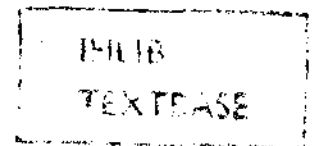INSTITUTE
OF
HYDROLOGY

IODIDE AND LITHIUM TRACERS IN
CHEMICAL DILUTION GAUGING
OF STORM SEWERS

by

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ABSTRACT

The potential use of iodide and lithium ions
as tracers in chemical dilution gauging
exercises for storm sewers is assessed.
It appears that iodide has considerable
limitations because of serious problems in
analysis and significant amounts of tracer
being sorbed from solution on to particulate
matter (adsorption during field storage
prior to analysis introduces serious systematic
errors in the flow estimates). Lithium can
be used in this application, however, provided
that representative background concentrations
are determined throughout the gauging. For
this tracer no significant sorption effects
were observed. The approach for testing tracers
prior to their application in chemical dilution
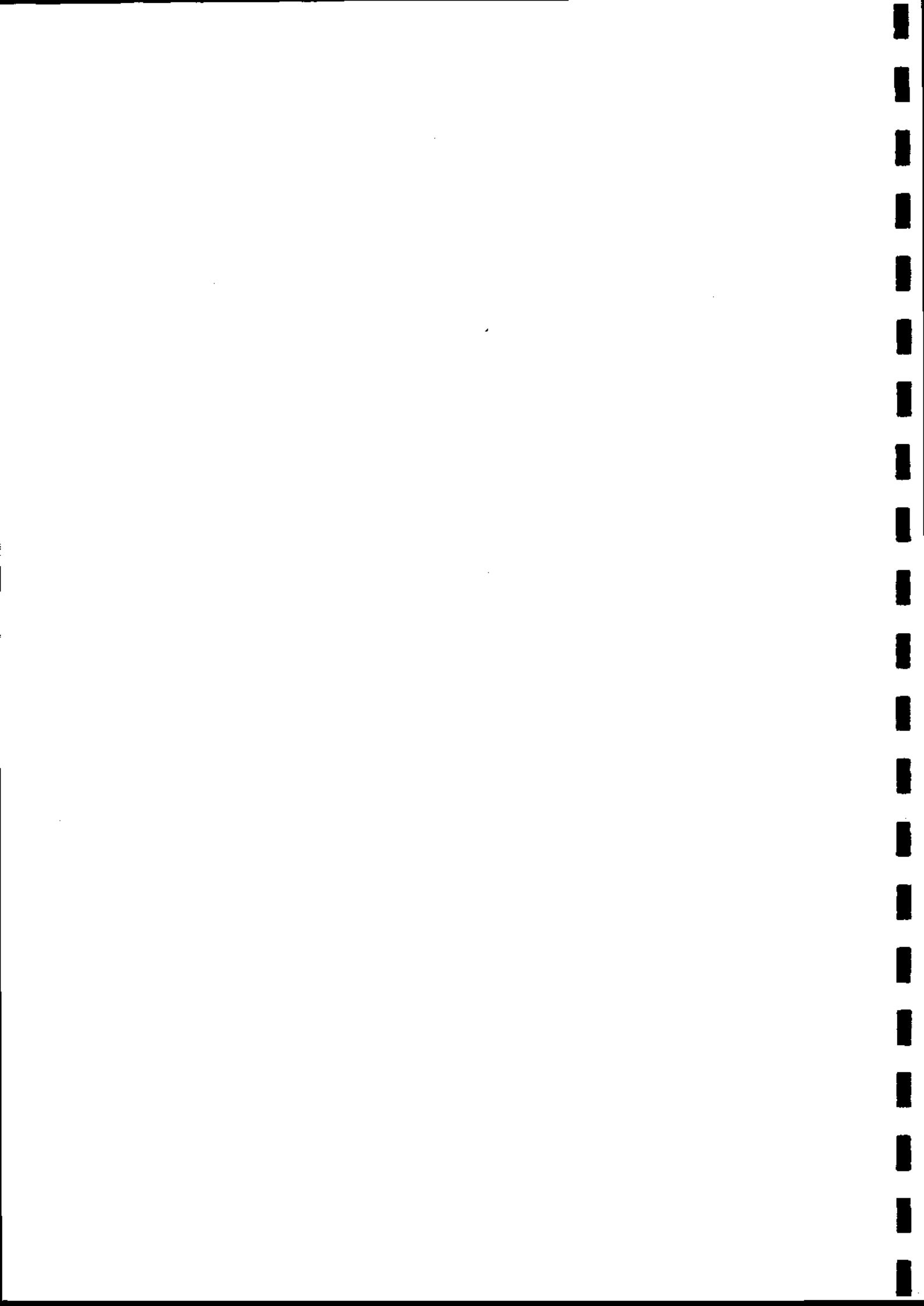gauging exercises is discussed.

