe the best practicable application of peroxide. However, these guidelines may well be revised in light of future experience and subsequent feedback.

Peroxide may be effective in the treatment of chemical pollutants that do not affect oxygen levels, for example cyanide, phenols, aldehydes and nitrogen compounds. Use of peroxide in these situations is subject to further research currently underway in the Agency and will ultimately form part of the Chemical Techniques Manual.

1.3 Toxicity

The Agency has accepted that as a response to an emergency, the addition of hydrogen peroxide as a remedial measure is an acceptable and legitimate practice. However, in all cases due regard must be given to the health and safety of operators and the public, as well as to environmental considerations.

Peroxide is toxic to plankton, invertebrates and fish, with plankton being the most sensitive organisms. Toxicity has been found to increase significantly with temperature, with an approximate five-fold increase observed with a doubling in temperature.

Peroxide is particularly toxic to algae, a concentration of 3 mg/l killing algae. Blue green species are very sensitive with death occurring at concentrations as low as 1.5 mg/l. However, the effect can be quite short lived with populations recovering within

48 hours. There is also evidence of temporary suppression of macrophyte growth following peroxide use.

Zooplankton are also sensitive to peroxide with mortalities in Daphnia being reported at concentrations of around 3 to 7 mg/l, although at much lower concentrations (0.1 mg/l) motor activity becomes supressed. Invertebrates such as Gammarus display a similar level of sensitivity to Daphnia, but molluscs (e.g. Physa), are significantly more tolerant, a typical LC_{50} being 17 mg/l. Whilst invertebrates are generally more sensitive to peroxide than fish, they are considered to recover relatively quickly following exposure due to recolonisation by drift from unaffected areas.

With respect to fish, recent studies on several species have revealed no observable effect when peroxide concentrations, over a period of exposure lasting 45 minutes, ranged from 250 mg/l (brown trout) through to 500 mg/l (variety of species). However, it is noticeable that larger individuals are more sensitive than smaller fish. To mitigate for impacts of peroxide use on fish it is advisable to avoid localised areas of high concentrations by ensuring adequate mixing during dosing. In addition, the influence of temperature on toxicity should be borne in mind, particularly as most problems will occur in the summer months. Therefore residual concentrations should not be allowed to accumulate.

Residual peroxide concentration has been set at an operational limit of 20 mg/l. This is for treatment of individual isolated pollution incidents. In addition, to ensure adequate protection of aquatic ecosystems following a single or infrequent dosing regime, it is recommended that *average* concentrations of peroxide over the 24 hour period following application should not exceed 1 mg/l.

1.4 Types of Peroxide

Three types of commercially available peroxide are currently used in waterways to alleviate oxygen sags and to remediate against pollution events:

- 35% strength liquid peroxide
- 50% strength liquid peroxide
- Sodium carbonate peroxyhydrate (PCS), a solid form of peroxide.

Very little work has been carried out which allows the comparison of the effectiveness of these different forms of peroxide. 50% liquid peroxide has the greatest peroxide content per unit volume, it should therefore release the most oxygen. It is more expensive than 35% peroxide, the most common form utilised to date. 35% liquid peroxide is cheaper than PCS and also releases a greater amount of oxygen for a given quantity, as well as being regarded by many as safer and easier to apply. PCS may also increase pH in the water body as it decomposes and is labour intensive. However, there are several advantages associated with the use of PCS, including suitability for extended storage, the need for no additional equipment and its slow decomposition, if placed in hessian sacks on the river bed.

1.5 Hydrogen Peroxide Transfer Efficiency

Hydrogen peroxide decomposes to form water and oxygen:

$2H_2O_2 \Leftrightarrow 2H_2O + O_2 + \text{heat}$

For every tonne of 35 % solution hydrogen peroxide, a maximum of 0.165 tonne of oxygen is theoretically available for release.

Estimations of the transfer efficiency of hydrogen peroxide range from 82.3% to 9%. These markedly different estimations highlight the difficulty of accurately estimating the quantities of hydrogen peroxide which need to be added to a water body to achieve a desired increase in oxygen concentrations.

