

THE ADSORPTION OF RHODAMINE-B ON TO MATERIALS CARRIED IN SUSPENSION BY INSHORE WATERS

By

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Experiments have been carried out to investigate the adsorption of Rhodamine-B on to suspended material when the dye is used in the turbid waters of some English east coast estuaries. This adsorption appears to be most serious when large dilution has taken place. The experimental results lead to an equation between observed dye concentration and that to be expected under otherwise similar conditions but without loss of dye from solution by adsorption. The equation takes the form $R = (r^n + KP)^n$ where R = Rhodamine concentration to be expected if there were no adsorption, r = measured Rhodamine concentration, P = suspended load in parts per million, and K and n are constants.

INTRODUCTION

Many workers have found that Rhodamine-B is a convenient tracer material for use in water movement studies. However, a tendency for the dye to be adsorbed on to particles carried in suspension may be a disadvantage when working in turbid inshore waters. Tracer experiments carried out in the east coast estuaries of the Rivers Blackwater, Thames and Medway during the spring and summer of 1966 indicated that this apparent loss of dye by adsorption might be appreciable. An investigation was therefore made to determine the magnitude of the effect and also to assess the possibility of applying a correction for adsorption loss to survey results.

EQUIPMENT

The instrument used for detection of dye was a G. K. Turner Model III Fluorometer. The usual optical filter arrangement was used as described by other workers (PRITCHARD and CARPENTER, 1960). For most measurements the standard 12×75 mm Pyrex cuvettes were used, but for the lower dye concentrations a greater sensitivity was obtained by fitting a 20 ml flow-through cuvette.

GENERAL PROCEDURE

The main part of this investigation was carried out in the laboratory during the summer and autumn of 1966, using dried solid material that had been obtained from the bed of the River Blackwater. This procedure was adopted for its convenience and because it seemed most likely to yield reproducible results, although it would no doubt have been better in principle to have worked directly on water samples carrying solid matter in suspension. However, there is a considerable variation in the suspended load in the Blackwater over a period of several weeks and, at the time the investigations started, the suspended load was considered to be too low to give satisfactory results in the experimental work. In any case there is a tendency for the suspended particulate matter to coagulate on standing. Thus water samples collected from the estuary would not necessarily have given results truly representative of conditions in the estuary, since there would have been an inevitable delay between collecting samples and using them in the tests.

The procedure adopted was to add a weighed quantity of the dry particulate material to a known volume of Rhodamine solution and to observe the resulting change in dye concentration. This was done using various combinations of salinity, temperature, initial dye concentration and mass of added material. Further experiments were made, using silt-laden water samples collected from the Rivers Blackwater and Crouch, in order to discover what difference would be expected between the adsorption loss obtained using dry material and that under conditions corresponding more closely to working conditions in these estuaries.

EXPERIMENTS USING DRIED SEDIMENT FROM THE BLACKWATER ESTUARY

Accurately weighed 500 mg samples of dried sediment obtained from the Blackwater Estuary were added to one-litre volumes of sediment-free water, also from the Blackwater Estuary. These one-litre volumes initially contained known concentrations of dye. The suspensions were mechanically agitated for one hour in a temperature-controlled water bath, a period which had been found to be sufficient for adsorption equilibrium to be attained. The concentration of dye in the solution at the end of this hour of agitation was then measured using the fluorometer.

Rhodamine-B is subject to photochemical and chemical decay (FEUERSTEIN and SELLECK, 1963), and in order to eliminate the effect of this from the results a control solution was used. This control was made up to the same initial dye concentration as the test solution and was placed alongside the latter in the water bath, where both solutions were similarly agitated. Any difference between the dye concentrations in the two solutions after this period of agitation was assumed to result from adsorption loss.

