FACTORS AFFECTING THE FORMATION AND OXIDATION OF SULPHIDES IN A POLLUTED ESTUARY

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(With 11 Figures in the Text)

INTRODUCTION

In Great Britain there are many estuaries which, although not polluted by discharges of sewage and industrial effluents, nevertheless contain deposits of mud. The lower layers of these deposits are frequently almost black owing to the presence of sulphides formed by decomposition of organic matter and reduction of sulphates under the anaerobic conditions prevailing. In these estuaries, however, the water is nearly saturated with dissolved oxygen at all times of the year and sulphides never appear in it. The estuary of the River Wye in Monmouthshire is an example of this kind.

Other estuaries, however, are heavily polluted by sewage and industrial effluents which are discharged after little or no treatment. Although there is evidence that, at least in some of the less extremely polluted of these estuaries, the discharges have little effect on the rate of formation of mud-banks or their erodibility (Southgate & Preddy, 1952), they have considerable effect on the chemical condition of the water. In certain estuaries the water becomes devoid of oxygen, and sulphides and noxious products of anaerobic bacterial action are then released to the water and atmosphere.

In the course of a survey of the estuary of the Thames now being made by the Water Pollution Research Laboratory, some experiments have been made to find how certain factors affect the formation and persistence of sulphide, which is now usually present in the middle reaches of the estuary during the summer months.

During a survey of the estuary of the River Mersey (Department of Scientific and Industrial Research, 1938), which is heavily polluted by sewage and industrial wastes, water containing dissolved oxygen was never found to contain sulphide, although there were deposits of anaerobic mud below the mud-water interface. Similarly, observations of the condition of the water in the Thames Estuary (Department of Scientific and Industrial Research, 1952) show that sulphide is found only when dissolved oxygen is absent or is present only in very small quantities. One of the objects of the work to be described has been to explain this and to decide either whether the dissolved oxygen inhibits the formation of sulphide in the water and mud, or whether its chief effect is to oxidize sulphide formed, for example, in mud deposits in which conditions below the surface would be anaerobic.

Generally, it has been assumed that sulphide formed in an estuary is produced from sulphates by sulphate-reducing bacteria. Clearly, sulphide might also be formed by the decomposition of sulphur-containing organic compounds present in sewage or in dead plant and animal material; the evidence available, however, suggests that the amount formed in this way is comparatively small.

The effect of temperature on the rate of formation of sulphide has also been investigated, as it is only during the summer months, when the water and deposits of mud in the estuary are warm, that the dissolved oxygen content falls to zero and sulphide appears. Dissolved oxygen is usually found to be absent from the water for a month or more before sulphide appears in the water. This lag period might arise either because the temperature of the water and mud is too low for sulphate-reducing bacteria to be active, or because there might be a reserve of oxidized matter in the estuary which would have to be reduced before the oxidation-reduction potential of the water was sufficiently low either for sulphate-reducing bacteria to grow or for sulphide to persist. Ferric iron, for example, is present in the suspended matter in the estuary and might be capable of oxidizing sulphide as it is formed.

FORMATION OF SULPHIDE

Effect of dissolved oxygen on conditions in deposits of mud

Sulphate-reducing bacteria are obligate anaerobes (ZoBell & Rittenberg, 1948), and their growth in artificial media is stimulated by traces of reducing agents, for example, ferrous iron and sulphide, which lower the oxidation-reduction potential of the media; metabolic products of the bacteria can then maintain the potential at a value suitable for growth. ZoBell & Rittenberg (1948) have reported that the optimum oxidation-reduction potential (Eh) for growth of sulphate-reducing bacteria is between -100 and -300 mV. at pH 7 and no growth has been observed at potentials more positive than $+27$ mV. (Aleshina, 1938). Observations of the potential in synthetic culture media and in the estuary of the Thames have supported these values. It was considered that a comparison of the oxidation-reduction potential at various depths in deposits of mud maintained below estuary water containing no dissolved oxygen, and below estuary water nearly saturated with oxygen, would indicate clearly whether oxygen in the water could affect the activity of sulphate-reducing bacteria in the mud.

Mud and water from the Gravesend reach of the estuary were placed in a glass tank to form two layers 20 and 24 cm. deep respectively. Platinum electrodes were then mounted at known distances above and below the surface of the mud. The system was left at room temperature without any mechanical agitation or aeration of the water for 6 days, and the potentials of the electrodes were measured at intervals.

Values of oxidation-reduction potential (converted to the hydrogen scale) obtained on the 5th day are shown in Fig. 1. The potential in the water decreased with depth, and no sudden change occurred at the mud surface. A value of -200 mV. was reached about 2 cm. below the mud-water interface, and below this depth the potential remained almost constant.

After the static period the water was aerated for 3 weeks. The concentration of dissolved oxygen in the water increased and became constant throughout its depth. A thin surface film of light-coloured mud which had formed gradually during the static period became steadily thicker after aeration was begun, and 3 weeks later this oxidized layer was 6 mm. thick. Values of the oxidation-reduction potential during this period are also shown in Fig. 1. The potential remained constant throughout the water and then decreased rapidly in the upper 2 cm. of mud reaching a constant value of -220 mV., that is, slightly lower than when static conditions were maintained. Similar values of the potential were obtained when a single clean platinum electrode was lowered in stages through the water and mud. Bubbles of gas were observed in the lower layers of mud from the 8th day, but none was observed in the upper 5 cm. A sample of gas was obtained by disturbing the mud and collecting the gas over water; no hydrogen sulphide could be detected with lead acetate paper.

