A risk assessment of the use of fluorescein in public fountains in Sheffield

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1 Introduction

It is proposed to introduce fluorescein dye into the fountains at Barker's Pool and at the Peace Gardens in order to make the water a bright lime yellow for the launch of Yorkshire's festival celebrating the Tour de France. This document is an analysis of the potential risks involved in this. The relevant literature has been examined and a number of experiments have been performed, which are reported here. It is concluded that the dye poses no risk to members of the public or to Sheffield City Council employeees. The architectural structure of the fountains is not at risk, nor will there be any environmental damage.

2 Fluorescein

Fluorescein is an organic dye with full name 2-(3-hydroxy-6-keto-xanthen-9-yl)benzoic acid and Chemical Abstracts Service registry number CAS 2321-07-5. It is most commonly encountered as the sodium salt of the acid which is a reddish powder, readily soluble in water to give a brilliant lime yellow fluorescent colouration. Confusingly, this form is also often called "fluorescein" and this is the substance we intend to use. Other names are "sodium fluorescein", "uranine", "Drugs and Cosmetics Yellow no.8" and "Colour Index Acid Yellow 73". It is identified as CAS 518-47-8 [6].

It is widely used as a fluorescent tracer for many applications, particularly for tracing water courses. It is used as a colourant in several domestic products, such as cleaners and windscreen wash. There are many suppliers of the substance, for example Aldrich Chemical, Mistral Laboratories, VWR International etc.

3 Proposed use

We intend to add fluorescein dye to the fountains in the Peace Gardens and Barker's Pool in order to produce a spectacular yellow colouration. The Peace Gardens has holding tanks of 55,000 litres while Barker's Pool has two tanks of 4000 litres each, giving a total of 63,000 litres. Typical concentrations for visual water tracing are 1 part-per-million (1ppm, 1mg/litre), but visual effects require greater concentration.

Experiments were performed to judge the concentration, a number of samples were made up with different levels of dye. At 1ppm the water the liquid is noticeably coloured, at 8ppm it is a lime yellow, while at 16ppm it is a vivid lime yellow. Increasing further to 32ppm does not produce a dramatic increase in effect. The dye comes in 500g packs, so adding three, a total of 1.5kg, would give 24ppm, which should give spectacular results.

Fluorescein is rapidly destroyed by sunlight. A solution of the dye exposed to three hours of sunlight was found have lost 50% of its intensity, while another test in an uncovered dish showed an almost complete destruction in two hours [10]. Admittedly this was Californian sunlight and some adjustment should be made for Yorkshire sunlight. Experiments with vials of 16 and 32ppm fluorescein solutions in glass vials placed on a south facing window ledge in Sheffield, showed that the solution lost its colouration substantially over four days in late February. It had been a fairly sunny period, but some account should be made for the fact that the solution was in glass, behind a double glazed window, so the ultraviolet content and consequently the bleaching would be reduced.

Fluorescein is also destroyed by chlorine. The solutions just described were all made with tapwater chlorinated at the normal level. It is understood that the water in the fountains in Sheffield is more strongly chlorinated, and indeed chlorine can be smelt close to the fountains. If at all possible, the chlorination should be stopped at least 24 hours before the dye is added, to allow time for the chlorine levels to drop. After the end of the project, the chlorine levels can be increased again and this should help clear any residual colouration at the point that the spectacular effect is over.

4 Impact on members of the public

Fluorescein is not considered hazardous. Its toxicity is stated as LD50 oral in rats 6,721 mg/kg [6], which suggests that the lethal dose in 80kg humans is around 500g of the pure dye. (Compare the toxicity of ethanol, LD50 oral in rats 9,000 mg/kg, lethal dose in 80kg humans is around 720g.)

We intend to use it at a concentration of 24ppm at which it is completely harmless. The dye has been licenced in the US and in Europe [3] for use in drugs and cosmetics, but it has not been permitted as a food additive.

