

ON THE UNUSUAL PATTERNS OF PHOSPHATE VERTICAL DISTRIBUTION IN THE TAMAR ESTUARY

By J. P. MOMMAERTS

Lab. voor Ekologie & Systematiek V.U.B.

(Text-figs. 1-4)

Chemical investigations in the Tamar estuary (Plymouth, Great Britain) have revealed marked variations of phosphate content in the water column. This pattern was usually not matched by that of salinity. The origin of the phenomenon and its possible use for the computation of the flushing time of the estuary are discussed.

INTRODUCTION

In two previous papers on the distribution of some nutrients and phytoplankters in the Tamar estuary, anomalies in the vertical profile of phosphate concentration have been demonstrated (Mommaerts, 1969*a, b*). In the top three metres the water column was stratified so that a dip of no more than 50 cm revealed a PO_4^{3-} (calculated as phosphorus) variation that would normally be accompanied by a marked change in salinity. On the other hand, salinity determinations revealed no dilution at all. Such unexpected variations occurred two or three times in the layer studied. There was an excellent correlation between the PO_4^{3-} and NO_3^- (calculated as nitrogen) concentrations on the one hand and between the silicate concentration and salinity on the other hand. Such a phenomenon could indicate either pollution or biological activity distributed along specific layers. The idea of pollution seemed to be most likely but, to fit the observations, the pollutant would have to match the salinity of the estuary at the precise spot where it enters.

Further measurements to give a better understanding of this problem were made during the spring of 1969 and are discussed here.

METHODS

Saltash sampling station (C in the 1968 survey) was visited on 27 March 1969 (at high water and on a neap tide) and on 30 May 1969 (at low water and also on a neap tide). On both occasions a neap tide was chosen to minimize the effects of water circulation on the sampling. For the same reason, the water samples were collected as rapidly as possible (30 min) with a Nansen-Petersen bottle. Duplicate samples were taken at every 50 cm from the surface to the bottom. Phosphate was determined without delay by the molybdate-antimony-ascorbic acid method of Murphy & Riley

(1962). The salinity was determined using the Mohr method modified after Harvey (1963). Some results not published in the previous work are included here. In this case salinity was determined by comparison of electrical conductivity with Copenhagen standard sea water with use of an Autolab inductively coupled salinometer, model 601. Table 1 summarizes all the sampling operations.

TABLE 1. SAMPLING DATA FOR THE PHOSPHATE RESULTS REFERRED TO IN TEXT AND TABLE 2

Date	Sampling station	Location	State of tide
8. iii. 68	B	4 km from the mouth	Ebb (1/3)
14. v. 68	B	4 km from the mouth	Ebb (1/3)
26. vi. 68	Cargreen	11 km from the mouth	Flood (1/3)
	B	4 km from the mouth	Flood (3/3)
29. vii. 68	Cargreen	11 km from the mouth	Ebb (1/3)
3. ix. 68	Cargreen	11 km from the mouth	Flood (1/3)
	D	8 km from the mouth	Flood (2/3)
	B	4 km from the mouth	Flood (3/3)
27. iii. 69	C (Saltash)	6 km from the mouth	High water
30. v. 69	C (Saltash)	6 km from the mouth	Low water

TABLE 2. PHOSPHATE CHANGES ($\mu\text{g at./l.}$) OBSERVED BETWEEN THE SURFACE AND 50 cm BELOW IN THE TAMAR ESTUARY

Strength of tide	Date	Low water	Flood			High water	Ebb	
			1/3	2/3	3/3		1/3	2/3
Spring	14. v. 68	—	—	—	—	—	+0.03	—
	26. vi. 68	—	+0.51	—	+0.541	—	—	—
	29. vii. 68	—	—	—	—	—	-0.05	—
Neap	8. iii. 68	—	—	—	—	—	+0.04	—
	3. ix. 68	—	-0.01	+0.173	+0.246	—	—	—
	27. iii. 69	—	—	—	—	-0.04	—	—
	30. v. 69	+0.101	—	—	—	—	—	—

PATTERNS OBSERVED

From the first cruises surface figures were much lower than expected. Later on it was found that this pattern occurred especially on the ebbing tide. However, smaller differences or even inverted patterns were also observed (Table 2). The flood-tide results were more consistent, the surface PO_4^{3-} concentration being generally much higher than immediately below. It should be remembered that the cyclical variation of concentration of a given nutrient is too intricate a phenomenon to be thoroughly related to tidal oscillations. Indeed, tidal oscillations and the strength of the tide, the river flow and the circumstances of pollutant emission act together and produce variable effects.

