

## “Organic” Phosphorus in Sea Water from the English Channel.

By

L. H. N. Cooper, Ph.D., F.I.C.,

*Assistant Chemist at the Plymouth Laboratory.*

THE amount of phosphorus in sea-water in organic combination has in recent years received considerable attention. For its determination various methods have been proposed of which the most promising is that of Kalle (1935). The writer has examined a method in which sea-water was evaporated in a platinum dish with sulphuric acid to remove halides, the resultant melt being dissolved in water and treated successively with permanganate and sulphite, made up to a known volume and its phosphorus content determined colorimetrically. This method promised well as a reference method by which others could be checked, but it was very tedious particularly as only a limited amount of platinum ware was available. As a routine method Kalle's modification of Winkler's procedure is much more promising but here it has not given results as concordant as could be wished, the main source of error being a rather large reagent blank which it has not proved possible to reduce. The total content of phosphorus and arsenic, calculated as phosphorus, as found by Kalle's method, appears to be somewhat less than by the evaporation-permanganate oxidation method. One sample gave 1.20 mg.-atom by the permanganate method and 1.00 mg.-atom per cubic metre by Kalle's. This suggests that there may be incomplete oxidation either of arsenite or of organic phosphorus compounds. When a solution of Waksman's ferri-ligno-protein complex (which may well be typical of some of the more resistant organic constituents of sea-water) was added to sea-water, so as to give 120 mg./m<sup>3</sup> of added iron, and then oxidized by bromine water as in the method for "total iron" (Cooper, 1935), only 40% of this iron was set free. It would thus appear that any practicable method of oxidizing organic material in sea-water without prior evaporation is likely to be incomplete. Nevertheless the possibility that iron or phosphorus, that cannot be set free by such drastic processes, has any immediate biological value is remote, so that Kalle's method may quite well give a figure for total biologically available phosphorus (+arsenic).

To reduce arsenate to arsenite and so to render the colorimetric determination of phosphorus free from interference by arsenic, Kalle advocates

thiourea. In trial experiments with known amounts of arsenic *in concentrations likely to be found in sea-water* the writer has been unable to effect any reduction whatever with thiourea, with bisulphite, with "Analytical Reagent" zinc or with a special activated zinc containing small percentages of cadmium, copper and tin. Dr. Kalle has very kindly supplied a sample of his own thiourea, but no better success was achieved with this. At high dilutions complete reduction of arsenate to arsenite and the converse oxidation are known to be difficult to bring about and to be very dependent upon the pH value of the solution. The precise conditions for the reduction, which Kalle has evidently found, are difficult to reproduce and investigators intending accurately to determine total phosphorus should make certain that they have succeeded in removing arsenic present.

The conditions governing the arsenate-arsenite equilibrium in sea-water may themselves be of biological interest since to a limited extent for a limited range of species arsenic is able to replace phosphorus (cf. Atkins and Wilson, 1927).

In Table I are given analyses of total phosphorus+arsenic,  $\Sigma(P+As)$ , in samples of sea-water either unfiltered or filtered through Schleicher and Schüll's filter paper No. 589 (Blueband) as recommended by Kalle. Judging from subsequent work in this laboratory on iron, a membrane filter ought to prove more efficient. The organic phosphorus+arsenic content of unfiltered water from Stations E1 and L4 in early spring and July appears to be very constant. The arithmetic mean of all determinations is 0.44 mg.-atom/m.<sup>3</sup> and it is of interest that the arithmetic mean of all Bôto's determinations (1935) of organic phosphorus by Kalle's method off the coast west and south of Portugal between the surface and fifty metres in August and September, 1934, average 0.30 mg.-atom/m.<sup>3</sup> and that the arithmetic mean of Seiwel's results (1934) between the surface and fifty metres for thirteen stations in the Western North Atlantic in February and March averaged 0.46 mg.-atom. Kreps and Osadchih (1933) by a somewhat different method found in the Barents Sea an annual mean of only 0.24 mg.-atom organic phosphorus (including arsenic) per cubic metre. An examination of all the records shows that organic phosphorus+arsenic in the surface layers of the North Atlantic averages about 0.4 mg.-atom per cubic metre. Around Iceland with an earlier provisional method, Kalle (1933) found values for the surface which were all consistently much higher, averaging 1.1 mg.-atom/m.<sup>3</sup> In an interesting set of analyses by his present method for a September station in the North Sea he found (mg.-atom/m.<sup>3</sup>):—

$PO_4-P.$	$\Sigma P$ in unfiltered water.	$\Sigma P$ in filtered water.	Org. P in unfiltered water.	Org. P in filtered water.
0.17	0.89	0.53	0.72	0.36

Arsenic was said to have been removed by thiourea.

Off Plymouth in July, 1935, results were also obtained on filtered water, but the two sets of analyses cannot be regarded as conclusive. Work here in 1934 had shown that seldom was more than 0.03 mg.-atom P/m.<sup>3</sup> present as plankton caught in a silk net with 200 meshes to the linear inch, while Harvey's investigations have also shown that nannoplankton able to pass such a net was unlikely to be present in such bulk as to equal the net catch. The origin of such a large organic phosphorus fraction removable by filtration through filter paper is therefore still unknown.

Rakestraw and Lutz (1933) carried out direct determinations of arsenic on the waters in the neighbourhood of Woods Hole; the arithmetic mean of all their results from the surface down to fifty metres was 0.19 mg.-atom per cubic metre. Again, in waters from seventy metres in the English Channel in November, 1921, the Government Chemist found 0.25 mg.-atom/m.<sup>3</sup> (Orton, 1924). Thus about 0.2 mg.-atom/m.<sup>3</sup> arsenic is present in sea-water, probably mostly as arsenite, which after oxidation in any of the methods used for determining total and organic phosphorus should yield arsenate which behaves like an equivalent amount of phosphate in colorimetric determinations.

