Metals pollution tracing in the sewerage network using the diffusive gradients in thin films technique

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ABSTRACT

Diffusive Gradients in Thin-films (DGT) is a quantitative, passive monitoring technique that can be used to measure concentrations of trace species in situ in solutions. Its potential for tracing metals pollution in the sewer system has been investigated by placing the DGT devices into sewage pumping stations and into manholes, to measure the concentration of certain metals in the catchment of a sewage treatment works with a known metals problem. In addition the methodology and procedure of using the DGT technique in sewers was investigated. Parameters such as temperature and pH were measured to ensure they were within the limits required by the DGT devices, and the optimum deployment time was examined. It was found that although the results given by the DGT technique could not be considered to be fully quantitative, they could be used to identify locations that were showing an excess concentration of metals, and hence trace pollution back to its source. The DGT technique is ‘user friendly’ and requires no complicated equipment for deployment or collection, and minimal training for use. It is thought that this is the first time that the DGT technique has been used in situ in sewers for metals pollution tracing.

Key words | DGT, metals, passive sampling, pollution tracing, sewer system

INTRODUCTION

Pollution caused by metals from trade effluent discharges and other sources can be difficult to trace, and hence control. At present the extent of metals pollution is usually measured by either taking grab samples or collecting samples with an autosampling device and having these analysed in the laboratory. This paper examines a relatively new technique for measuring the concentration of metals in solutions, and reports on field trials undertaken in a catchment.

In 2005 a sewage treatment works (STW) in the Thames Water region was receiving high concentrations of metals in the incoming sewage. The catchment of the STW contained a number of businesses that were consented to discharge some metals, but the concentrations of metals arriving at the STW were much higher than these consents. It was decided to trace back the metals pollution through the catchment to identify its source and ensure that it could be stopped.

Thames Water’s Research and Development department were asked to assist in the pollution tracing using the technique of Diffusive Gradients in Thin-Films (DGT). This is a quantitative, passive monitoring technique that can be used to measure concentrations of trace species in situ in solutions. In this trial the DGT technique has been used to measure the concentration of certain metal species in sewage.

The DGT technique was developed at Lancaster University (Davison & Zhang 1994), and it is from here that the majority of the research has been carried out. The DGT technique was originally developed for use in natural waters, but has since been extended to sediments and soils. It is thought that this study is the first time that...
the DGT technique has been used in situ in sewers for metals pollution tracing. A recent study (Buzier et al. 2006) evaluated the DGT technique in wastewater, but took samples from STW and performed the studies in the laboratory.

A major difference between the DGT technique and more traditional sampling techniques is the species of metals which are detected by the DGT devices. Traditional laboratory analysis of sewage samples measures the concentration of dissolved metals or the total concentration of metals in the sample. DGT only measures those metals which can diffuse across a hydrogel and bind to an ion exchange resin; these are known as labile metals.

The main advantage of the DGT technique over grab sampling techniques, in sewers, is that grab samples only sample a small volume of the sewage, at a specific point in time. The DGT devices can accumulate metals over a period of days, and measure an average concentration, meaning that if the pollution is intermittent there is a greater likelihood of it being measured by the DGT device than by a grab sample. The reliability of discrete sampling was discussed in Ort & Gujer (2006), who show that large errors occur with discrete sampling if the substance of interest is contained in a low number of wastewater pulses. The accumulation of metals on a DGT device also means greater sensitivity than can be achieved by grab samples, metals are pre-concentrated on an ion exchange resin which means that detection of lower concentrations is possible with DGT.

Analytical techniques for metal speciation in freshwaters were evaluated by Sigg et al. (2006), who compared DGT, gel integrated electrodes combined to voltammetric in situ profiling system (GIME-VIP), stripping chronopotentiometry (SCP), flow through and hollow fiber permeation liquid membranes (FTPLM and HFPLM), Donnan membrane technique (DMT), and competitive ligand exchange/stripping voltammetry (CLE-SV). It was found that no single analytical method could provide a detailed description of all the metal species present, but each would measure a certain proportion of the total complexes that lie within a given characteristic thermodynamic and kinetic window. It was also noted that it was advantageous that all methods examined contained a preconcentration step (either by accumulation at an electrode, or within an acceptor medium) and that in situ methods do not have the problems of sample handling and filtration, which may induce changes in the samples and induce artifacts. The detected concentrations of Cu, Pb, and Cd were found to decrease in the order DGT > GIME > FTPLM > HFPLM ~ DMT, which follows the order of decrease of effective measurement time of the techniques.