1.6 Determining the Quantities of Peroxide Required – Feedback Monitoring

The amount of oxygen released into the water column and the speed of its release by peroxide are dependent on numerous factors including; site characteristics, peroxide dose, type of pollutant, BOD, antecedent conditions, degree of mixing, speed and position of application and the size of water body. It is therefore very difficult to predict accurately the amount of peroxide which will be required for a given pollution incident.

Peroxide addition can be regulated by monitoring upstream and downstream oxygen concentrations. Monitoring at several points downstream allows both the effects of the peroxide and its progress downstream to be determined. Residual peroxide concentrations should also be monitored and should not exceed 20 mg/l.

1.7 Suppliers of Hydrogen Peroxide

Companies who supply hydrogen peroxide are listed in the table below. It should be borne in mind that the nature of the stabiliser and the specification of commercial products should be established before they are used.

Supplier	Contact number
Solvay Interox Ltd	01925 651 277
Ellis and Everard	0151 420 7616
Tennants	0161 205 4454
Hays Chemical Distribution Ltd	0161 848 7938
Univar plc	01256 312073

1.8 Specification for Liquid Peroxide

Solvay Interox has supplied the following specification for 35% hydrogen peroxide.

Specification for Hydrogen peroxide 35%m/m (commercial) – 411 grade

Physical description	Clear liquid with characteristic odour and free from visible impurities
Strength (as H_2O_2, %m/m) **(as H_2O_2, g/kg)**	34.8 – 35.6 %m/m 348 – 356 g/kg
Chloride (as Cl mg/l)	10 mg/l maximum
Non volatile matter (mg/l at 105°C)	1000 mg/l at 105°C maximum
Contaminants	Free from substantial chemical impurities

1.9 Suppliers of Equipment for Peroxide Application

A specification for a venturi pump arrangement for peroxide application to water-bodies is provided in the more detailed R&D Technical Report P2/095/1/M. However, the following company supplies a purpose built venturi based system specifically for remediation of aquatic pollution events.

Supplier	Equipment Supplied
Ospray Ltd **01823 680043**	Oxyjet system & Oxyjet Boat – venturi based systems for peroxide application

Liquid peroxide is supplied in a variety of volumes and appropriate containers. Small quantities are supplied in 30kg plastic carbouys. Larger quantities (1 tonne) are supplied in IBC's (Intermediate Bulk Containers) dedicated to the transportation of peroxide, whereas, bulk quantities can be provided by road tanker. IBC's are perhaps the most convenient size for many applications but logistical problems may be encountered as a fork-lift truck is required for off loading which must be hired separately. An outlet valve is however built into the bottom of IBC's.

PCS is supplied in 25kg polythene bags. Individual bags & quantities up to 5 tonnes can be obtained from Ellis & Everard, whereas, bulk requirements (supplied in palettes of 40 x 25kg bags, with a minimum quantity of 5 palettes per order) can be met by Solvay.

1.10 Suppliers of Equipment for Measuring Residual Peroxide

Various types of equipment are available for the measurement of residual peroxide concentrations in water. Examples of the equipment available, along with suppliers, are listed in the table on page 5.

Supplier	Equipment Supplied
Merck, Lutterworth **0800 22 33 44**	RQflex – quantitative test strip analyser Merckoquant – peroxide test strips
Palintest **0191 491 0808**	Standard photometer 5000 – digital colorimeter + standard comparator kit
Reagacon **01865 774677**	Lamotte – various test kits
Galco UK Ltd **01727 850267**	CHEMetrics test kit – self-filling reagent glass ampoules
Camlab, Cambridge **01223 424222**	Kit containing thiosulphate solution for determination by drop count method

1.11 Methods of Peroxide Application

A variety of methods have been used to add hydrogen peroxide to water bodies ranging from the more basic methods of pouring liquid peroxide into the water body to more complex pump assisted commercially available systems. Methods of administering peroxide to water bodies are described in the summary below:

1.11.1 Direct Addition Using Liquid Peroxide – Drip Feed & Pouring

The simplest method of liquid peroxide addition is to pour or drip the liquid at an appropriate rate into the receiving water body. However, in order to dissipate the liquid and maximise the oxygen generation efficiency, some form of mixing is required. In running waters this can be achieved via the natural flow within the stream or river. At sewage treatment works the final effluent channel can provide a very effective mixing zone combined with a secure location for dosing. However, in large still waters artificial mixing may be required. In its simplest form this could be undertaken using the outboard engine on a small boat. Alternatively, a water pump can be used to extract water from the area to which peroxide is being added and spraying the discharge hose over as wide an area of the zone of affected water as is necessary and/or feasible.