In presenting these results reference will be made to an adsorption coefficient (a) defined by the equation:

$$a = \frac{\Delta r}{r}$$

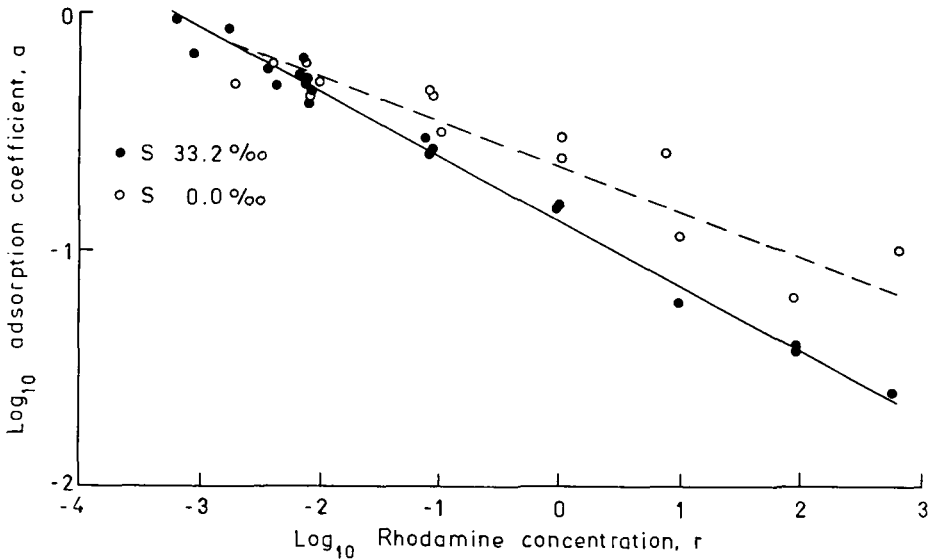


Figure 1. The relation between Rhodamine-B adsorption and the dye concentration in saline and fresh waters, as indicated by experiments using dried sediment.

where Δr = fall in dye concentration resulting from adsorption,
 r = mean dye concentration during adsorption.

Although a varies with r it will be assumed that the variation of the adsorption coefficient over the fall in dye concentration (Δr) resulting from adsorption will be sufficiently small that no distinction need be drawn between the mean adsorption coefficient over the range Δr and the actual adsorption coefficient at concentration r .

Figure 1 illustrates the results obtained using Rhodamine dissolved respectively in saline estuarine water and in fresh water. These results show, in both cases, a significant increase of the adsorption coefficient with decrease of the dye concentration. This observation is consistent with the results quoted by LEDERER and LEDERER (1957) for adsorption of organic compounds on to chromatography columns; these authors comment that adsorption frequently increases strongly with dilution of the solution.

A comparison of the two sets of results shows that adsorption is greater in fresh than in saline water. FEUERSTEIN and SELLECK (1963) have also commented on the marked increase in adsorption observed in fresh water, but their results suggest that the effect may be unimportant over the salinity range likely to be met in an estuary. A few experiments were therefore carried out to investigate further the dependence of the adsorption coefficient on salinity, but no variation could be detected for salinities in the range 8‰ to 33‰. It is therefore assumed that, when considering adsorption loss of Rhodamine, no account need be taken of salinity variation for the range of salinities likely to be met in estuaries such as the Blackwater.

The dependence of adsorption on temperature was also investigated and the results confirmed the statement by FEUERSTEIN and SELLECK that there is no

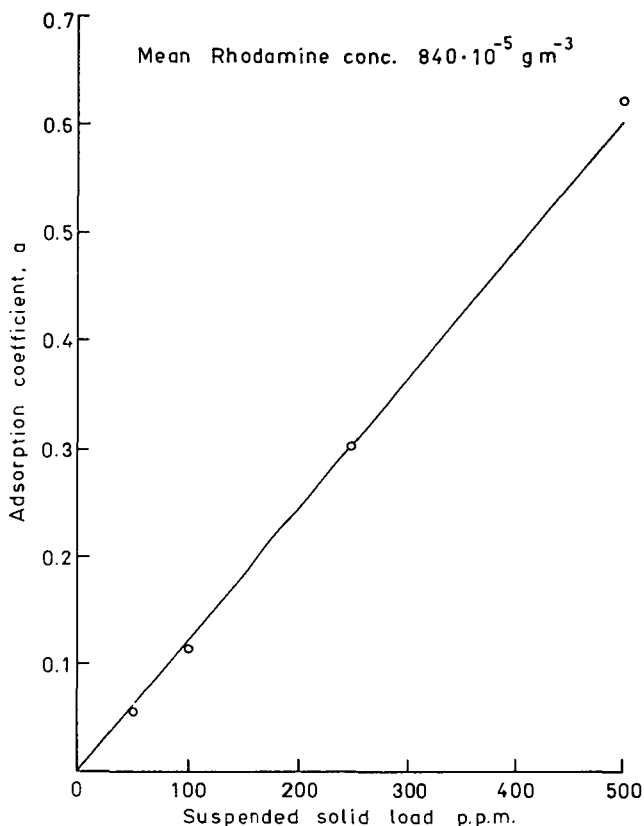


Figure 2. The relation between Rhodamine-B adsorption and the suspended solid load, as indicated by experiments using dried sediment.

significant variation of adsorption over the temperature range likely to be encountered in an estuarine environment.

