

DISTRIBUTION OF CHEMICAL SPECIES

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Introduction

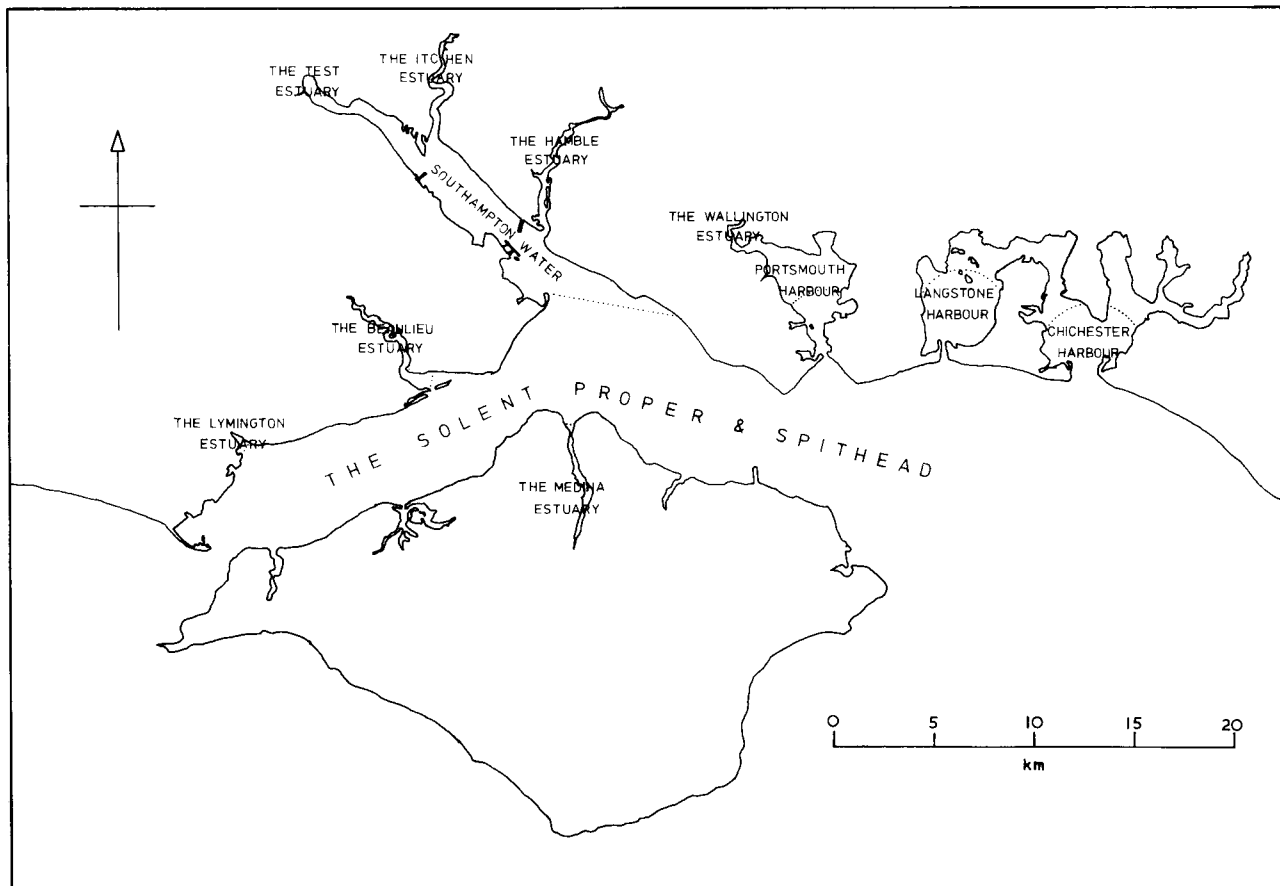
Following a brief discussion of the distribution of salinity throughout the Solent estuarine system as a whole, the region has been divided into twelve areas (Fig. 1), each of which will be considered separately. Basic data have been considered from three main sources, academic research, studies designed to answer specific questions and water quality surveys. Only the last which is the responsibility of the Water Industry can provide the long-term and wide geographical coverage that is required for a general assessment of chemical status as the others are often limited in time and space. It is thus not surprising that most of the information relates to the conventional measurements of water pollution such as dissolved oxygen, biochemical oxygen demand, and levels of nutrients and heavy metals. However, this type of approach does not always reflect underlying mechanisms since it is primarily intended to study effects rather than causes. For example, few chemical parameters are unaffected by seasonal cycles in biological activity and/or hydrographic conditions and many are also subject to diurnal and tidal variations. It is in these circumstances where specific, once-off investigations are of greatest importance.