> *Peroxide can be obtained from the list of suppliers on page 3. A 2" pump (or larger) should be used and can be easily hired from appropriate outlets.*

1.11.2 Direct Addition Using PCS – Pouring & Slow Release Sacks

Although less efficient than liquid peroxide, powdered PCS offers an alternative which may be useful in particular scenarios. It can be added directly into a water body or stream in the same way as liquid, in small or large amounts. However the main advantage of this form of peroxide is that it can be deployed in paper or hessian sacks which allow the PCS to decay slowly. For example, sacks of PCS can be taken to remote areas quickly for events such as a silage spillage in a small stream with no convenient vehicular access. Sacks can be laid on the stream bed in flowing waters, allowing the PCS to gradually be dissipated, being restricted within the fabric of the bag. In still waters, sacks of PCS can be deployed in precise locations from the side of

a boat, sinking to the bottom of the water body, where the PCS dissolves over a period of several hours, elevating bottom water concentrations.

PCS can be obtained from the list of suppliers on page 3 in sacks as required.

1.11.3 Venturi Pump – Custom-built systems & the Oxyjet

For versatility and rapid speed of deployment, combining a drip feed system with a venturi pump offers an excellent method of delivery and mixing. Simple custom-built systems have been used in several regions to good effect, although a commercially developed peroxide dosing system, Oxyjet, is now available for both bankside and boat deployment. A venturi unit is fitted to the inlet side of the pump, it creates a vacuum drawing peroxide from upright drums into the outflow stream of the pump, effectively mixing the peroxide with the outflow jet, which can then be returned to the water body. Fine control of peroxide addition can be achieved with good dispersion, negating the need for additional mixing.

1.12 Advice & Guidance

Considerable practical expertise in the field use of Peroxide has been built up by the Agency. Below is a list of Agency staff who have operational experience in the use of H_2O_2 and would be pleased to offer advice:

Contact Name	Agency Region	Contact Number
Alan Hunter	North East	0191 203 4113
Doug Freakley	Midlands	01543 444141
John Batty	Midlands	0121 711 5866
Brian Franklin	South West	01392 444000
Peter Lloyd	Thames	0181 310 5500
Richard Maile	Thames	0181 310 5500
Chris Hazleton	Thames	0181 310 5500
Neil Dunlop	Thames	0181 310 5500
Mark Pilcher	Thames	0181 310 5500

In addition, the following individuals from Solvay Interox, suppliers of peroxide and PCS, would be pleased to provide advice:

Technical Advice Alun James, Tel: 01925 651277
Commercial Advice Steve Davidson Tel: 01925 651277

2. HEALTH AND SAFETY

2.1 Risks Associated with Hydrogen Peroxide and PCS

Hydrogen peroxide is a strong oxidising agent which could create a hazard if incorrectly stored, transported or handled. A number of toxic effects are associated with hydrogen peroxide, principally related to its corrosive properties. It is damaging to mucus membranes, eyes and skin, with the severity of the lesions and the prognosis of intoxication depending directly on the concentration and duration of exposure. It is not flammable but will contribute to the combustion of other materials, as will PCS. PCS is similarly irritating to mucus membranes, eyes and skin.

Materials used for the construction of storage vessels, valves, pumps and pipework should be selected with care, as some metals can not be used due to the risk of oxygen gas production. Aluminium and stainless steel can, however, be used if chemically passivated. Suitable plastic materials include PTFE, polyethylene and unplasticised pvc.

2.2 Safe system of work

Before hydrogen peroxide or PCS is purchased and/or used in any circumstances, a safe system of work for its storage and use should be devised. A safe system of work should:

- Detail the hazards, the precautions and safe working conditions.
- Be used in all aspects of training.
- Be referred to in the company's health and safety policy.

In addition, details should be added concerning:

- The correct use of equipment and tools.
- The working environment.
- Safety rules.
- Formal issue, correct use and maintenance of all necessary protective clothing and equipment.
- Relevant chemical/product safety information.
- Correct and safe working methods with all relevant safety precautions.