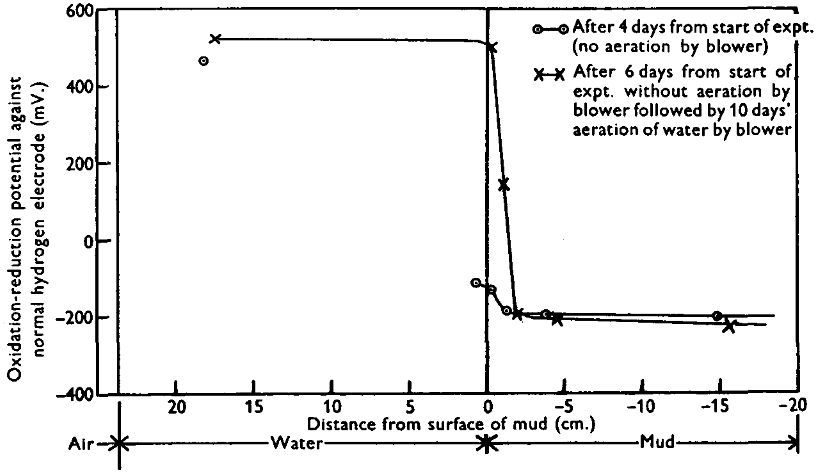

Fig. 1. Effect of aeration on the oxidation-reduction potential of platinum electrodes at different depths in a tank containing water and mud from the Gravesend Reach of the Thames Estuary.

During a third period the water overlying the mud was covered with paraffin wax. The oxygen content of the water decreased and became constant at a value less than 1% of the saturation value. Oxidation-reduction potentials were measured each day. Steady values were obtained after 20 days, and these are compared in Fig. 2 with those obtained when the water was aerated. Reducing access of oxygen to the water by covering it with a layer of wax had less effect on the potentials of the water than had been expected. This was due, presumably, to the absence of fresh polluting matter in the water and mud and to the comparatively low temperature of the system.

Measurements of pH value in the mud showed that this decreased from pH 8·0 at the interface to pH 6·6 at 2 cm. depth and then increased slightly to pH 6·7 (Fig. 3); similar observations are reported by Debyser (1952). This change in pH value would have caused a variation of oxidation-reduction potential with depth in the mud, but its range would have been of the order of 90 mV. or less, whereas the variations actually observed were near 600 mV.

These experiments showed that the presence of dissolved oxygen in the estuary would have no effect on the oxidation-reduction potential and conditions prevailing in deposits of mud at distances greater than about 2 cm. from the mud-water interface, and that conditions in the lower layers would be suitable for growth of

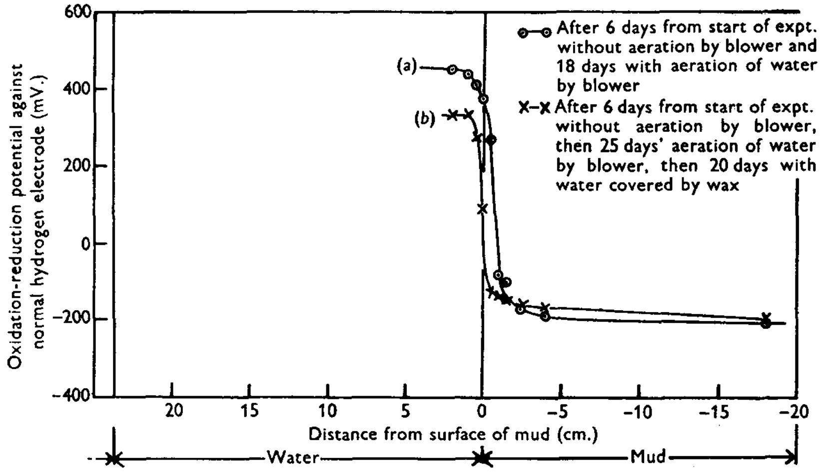

Fig. 2. Oxidation-reduction potential at various distances from the surface of mud when (*a*) aerobic and (*b*) anaerobic conditions were maintained in the supernatant water.

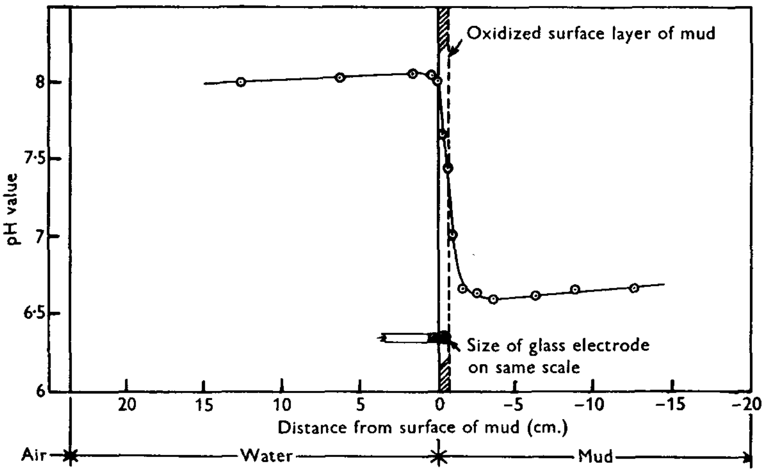

Fig. 3. Variation of pH value with distance from the surface of a layer of mud from the Gravesend Reach of the Thames Estuary. Concentration of dissolved oxygen in the water: 0·07 p.p.m.

anaerobic bacteria whatever the oxygen content of the water. The findings of these experiments apply only to firm deposits of mud and not to those deposits, such as are found near the Royal Docks, which may be eroded and carried in suspension in the water when disturbed by large vessels or by fast tides.

Effect of concentration of dissolved oxygen on the activity of sulphate-reducing bacteria

In the Thames Estuary sulphide is usually found only when dissolved oxygen is absent. This might be either because traces of dissolved oxygen inhibit the growth of sulphate-reducing bacteria and sulphide is not formed or because sulphide is oxidized by dissolved oxygen at a much higher rate than it is formed in the water. An experiment was made, therefore, to determine the minimum concentration of oxygen needed to stop the formation of sulphide.