A few experiments were carried out using different masses of added dry material. The results of these experiments are illustrated in Figure 2, which shows that over the range of values likely to be met in practice the adsorption coefficient should be directly proportional to the mass of solid material in suspension per unit volume of liquid.

EXPERIMENTS USING SEDIMENT-LADEN WATER FROM THE RIVERS CROUCH AND BLACKWATER

In November 1966, at the conclusion of the laboratory experiments described above, it was decided to check the results obtained by using water samples more closely representative of the conditions found in an estuary. The experimental procedure adopted was as follows:

A series of 15 litre water samples was taken from points in the Rivers Crouch

TABLE I. Results of serial dilution of Rhodamine-B, shown as Rhodamine concentration (r) $\text{g}\cdot\text{m}^{-3}$, in waters of various salinities and suspended loads

(i) River Crouch water sample, S 30.4‰, suspended load 250 p. p. m.

Temp. °C.	Measured r	Expected r
6.5	0.0084	0.014
7.0	0.0030	0.0070
8.0	0.0015	0.0035
8.5	0.00063	0.00175
9.0	0.00035	0.00088
9.5	0.00017	0.00044

(ii) River Crouch water sample, S 31.2‰, suspended load 365 p. p. m.

Temp. °C.	Measured r	Expected r
6.0	0.028	0.058
7.0	0.0154	0.029
7.5	0.0056	0.014
8.0	0.0032	0.0072
8.5	0.0019	0.0036
9.0	0.00073	0.0018
9.5	0.00036	0.0009
9.5	0.00017	0.00045
9.5	0.00007	0.00023

(iii) River Crouch water sample, S 30.2‰, suspended load 115 p. p. m.

Temp. °C.	Measured r	Expected r
12.5	0.053	0.057
7.5	0.022	0.028
8.0	0.0085	0.014
8.5	0.0034	0.0071
9.0	0.0020	0.0035
8.5	0.00074	0.0018
9.0	0.00046	0.0009
8.5	0.00026	0.00045

(iv) River Blackwater sample, S 28.4‰, suspended load 170 p. p. m.

Temp. °C.	Measured r	Expected r
7.0	0.0169	0.029
7.5	0.0064	0.014
8.0	0.0039	0.0072
8.0	0.0016	0.0036
8.5	0.00066	0.0018
8.5	0.00037	0.0009
8.5	0.00020	0.00045
8.5	0.00009	0.00023

and Blackwater where the suspended solid load was observed to be high. In every case the sampling position was in shallow water over mud flats where wave action was sufficient to keep a high sediment load in suspension. The samples were then immediately returned to the laboratory, where the sediment load was kept in suspension by mechanical stirring. After the suspended sediment load of each water sample had been determined gravimetrically, a small, known volume of high-concentration dye solution was made up to one litre with the sediment-laden water. This gave a solution whose dye concentration could be calculated, ignoring any loss due to adsorption. After the solution, containing suspended solids and dye, had been allowed to stand for one hour in a light-proof case, the actual dye concentration was measured. The difference between the calculated and measured dye concentrations gave the adsorption loss.

A 500 ml portion of the solution was then made up to one litre with fresh sediment-laden water and this one litre solution was allowed to stand for one hour until adsorption equilibrium had again been reached. The dye concentration remaining after this second addition of sediment-laden water was then measured. Thus, using successive dilutions with sediment-laden water, it was hoped to follow more closely the conditions experienced in a field experiment, in which the dye continuously comes into contact with fresh sediment as diffusion progresses.