As the safe system of work will vary for different types of incident, a risk assessment should be carried out for each proposed peroxide addition, to determine the potential hazards and remediative actions which can be taken. The actions identified in the risk assessment should then be used to tailor the safe system of work to the site and working conditions.

Every safe system of work should include details of the following 8 points. Examples of the details that should be included are given under each heading.

2.2.1. Storage

Hydrogen peroxide should be stored:

- In a cool, well ventilated place in original containers.
- Upright, as container tops are pressure vented and may leak if not stored upright.

- Away from combustible and flammable materials.
- Away from acids, alkalis, metals, organic materials and flammable substances.
- Away from PCS.
- In specifically treated storage vessels of 304L or 316L stainless steel or HDPE which should be used exclusively for hydrogen peroxide.
- State and temperature of the containers should be regularly checked.

PCS should be stored:
- In a cool, dry area, protected from direct sunlight.
- Away from acids, alkalis, metals, organic materials and flammable substances.
- In original containers.
- Away from combustible or flammable materials and heat sources.
- Away from hydrogen peroxide.

In addition:
- An emergency shower, first aid kit, fire extinguisher and eye wash bottles should be provided.
- Warning signs should be in place.
- A no smoking policy must be observed.
- The product should never be returned to the container.

2.2.2 Transport to the site

Hydrogen peroxide should be transported:
- On open-backed vehicles, trailers or boats.
- With appropriate warning signs.
- In an upright position and restrained.
- According to storage requirements.
- In enclosed vehicles with an airtight bulkhead between load and driver.
- By trained drivers certified to transport chemicals (specifically peroxide) on the public highway[1].

PCS should be transported:
- On open backed vehicles, trailers and boats. Packages should be restrained and protected from direct sunlight and rain. Sheeting may be required.
- With appropriate warning signs.
- In enclosed vehicles, packages must be restrained.
- According to storage requirements.
- By trained drivers certified to transport chemicals (specifically peroxide) on the public highway.[1]

In addition:
- Fire extinguishers, first aid kit and eye wash bottles must be provided.
- Drivers must be prepared for spillages and hence must carry appropriate equipment; PVC suit, rubber boots, visor, PVC gloves, hard hat.
- A no smoking policy must be observed.

[1] Rules on transport of dangerous goods should be observed. Quantities of more than 200 kg of peroxide require properly trained drivers.

2.2.3 Storage and use on site

- On site, procedures should be implemented to prevent spillage, splashing or dust emission from the use of hydrogen peroxide or PCS e.g. storage on a plastic sheet to prevent spillages reaching dry grass.
- Personal protective equipment should be worn at all times.
- The hydrogen peroxide or PCS should be used and stored in such a way as to limit risks to other employees and members of the public.
- Barriers and warning signs should be used.
- An emergency shower, first aid kit, water fire extinguisher and eye wash bottles should be provided.
- A no smoking policy must be observed.
- The importance of prevailing weather conditions should be defined e.g. PCS may be unsuitable for use in windy conditions.

2.2.4. Staffing

- The use of hydrogen peroxide or PCS on site is not suitable for lone working.
- The site must not be left unattended during the use of hydrogen peroxide or PCS.
- Minimum staff numbers should be defined and specific tasks allocated to each staff member.
- All staff must be aware of the safe system of work.

2.2.5. Safety clothing and equipment

Hand protection:

- Protective gloves which are chemical resistant.
- Recommended materials are PVC, neoprene or rubber.

Eye protection:

- Protective goggles should be worn for all operations.
- Chemical proof goggles or a face shield should be worn if there is any risk of splashing.

Skin protection:

- Overalls should be worn for all operations.
- Apron or splashsuit and boots of PVC, neoprene or rubber should be worn if there is any risk of splashing.

Other precautions:

- A shower (or emergency hose) and eye wash stations should be on site.
- Consult safety manager for the selection of personal protective equipment suitable for the working conditions.
- A trained first-aider should be present during dosing.

2.2.6. Action in emergencies

General:

- 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 water.

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

Eye contact:
- Flush eyes immediately with eye wash or running water for 15 minutes, keeping eyelids wide open.
- Seek medical attention.