Water quality monitoring is undertaken by large-scale users and by the Southern Water Authority who have the statutory responsibility for the area. Any reference to the Authority in the context of surveys commenced before April 1974 should be understood to include one or more of its predecessors, the Hampshire River Authority,

the Isle of Wight River and Water Authority and the Sussex River Authority. The Authority's current programme includes quarterly surveys from all parts of the region except for Chichester Harbour which receives greater attention and the Beaulieu, Lymington and Medina Estuaries which are not at present surveyed regularly. The Solent, Southampton Water, the Test and Itchen Estuaries and Langstone Harbour are also subject to individual monitoring programmes undertaken by the Authority and special projects are commissioned from time to time. In addition, the more important streams in the area are sampled at least six times a year. Sea water penetrates the lower reaches of some of these streams and sampling points at which chloride concentrations greater than 1g l^{-1} have frequently been observed include those on the Avon Water at Keyhaven, the Dark Water at Lepe, the Bartley Water at Brokenford, the River Meon at Hill Head and the River Alver at Privett. A number of minor estuaries on the northern coast of the Isle of Wight, however, are virtually unknown from a chemical standpoint.

The comparison of data from different sources collected over a long period inevitably involves a risk of inconsistency since analysts and their methodologies change. This problem was highlighted by the results of a recent interlaboratory comparison exercise between five laboratories in the Solent region (Phillips, 1977) and should be borne in mind when interpreting the

Fig. 1 Parts of The Solent Estuarine System. Areas landward of the dotted lines may experience salinities below 30‰



information presented in this review. An Appendix tabulates data on trace elements, organochlorine residues and hydrocarbons in marine organisms.

Salinity

The composition of a water body is the result of its material exchanges with other environments, modified by processes occurring within it. In the case of the Solent, and most other British estuaries, the chemical inputs to the system reflect its natural setting and human activities in the surrounding region. These inputs, together with mixing processes, largely dictate the distribution of constituents within the system. Many of the less abundant chemical species have higher concentrations in fresh than in sea water and inverse relationships between concentration and salinity are commonly found. However, some minor constituents show a positive correlation with salinity and others vary little. Deviations from conservative behaviour are mainly due to interaction with particulate phases, both mineral and biological.

The general distribution of salinity forms a useful background to the behaviour of other constituents and the information in subsequent sections relates concentrations to this parameter. Figure 1 delimits the zones in which salinities of less than 30‰ have been observed. Ideally such a boundary would represent the average position of the 30‰ surface isohaline at mean low water springs, but lack of data makes it impossible to provide more than a rough approximation. The trend of the line outside Southampton Water reflects the presence of an east-going tidal stream that runs in this area for several hours after low water and the lines inside the harbours to the east of Spithead serve to emphasise their partially marine character.

The Solent proper and Spithead

This region forms the greater part of the total estuarine system but for reasons of its size, its relatively unpolluted state and the lack, until recently, of any pressing need for information, relatively little is known about its chemistry. The mean surface salinity as a whole is 34.3‰ although the winter months are poorly represented. Relative to this mean value, the central part which receives the bulk of the fresh water entering the system, is up to 0.5‰ fresher, and Spithead which is more exposed to the open sea, about 0.2-0.3‰ more saline. Although there are few salinity profiles available little variation with depth is to be expected over most of the region.

Routine monitoring for dissolved oxygen by the Hampshire River Authority had been in progress for about a decade recording levels consistently around the saturation value (Wright and Barnard, 1964), when it was interrupted in 1971 by a more intensive study conducted by Messrs J D and D M Watson on behalf of the South Hampshire Plan Advisory Committee. During this study which was undertaken in connection with the disposal of sewage and sewage sludge in the Solent area, near-surface water samples were collected at 16 stations between the Needles and Nab Tower on 8 occasions from March to November, for analysis by the River Authority. Over the same period zinc analyses were carried out by Clark (Department of Oceanography, Southampton University) and approximately 2000 measurements of temperature, salinity and dissolved oxygen were made. The results have been published (South Hampshire Plan Advisory Committee, 1972) and means and ranges for each month of the study are listed in Table 1. Some values are also given for compara-