REPORT NO 50

June 1978

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1. INTRODUCTION

Although iodide has been used successfully as a dilution gauging tracer for fluvial studies (Greenland, 1975; Smith *et al*, *in press*) its usefulness for intended IH studies of storm-sewers has not been confirmed. An alternative tracer, lithium, has been employed for several years for storm and foul-sewer studies with some success (Blakey, 1969; Gizzard and Harms, 1974; White, Lee and Belcher (WRC) Manse (WRC) unpublished data). Before field studies are undertaken, it was essential to establish which, if either, of these tracers could be used satisfactorily. Further, the testing of tracers is important in general to categorise under what circumstances they can or cannot be used. This is especially true for the tracers under consideration since not only are they commonly, and increasingly, used in chemical dilution gauging studies but they also are two of the few practicable tracers used which are environmentally safe. In addition, in storm-sewers, suspended loads, containing a high proportion of organic material, are large and this is conducive to loss of tracer from solution (Neal and Truesdale, 1976), a situation not previously encountered in chemical gauging studies at IH. Thus if loss of tracer from solution (within the expected time period between sample injection and sample analysis) is demonstrated to be significant then that particular tracer cannot be used for these intended studies since this would introduce systematic errors of unknown magnitude.

A comparison of the removal of lithium and iodide from solution is of particular relevance since these tracers have contrasting hydrochemical characteristics. For example, lithium exists in solution as the cation $Li^+_{(aq)}$ and could be removed from solution by particulate matter having high cation exchange capacities (clay minerals). Iodide, however, exists in solution as the anion $I^-_{(aq)}$ (or oxidised to $IO_{3(aq)}$) and could be removed from solution by particulate matter having high anion exchange capacities (organic matter) as well as by biochemical processes. Thus the choice of either of these two tracers for dilution gauging studies may be determined by the major differences in their hydro/geochemistry in the particular aquatic environment under study.

2. METHOD

Analysis

All the laboratory reagents used were of Analar grade. Iodide and lithium standards were prepared from sodium iodide and lithium chloride respectively. Samples of storm-sewer water were collected using an Automatic Liquid Samplers Ltd 4BE vacuum sampler with

24 bottles (Harvey *et al.*, 1976) from storm-sewers at Bracknell and Stevenage during individual storm events. The suspensions collected were stored unfiltered and returned to the laboratory for analysis within seven days of sampling. Subsequent filtration was performed using Whatman GFC glass fibre filter circles.

Total dissolved iodine in the filtered waters was determined by the method of Truesdale and Smith (1975) using a Technicon Auto Analyser I. Each sample and standard was analysed in duplicate and, to minimise interference effects from other components present in the waters analysed, calibration standards were always made up in the appropriate, filtered, background material. Calibration was performed using 10 iodide standards in the range 10.0 to 100.0 μg l^{-1} total iodine. Initial experiments using the above and other storm-sewer waters (Harvey *et al.*, 1977) indicated that the total dissolved iodine method of Truesdale and Smith (1975) could not be applied directly for these waters. This was because most cases gave spurious results, the cause of which was not identified, although it was established that it was a function of the water type analysed rather than an Auto Analyser malfunction. However, before modifying or changing the method of iodine analysis, which would be very time consuming, simplified sorption experiments for a similar system having no analytical difficulties were undertaken, i.e. using filtered suspended matter from these sewer waters with distilled water rather than storm-sewer water. Thus if sorption were observed in these simplified experiments then it would be reasonable to assume that, irrespective of the method of analysis, iodide would not be a suitable chemical tracer for storm-sewer waters containing similar suspended matter loadings.