Skin contact:
- Remove contaminated clothing, under the shower if necessary.
- Wash the affected skin with running water.
- Cover to avoid loss of body heat – provide clean clothing.
- Seek medical attention.

Ingestion:
- Seek medical attention in all cases.
- If conscious, rinse mouth, administer fresh water, do not induce vomiting.
- If unconscious, loosen collar and tight clothing, lay on left side, resuscitate and administer oxygen if necessary, keep warm.

Fire:
- Extinguish with large quantities of water if safe to do so.

Spillage:

Precautions - Try to stop the spillage **if safe to do so.**
In case of leak, isolate the area.
Avoid materials and products which are incompatible.

Clean up - If possible, dam large quantities of liquid with sand or earth.
Dilute with large quantities of water.
Do not add chemical products.
Do not return recovered product to original container, to avoid contamination.
Small quantities can be discharged to sewer with large quantities of water.
Notify appropriate authorities in case of important discharge.

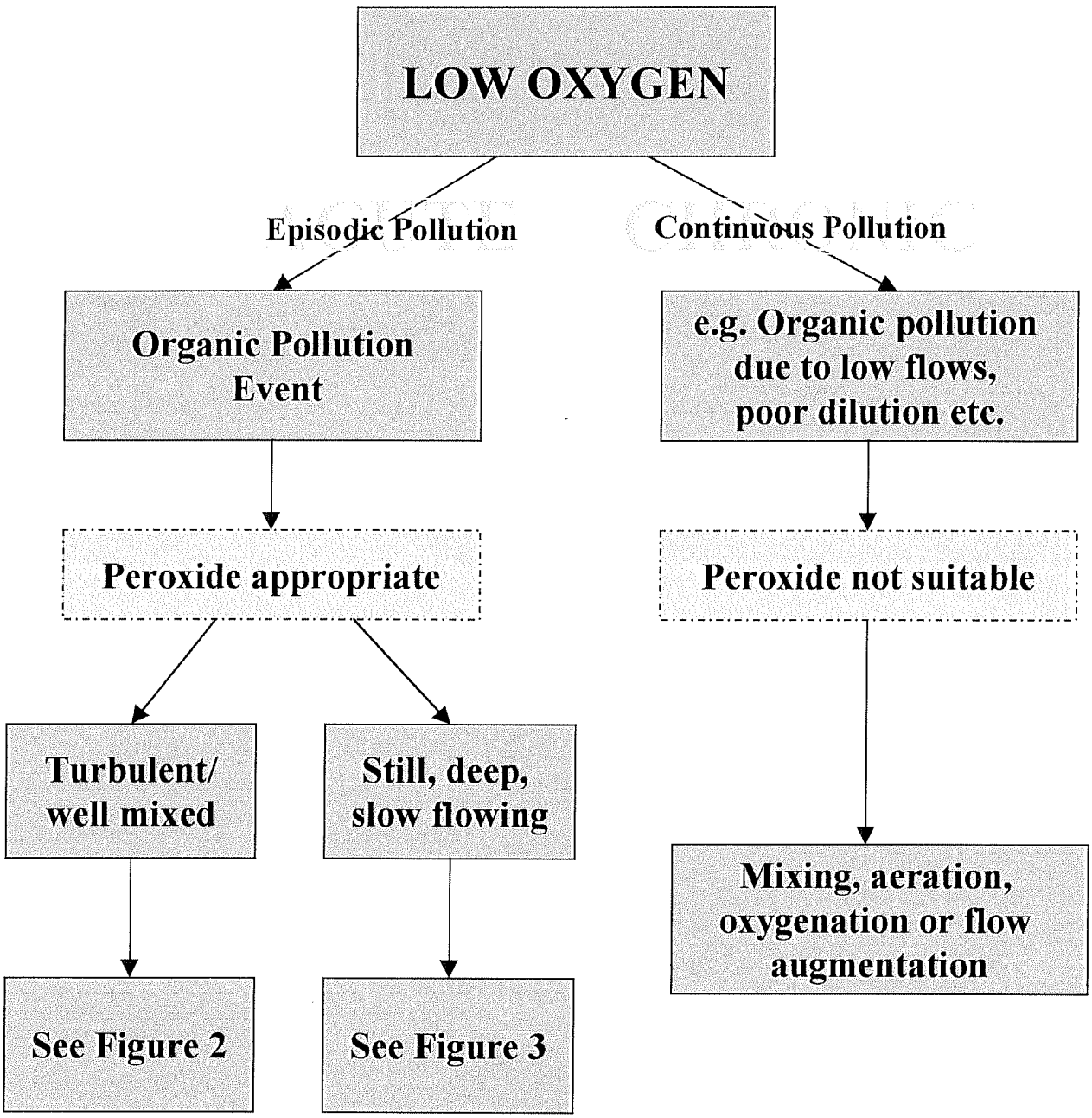
In addition:
- Downstream users must be made aware of the intention to use peroxide before dosing is commenced.
- Staff should always be aware of their location and be able to supply road names or a six-figure grid reference to the emergency services.
- All staff should be aware of details of the nearest hospital.