Theory of DGT technique

The DGT technique works by accumulating the metal ions on an ion exchange resin, separated from the solution by an ion-permeable hydrogel membrane of known thickness (see Figure 1).

Mass transport through the gel is diffusion controlled and thus well defined, making it possible to obtain quantitative data. A cellulose nitrate membrane covers the hydrogel membrane and acts as a filter. The DGT devices are approximately 40 mm in diameter with a gel thickness of approximately 1 mm. The DGT devices for this study were supplied, ready constructed by Lancaster University, and were stored refrigerated at around 3°C before use.

The DGT technique is based on Fick’s first law of diffusion. If the mass of the metal ions which diffuse into the resin layer can be analytically determined, and the deployment time is known, then the concentration of metal ions, in the bulk solution can be quantified. A detailed description of the theory can be found in Zhang & Davison (1995). The diffusion coefficient for each type of metal ion in the hydrogel is assumed to be the same as the diffusion coefficient for the metal ion in water. The hydrogel used is approximately 95% water when fully hydrated, and has pore sizes of approximately 2 to 5 nm, which is much bigger than the hydrated radius of 0.2 to 0.3 nm for the ions involved in this study. An initial study (Davison et al. 1994) showed that the diffusion coefficient for Mn$^{2+}$ within the hydrogel is effectively the same as in water. A more detailed study (Garmo et al. 2003) looking at a larger selection of elements found that for all the elements of interest to this study (except Fe) the diffusion coefficients measured using DGT were close to previously published values in water. It has also been found that above a low threshold flow of
The mass of metal accumulated by DGT is independent of flow (Gimpel et al. 2001).

The ion exchange resin used in the resin layer (see Figure 1) is Chelex 100, an ion exchange resin that strongly binds multivalent metal cations. Hence the DGT technique does not measure the total metal concentration in a solution, only those metal ions that are available to bind to the ion exchange resin; i.e. the labile metal ions. Thus, the proportion of metal ions detected by the DGT technique is similar to those which are bioavailable. It also means that direct comparison between the concentration measured by the DGT technique and the concentration measured by grab samples (both total metals and dissolved metals) is not possible, as they are measuring slightly different quantities. An important point to note in terms of pollution tracing is that if the metals pollution is in the form of particulate metal species then it may not be detected by the DGT technique.

To calculate the concentration measured by the DGT devices the temperature of the solution needs to be known, so that the diffusion coefficient of the metal across the hydrogel can be estimated. It was not possible to log the temperature at all sample locations during this trial, and hence the temperatures had to be estimated from readings taken when the grab samples were taken. The temperature loggers that were available were placed in wet wells and showed a maximum temperature variation of approximately 3°C during the deployment period. This variation leads to changes in the diffusion coefficient of less than 10%. However, the temperature variations in the sewers could be greater than this, and there is also the possibility that in the sewers the devices may not always be immersed in the flow. For this reason the results from the DGT devices may not be fully quantitative, but can provide a comparison between locations to trace back the route of the metals pollution.

**METHODS**

DGT devices were purchased from DGT Research Ltd. and used as received. The DGT devices were deployed in purposely designed holders, which hold three DGT devices in a linear configuration. The holders were attached to the wet wells or manholes using a length of rope, attached to some point either in the wet well or manhole, or just outside. The DGT devices were kept sealed until immediately prior to deployment when they were loaded into the holder, with care being taken not to touch the filter surface. For deployment in sewage pumping stations (SPS) the wet well was pumped to its lowest level and the holder was deployed just below this to ensure coverage at all times. For deployment in manholes the holder was deployed face down in the invert of the sewer. The time of deployment was noted, and any other samples and measurements, eg grab samples, temperature, or pH, were taken. Grab samples were sent to the Thames Water Laboratories for analysis of dissolved metals and total metals for: Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd, As, and Pb.