By this method of successive dilution the dye concentration was reduced to about $0.0001 \text{ g}\cdot\text{m}^{-3}$, below which the variation in background caused by the suspended solids made measurements unreliable. No control solution was used in this series of tests, but by keeping the test solutions in total darkness without agitation it was hoped to reduce both photochemical and chemical decay to negligible levels.

Table 1 gives the results of the experiments carried out using water from the Rivers Crouch and Blackwater. In this table the "expected" values quoted are the concentrations calculated on the assumption that adsorption loss is negligible. Microscopic examination of the suspended solids obtained from the four water samples used revealed that the suspended load consisted of fine grained sand, colloidal clay particles and organic matter. Significant differences in particle size composition were noticed between the four samples.

DISCUSSION OF RESULTS

The first experiments cover a range of concentrations from $6 \cdot 10^2$ to $10^{-3} \text{ g}\cdot\text{m}^{-3}$. We shall assume that these results may be extrapolated to cover the range of concentrations met in a Rhodamine-diffusion experiment, namely $2 \cdot 10^5$ to $2 \cdot 10^{-5} \text{ g}\cdot\text{m}^{-3}$. The need to extrapolate at this stage partly reflects the large range of concentrations met in a Rhodamine-diffusion experiment. Although the extrapolation is towards both higher and lower concentrations, the inclusion of the latter probably introduces the greater uncertainty. In this range, close to the lower detectable limit, considerable difficulty is met in trying to obtain experimental results. Similar difficulties are encountered when carrying out field work in water carrying a high suspended load and in such cases the minimum detectable Rhodamine concentration would be higher than that quoted above, that is to say about $10^{-4} \text{ g}\cdot\text{m}^{-3}$. Thus, in practice, the extrapolation may not be quite as serious as at first appears, since in those cases where particularly high suspended loads lead to large adsorption effects survey results will not be available to such low dye concentrations.

It appears from Figure 1 that the adsorption coefficient (a) is related to the Rhodamine concentration (r) by an equation of the form:

$$\log a = k \log r + \log C \quad (1)$$

$$\text{or } a = Cr^k, \quad (2)$$

where C and k are constants which may be determined from the experimental results. For a suspended load of 500 p.p.m. it follows from Figure 1 that

$$C = 0.13$$

$$\text{and } k = -\frac{1}{3.6} \text{ in saline water.}$$

The observed variation of C with suspended load is illustrated in Figure 2, which shows that adsorption is directly proportional to suspended load over the range investigated,

$$i.e. \quad C = KP$$

where P = suspended load in parts per million,

$$K = 2.6 \times 10^{-4}.$$

Consider a volume v m³ of Rhodamine solution of concentration r g·m⁻³ and suppose this to be diluted by the addition of a volume δv of sediment-laden water. For the present we shall assume that the same adsorption is obtained by the introduction of sediment already in suspension as in the experimental work when dry silt was introduced. The Rhodamine concentration, after dilution, should be given by

$$r' = \frac{rv - ar\delta v}{v + \delta v};$$

or, using (2), we may write

$$r + \delta r = \frac{rv - Cr^{(k+1)}\delta v}{v + \delta v};$$

or, considering δv and δr to be small, we may neglect second order small quantities,

$$\text{thus, } \frac{dr}{r(1 + Cr^k)} = -\frac{dv}{v}.$$

Substituting $r^k = u$ this gives:

$$\frac{1}{k} \int_{u_0}^u \left(\frac{1}{u} - \frac{C}{1 + Cu} \right) du = - \int_{v_0}^v \frac{dv}{v},$$

where u_0 , r_0 , v_0 represent the initial conditions.

Solving this equation and eliminating u gives:

$$r = [(r_0^{-k} + C) \left(\frac{v_0}{v} \right)^{-k} - C]^{\frac{1}{k}}. \quad (3)$$

Let R = the Rhodamine concentration that would have been produced after the same dilution if there had been no adsorption;

$$\text{then } R = \frac{v_0 r_0}{v} \quad \text{or} \quad \frac{1}{v} = \frac{R}{v_0 r_0}.$$