Total dissolved lithium in filtered water was determined by flame emission spectrophotometry using a Pye Unicam SP 1900 spectrophotometer. An air/acetylene flame (flow rates 5.0 to 1.0 l min^{-1} respectively was used with an emission head for a burner height of 15 mm. Samples and standards were filtered and analysed singly. Calibration standards were always made up in the appropriate background solution and a correction was made for instrument drift. This correction was effected by introducing known standards (1.00 mg l^{-1} lithium) after every 9th sample being analysed and assuming a linear decrease or increase in response between successive standards. If the variation in response between successive known standards was erratic and greater than $\pm$ 3% the analysis batch was discounted and the samples were redetermined after readjustment of the spectrophotometer. Calibration was performed using seven lithium standards in the range 0 to 1.5 mg l^{-1} lithium. Samples and standards were determined for repeat 10-second aspiration times until consecutive determinations were within 1% of each other and between each solution a distilled water wash was aspirated for approximately 20 seconds.

Sorption studies

The sorption experiments used in this study are essentially similar to those used by Neal and Truesdale (1976).

The iodide tracer sorption experiments consisted of mixing six 250 ml portions of filtered damp suspended matter from Stevenage storm-sewer waters with distilled water solutions containing 60.0 µg l^{-1} total iodine in 300 ml stoppered glass bottles and determining loss of total iodine from solution. The sediment loadings used were in the range 3.56 to 7.00 g l^{-1}. The suspensions were mixed thoroughly and 25 ml subsamples were taken after periods of 1, 2, 3, 4, 7 and 8 days for analysis. These samples were filtered through separate Whatman GFC filter circles and analysis was performed within one hr of filtration.

The lithium tracer sorption experiments consisted of adding the tracer to Bracknell and Stevenage storm-sewer waters and determining the rate and degree of removal of lithium from solution. The limited amount of storm-sewer water collected by the automatic sampler in the field for these studies necessitated mixing of the subsamples collected to ensure sufficient water volumes for full analysis. The subsamples (15 to 24) were divided into groups containing low to progressively high sediment loadings and these sorted samples were mixed to give four bulk solutions containing low to progressively high sediment loadings for both sewer waters. Lithium concentrations of 1.00 mg l^{-1} lithium (+ blank lithium concentration) were obtained by dilution of a stock 1000 mg l^{-1} lithium standard solution with these bulked suspensions. These suspensions with added tracer were thoroughly mixed and 25 ml portions were removed for analysis after periods of 1 hr, 1, 2, 3, 4 and 7 days. Analysis was performed on the filtered subsamples within two hours of collection. Standard solutions were prepared, on the first day of analysis, for each bulked filtered sewer water and these were stored and used for calibration of the different sample-types analysed.

Initial experiments on Stevenage storm-sewer water demonstrated that, within experimental error, stored lithium calibration standards could be used during analysis for periods up to 14 days of initial mixing. No tests were performed for greater storage times.

3. RESULTS

Iodide

The results of the iodide sorption experiments (Table 1) indicate that significant uptake (> 2%) of this tracer occurred, within one day of mixing for all but one of the suspensions analysed. The exceptional sample (no 4; 5.9 g l^{-1} sediment loading, time = 1 day) is probably caused by iodine contamination since the level of total iodine measured is higher than that introduced at the initial stage of the experiment. In all other cases the results are consistent, in that the amount of total iodine lost from solution increases with prolonged

TABLE 1.   THE SORPTION OF IODIDE ON TO SUSPENDED STEVENAGE STORM-
            SEWER SEDIMENTS

Equilibration time (days)	Suspended load (gl^{-1})					
	3.6	3.7	4.6	5.9	6.3	7.0
	% I^- removed from solution					
0	0.0	0.0	0.0	0.0	0.0	0.0
1	4.6	2.0	-8.3	2.5	1.5	2.4
2	4.8	5.3	4.5	2.5	2.9	4.9
3	6.3	11.6	7.9	7.0	3.1	4.6
4	9.8	20.9	9.4	6.7	4.7	4.5
7	23.3	31.1	22.2	20.0	15.0	13.5
8	23.3	35.3	19.7	16.7	13.6	11.3

storage time. Major removal of total iodine (> 10%) was observed for
all the samples analysed after storage times $\geq$ 7 days. The results
are similar to those observed previously for iodide sorption on to
peat (Neal and Truesdale, 1976) with the curious exception that in the
present study the amount of total iodine sorbed decreased rather than
increased with increasing sediment load as would be expected from
theoretical considerations. The cause of this discrepancy is unknown.