Mixtures of settled sewage, nutrient solution, and a mixed culture of sulphate-reducing bacteria derived from sewage were incubated in 2 l. bottles at 25° C. Nitrogen from which all traces of oxygen had been removed was passed as a stream of fine bubbles through one bottle, and nitrogen containing 1, 2 and 3 % air was similarly passed through others. The issuing gases were passed through a solution of cadmium acetate to absorb hydrogen sulphide, the quantity of which was determined at intervals (Fig. 4). When 2 % air was added to the nitrogen the production of sulphide was negligible. The concentration of oxygen in solution in equilibrium with nitrogen containing 2 % air would have been 2 % of the saturation value or about 0·16 p.p.m., but in the culture solution it was probably less than this, since oxygen was being consumed by bacterial action. This experiment indicates that it is unlikely that reduction of sulphate would occur in the water of the estuary if any significant amount of oxygen was present. Sulphide might, however, be formed in deposits of mud and the rate of oxidation of sulphide in the water would then be of importance.

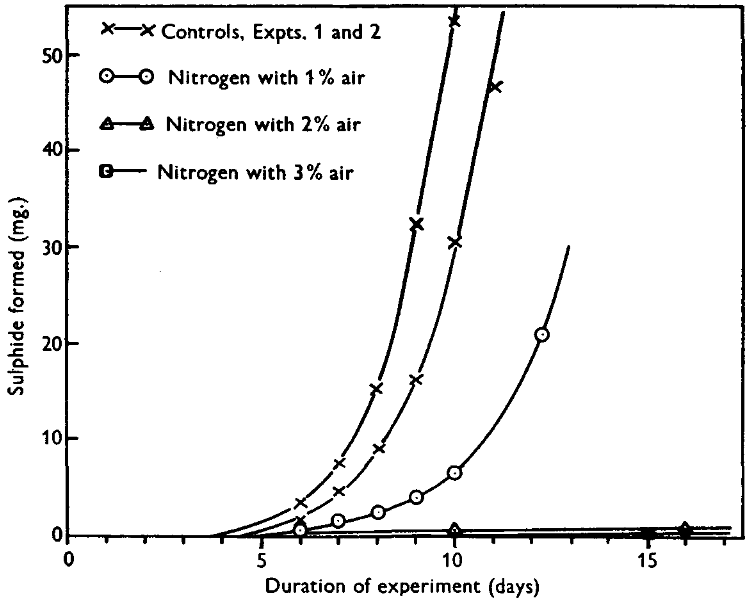

Fig. 4. Variation with time of the amount of sulphide formed by sulphate-reducing bacteria in culture solutions through which nitrogen containing various proportions of air was passed.

Effect of temperature on the formation of sulphide

Three series of experiments were made, to investigate the effect of temperature, (*a*) using synthetic culture media, (*b*) using mixtures of mud and estuary water and (*c*) using mud, estuary water and periodic additions of nutrient.

(*a*) *Experiments with synthetic culture media*

A culture solution (350 ml.) inoculated with sulphate-reducing bacteria grown at 30° C., and containing, per litre, 5·2 g. of sodium sulphate decahydrate, 2·5 ml. of sodium lactate (70 % solution), 0·036 g. of ferrous ammonium sulphate and buffered at pH 7·4 with 13·6 g. of potassium dihydrogen phosphate was incubated in 16 oz. bottles at temperatures of 5, 10, 15, 20 and 25° C. Nitrogen was passed through the solution in each bottle and then through pairs of Dreschel bottles containing cadmium acetate. These were replaced at intervals and the quantity of sulphide in them was determined iodimetrically. At 25° C. sulphide was formed rapidly and formation was complete after 6 days (Fig. 5). At 20° C. sulphide was produced during the first few days, but more slowly, and its formation continued for 11 days. At 15° C., 25 days elapsed before an appreciable quantity of sulphide was formed; production ceased after 31 days, and the total quantity formed was only about one-third of that at 25° C. Addition of a further quantity of sodium lactate, however, caused an immediate increase in the rate of formation of sulphide showing that the supply of nutrient was a limiting factor. Presumably other types of bacteria had consumed most of the nutrients before the sulphate-reducing bacteria had proliferated. At temperatures of 5 and 10° C. no sulphide was formed in 45 days, even though extra lactate was added after 31 days.

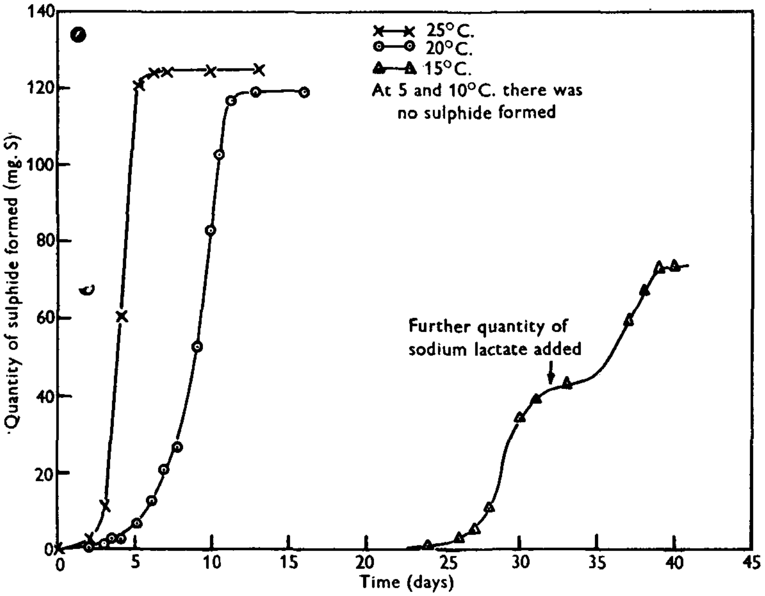

Fig. 5. Effect of temperature on the rate of formation of hydrogen sulphide by sulphate-reducing bacteria in a culture solution containing sodium lactate.

The reason for the slow growth of sulphate-reducing bacteria at 15° C. was possibly that the inoculum was grown at 30° C. and the bacteria could not rapidly accustom themselves to the change in temperature. A new culture of bacteria was therefore grown at 15° C. and the experiment was repeated. The results were similar to those previously obtained, and sulphide was not formed in the bottle at 15° C. until 18 days had elapsed. These experiments showed that the effect of temperature on sulphate-reducing bacteria growing in synthetic culture solutions was most marked between 10 and 20° C., but these results were not wholly supported by the second series of experiments using mud and estuary water.