Collection was essentially the reverse of this process. The DGT holders were pulled up using the rope. The DGT devices were removed from the holder before being rinsed.
in deionised water, and then labelled and put into small sealable plastic bags to be sent to Lancaster for analysis for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, and Pb. The analysis involves eluting the metal ions from the ion exchange resin using nitric acid and analysing the resulting solution using atomic adsorption spectroscopy or inductively coupled plasma mass spectrometry (see Zhang & Davison 1995 for full details of analysis). The time of collection was noted, and samples were taken as needed.

Field trials were carried out in the catchment area of the STW in two stages. Stage 1 involved deploying the DGT devices in six SPS throughout the catchment to identify those where metals were present in high concentrations. DGT devices were also deployed at the STW inlet, the STW outlet, and the river immediately downstream of the STW outlet. Stage 1 was also used to determine the optimum deployment time for the DGT devices, and to ensure that the pH levels in the SPS wet wells were in the correct range for the DGT devices to operate. Previous laboratory experiments involved deploying DGT devices in sewage samples for between 4 and 145 hours, where it was found that the short timescales did not give an accurate indication of the metals present. Three sets of three DGT devices were deployed in each location, with one set of three collected after 24 hours, the next after 48 hours, and the final set collected 120 hours after initial deployment. The pH values measured at the nine locations all fell within the range pH 7.0 to pH 8.6, when measured at deployment and at each collection. This is well within the optimum range pH 5 to pH 10 for DGT devices with Chelex 100 resin (Gimpel et al. 2001). The temperature of the wet wells was measured on deployment and collection of the DGT devices, and was logged over a period of five days at one of the SPS wet wells. Temperature variation was a maximum of 3°C over this period.

Stage 2 investigated in more detail the catchment of the SPS found to have high metals concentration in stage 1. This involved placing DGT devices in manholes as well as SPS, to further narrow the search for sources of metals pollution. In stage 2 DGT devices were deployed into three manholes, two SPS, and the STW inlet for 120 hours. Grab samples were taken at the time of deployment and the time of collection from all locations. The pH was measured at all locations, and found to be in the correct range. Temperature was also measured on deployment and collection of the DGT devices.

RESULTS AND DISCUSSION

Stage 1

The DGT results for all metals measured in stage 1 are shown in Table 1. Figure 2 shows the metals of interest at six SPS, the STW inlet and outlet, and the river immediately downstream of the STW outlet. Due to the wide range of concentrations between the different metal species the relative concentrations of the metals are shown, i.e. the location with the highest concentration is given a concentration of 100, and the concentrations at the other locations are shown relative to this value. From Figure 2 it can be seen that SPS 2 clearly has the highest concentration of Ni, Cu, Zn, and Cd of any of the locations.

| Metals concentrations measured by DGT during stage 1 (all in μg litre⁻¹) |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                | Al  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  | Cd  | Pb  |
| SPS 1           | 10.62 | 37.47 | 425.33 | 0.15 | 1.71 | 0.76 | 10.54 | 0.01 | 0.54 |
| SPS 2           | 32.02 | 7.91 | 21.96 | 0.06 | 33.08 | 104.50 | 35.57 | 0.09 | 0.58 |
| SPS 3           | 52.99 | 39.13 | 1196.09 | 0.18 | 2.35 | 2.48 | 29.08 | 0.02 | 0.82 |
| SPS 4           | 32.26 | 36.84 | 342.49 | 0.15 | 1.00 | 1.87 | 15.98 | 0.02 | 0.84 |
| SPS 5           | 37.06 | 22.88 | 357.65 | 0.19 | 1.89 | 3.11 | 29.01 | 0.04 | 1.15 |
| SPS 6           | 27.68 | 15.43 | 59.02 | 0.15 | 1.30 | 1.63 | 15.70 | 0.02 | 0.27 |
| Inlet           | 27.55 | 24.22 | 62.67 | 0.14 | 2.37 | 7.37 | 27.61 | 0.03 | 0.68 |
| Outlet          | 11.96 | 8.37 | 7.44 | 0.04 | 1.40 | 1.98 | 11.17 | 0.01 | 0.15 |
| River           | 25.38 | 24.00 | 39.13 | 0.15 | 1.63 | 2.96 | 19.84 | 0.01 | 0.44 |
sampled. From these data it was a straightforward decision to choose SPS 2 as the pumping station to investigate further in stage 2.