Thus equation (3) gives

$$r = [(r_0^{-k} + C) \left(\frac{R}{r_0} \right)^{-k} - C]^{\frac{1}{k}}$$

which, on rearrangement, gives

$$R = \left(\frac{1}{1 + Cr_0^k} (r^{-k} + C) \right)^{\frac{1}{k}}. \quad (4)$$

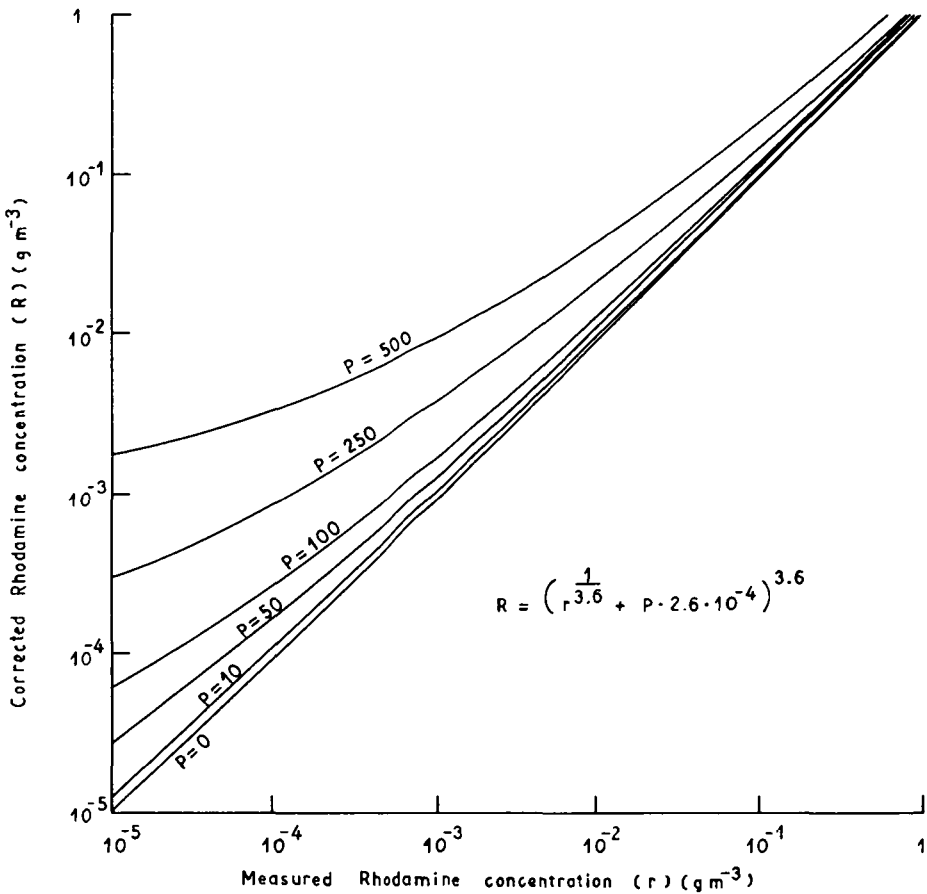


Figure 3. Calculated correction curves for Rhodamine-B adsorption, for various values of the suspended solid load.

In practice $r_0 = 2 \times 10^5$ and the experimental results have indicated that

$$k = -\frac{1}{3.6}$$

and $C = 0.13$ for a suspended load of 500 p.p.m. Actual suspended loads are likely to be appreciably smaller than this, so that it is reasonable to regard