It is routinely used on humans in opthalmic and other medical procedures [5]. Strong solutions of the dye are dropped into the eyes to check the fitting of contact lenses. The most dramatic medical application is ocular angiography which is intended to reveal the arteries and veins at the back of the eye. It is performed by injecting fluorescein solution into a vein in the arm and photographing the back of the eye through the lens. For an adult, typically 500mg of the dye is injected [1]. This is performed routinely with negligible problems. A side effect is a yellowish discoloration of the skin which disappears within 12 hours.

It is possible that members of the public might drink the liquid in the fountain. At 24 ppm, the consumption of a litre of fountain water would give 24mg of fluorescein in the alimentary canal. Even if all this was absorbed into the blood, the dose would be considerably less than the medical injected dose, and can be considered safe. Similarly, inhalation of spray or getting the dyed water in the eyes can be considered non-hazardous.

5 Impact on personnel

Personnel deploying the material are likely to come into greater contact with the material. To avoid handling the powdered material outdoors in potentially windy conditions, the powder will be measured out and made up into a strong solution indoors before the event. This solution will be brought to the sites in labelled one litre PET bottles (re-cycled mineral water bottles). To lessen the possibility of contamination, long-sleeve rubber or plastic gloves will need to be worn during all dye-handling operations. Sufficient clean water and kitchen towels will be provided to deal with spillages or other problems.

6 Achitectural impact

An assessment has been made of the possibility of damaging the structures of the fountains by permanently dyeing the materials.

6.1 Stonework

The Peace Gardens fountains and rills have a range of stone and ceramic surfaces which might take up dye. To test this, a number of stone samples, gritstones, sandstones, slate and granite and also brick and concrete were tested. Each sample was a few hundred grams and few tens of centimetres across. Available pieces were used, rather than specially prepared material. A thick paste was prepared from fluorescein powder and water. This paste was applied liberally to one side of the material samples which were then allowed to dry. They were then placed outside with the dyed side upwards in Sheffield S8 and allowed to weather for about one month (January-February 2014). At the end of this they were washed and examined in a dark room under ultraviolet light. No colouration or fluorescence was visible on any sample. Admittedly it had been an excessively wet period, but it suggests that the great solubility of the dye ensures that it is easily washed out of porous materials. The conclusion is that stone and concrete materials will not be stained by fluorescein.

6.2 Acrylic

The Barker's Pool fountains contain significant slabs of acrylic. In order to assess the impact on these, experiments were performed on small samples to establish whether acrylic (PMMA, Perspex, Plexiglas, Lucite…) was susceptible to permanent staining by exposure to aqueous solutions of the dye. It was decided to do an extreme case experiment, which could be undertaken on a short time scale. This was to test the susceptibility of samples to a concentrated solution of fluorescein at elevated temperature. Both increased concentration and increased temperature would accelerate the penetration of dye into the acrylic. If the acrylic could be demonstrated to be resistant to this, it would certainly be resistant to lower concentrations at ambient temperatures, even if the exposure was for a longer period.

Material

Two small samples of acrylic were tested. The first was unbranded extruded acrylic rod, 30mm long by 10mm square. The second was cast acrylic branded "Perspex" from Lucite International. It was saw cut to about the same size as the first sample from 10mm thick sheet. For both samples, there were faces with the manufacturers' original polish and roughly saw cut surfaces. It was intended that examination of the saw cut surfaces would show whether dye penetration via scratches was possible.

The difference between the materials is that the extruded material has polymers of lower average molecular mass and may have a grater plasticizer content. The cast material is polymerized from the monomer between glass sheets to provide high optical quality. It is generally of high average molecular mass but may contain unpolymerized monomer and catalysts. There are many grades of acrylic on the market and it is clearly impossible to test them all. These two grades are taken as typical. The material used in the Barker's Pool fountains is almost certainly a cast grade. It is the experience of the author that the cast material is very resistant to dye uptake from aqueous solutions or to attack by solvents, while the extruded material is softer and is more susceptible.