2.2.7 Dosing procedure
- The method of dosing and associated monitoring should be clearly defined. Some methods of dosing will have more associated risks than others.

2.2.8 Cleaning of equipment/disposal of waste

- All pumping plant, hoses, Venturis etc. should be thoroughly flushed with water to remove all traces of hydrogen peroxide prior to leaving the site.
- Peroxide containers should be returned to the supplier without rinsing. Empty containers present a hazard and should not be left unattended. They should be cleared away as soon as practicable to a safe storage area or returned directly to the supplier.
- PCS sacks should be collected and sent to a licensed authority who deal specifically with the disposal of hazardous goods (oxidisers).

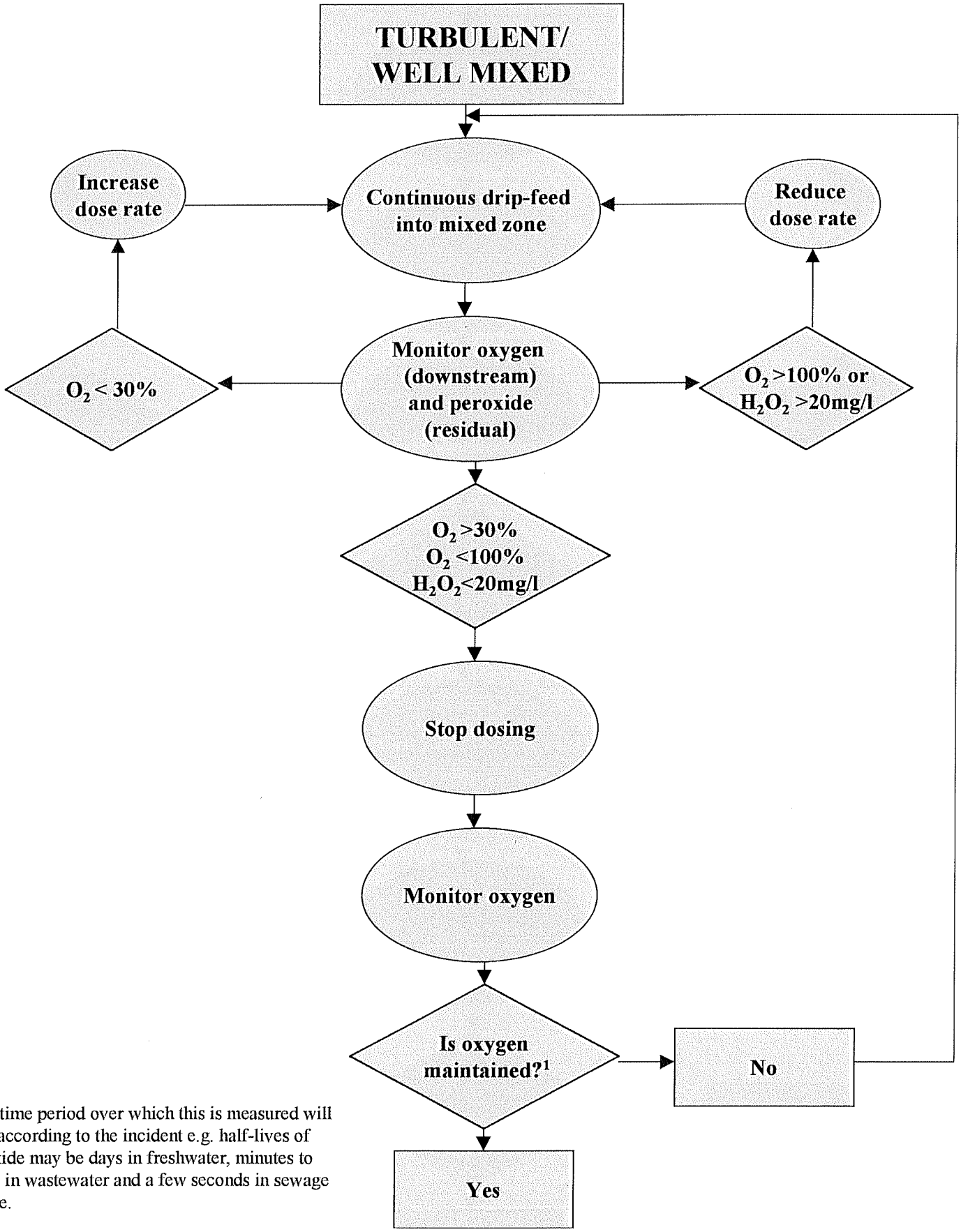
Figure 1
Peroxide Use - Operational Guidelines