TABLE 1: Summary of Chemical Information for the Solent in 1971

Month	Salinity ‰	pH	Dissolved oxygen % saturation	Biochemical oxygen demand ppm	Ammonia-N µg-atoms l ⁻¹	Nitrate-N µg-atoms l ⁻¹	Phosphate-P µg-atoms l ⁻¹	Synthetic detergents (as Manoxol OT) µg-atoms l ⁻¹	Zinc (dissolved) µg-atoms l ⁻¹
March	33.00 (32.25-33.90)	7.6 (7.6-7.8)	104 (87-116)	1.6 (0.1-2.8)	2.6 (0.6-4.9)	7.3 (2.0-12.9)	1.5 (0.4-3.2)	15 (0- 40)	9.7 (0.8-31.7)
April	34.07 (33.39-34.98)	7.8 (7.7-8.0)	104 (100-112)	2.5 (1.1-3.7)	3.5 (1.5-7.9)	7.3 (0.3-14.5)	—	43 (15- 92)	5.5 (0.6-25.1)
May	33.96 (33.45-34.60)	8.1 (8.0-8.1)	112 (104-116)	2.8 (1.9-3.8)	1.5 (0.4-5.0)	5.9 (2.1- 9.6)	2.9 (1.6-6.7)	14 (5- 18)	3.7 (1.1-12.2)
June	33.90 (33.06-34.47)	7.9 (7.9-7.9)	105 (98-110)	2.6 (1.5-3.5)	1.7 (1.0-4.9)	6.1 (3.4-10.3)	0.6 (0.3-1.3)	154 (147-165)	6.6 (0.3-31.1)
July	34.07 (32.95-34.60)	7.8 (7.6-7.9)	107 (100-122)	1.5 (0.2-4.0)	3.1 (1.3-6.6)	8.8 (4.5-12.8)	1.0 (0.6-2.4)	58 (51- 67)	6.0 (1.3-15.6)
August	34.29 (33.18-34.71)	7.8 (7.6-7.9)	101 (93-108)	0.5 (0.1-0.8)	1.8 (0.0-4.4)	3.1 (0.0- 7.4)	0.6 (0.2-1.3)	36 (28- 43)	3.8 (1.1- 8.2)
September	34.51 (33.62-35.80)	7.7 (7.6-7.8)	105 (96-113)	1.0 (0.3-1.6)	2.7 (0.4-6.7)	7.4 (2.1-12.4)	0.3 (0.1-0.8)	—	6.6 (1.7-24.1)
October	—	—	93 (86- 98)	—	—	—	—	—	—
November	—	7.8 (7.7-7.8)	93 (86- 98)	0.9 (0.3-2.0)	4.3 (1.9-7.8)	—	1.1 (1.0-2.0)	—	5.5 (1.1-15.2)
Averages	33.97	7.8	103	1.7	2.6	6.6	1.1	53	5.9
Data for comparison (see text)	35.14	~8.0	~100	—	—	2.7	0.27	—	4.2

TABLE 2. Trace metals in the Solent (data collected by M.A.F.F. Fisheries Laboratory, Lowestoft).

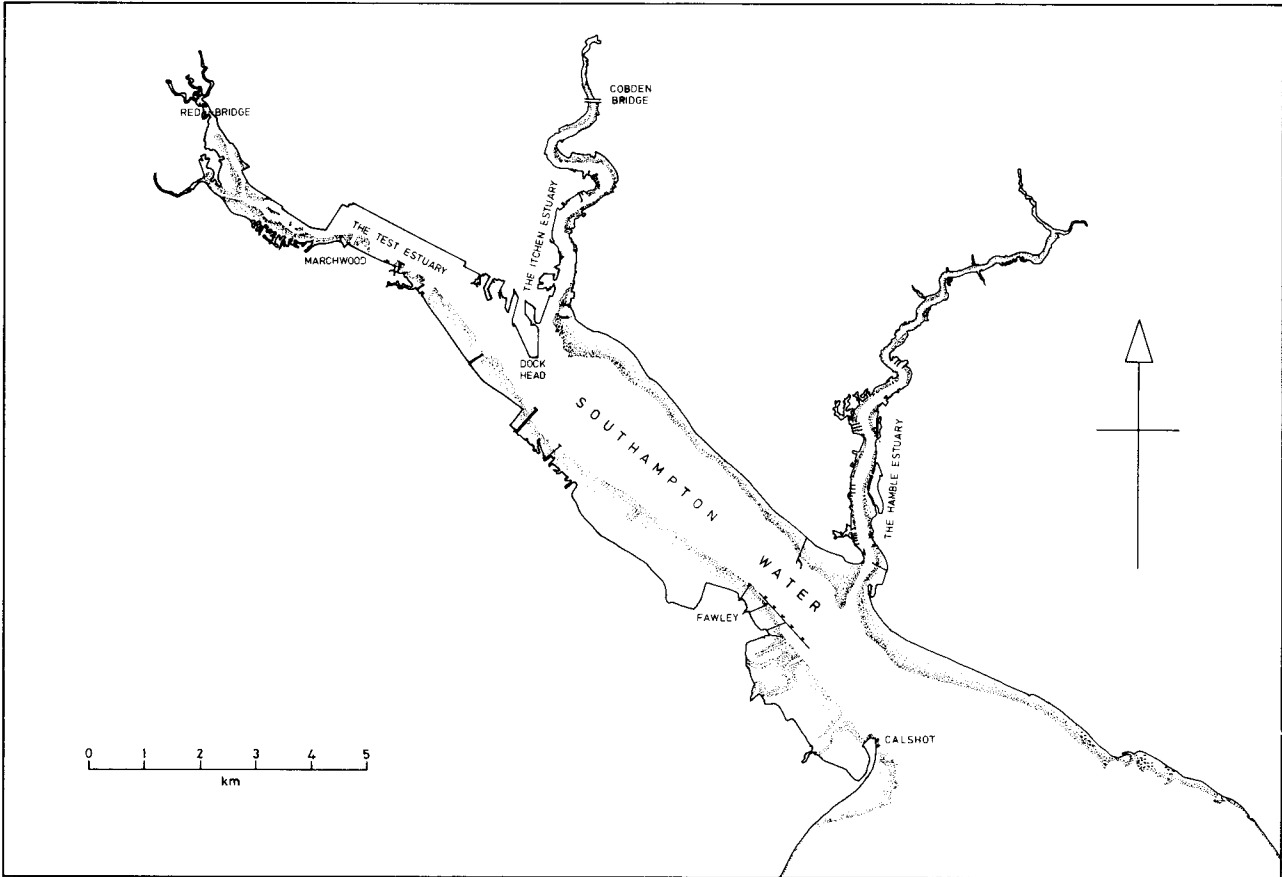
Date	Position	Depth	Concentration ($\mu\text{g l}^{-1}$)			
			Cadmium	Copper	Nickel	Zinc
March 1973	50°45'N 01°08'W	surface	0.05	0.58	0.4	2.8
		near bottom	0.05	0.51	0.4	8.7
June 1973		surface	0.11	0.51	0.4	4.7
		near bottom	0.02	0.44	0.4	3.2
August 1974		surface	0.05	0.68	0.5	2.5
		near bottom	0.05	0.63	0.5	1.6
	50°43'N 01°31'W	surface	0.05	0.42	0.4	1.5
		near bottom	0.06	0.42	0.5	1.2
	50°47'N 01°18'W	surface	0.04	0.63	0.6	2.5