Later on, narrowing the gap between the sampling depths, it was shown that such shifts occurred two or three times in the top three metres. They

were always more significant than the unavoidable variations due to experimental techniques. Moreover that pattern occurred at several adjacent stations (Fig. 1). The intensity of the phenomenon was variable depending on the sampling time. On only one day was this peculiar phosphate profile matched by similar profiles of salinity, silicate and temperature (Fig. 2).

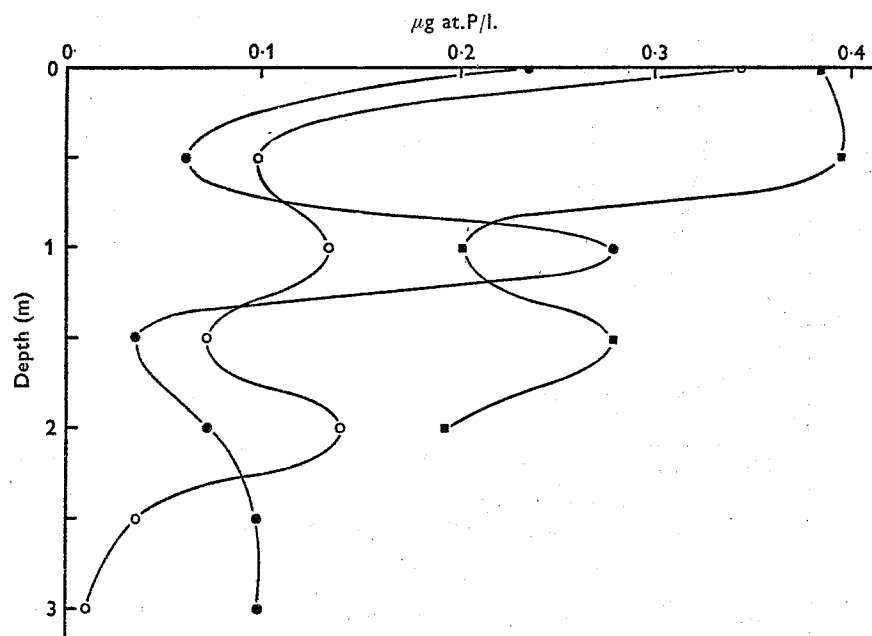


Fig. 1. Phosphate profiles in the Tamar estuary, 3 September 1968. ●—●, Station D (flood tide); ○—○, station B (flood tide); ■—■, Cargreen station (low water).

The cruises of 27 March and 30 May 1969 gave results shown in Fig. 3. The shifts observed this time were less dramatic than demonstrated before. This could be because the samples were taken during bad weather. Moreover, on 30 May water was very turbid so that the precision of the PO_4^{3-} analysis was reduced. However, standard deviations of replicates never exceeded 5%, whereas observed variations with depth were of the order of 10%. Under more favourable circumstances (e.g. 27 March 1969) standard deviations for replicates never exceeded 1%.

These fluctuations extended from the surface to the bottom. Simultaneous measurements of salinity once more failed to reveal the PO_4^{3-} anomaly. It has been calculated that if salinity was strictly correlated with the PO_4^{3-} content, according the regression lines in Fig. 4, changes of 1‰ in salinity should have been observed. Any rough method of salinity determination could detect changes of this order.