Examples of episodic events
- Silage spillage
- Storm sewage
- Sewage works failure
- Foodstuffs + by-products spill
- Industrial pollution incidents
- Pulp mill spillage
- Oxygen sags - algal blooms

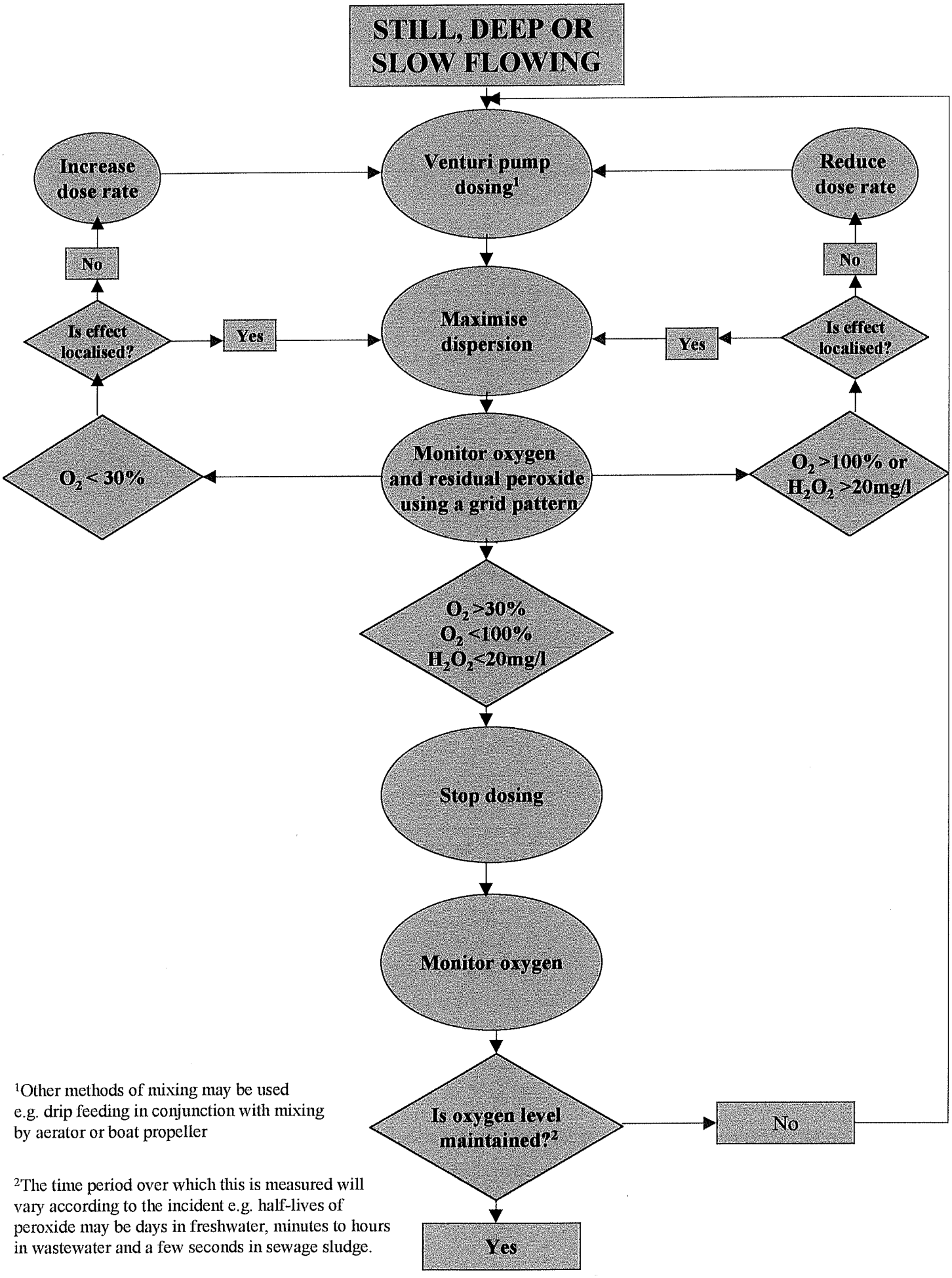
Examples of continuous events
- Treated sewage effluent
- Background BOD/SOD