tive purposes. Data on salinity and nutrient concentrations are from the International Hydrographic Station E1, 40km off Plymouth, in 1968 (Banoub, 1971), the value for zinc is the mean of eight surface water samples from the English Channel and Celtic Sea in 1969 and 1970 (Preston *et al.*, 1972) and the remainder are typical figures for UK coastal waters. It can be seen that the waters of the Solent are slightly diluted with respect to English Channel water with surface salinities approximately 1‰ lower. The nutrient concentrations were several times greater than those at E1 and their variations showed surprisingly little regularity through the year. However, biochemical oxygen demand was

relatively high in the spring and early summer and dissolved oxygen displayed a mild degree of supersaturation until October. There is no clear indication of a long-term trend in dissolved oxygen concentration, the only parameter for which a substantial body of earlier data is available.

Water quality deteriorates towards the middle of the Solent as a result of the reduced salinity and higher levels of ammonium and biochemical oxygen demand of Southampton Water. Although nutrient concentrations are somewhat lower in Spithead than at the western end of the Solent reflecting the salinity distribution,

Fig. 2 Southampton Water and associated estuaries



in general longitudinal gradients are not pronounced. Southgate reviewed the chemical and bacteriological aspects of the area in a report to the South Hampshire Plan Advisory Committee (1972) and concluded that "From surveys made in 1971, as judged by dissolved oxygen content, concentration of phosphate, ammonia and nitrate and count of coliform bacteria, it is evident that the present concentration of polluting substances in the Solent, derived from sewage, is very small". Since this time a much expanded monitoring programme in the Solent has been initiated by the Southern Water Authority.

The levels of dissolved cadmium, copper, nickel and zinc were measured on three occasions in 1973-74 by the Ministry of Agriculture, Fisheries and Food (Table 2) and the information from the first two surveys has been published (ICES, 1974). Silicate concentrations approaching $15 \mu\text{g-atom Si l}^{-1}$ were recorded in the Solent in December 1966 (Banoub and Burton, 1968) and up to $1 \mu\text{g-atom N l}^{-1}$ has been found in the eastern Solent during studies of the vertical distribution of urea (Pineda, 1974), with the highest levels at the surface. Swain (1973) reported somewhat higher levels in the western Solent the following June. Surveys of dissolved inorganic and organic carbon in the surface waters of the Solent were carried out in February and October 1975 and provided mean values of 27 and 1.2 mg l^{-1} respectively (Collins and Williams, 1977; Collins, 1979). Although there was only slight variation about these means, there was a general tendency towards lower levels with increasing salinity in the October samples. Additional sources of information on nutrients in the Solent can be found in Table 3.

In 1976 work commenced on a large sewage treatment works near Gosport to serve most of south-east Hampshire. When the initial stage is completed in 1982 it will treat a dry-weather flow of $86,000 \text{ m}^3 \text{ d}^{-1}$, discharging a fully treated effluent 1 km offshore. Although the volume of sewage discharged directly to the Solent will be increased, the scheme will relieve pressure on the Wallington Estuary and may eventually replace all the outfalls on the north-eastern shore as far as Southampton, including the Hamble Estuary. Most of these at present discharge untreated sewage.