The results differ from those obtained by Harvey et al., for a similar
experiment in that they observed normal sorption behaviour (i.e.
greater uptake with higher sediment loadings) for a lower range of
sediment loadings with storm-sewer samples collected from a different
storm event. However, the degree of iodide tracer removal for
sediment loadings greater than 1.0 g l^{-1} were in a similar range for
the two studies. Thus after eight days storage Harvey et al. (1976)
observed removal of total iodine from solution of 18% and 25% for
sediment loadings of 1.1 and 2.0 g l^{-1} compared with 23% and 11% for
sediment loadings of 3.56 and 7.00 g l^{-1}, respectively, in the present
study. The results obtained in the two studies cannot be compared
directly since the sediments were collected on different days and
hence they may possess different sorption characteristics.
Nevertheless, both sets of results demonstrate that significant
removal of total iodine from solution does occur within one day where
there are storm-sewer sediment loadings greater than 1.0 g l^{-1}.

Lithium

The results of the lithium sorption experiments (Table 2) indicate that, irrespective of acid pretreatment, no significant uptake of this tracer occurred within seven days of tracer addition for either Bracknell or Stevenage storm-sewer waters, even at high sediment loadings.

TABLE 2. THE SORPTION OF LITHIUM ON TO UNFILTERED BRACKNELL AND STEVENAGE STORM-SEWER WATERS

(a) UNTREATED SAMPLES

Equilibration time	Bracknell				Stevenage			
	% Lithium removed from solution							
Sample No*	1	2	3	4	1	2	3	4
1 hr	2	2	2	2	2	-3	1	2
1 day	-2	0	-2	0	1	-2	0	2
2 days	-1	1	-2	0	2	1	3	3
3 days	2	3	0	-2	-1	-2	1	1
4 days	2	2	1	2	0	0	0	0
7 days	-1	1	-3	-3	1	-2	0	1

(b) ACID TREATED SAMPLES

Equilibration time	Bracknell				Stevenage			
Sample No*	1	2	3	4	1	2	3	4
1 hr	-1	1	0	1	-1	0	0	1
1 day	-3	-3	-2	-2	1	-1	1	-1
2 days	-1	-2	-1	-2	0	1	1	0
3 days	-2	-1	-1	-1	-1	-2	-2	0
4 days	-1	-4	2	1	-1	-1	-1	0
7 days	-1	-1	-1	-2	-2	-3	-3	1

* Samples 1 to 4 are listed in order of progressively increasing suspended load.

4. ANALYSIS OF LITHIUM IN STORM-SEWER WATER

Although the initial sorption experiments presented above suggest
that lithium should be used as a tracer for storm-sewer dilution
gauging studies in preference to iodide, a method for its analysis
has not been fully established at IH to date. For this reason the
following trials were undertaken.

The analysis of lithium in storm-sewer waters using flame emission
spectrophotometry is complicated by errors introduced due to
interference (matrix) effects from other components present in the
waters analysed. These effects are functions of the chemical
variability of waters analysed and are primarily the result of
variations in flame ionisation (associated with variations in the
content of easily ionisable salts; Slavin, 1968 and Price, 1975) as
well as surface tension changes (e.g. associated with variations in
the amount of detergent in storm-sewer waters; Price, 1975). For
reliable determinations it is essential that these effects are
minimised either by adding "masking" reagents to both standards and
samples or alternatively using standards made up in the same
background solutions (i.e. storm-sewer waters) as the samples. In
the present study only the latter technique was considered because it
would be more convenient for routine analysis although it has to be
demonstrated that these matrix effects are constant within a storm-
sewer during a chemical dilution gauging exercise. To test if this
condition held, the following experiments were performed in addition
to the above sorption studies.

Storm-sewer waters from Bracknell and Stevenage were collected during
individual storm events and these were subdivided into two separate
ordered groups to ensure that sufficient solution was available for
subsequent analysis. These samples were filtered and standard
calibration solutions (0 to 1.5 mg l^{-1} lithium) were made up for each
of these batches as well as for a reference distilled water solution.
The calibrations obtained all gave a linear relationship between
added lithium and instrument response. The calibration curves fitted
well a linear regression model for the equation $y = mx + c$ where x is
the instrument response, y is the concentration of lithium added and
m and c are constants. The results, expressed in terms of linear
regression coefficients (Table 3), show that the gradients (m) are
constant individually for Bracknell and Stevenage storm-sewer water
calibrations but are significantly different from each other as well
as for distilled water. In all cases the multiple correlation
coefficient was greater than 0.9995.