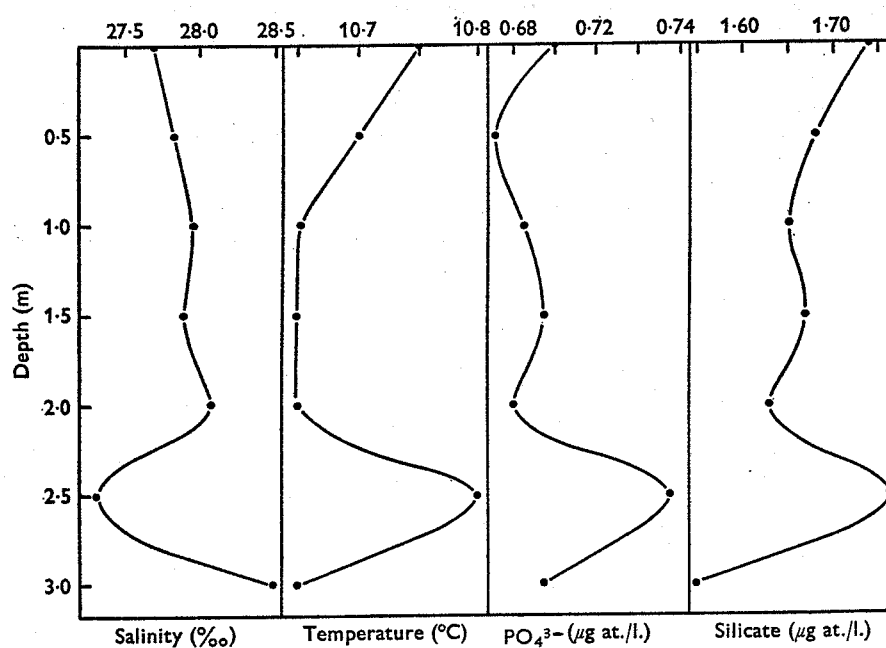


Fig. 2. Salinity, temperature, phosphate and silicate profiles in the Tamar estuary at sampling station B, 14 May 1968.

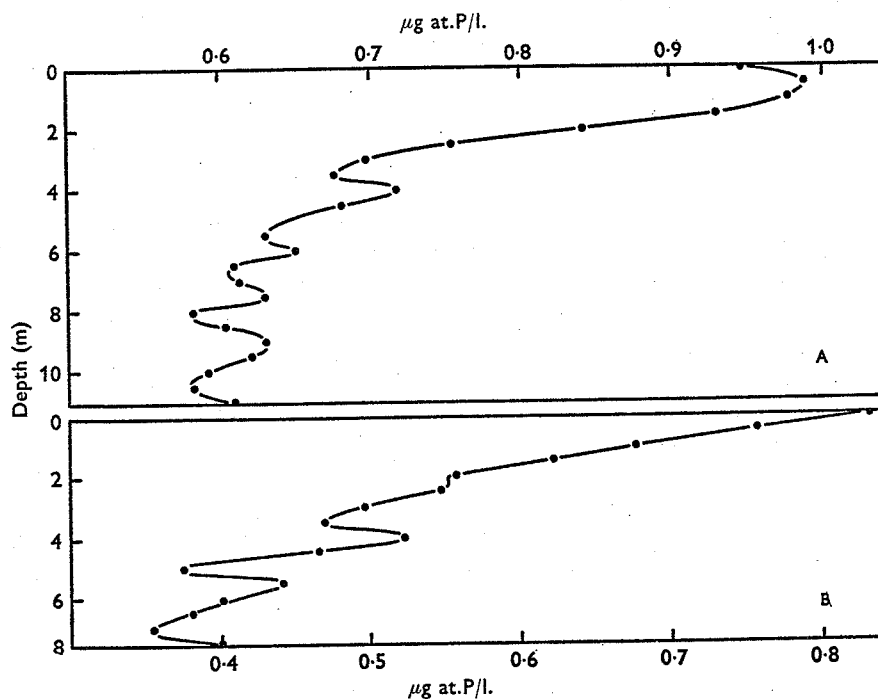


Fig. 3. Phosphate profiles in the Tamar estuary at Saltash sampling station.

Incidentally, the regression lines with their unchanged slopes give a good idea of the PO_4^{3-} depletion which occurred between March and May 1969. This is of the order of $0.400 \mu\text{g at. P/l.}$