Southampton Water

Southampton Water, the most intensively studied part of the Solent estuarine system, is a roughly linear body of water about 10 km long and 2 km wide, forming a north-westerly extension of the central Solent (Fig. 2). Its shipping channel is dredged to a depth of about 13 m below mean tide level and bordered by broad intertidal mudflats fronting shingle and sand on the eastern side and saltmarsh to the west. It is bifurcated at its landward end, the western and eastern arms forming the estuaries of the Rivers Test and Itchen respectively. Although these estuaries are being considered separately, they have been included in many surveys of Southampton Water and where appropriate these data are presented below. The general situation in Southampton Water and the Test Estuary has been discussed by Woolley (1973) and a similar report deals with the Itchen Estuary (Snell, 1972). Both are based largely on data supplied by the Hampshire River Authority. The position has also been summarised by Raymont (1972) who stated that "Investigations of concentrations of primary nutrients and of certain metallic ions in addition to oxygen data suggest that Southampton Water is not a grossly polluted area. However, the present

quantities of nutrients and some metallic ions suggest that further increases in Southampton Water might have deleterious effects".

Southampton Water is a partially mixed estuary (Dyer, 1970) but its salinity structure depends very much on tidal state and, to a lesser degree, the seasonal cycle in freshwater flow. At high water it shows little stratification and the surface salinity normally exceeds 30‰ at Dock Head during summer and autumn. On the other hand, at low water the surface salinity at Calshot may fall below 30‰ in the wetter months and stratification is markedly increased. The vertical salinity difference at the seaward end typically ranges from 0.5 to 2.3‰. This changing situation underlines the value of relating chemical data to salinity.

The first analyses of water from the estuary were carried out for the Royal Commission on Sewage Disposal (1908, 1911). Although few in number, they suggest that concentrations of ammonium and nitrate were lower than they are today. Unfortunately no further data were gathered until 1958-59 when Raymont and Carrie (1964) measured the concentration of phosphate in samples from Marchwood and Calshot. Their figure for the winter maximum was slightly higher than those found subsequently. In addition to the measurements made by the Southern Water Authority and its predecessors over the last 20 years, a number of extensive surveys have been undertaken in recent years by Phillips in 1969-74, the Port Health Authority (analyses by the Public Analyst) in 1971-72 and Collins (1979) in 1974-75 to investigate the distribution of nutrients and related parameters in Southampton Water (Table 3).

Examples of the distribution of dissolved oxygen in Southampton Water and the Test and Itchen Estuaries during the early 1960s have been published by Wright and Barnard (1964). Concentrations in Southampton Water rarely fall below 80% saturation and may exceed 150% during algal blooms. The ranges of nutrient concentration encountered at the extremes of the estuary are summarised in Table 4 and the winter distribution of salinity, dissolved oxygen and nutrients at high water is illustrated in Figure 3. Nutrient concentrations are much depleted in the summer when phytoplankton activity is at a peak. When plotted against salinity, nitrate and silicate behave conservatively, whereas phosphate and ammonium display anomalies which are attributable to sewage effluents, mainly discharged from the city of Southampton.

The concentration of particulate silicon varies widely and irregularly (Banoub and Burton, 1968), with an average value in winter about 2.5 times that for (dissolved) silicate. Pineda (1974) investigated the distribution of urea in Southampton Water during 1972 and concluded that it was not a suitable tracer for sewage effluents in the estuary because of contributions from other significant but unidentified sources. Concentrations in the spring and summer decreased from about 4.5 to approximately $1.5 \mu\text{g-atoms N l}^{-1}$ in a seaward direction and were generally lower and more uniform at about $2 \mu\text{g-atoms N l}^{-1}$ in the autumn-winter period. The highest annual mean concentration of urea was found in the Test Estuary.

The surveys by Collins (1979) also recorded pH values of 7.4-8.2 with a mean of 7.8 and included analyses of particulate organic, dissolved organic and dissolved inorganic carbon. In general, concentrations of particulate and dissolved organic carbon were 0.2-1.0 and

TABLE 3: Sources for data on nutrients and associated parameters in Southampton Water and the adjacent areas.

SOURCE	PARAMETER	YEARS OF SURVEY	ADJACENT AREA INCLUDED
Banoub & Burton 1968	pH Dissolved oxygen Silicate Particulate silicon Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1966	ST
Birks 1972	Silicate Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium	1972	SI
Chan 1978	pH Dissolved oxygen Nitrate Nitrite Ammonium	1978	I
Collins 1979	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1974-75	STI
Mayo 1970	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1970	STIH
Mendez in Raymont (1972)	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1971	T
Moore 1978	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1977	I
Pineda 1974	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1972-73	ST
Port Health Authority (incl. McGregor, 1975)	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1971-72	STIH
Phillips (author)	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1969-74	ST
Raymont & Carrie 1964	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1958-59	T
Royal Commission 1908	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1904	TI
Royal Commission 1911	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1910	TH
Southern Water Authority	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	~1960 to date	STIH
Spencer 1970	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1970	T
Swain 1973	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	1973	ST
Wright & Barnard 1964	pH Dissolved oxygen Phosphate Polyphosphates Dissolved organic phosphorus Particulate organic phosphorus Nitrate Nitrite Ammonium Urea Albuminoid nitrogen Dissolved organic nitrogen Particulate organic nitrogen Dissolved inorganic carbon Particulate inorganic carbon Dissolved organic carbon Particulate organic carbon Permanganate value Biochemical oxygen demand Ultraviolet absorbance	early 1960s	STIH

Key: S, Solent; T, Test Estuary; I, Itchen Estuary; H, Hamble Estuary.