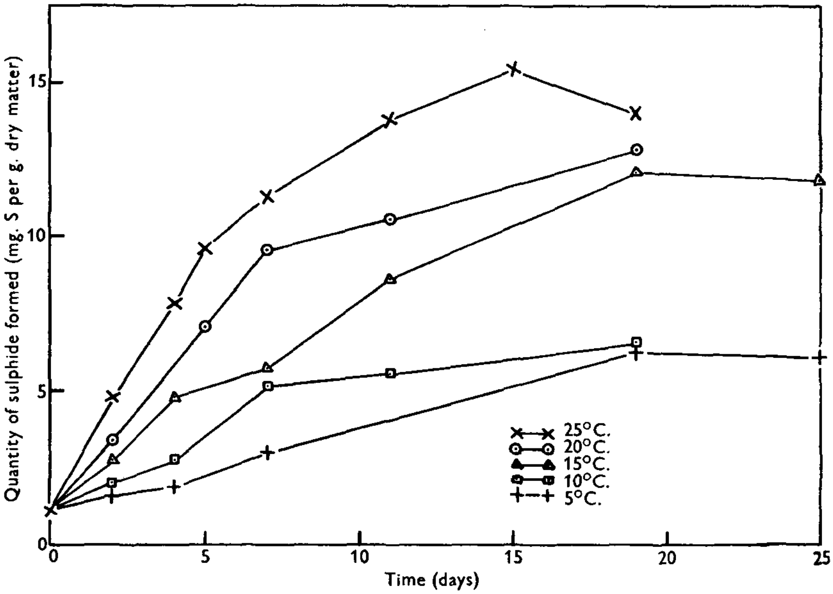

Fig. 6. Effect of temperature on the quantity of sulphide formed in a mixture of mud, sewage sludge and sea water.

(*b*) *Experiments with mixtures of mud and estuary water*

Mixtures of mud and estuary water are able to retain appreciable quantities of sulphide as ferrous sulphide, so that the type of experiment adopted with synthetic culture media could not be used.

120 ml. of mud from the estuary was intimately mixed with a suspension of sewage sludge (dry weight of sludge was 1 % wet weight of mud) and was diluted to 1 l. with estuary water. 100 ml. quantities were incubated in bottles at temperatures of 5–25° C., and at intervals the sulphide contents of bottles were determined (Fig. 6). Because of variations in the rate of formation of sulphide in similar bottles at the same temperatures the curves obtained were not smooth, but the results show that some sulphide was formed even at 5 and 10° C. and that the quantity formed increased with temperature. During the first 10 days the quantity of sulphide formed approximately doubled for each 10° C. rise in temperature, which is of the same order as the variation with temperature of the rate of simple chemical reactions. The results differed from those obtained when synthetic

culture media were used, as in the latter no sulphide was formed at 5 or 10° C. It is possible the conditions were more anaerobic and the organisms were more varied and better adapted to the culture medium when the mixture of mud and estuary water was used. This big difference in the results from two kinds of experiment shows the danger of predicting from the results of laboratory experiments what might occur in an estuary. In both these experiments the conditions differed from those in an estuary where nutrients are continually replenished by discharges of polluting matter and by mixing with sea water. A further series of experiments was made, therefore, in which the concentration of nutrient was kept almost constant and the steady rate of evolution of sulphide at different temperatures was measured.

(c) *Experiments with mixtures of mud and estuary water and periodic additions of nutrient*

300 ml. of a mixture of mud, estuary water and settled sewage were placed in a series of 16 oz. bottles and the mud was allowed to settle; it formed a layer $\frac{1}{2}$ in. deep. Bottles were immersed in water baths at temperatures of 5, 10, 15, 20, 25 and 36° C. Nitrogen was bubbled through the water above the mud in the bottles and then through Dreschel bottles containing cadmium acetate. These were replaced at intervals and the sulphide in them was estimated. Each day, 100 ml. of supernatant liquid was removed from each bottle and 100 ml. of fresh liquid was added. This consisted of 50 ml. of settled sewage, sea water to give a salinity the same as that in the bottles, namely, 16·25 g. per 1000 g., and sodium sulphate equivalent to the sulphide collected in the Dreschel bottles. In this way a supply of nutrients was maintained in each bottle. In this experiment some sulphide must have remained in the mud, but once the mud had become saturated with hydrogen sulphide some would be expected to be evolved each day, and the quantity of this would give a reliable indication of what might be evolved at different temperatures from mud deposits in the estuary.

Sulphide appeared in the gas from the bottle at 36° C. after 3 days but was not present in the gas from the bottle at 5° C. until 30 days had elapsed. If, as is believed, the mud was absorbing hydrogen sulphide during this period, then the time taken for sulphide to appear in the gas can be used as an indication of the rate of formation of sulphide at the different temperatures. The times, plotted against temperature, give a smooth curve (Fig. 7). As in the previous experiment the rate of formation of sulphide was approximately doubled for each 10° C. rise in temperature. Figures for the amount of sulphide produced each day after it first appeared are given in Table 1. These values vary considerably from day to day, perhaps because of the variation in the volume of nitrogen passed through the bottles and it is not possible to obtain from them any simple relation between the rates at various temperatures. Comparison of the average values leads to the conclusion that the rate of formation of sulphide in the estuary during the summer when the temperature of the water is 20–25° C. might be about three times as great as during the winter, other factors being constant.