Figure 2
Peroxide Use - Well-mixed Environments



[1]The time period over which this is measured will vary according to the incident e.g. half-lives of peroxide may be days in freshwater, minutes to hours in wastewater and a few seconds in sewage sludge.

Figure 3 Peroxide Use - Still Waters



[1]Other methods of mixing may be used e.g. drip feeding in conjunction with mixing by aerator or boat propeller

[2]The time period over which this is measured will vary according to the incident e.g. half-lives of peroxide may be days in freshwater, minutes to hours in wastewater and a few seconds in sewage sludge.

3. RECORD OF HYDROGEN PEROXIDE APPLICATION TO A WATER BODY

Following a review of information available on the use of hydrogen peroxide in waterways, it has become apparent that more data need to be collected to determine the efficiency of oxygen transfer from hydrogen peroxide in the field. This could be achieved by the standardisation of the data which are collected when peroxide is used following low DO incidents.

The minimum data which are required are summarised below. Sample collection should be at the point of dosing but should also be upstream and at regular intervals downstream of the dosing in flowing water bodies. The size of incident and resources available will obviously dictate the level of investigation and therefore the quality and quantity of data available for reporting.

A minimum requirement however, should be the completion of the proforma reporting sheet on the following page. This sheet is designed to provide a summary of the main aspects of a pollution incident and the addition of hydrogen peroxide in a standardised reporting format. It is not intended to act as a substitute for scientific or operational project reports.

Following completion of forms, data should be recorded onto a national or regional database, to allow the dissemination of results irrespective of the success or otherwise of the hydrogen peroxide application. Failures are as important as successes. Only by extending our knowledge of the effectiveness of hydrogen peroxide in different types of water bodies with variable water quality will peroxide become an established and valuable pollution incident management tool.

3.1 Data to be collected during hydrogen peroxide application to a water body

1. Date of application.
2. Location.
3. Size of water body (depth, width, length).
4. Flow rate in the water body.
5. Reason for application.
6. Amount of peroxide added.
7. Type of peroxide used (liquid/solid/strength).
8. Method of application (Drip feed/Venturi/etc).
9. Date/time dosing began.
10. Date/time dosing ended.
11. Temperature at start of dosing/end of dosing/regular periods afterwards.
12. Dissolved oxygen at start of dosing/end of dosing/regular periods afterwards.
13. pH, BOD, COD, SOD (if appropriate), ammonia at start of dosing/end of dosing/regular periods afterwards.
14. Residual peroxide concentrations during dosing and at regular periods afterwards.

Once complete, the proforma reporting sheet should be returned to the regional representative who sits on the Pollution Alleviation Working Group (PAWG).

4. REPORTING PROFORMA

Contact Name:	Address: Phone No:
Water body: Size: Flow:	EA Region:
Description of incident: Pollutant: Volume: Type: Strength:	
Types of peroxide added: Method of application: Time period: Quantities used:	
Results of application – successful or unsuccessful?	
Data available. Please tick Oxygen data Residual peroxide data Water quality data Biological data Details of water body Health & Safety Issues Report available yes/no (delete as appropriate)	

5. INDEX