This table should not be taken to imply that a particular source necessarily contains information on all the marked parameters in all the adjacent areas included.

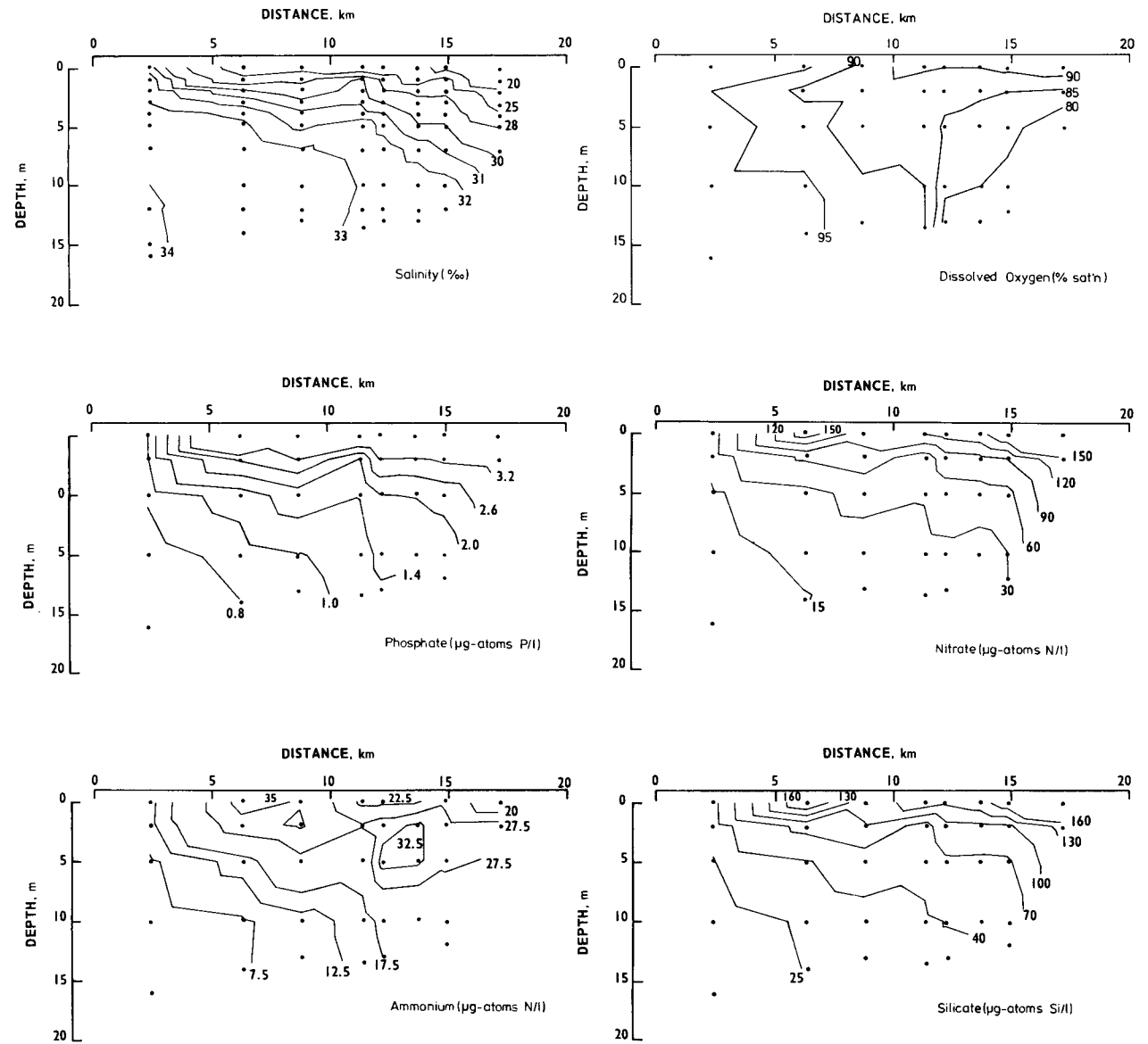
1.0-3.0 mg l⁻¹ respectively. Higher levels of particulate organic carbon were associated with the resuspension of sediments in rough weather and with an algal bloom in July-August. Although no seasonal cycle was observed in dissolved organic carbon levels, two more detailed surveys have revealed longitudinal gradients declining towards the Solent. Moore (1978) investigated the composition of dissolved organic carbon from Calshot by ultrafiltration. In conjunction with his studies on nutrient and carbon flux, Collins developed a one-dimensional steady-state model incorporating photosynthesis and respiration. This approach was extended by Peters (1977), who produced a time-dependent model of plant carbon, total inorganic nitrogen (ammonium plus nitrate) and phosphate in the estuary. Many of the nutrient data and related measurements for Southampton Water have

been stored in a computer archive at the Department of Oceanography, Southampton University.