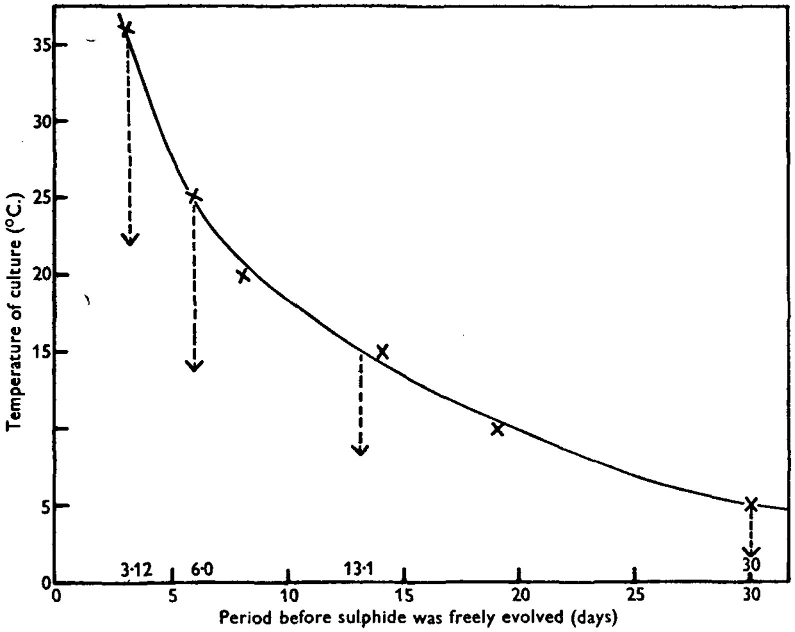

Fig. 7. Variation with temperature of the time elapsing before sulphide was freely evolved from mixtures of mud, sewage and estuary water

Table 1. *Quantity of sulphide collected during periods of* 24 *hr. from mixtures of mud, estuary water and sewage incubated at temperatures between* 5 *and* 36° C.

Time from start of experiment (days)	Quantity of sulphide collected in 24 hr. (mg. S)					
	5° C.	10° C.	15° C.	20° C.	25° C.	36° C.
5	—	—	—	—	Trace	6·2
6	—	—	—	Trace	1·9	2·7
8	—	—	—	2·1	2·2	4·7
10	—	—	—	1·3	1·6	1·9
13	—	—	Trace	1·7	1·8	3·5
17	—	Trace	—	—	—	—
21	—	—	1·6	—	1·6	3·0
22	—	0·6	1·2	—	1·8	2·9
23	—	0·5	1·0	—	1·2	3·3
24	—	0·2	0·8	1·8	1·8	4·8
27	—	1·0	3·0	4·9	3·0	5·2
28	—	0·4	0·9	3·4	4·4	5·1
29	—	1·5	3·9	6·7	2·8	6·7
30	0·93*	1·6	2·7	4·8	3·6	4·2
34	—	0·7	3·2	4·8	2·9	2·3
Average	—	0·8	2·0	3·5	2·4	4·0

* Total to date.

Mixing of mud and estuary water

In many parts of the Thames Estuary there is no sharp division between supernatant water and mud deposits, but there is instead a zone in which large amounts of mud are carried in suspension. It seemed desirable to know whether the rate of formation of hydrogen sulphide in a suspension of mud in estuary water was greater or less than that in a compact layer of mud in which conditions might be somewhat different.

Twelve 8 oz. bottles were completely filled with a mixture of mud, estuary water and sewage. Six were shaken continuously and the others were left undisturbed during the experiment. In the latter the mud settled to form a layer 4 cm. deep. The salinity of the mixture was 20 g. per 1000 g. After various periods of time pairs of bottles were taken, the contents were acidified, and the sulphide was blown off, reabsorbed and estimated. There was no significant difference between the amount of sulphide formed in the mixed and in the quiescent cultures (Table 2). This indicated that both freshly deposited mud and mud in suspension would play equal parts as sources of sulphide in the estuary when the water was anaerobic. When, however, traces of dissolved oxygen are present in the water the amount of sulphide formed from mud in suspension would probably be much reduced.

Table 2. *Quantity of sulphide formed after various periods of time in a mixture of mud, estuary water and sewage*

Time (days)	Quantity of sulphide present in bottle (mg. S per 250 ml. mixture)	
	Quiescent	Mixed
0	7·95	7·95
2	11·52	11·48
5	13·75	13·75
7	15·95	15·25
13	20·25	19·85
15	21·14	20·95

OXIDATION OF SULPHIDE

Nature of oxidation process

Factors have been considered which would affect the quantity of sulphide formed in the estuary, but these cannot account for the disappearance of sulphide during the autumn when the oxygen content of the water increases. Neither do these factors decide entirely what concentration of sulphide might be present in the water.

Hydrogen sulphide, once it has been formed in an estuary, can be dispersed by escape to the atmosphere or destroyed by reaction in solution with dissolved oxygen or another oxidizing substance; this oxidation may be brought about by sulphur-oxidizing bacteria or may be of a purely chemical nature.

Because it was known that the chemical oxidation of sulphide is complex and that traces of certain metals catalyse the reaction (Krebs, 1929; Meunier & Kapp, 1931; Jahn, Kröller, Shin & Kunt, 1948), experiments were made using sea and river water from the Thames Estuary so that the results could be applied with certainty to show how quickly the oxidation could proceed under natural conditions. In the first experiments the rates of oxidation of sulphide in sterile and non-sterile mixtures of mud and estuary water were compared to find whether sulphur-oxidizing bacteria play any significant part in the oxidation process.

Duplicate sterile and non-sterile mixtures of 95 ml. of sea water and 5 ml. of a suspension of mud from the surface of a deposit near Gravesend were put into 1 l. bottles. A known amount of sulphide was added, the bottles were shaken for 100 min. on a 'wrist action' type shaking machine, and then the quantity of sulphide remaining in each bottle was estimated. Results of three similar experiments (Table 3) showed there was no significant difference between the amounts of sulphide oxidized in the sterile and non-sterile samples, and it was concluded that the oxidation of sulphide in the Thames Estuary is predominantly of a chemical nature. In further experiments only unsterilized samples of mud, river water and sea water were used. Changes were also made so that the amount of shaking given to the bottles could be accurately reproduced.