Experimental procedure

A strong solution of fluorescein was prepared by dissolving 0.5g fluorescein in 30ml water. This concentration is vastly in excess of that normally used for tracer studies and vastly in excess of what is intended in the fountain project. A solution of this strength is not the familiar bright yellow or lime green, but rather a dark orangish red. The samples were carefully cleaned with detergent and running water to remove any grease. They were placed in the solution in capped vials and these were then placed in a bain-marie which was brought up to boiling point and then left simmering. The samples remained in the dye solution at around 95°C for an hour. At the end of this, they were allowed to cool, and the samples were taken out and washed in running water. They were then examined visually in daylight and in a darkened room with exposure to ultraviolet and blue light to look for any fluorescence.

Neither sample showed any sign of colouration or fluorescence on any surface. It can be unequivocally stated that acrylic is unaffected by fluorescein in aqueous solution.

6.3 Silicone sealant

It is possible that silicone sealants have been used in the construction of the fountains. They are commonly used where a flexible waterproof joint is required. There are many types on the market, coloured and transparent, some containing mineral fillers. They are largely RTV (Room Temperature Vulcanizing) silicone rubber applied either as a two-component system or as an actoxy cure. Again it is impossible to know exactly what materials have been used in the fountains, so a test was performed using available material.

Experimental procedure

A disused aquarium was obtained that had been constructed from sheet glass held together at the seams with clear silicone aquarium sealant. This aquarium was about fifteen years old, so the silicone was fully set and well aged. Small sample strips of the silicone sealant were cut away from the aquarium. These were simmered in a strong solution of fluoroscein for an hour in exactly the same way that the acrylic samples were treated. At the end they were washed and examined to look for any fluorescence. None was found, and it can be concluded that this grade of silicone sealant is unaffected by fluorescein in aqueous solution. As silicones are highly hydrophobic it is thought that all grades of silicone sealant will be resistant to staining from fluorescein.

6.4 Biofilm

Fluorescein is capable of staining biological materials, as anyone who has handled the dye knows when they get it on their fingers. It is possible that if the acrylic in the fountains has a biofilm deposit, this will take up dye and show some temporary colouration. When immersed in clean water the dye would be expected to leach out again and in any case the dye will bleach out in sunlight. Cleaning of the surfaces to remove any biofilm will also restore the acrylic.

Experimental procedure

In order to make tests on this, recourse was again made to available objects. A glazed earthenware dish and a 1lb. glass jam jar were used. These had spent in excess of a year in a garden in Sheffield S8 and were half full of stagnant water. The interior surfaces had a clearly visible layer of biofilm, in places thick enough to support algal growth. These vessels were emptied, then filled with the strong flourescein solution (0.5g dye in 30ml water) and left overnight at ambient temperature. The next day they were carefully washed out with clean water several times. On examination it was clear that the biofilm had absorbed some fluorescein. The vessels were then refilled with clean water and left for some hours before re-examination. This time the fluorescence was far less. Further changes of the water revealed that the fluorescein was not bound to the biofilm and gradually washes out.

6.5 Achitectural Impact Conclusion

The experiments suggest that none of the materials in the fountains at Barker's Pool or the Peace Gardens are likely to be discoloured by adding fluorescein to the water. If there is any slight surface penetration or absorption by biofilms it will subsequently wash out when exposed to clean water. The natural bleaching due to sunlight and the presence of chlorine in the water will further prevent problems.

7 Environmental impact

At the end of the event, the fluorescein will largely have been degraded to simple organic molecules. It is not expected that large volumes of the dye solution will be discharged to the sewers or to storm drains. However, it is worth examining the likely effect on the environment if the material is released.

A number of studies of the environmental and ecological effects of tracer dyes have been performed [7, 4, 2]. All of these suggest that of all the dyes trialled, fluorescein was the safest and that at low dye concentrations it had no detectable effects. Very high concentrations, vastly in excess of those we intend to use, have been found detrimental to fish [9] and snails [8].

8 Conclusion

The use of fluorescein dye in the Sheffield fountains poses no risk to members of the public or to Sheffield City Council employeees. The architectural structure of the fountains is not at risk, nor will there be any environmental damage.

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