Table 4: Typical nutrient concentrations (µg-atoms l⁻¹) in the River Test and at Calshot.

	River Test	Calshot	
		winter	summer
Phosphate	1.5 - 2.5	0.7	0.2
Nitrate	250 - 300	15	2
Nitrite	1 - 2	0.2	0.2
Ammonia	1 - 10	5	1
Silicate	150 - 400	20	4

Fig. 3 The high-water distribution of salinity, dissolved oxygen and nutrients in Southampton Water on 14th January 1972. (Nitrate includes nitrite, which rarely amounts to more than a few percent of the total).



Trace element data from Southampton Water and for nearby river waters are numerous and, together with information on the trace element content of sediments, are summarised in Table 5.

The presence of a large oil refinery at Fawley has stimu-

lated the investigation of hydrocarbons in the water, sediments and biota of the estuary (Knap, 1979). A more detailed study of the distribution of hydrocarbons in the water was carried out in 1977 by Lysiak (Department of Oceanography, Southampton University). Samples of

TABLE 5: Summary of data on trace elements in Southampton Water and the adjacent areas.

[illegible]

Cu	Water (0.45μ)	Chelex-100; AAS.	Organic fraction investigated by UV Photolysis and CHCl ₃ extraction.	Matharu 1975
V	Water (~0.5μ)	Coprecipitation with Fe(OH) ₃ ; anion exchange; spectrophotometry of 3,3'-dimethylnaphthidine complex.	—	McHugh 1972
Se(IV))	Electron-capture GLC of 5-nitropiaselenol derivative extracted into toluene.	—)
Total dissolved Se)	UV photolysis	—) Measures 1978
Co Cu Ni Zn (total and fractions associated with various mineral components)	Sediment	HF digestion, sequential leaching or solvent extraction; dithizone; AAS.	—) Measures & Burton 1978
Cu	Water (~0.5μ)	Chelex-100; spectrophotometry of neocuproin complex.	—	Mierzejewski 1977
Cu	Water (0.45μ)	Chelex-100; flameless AAS.	Organic fraction investigated by UV photolysis, CHCl ₃ extraction and adsorption on XAD-2.	Miles 1968
Iodide, iodate	Water (filtered)	Precipitation by Ag citrate before and after reduction with NaH ₄ ; Spectrophotometric determination as tri-iodide.	—	Moore 1978
Ni Zn	Water (0.45μ)	Chelex-100; AAS	—	Morrant 1973
Cu Fe Zn	Littoral sediments (total and < 204μ)	HNO ₃ digestion; AAS.	—	Raymont 1972
Mn V	Sediment cores	HF digestion; oxidation to permanganate and spectrophotometry (Mn); cation exchange and spectrophotometry of 3,3'-diaminobenzidine complex (V).	Samples washed in deionised water.	Romeril 1974, 1979
Sn (dissolved))	Adsorption on quartz wool; solvent extraction (of eluate); spectrophotometry of phenylfluorone complex.	—	Smith 1969
Sn (particulate))	H ₂ SO ₄ digestion replaces adsorption.	—	Smith 1971
Cd Cr Cu Pb Hg Ni Zn	Water (0.45μ)	SDDC extraction; AAS.	Total and inorganic Hg by a cold vapour technique.	Smith & Burton 1972
Cd Cr Co Cu Fe Pb Mn Ni Zn	Sediment	HNO ₃ digestion ± H ₂ O ₂ .	—	Smith 1971
Mn Zn (total and non-lattice-bound)	Sediment cores	HF digestion or leaching with Chester-Hughes reagent; AAS.	Also Zn in interstitial water using Chelex-100.) Southern Water
Cr U	Sediment cores	Neutron activation; HF digestion; radiochemical separation; counting.	U measured as ¹³¹ I.) Authority (unpublished)

Footnotes:

1. Unless stated otherwise, water analyses are for the dissolved element.
2. The average pore size or type of filter is shown in brackets.
3. Sediment analyses refer to surface grab samples.
4. Some sediment cores also include grab samples.