Table 3. *Amount of sulphide oxidized in* 100 *min. in sterile and non-sterile mixtures of sea water and surface mud. Temperature* 22° C.

Experiment	Condition of water	Sulphide in bottle (mg.)		Sulphide 'oxidized' (%)
		Initially	After 100 min.	
1	Sterile	28·8	7·15	75
	Non-sterile	28·8	7·47	74
2	Sterile	28·8	7·48	74
	Non-sterile	28·8	7·48	74
3	Sterile	28·8	9·8	66
	Non-sterile	28·8	9·9	66

The apparatus consisted of 16 oz. bottles closed by waxed bungs carrying one long and one short glass tube so that, at the end of the experiment, nitrogen might be passed through the bottles to sweep out hydrogen sulphide. During experiments each bottle contained 55 ml. of solution and 505 ml. of air containing 106 ml. of oxygen (0·15 g.) sufficient to oxidize 75 mg. of sulphide to sulphate or 300 mg. to sulphur. In experiments only about 12 mg. of sulphide was present, so the partial pressure of oxygen in the air would change by no more than 16 % under any conditions and usually by no more than 5 %. It was assumed that during an experiment sulphide in the vapour phase would redissolve rapidly as sulphide in the solution became oxidized. It was also assumed that the rate of oxidation of sulphide in solution would be much greater than in the vapour phase. This was shown to be true by the fact that the composition of the water had a large influence on the amount of sulphide oxidized. All the experiments were made in a constant-temperature room at 22–23° C., and all solutions were adjusted to this temperature before use.

Effect of salinity and amount of suspended matter

The rates of oxidation of sulphide in two samples of water, one taken at low water off the entrance to the Royal Docks, the other taken at mid-tide off Tilbury, were compared in the first experiment. These samples are referred to, respectively, as 'river-water' and 'sea water'.

50 ml. samples of water were placed in a series of 16 oz. bottles and 5 ml. of a solution containing approximately 14 mg. of hydrogen sulphide was added to each below the surface of the water. The bottles were closed immediately and fixed to the shaking machine. After various periods bottles were removed and the amount of sulphide in each was determined. These values were then plotted on a logarithmic scale against the period of shaking (Fig. 8). The lines drawn through the points were nearly straight, indicating that under the conditions of the experiments the oxidation was predominantly a pseudo-first-order reaction, the rate of oxidation depending on the concentration of sulphide, other factors being constant. Oxidation of sulphide in the sample from Tilbury took place more rapidly than in the one of lower salinity, and it was thought this might be due to a difference in the concentration of iron present, as ferric iron is known to act as a catalyst. The filtered 'sea water' contained a total of 0·32 p.p.m. iron; the 'river water' contained 0·24 p.p.m., but not all this was present in a simple ionized form. Some was present in colloidal suspended matter, so the effect of this on the rate of oxidation of sulphide was investigated.

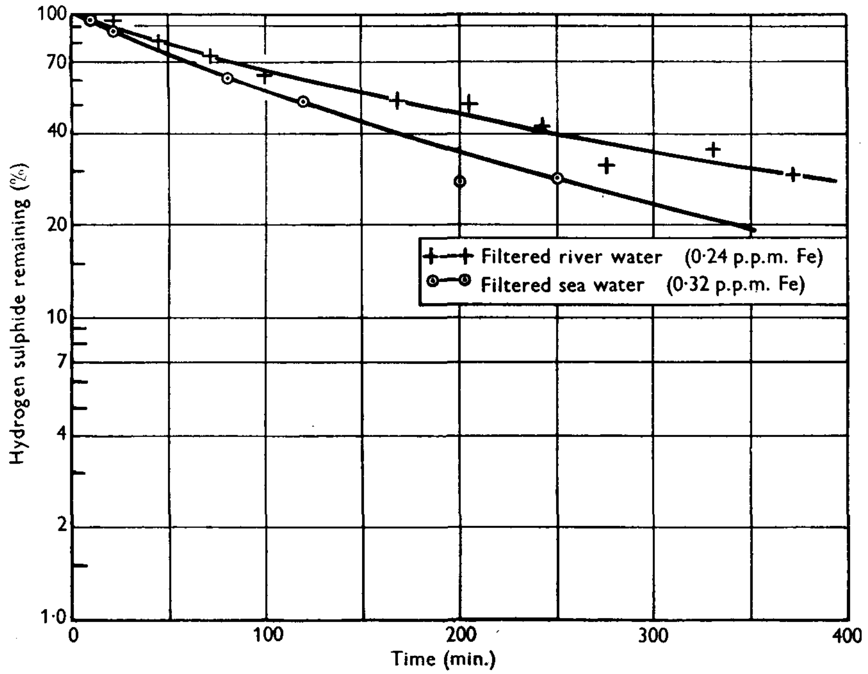

Fig. 8. Variation with time of the concentration of sulphide remaining when sulphide is added to water from the Thames Estuary and is shaken in a closed bottle with an excess of air.

A quantity of the same water was treated with coagulant and filtered to remove colloidal suspended matter, and the pH of the water was then restored to its original value. The total concentration of iron in the treated water was determined, and the iron content of one portion of it was raised to that of the original by addition of 0·07 p.p.m. iron as ferric chloride. Rates of oxidation of sulphide in the original and the two types of treated water were then determined as before. Results are shown in Fig. 9, together with that of a similar experiment in which 1 ml. of a suspension of mud was added to 50 ml. of filtered sea water. The rate of oxidation of sulphide in the coagulated sea water was appreciably less than in the untreated water, but when 0·07 p.p.m. iron was added the rate was increased nearly to its original value. When mud was present the rate of oxidation was much increased.