The mean gradients, 1.688×10^{-3} and 1.538×10^{-3} for Bracknell and
Stevenage storm-sewer water respectively, compared with a gradient of
1.708×10^{-3} (single determination) for a distilled water calibration.
Varitions in the gradient m were higher for the Bracknell storm-sewer
water calibrations. For example, all values of m were within 3.3%
($\sigma = 0.028 \times 10^{-3}$) and 0.7% ($\sigma = 0.003 \times 10^{-3}$) of the mean gradient

TABLE 3.   REGRESSION LINES FOR THE CALIBRATION OF LITHIUM STANDARDS IN BRACKNELL AND STEVENAGE STORM-SEWER WATER

Sample No*	m $(\times 10^{-3})$	c $(\times 10^{-3})$	Multiple correlation coefficient
(1) Bracknell storm-sewer water			
1	1.657	-14.62	0.9999
2	1.743	-20.69	0.9996
3	1.682	-8.37	0.9999
4	1.668	-19.78	0.9995
5	1.684	-13.53	0.9999
6	1.661	-19.58	0.9997
7	1.693	-5.13	0.9997
8	1.723	-14.13	0.9998
9	1.684	-12.97	0.9999
(2) Stevenage storm-sewer water			
1	1.527	-24.72	0.9999
2	1.540	-30.88	0.9998
3	1.527	-21.93	0.9999
4	1.540	-25.64	0.9999
5	1.548	-31.17	0.9999
6	1.541	-23.13	0.9998
7	1.533	-23.03	0.9999
8	1.544	-52.99	0.9999
(3) Distilled water			
1	1.708	-4.06	0.9999

* The samples are arbitrarily numbered in a time sequence. All samples were collected from single storm events and waters low sample designated numbers were collected during high flow and high sample numbers during low flow.

for Bracknell and Stevenage storm-sewer waters respectively; the reason for this difference was not established. These results indicate that the magnitude of the matrix effects is significant for different storm-sewer waters but is not significant for individual localities over single storm event sampling periods. However, it is concluded that in general a representative "bulked" background water may be taken for use in calibration of these storm-sewer waters to minimise any matrix effects. If greater precision is necessary for calibration purposes many sets of standards would be required throughout a storm event and comparisons with samples collected for particular times during that event would have to be made.

Although these matrix effects were constant for each locality the background concentrations of lithium (i.e. samples without tracer addition) varied systematically with time of sampling for the Stevenage but not Bracknell storm-sewer waters (Table 4). The background values varied between 0.4 and 1% and 1 and 6% of those with 1.00 mg l^{-1} lithium addition for Bracknell and Stevenage storm-sewer waters respectively. Hence if the minimum tracer concentration after dilution in the sewers is 1 mg l^{-1} lithium a continuous representative background correction would be required to give sufficient accuracy in chemical dilution gauging of Stevenage storm-sewers only. If however to save on the cost of each gauging the amount of tracer injected is decreased and hence lower lithium concentrations are to be measured, the background lithium concentration becomes highly significant for both storm-sewers and representative background values are essential. For example, if the minimum tracer concentration after dilution in the sewers is 0.1 mg l^{-1} lithium the background values would be in the range 5% to 10% and 8% to 40% of the determined value for Bracknell and Stevenage storm-sewer waters respectively.

Therefore representative backgrounds are required throughout a lithium chemical dilution gauging of Bracknell and Stevenage storm-sewers whenever diluted concentrations of less than 1 mg l^{-1} of tracer are predicted in the field.

TABLE 4.   THE VARIATION IN BACKGROUND AND BACKGROUND PLUS 1.00 MG LITHIUM l^{-1} LITHIUM RESPONSE FOR STEVENAGE AND BRACKNELL FILTERED STORM-SEWER WATERS COLLECTED DURING INDIVIDUAL STORM EVENTS

	INSTRUMENT RESPONSE				
Sample No.*	Stevenage		Sample No.*	Bracknell	
	Background	Background + 1.00 mg lithium l^{-1}		Background	Background + 1.00 mg lithium l^{-1}
1	37	598	1	7	616
2	29	595	2	3	587
3	9	576	3	3	597
4	11	573	4	6	612
5	16	587	5	4	599
6	11	583	6	5	618
7	5	585	7	4	605
8	11	589	8	5	587
9	8	562	9	7	595
10	9	556			
11	9	581			
12	26	567			
13	9	552			
14	22	562			
15	23	561			
16	25	574			
17	16	564			

* Samples numbered in time sequence. Sample 1 was collected at the highest flow and sample 17 at the lowest flow during each storm event.