The DGT results can be compared with those from the grab samples. Figure 3 shows the dissolved Zn concentrations measured on four different days. It shows that on only one of the four days are elevated Zn levels seen at SPS 2. Had the investigation been conducted using grab samples only it is highly likely that the high Zn concentrations found at SPS 2 could have been overlooked due to the fluctuating concentration levels.

**Length of deployment**

A further objective of stage one was to determine the optimum length of time that the DGT devices should be deployed in sewers to give the most useful results. The optimum deployment time should be a balance between the devices being in place long enough to see any significant metals concentration that could be present, but not being there so long that the capacity of the devices is exceeded, or that they become so ragged up that they stop accumulating metals. The total capacity of the DGT devices is around 0.5 mg of metals. For SPS 2 (the location with the largest overall concentration of metals in stage 1) the maximum amount of metals absorbed by the DGT devices after 120 hours was 87 μg, hence nowhere near capacity. The amount of ragging varied from location to location, but showed no overall trend between the devices that were removed after 120 hours compared to those removed after 24 hours. From all these results it was decided that for future deployment the devices should be kept in place for approximately five days, but this trial has shown that a period as short as 24 hours is enough to see variations in metals concentrations between different locations.

**Stage 2**

The catchment of SPS 2 is split into two branches, a northern branch and a southern branch. Three manholes were chosen as sampling points, two on the northern branch (MH 1 and MH 3) and one on the southern branch (MH 2). DGT devices were also deployed at SPS 2, SPS 3, and the STW inlet. The devices were deployed at SPS 3 to ensure that SPS 2 still had an elevated metals concentration in the time between stages 1 and 2.

Figure 4 shows the relative concentrations as recorded by the DGT technique at the six locations. It can clearly be seen that of the three manholes it is MH 2 that has the highest metals concentrations, thus indicating the metals pollution is coming from the southern branch of the SPS 2 catchment.
Comparing DGT results and grab samples

It is not possible to directly compare the results obtained by the DGT technique with those obtained by taking grab samples. The grab samples could be analysed for either total metals concentration, or dissolved metals concentration, whereas the labile metals concentration measured by the DGT technique is expected to fall between these two measures. In addition the grab samples only measure the metals concentration at the time the sample is taken, whereas the DGT technique provides an average concentration over the deployment time.

CONCLUSIONS

This trial has shown that the DGT technique is well suited for use in the sewerage system for determining locations that show an excess concentration of metals, and hence tracing the pollution back to its source. The DGT technique only measure labile metals, it will not detect those that are in highly stable complexes or adsorbed onto the surface of solids in the sewer flow. However, this trial proves that the difference in labile metals concentration is sufficient to resolve those locations where metals pollution is a problem. The DGT technique is a cumulative technique, and hence measures an average concentration over the length of the deployment. The DGT technique therefore has the advantage over instant grab samples that it may detect short lived peaks in metals concentration that could otherwise be missed. The DGT probes are easy to use, and would require minimal training for deployment and retrieval.

Future work is planned to follow up on the two stages reported here to trace the metals pollution further back up the catchment to definitively establish its source.

Key findings:

- The effectiveness of the DGT technique for the tracing of metals pollution in sewers has been established.
- The technique is easy to use, and provides an average concentration allowing “24 hour” monitoring of the sewerage system.
- It is thought that this study is the first time that the DGT technique has been used in situ in sewers for metals pollution tracing.

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REFERENCES