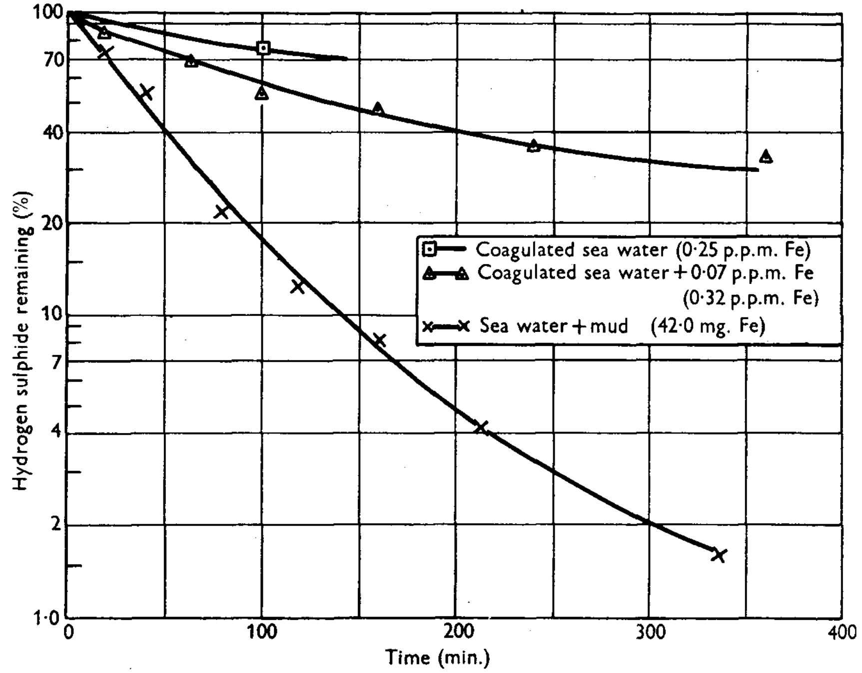

Fig. 9. Variation with time of the concentration of sulphide remaining when sulphide is added to sea water containing various quantities of suspended matter and iron and is shaken in a closed bottle with an excess of air.

The effect of suspended mud was shown in a separate experiment. Quantities, up to 5 ml., of a suspension of mud, containing 66 mg. of solids and 2 mg. of iron per ml., were added to 50 ml. samples of filtered sea water. Sulphide was added and the amount of sulphide remaining after a period of 220 min. was determined (Fig. 10). Addition of successive increments of mud had a progressively smaller effect on the rate of oxidation. This may have been due to the fact that the rate of solution of oxygen in the water was becoming a limiting factor.

Rate of supply of oxygen to the estuary

The experiments made using estuary water and mud showed that sulphide could be oxidized chemically by dissolved oxygen at a much higher rate than had been supposed. In one experiment, for example, the half-life period was of the order of 1 hr., and it seemed that if the oxidation of sulphide proceeded at such a rate in the Thames Estuary sulphide would not remain for long in the water. Obviously, some other factor, probably the rate of entry of dissolved oxygen, must limit the rate of oxidation in the estuary.

This view was supported by an experiment in which the rate of entry of oxygen per unit volume of water was similar to the rate in the estuary and the rate of oxidation of sulphide was measured. About 50 l. of estuary water was placed in a carboy; the ratio of the area of the surface of the water to its volume was then the same as that of a river 30 ft. deep. The carboy was fitted with a stirrer to keep the solids in suspension and the surface of the water free from any film, for example, of iron sulphide. The water was stirred as fast as was possible without forming a vortex in it. Hydrogen sulphide dissolved in estuary water was added, and the water was then left a few hours for any traces of dissolved oxygen to disappear. At intervals after this, samples were removed and the concentration of sulphide in them was determined. Water removed with each sample was replaced with an equal volume of estuary water; the surface area of the water was thus kept constant throughout the experiment. Four experiments were made using similar samples of water. In three air was in contact with the water, in the fourth, oxygen (Fig. 11). The rates of oxidation were much slower than in the bottle experiments and the variation of the concentration of sulphide with time was linear, i.e. the reaction was of zero order. This indicated that the rate of entry of oxygen, which was constant during any particular experiment, was controlling the rate of oxidation of sulphide. The rate of oxidation increased when the rate of entry of oxygen was increased by passing pure oxygen over the surface of the water. In experiments

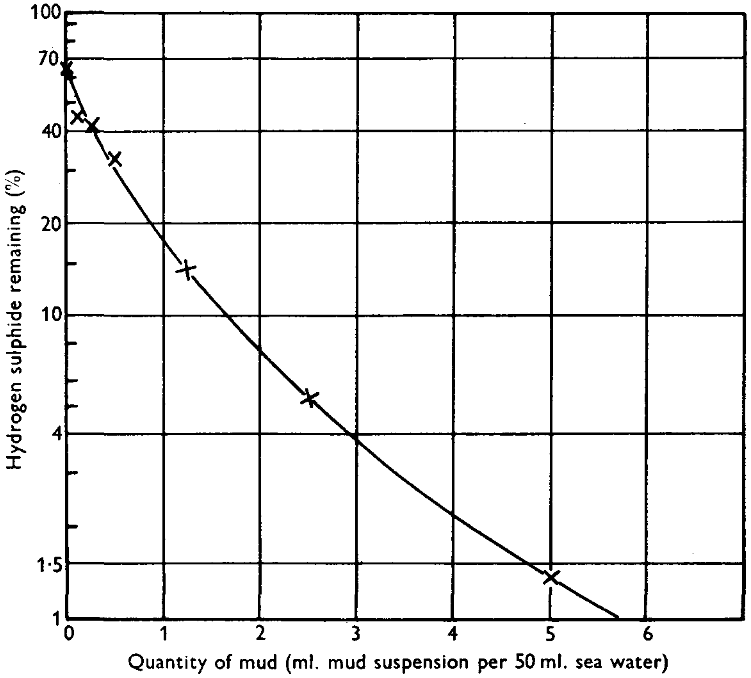

Fig. 10. Variation, with concentration of mud, of the amount of sulphide remaining in sea water shaken for 220 min. with an excess of air in a closed bottle.

when air was used the rates of oxidation were not identical because the rate of entry of oxygen from the air was not kept constant. The highest rate was obtained when air was passed over the surface from a jet, as this increased the disturbance of the surface film on the water. The lower rates were obtained when the air was stagnant. When oxygen was used this was passed over the surface from a jet but more slowly than when air was used. In view of these differences the relative rates of oxidation of sulphide agree with those that might be expected from the rate of solution of oxygen.