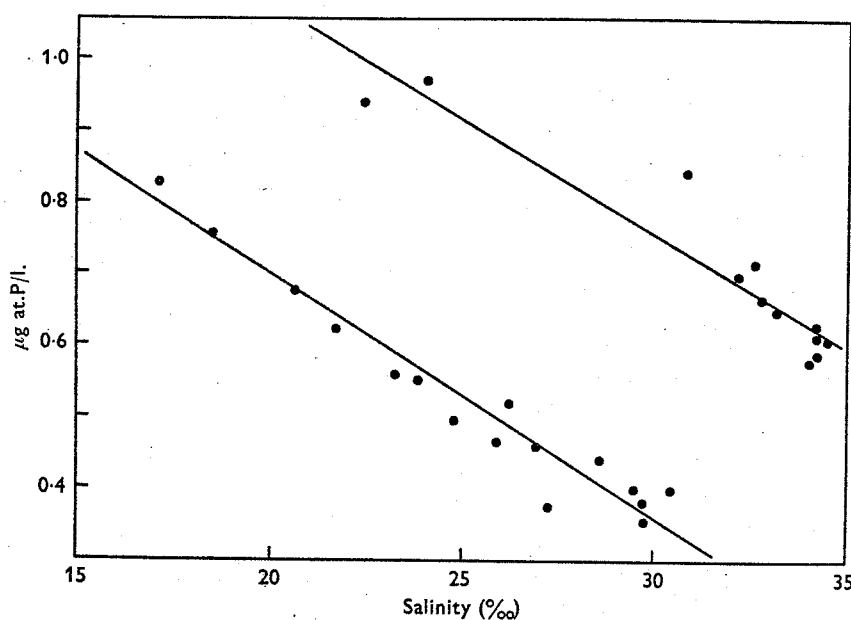


Fig. 4. Regression lines computed from paired determinations of phosphate and salinity at Saltash sampling station. Above, 27 March 1969; below, 30 May 1969.

DISCUSSION

Enough data have been gathered to demonstrate an unusual pattern of phosphate distribution in the Tamar estuary. The significance of the fluctuations was not as marked on the later cruises because the standard deviations of the replicates were much higher. This emphasizes the need for extreme care in chemical analysis.

The first question concerns the origin of the phenomenon: whether biological (e.g. layers with phytoplanktonic activity where PO_4^{3-} depletion is higher) or physico-chemical (e.g. currents, chemical pollution). The biological explanation was not impossible, for an excellent PO_4^{3-} - NO_3^- correlation was found on 26 June 1968 (Mommaerts, 1969*a*), but analyses of chlorophyll *a* gave divergent results.

The introduction of a pollutant was more likely, but the salinity determinations, even when carried out with sophisticated techniques, failed to demonstrate any addition of extraneous water (except on one occasion). There is, however, a possibility that should be checked and that would permit the

apparent contradiction. This is sewage from the ships in Devonport dockyard where sea water is used for sanitary purposes.

The other question concerns the practical use of the phosphate curve. Possibly this curve could be used to measure the flushing time of the estuary and thus help in the solution of sanitary engineering problems. Indeed, flood and ebb tides appear to bring about inversions in surface PO_4^{3-} content. During the ebb tide there is a downstream flow of water contributed by the river and this displaces water seawards, especially at the surface. On the flood tide it appears as if the previously polluted body of water is moved back up the estuary underneath the surface water which continues to move seawards. Each bend in the curve could then result from a bygone tidal oscillation.

At Saltash the time for all the water present at a given time to be thoroughly removed would then be 5 or 6 tides. A check of this hypothesis should be relatively simple: rhodamine B released at the surface could be used as a tracer and its diffusion followed for several tidal oscillations, using fluorometry. This is a situation in which tracer technique (using a pollutant normally present or any indicator introduced) could advantageously replace theoretical computations.

In the steady state distribution theory (Ketchum, 1951) which is a sensible approach to this problem, it is assumed that water within a volume segment (defined so that the distance between its inner and outer boundaries is equal to the average excursion of a particle of water on the flooding tide) is completely mixed at high tide.¹ The exchange ratio for such a segment can be defined as $P/(P+V)$, where P is the local intertidal volume and V the low tide volume of the segment. One can see that a theoretical infinite number of tides is required to replace all the water in a segment. But a simple calculation as well as the application to natural estuaries show that half of the water in a segment is replaced after only a few tidal oscillations (between 1 and 10 according the range of exchange ratios usually measured). This is in good agreement with our empirical result using dissolved PO_4^{3-} as a tracer of estuarine flushing.

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¹ In estuaries with incomplete vertical mixing, only the mixed volume of water is considered and the exchange ratio equation is modified correspondingly.

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