$$Cr_0^k \ll 1;$$

i.e. we may write

$$R = (r^{-k} + C)^{\frac{1}{k}},$$

or, remembering that $C = KP$,

$$R = (r^{-k} + KP)^{\frac{1}{k}};$$

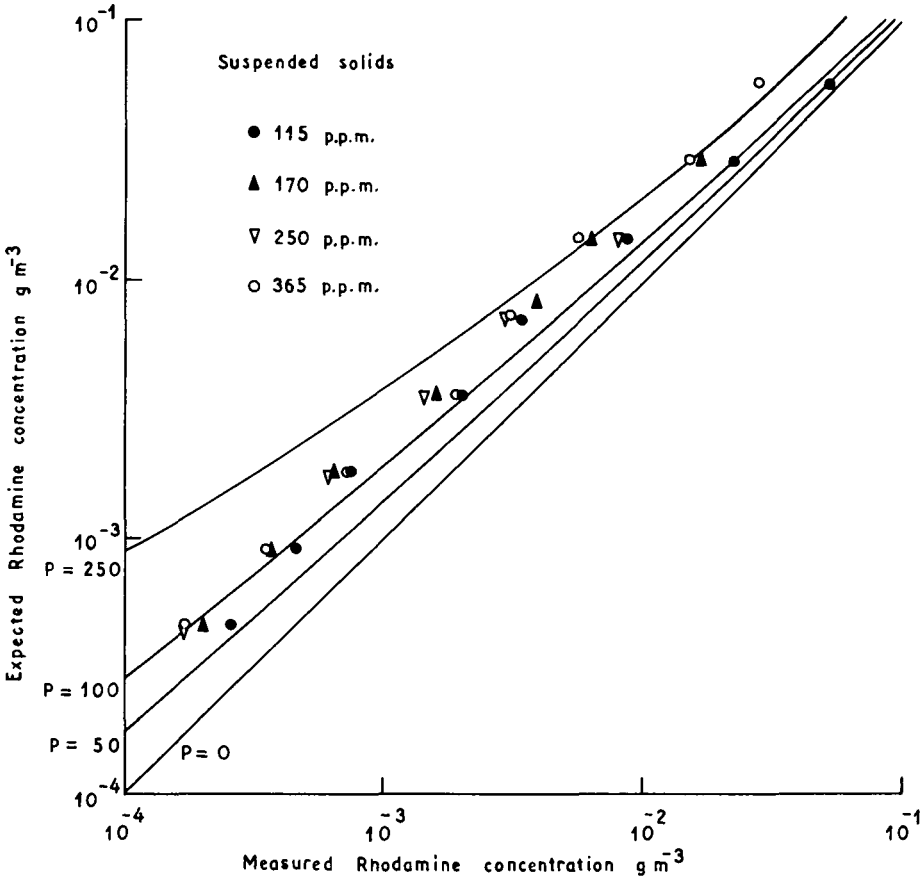


Figure 4. The relation between the measured and the expected Rhodamine-B concentrations obtained by serial dilution, using water samples from the Rivers Crouch and Blackwater.

or, since

$$k = -\frac{1}{3.6}$$

and

$$K = 2.6 \times 10^{-4}$$

$$R = (r^{3.6} + P \times 2.6 \times 10^{-4})^{3.6} \tag{5}$$

This relation between R and r is illustrated in Figure 3 for various values of P .

The above discussion has been based upon the results of the first experiments, which used dry silt. The second experiments were carried out in order to compare these predictions with the results of a series of successive dilutions using water carrying a suspended load. In Figure 4 we see these experimental results compared with the predicted curves.

Only a few days were available in which to carry out the second experiments, and a close examination of the results reveals a greater variation than was obtained in the first series of experiments. Two features of the results illustrated in Figure 4 may be worthy of comment. In the first place it appears that less adsorption took place at lower concentrations than is predicted by equation 5. Secondly, the differences in adsorption for different suspended loads are less marked than expected, and this is particularly true for the lower concentrations of Rhodamine. It is probable that some fractions of the suspended loads, and particularly the larger particles, were lost from the solutions as the successive dilutions were carried out and that this loss of suspended load accounts, at least in part, for the discrepancy between the observed results and the values that have been predicted above. Within the limits of experimental error the variation of adsorption loss with Rhodamine concentration appears to be consistent with that given by the theoretical discussion.

In practical work it would be necessary to select the appropriate adsorption correction curve by carrying out one or more test dilutions just before a Rhodamine release.

The authors have been involved in no inshore Rhodamine experiments since this investigation of adsorption was completed, but the results of the Rhodamine survey carried out in the Blackwater in April 1966 give some indication of the need for a correction for adsorption in such cases. It was clear that the Rhodamine released could not all be accounted for without the assumption of some loss, probably associated with adsorption. At various times the suspended load in the Blackwater Estuary has been determined, although unfortunately no direct measurements of this were made during the April 1966 Rhodamine surveys. We find that a value of $P = 80$ (corresponding to a suspended load of 80 p.p.m.) leads to a set of results which appears to account for all of the dye released. This is the order of magnitude of suspended load that would be expected on the basis of other measurements by the authors and others (see for example WAUGH, 1966). Thus it appears that significantly improved results are obtained when we take account of adsorption as suggested above, although it is clear that the assumption of a constant value of the suspended load must be an approximation which will limit the accuracy attainable.

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