Measurements of the rate of solution of oxygen when deoxygenated water is stirred in a beaker show that just before a vortex is formed the rate of entry of oxygen is about 0·244 g. per sq.ft. of surface per day per p.p.m. oxygen deficit (G. A. Truesdale, unpublished). At this rate 46·2 mg. of oxygen would have entered the carboy in 10 hr. and could have oxidized 92·5 mg. of sulphide to sulphur. In the two experiments with 'stagnant' air 120 mg. of sulphide was oxidized. When oxygen was in contact with the water the corresponding value was 730 mg., that is, the rate was about six times as fast.

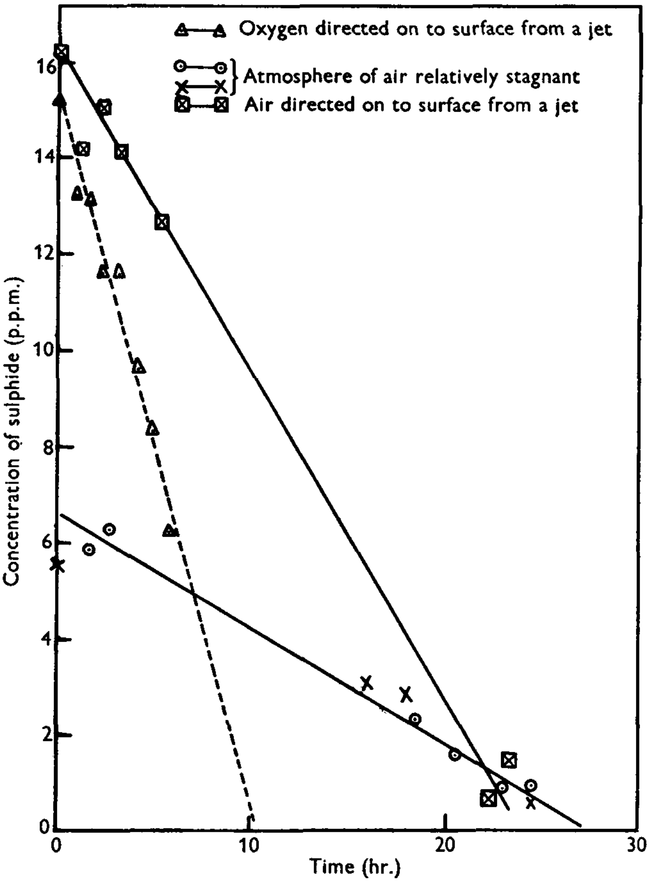

Fig. 11. Variation with time of the concentration of sulphide remaining in water from the Thames Estuary when the ratio of the area of the surface of the water to its volume is the same as that of a river 30 ft. deep. Temperature 22° C.

It is concluded, therefore, that in the Thames Estuary the rate of entry of oxygen through the surface limits the rate of oxidation of sulphide. This also explains why sulphide is not found in water when any trace of dissolved oxygen is present.

GENERAL CONCLUSIONS

A general picture emerges of some of the processes occurring in a polluted estuary such as the estuary of the Thames.

During the winter the natural flow of the river and the disturbance of the surface of the estuary are greatest and oxygen is present in the water. In addition, the water and deposits of mud are at their lowest temperature. Conditions in the mud, however, are still quite suitable for formation of sulphide. The deposits are anaerobic, the oxidation-reduction potential is low, and the temperature is not low enough to stop the growth of sulphate-reducing bacteria. When oxygen is present in the water, sulphide formed in the mud, but not retained as ferrous sulphide, would be oxidized before it could diffuse into the water. If no such oxidized layer was present, or the mud was in suspension, and traces of sulphide were formed, these would become oxidized to sulphur by the rapid chemical reaction in the presence of suspended matter and dissolved oxygen. If gases containing hydrogen sulphide escaped from deposits of mud the sulphide which dissolved in the water would be oxidized rapidly in a similar way. (Experiments not reported have shown that practically all the sulphide in bubbles would dissolve in the water before the bubbles reached the surface.)

During the period when the water becomes steadily warmer and the natural flow of fresh water into the estuary is low, then the oxygen content of the water decreases steadily to zero. After the disappearance of dissolved oxygen there would be a lag period when sulphide, if it was being formed, would be oxidized only at the expense of other oxidized substances in the water, for example, ferric iron. During this lag period the oxidation-reduction potential in the water would steadily become more negative and eventually sulphide would appear. During this stage it is likely that sulphide would be formed in suspended mud and in the water itself, and the sulphide content of the water would increase until its rate of formation was balanced by its loss to the air and its oxidation in solution by oxygen which, of course, would be entering at a high rate through the surface of the estuary. During the autumn the rate of entry of oxygen would increase as the water became rougher, and when the supply of oxygen exceeded the demands for it sulphide would disappear once more from the water.

To prevent liberation of hydrogen sulphide from such an estuary therefore, it would be necessary to maintain a small concentration of dissolved oxygen in the water throughout the year.

SUMMARY

Factors affecting the formation and destruction of sulphide in the Thames Estuary have been discussed. Measurements of oxidation-reduction potentials show that the effect of oxygen in the water on conditions in deposits of mud is limited to the surface layer. The rate of formation of sulphide increases with temperature,

doubling approximately for each 10° C. rise. Reduction of sulphate to sulphide will occur at temperatures as low as 5° C., but even at 25° C. is inhibited by traces of dissolved oxygen. Mud in suspension in the estuary can produce as much sulphide as compact layers of similar mud which might be more anaerobic.

Oxidation of sulphide in the Thames Estuary is shown to be of a purely chemical nature; the rate of oxidation, when oxygen is present, is increased by the presence of suspended matter and iron. In the Thames Estuary, however, the rate is limited by the rate at which oxygen enters the water.

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