The inference is therefore that at least one-half of the so-called organic phosphorus is really arsenite (cf. Atkins and Wilson, 1927) and that the quantities of phosphorus in organic combination present in the surface layers of the Atlantic are not in general such as to play any large part in the food chain in the sea.

The measurements of "organic phosphorus" by Kreps and Osadchih (1933) and by Seiwel and Seiwel (1934) evidently include arsenic since no steps were taken to remove it.

#### SUMMARY.

Determinations of organic phosphorus (so called) have been made in waters from off Plymouth. The amount varies little with the time of year and averages 0.44 mg.-atom per cubic metre. This is of the same order as determinations in other parts of the North Atlantic. About one-half of this "organic phosphorus" is considered really to be arsenite.

## REFERENCES.

- ATKINS, W. R. G., and WILSON, E. G. 1927. The Phosphorus and Arsenic Compounds of Sea-Water. *Journ. Mar. Biol. Assoc., N.S.*, Vol. XIV, pp. 609-614.
- BÔTO, R. G. 1935. Observações Oceanográficas, "Albacora," 1934. *Trav. Station Biol. Maritime Lisbonne*, No. 35, p. 31.
- COOPER, L. H. N. 1935. Iron in the Sea and in Marine Plankton. *Proc. Roy. Soc., Series B*, Vol. 118, pp. 419-438.
- KALLE, K. 1933. Phosphat und Gesamtphosphor in Beziehung zu Temperatur, Salzgehalt und Plankton an der Oberfläche der isländischen Küstengewässer. *Ber. deutsch. wiss. Komm. Meeresforschung, N.F.*, Bd. 6, pp. 273-299.
- 1935. Meereskundliche chemische Untersuchungen mit Hilfe des Zeisschen Pulfrich-photometers. V. Die Bestimmung des Gesamt-Phosphorgehaltes, des Plankton-Phosphorgehaltes (lebende Substanz) und Trübungsmessungen. *Ann. d. Hydrographie*, Jahrg. 63, pp. 195-204.
- KREPS, E., and OSADCHIH, M. 1933. The Organic Phosphorus in the Sea. *Internat. Rev. d. ges. Hydrobiol. u. Hydrographie*, Bd. 29, pp. 221-228.
- ORTON, J. H. 1924. Ministry of Agriculture and Fisheries Invest., Series 2, Vol. 6, No. 3, p. 166.
- RAKESTRAW, N. W., and LUTZ, F. B. 1933. Arsenic in Sea-Water. *Biol. Bull.*, Vol. 65, pp. 397-401.
- SEIWELL, H. R., and SEIWELL, G. E. 1934. Über den Gesamtphosphorgehalt des Seewassers im westlichen Nordatlantischen Ozean. *Ann. d. Hydrographie*, Jahrg. 62, pp. 7-13.

TABLE I.

TOTAL AND ORGANIC PHOSPHORUS (INCLUDING ARSENIC  
CALCULATED AS PHOSPHORUS).

MILLIGRAM-ATOMS PHOSPHORUS PER CUBIC METRE.

Date.	Station.	Depth m.	PO <sub>4</sub> -P.	Analyses on unfiltered water.		Analyses on filtered water.	
				Σ (P+As)	Org. P+As	Σ (P+As)	Org. P+As
12-ii-34*	L4	0 & 25‡	0.39	0.84	0.45	—	—
	E1	0, 5 & 50‡	0.32	0.64	0.32	—	—
26-ii-35†	L4	0	0.39	0.79	0.40	—	—
		25	0.42	0.86	0.44	—	—
		45	0.42	0.87	0.45	—	—
		<i>Average</i> §	<i>0.41</i>	<i>0.84</i>	<i>0.43</i>	—	—
	E1	0	0.42	0.82	0.40	—	—
22-iii-35†	L4	0	0.37	0.77	0.40	—	—
		5	0.32	0.84	0.52	—	—
		25	0.39	0.79	0.40	—	—
		45	0.39	0.79	0.40	—	—
		<i>Average</i>	<i>0.37</i>	<i>0.80</i>	<i>0.43</i>	—	—
	E1	0	0.52	0.97	0.45	—	—
		5	0.37	0.81	0.44	—	—
		50	0.35	0.87	0.52	—	—
		67	0.35	1.10	0.75	—	—
		<i>Average</i>	<i>0.36</i>	<i>0.88</i>	<i>0.52</i>	—	—
4-vii-35†	L4	0	0.04	0.42	0.38	0.14	0.10
		5	0.02	0.58	0.56	0.29	0.27
		25	0.17	0.53	0.36	0.50	0.33
		45	0.20	0.53	0.33	0.50	0.30
		<i>Average</i>	<i>0.13</i>	<i>0.53</i>	<i>0.40</i>	<i>0.45</i>	<i>0.29</i>
	E1	0	0.07	—	—	0.30	0.23
		5	0.05	—	—	0.35	0.30
		15	0.07	—	—	0.30	0.23
		25	0.12	—	—	0.48	0.36
		50	0.22	—	—	0.81	0.59
		<i>Average</i>	<i>0.16</i>	—	<i>0.59</i>	<i>0.43</i>	

\* Analyses on 12-ii-34 by evaporation—permanganate oxidation method.

† Analyses in 1935 by Winkler-Kalle method.

‡ Mixed sample from depths stated.

§ Average content of water column; for definition and method of computation see J. Mar. Biol. Assoc., N.S., 1933, Vol. 18, p. 722.