5. DISCUSSION

The present study has shown that lithium tracer is not removed from solution in Bracknell and Stevenage storm-sewer waters containing suspended matter whereas iodide tracer is. However this does not imply that either of these tracers can or cannot be used as general dilution gauging materials for either storm-sewer, foul-sewer, river or estuarine studies. For example, the conclusions of this and previous work (Neal and Truesdale, 1976) do not indicate that in general iodide cannot be used in chemical dilution gauging studies, but they do indicate that this tracer is highly suspect for waters containing a high concentration of organic-rich suspended load. Indeed, for either low suspended loadings or high suspended loadings where the particulate phases contain small amounts of organic matter, loss of iodide tracer from solution can be insignificant (Neal and Truesdale, 1976; Smith *et al., in press*).

Similarly, the evidence of this or any other study cannot be used on its own to suggest that lithium can or cannot be employed as a general tool for chemical dilution gauging exercises. Thus, for example, although lithium is not sorbed on to organic-rich suspended sediments, significant sorption of lithium may occur in systems where the suspended load is high and where these sediments contain a high proportion of components having large cation exchange capacities (e.g. clay minerals) and alternatively will not be significant when the sediments contain a high proportion of components having low cation exchange capacities (e.g. silica).

In addition, the decision as to whether a specific tracer can or cannot be used for chemical dilution gauging in particular environments cannot be assessed on the basis of previous indirectly related studies. This is because the nature of tracer-sediment interactions is sufficiently complex and inadequately understood (Duursma and Bosch, 1970; Duursma and Gross, 1971) as to preclude general statements e.g. that for waters containing high sediment loadings lithium and iodide can be used as tracers where the particulate matter contains high proportions of organic and inorganic components respectively. Hence it is worthwhile re-emphasising the conclusions of Neal and Truesdale (1976) that it is essential to test for sorptive processes each time tracer techniques are applied either at new sites or specific sites where great variations in suspended matter type occur.

Unfortunately a rigorous method of testing whether sorptive as well as chemical/biological/analytical effects are significant is impracticable since laboratory experiments would have to be designed to allow for factors such as variation in mixing parameters, flow lengths, temperature, times of transport and chemical quality. However, as a basic test of tracer removal from solution the following experiment, as described by Neal and Truesdale (1975), could be conveniently performed at every chemical gauging. A set of test solutions should be made up as soon as possible after sample collection using unfiltered

representative background solutions. Prior to analysis, these test solutions should be stored for a period equivalent to that between the collection and subsequent analysis of the samples obtained during the gauging. These test solutions should be filtered on the day of analysis. After the test samples have been stored for the appropriate period, a set of standard solutions should be made up in filtered background water and both sets of solutions analysed. If there is no significant variation between the two sets of solutions then the results obtained for that gauging exercise can be used. If the results differ, however, then supporting evidence must be provided to demonstrate that those gauging results can still be used.

Further, even if it is demonstrated in the laboratory that removal of tracer from solution can be inhibited chemically when samples are collected (e.g. by acidification) or corrected for by the use of representative stored standards, it is insufficient evidence to conclude that, during transport along the pipeline or in the river/ estuary prior to sampling, loss of tracer from suspension would not be significant. Thus in these cases it must be additionally demonstrated that one or both of two conditions hold before the tracer is accepted for use. Firstly, that tracer removal from solution is slow (i.e. very little tracer is lost from solution during the time between injection and sampling of tracer). Secondly, that the suspended sediment remains in the same parcel of water as the tracer over the injection and sampling stretch (i.e. sediment is not lost from suspension or transferred through solution at a different rate from that of the tracer). In the case where a chemical inhibitor is added to the samples it must also be demonstrated that particulate matter does not release significant amounts of the naturally occurring tracer that may be associated with it. Similarly it must also be demonstrated that the chemical inhibitor does not remove components from the particulate matter which would introduce significant interference effects during subsequent chemical analysis.

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