water collected just below the surface and analysed by thin-layer chromatography contained 10-40 $\mu\text{g l}^{-1}$ of non-volatile hydrocarbons expressed as carbon, with a mean value of about 20 $\mu\text{g l}^{-1}$. Water from the Solent contained somewhat lower concentrations of about 15 $\mu\text{g l}^{-1}$. These results confirmed Knap's general conclusions without revealing any systematic pattern. His measurements of the same parameter in surface sediments, however, showed a clear pattern centred on the area off the refinery outfalls, where concentrations exceeded 3 mgC g^{-1} (dry weight), falling to levels below 0.5 mgC g^{-1} in the more distant parts of the estuary. A sample from the western Solent contained only 0.1 mgC g^{-1} . Similar data have been reported by Levell (1978). The vertical profiles of hydrocarbon concentration in sediment cores sometimes displayed an 'oil horizon' whose depth indicated a very high rate of sedimentation near the outfalls. This is presumably associated with the start of large scale refinery operations in the early 1950s. The significance of petroleum hydrocarbons particularly the volatile fraction, to the organic carbon budget of the estuary has been discussed by Knap *et al.* (1979). Sites within the region were also included in a survey of hydrocarbon concentrations in the surface film, sub-surface waters and sediments around the UK undertaken jointly by the Department of Agriculture and Fisheries for Scotland and the Ministry of Agriculture, Fisheries and Food (Hardy *et al.*, 1977). Hydrocarbon analyses of marine organisms are listed in the Appendix.

The Test Estuary

The River Test supplies most of the fresh water entering Southampton Water. Its estuary has been much altered by dredging and land reclamation for dock facilities to within 2km of Redbridge, where it undergoes a second abrupt change in character, dividing into several winding marshland channels whose tidal limits lie a further kilometre or so upstream. The estuary receives effluent from two sewage treatment works about 3km downstream of Redbridge. The larger, on the Southampton side, was commissioned in 1965 after complete reconstruction and the smaller, almost opposite on the Marchwood side, is currently undergoing a programme of extensions.

Although surface salinities occasionally fall below 20‰, bottom salinities of less than 30‰ have not been observed off Marchwood at high water. The situation at low water has not been adequately investigated but stratification is known to increase, particularly in the upper reaches of the estuary. At Redbridge the salinity frequently covers a range from almost zero to about 25‰ in the course of a single tidal cycle. Although hydrographic anomalies caused by the discharge of cooling water from Marchwood Power Station have been detected in the past (Dyer, 1970), the station

is now little used outside the winter months. The estuary is generally well oxygenated, but levels below 50% saturation have recently been encountered at depth in the summer months, probably due to the extension of its dredged channel upstream.

Few chemical studies have been concerned specifically with the Test Estuary as it has often been treated as part of Southampton Water. However, the majority of the work by Burton *et al.* (1970) on the distribution of silicate was carried out in the Test and Collins (1979) surveyed particulate inorganic carbon at Redbridge over half a tidal cycle, finding concentrations widely scattered about a mean of 0.1 mg l^{-1} .

The Itchen Estuary

The shape of this estuary has been subject to less artificial modification than that of the River Test which has a freshwater flow of approximately double the Itchen. As a result, the Itchen Estuary displays a more "natural" salinity regime with considerable stratification at all states of the tide and fairly regular longitudinal salinity gradients. On the other hand, it receives a greater pollution load in relation to its size. This arises from two sewage treatment works, one at the mouth of the estuary and the other near its head. The quality of effluent from the former has improved steadily in recent years and major improvements to the latter were completed in 1978. Previously, dissolved oxygen levels below 50% saturation were not uncommon in some parts of the estuary.

The Water Research Centre has developed a two-dimensional tidally averaged model of mixing in the Itchen Estuary. The associated fieldwork included a study of photosynthetic oxygen production and nutrient distributions. Data obtained in the summer of 1975 (Hugman and Mallet, 1979) indicated that phosphate and nitrate concentrations were related to salinity in a similar fashion to those found in Southampton Water and the Test Estuary (see Fig.3 for the winter situation). Nitrite concentrations, however, were significantly higher and ammonium significantly lower than would have been expected on this basis. The concentrations of phosphate and ammonium near the surface showed distinct peaks in the upper reaches of the estuary due to the presence of sewage effluent. Despite nitrification, however, no corresponding peak was observed for nitrate, probably because of its relatively high concentration in the river water, which has a similar nutrient composition to that of the River Test (Table 4). Further information collected by the Southern Water Authority at their routine sampling point at Cobden Bridge, 1.5 km below the tidal limit, can be found in Table 6. Some analyses for silicate have been made on surface water collected from the estuary in August (Birks, 1972) and additional information is presented in Table 3.

Table 6 Long-term averages of water quality parameters at Southern Water Authority routine sampling points (9th annual report, Hampshire River Authority)

	Dissolved oxygen (%)	Ammonia-N ($\mu\text{g-atoms l}^{-1}$)	Nitrate-N ($\mu\text{g-atoms l}^{-1}$)	Phosphate-N ($\mu\text{g-atoms l}^{-1}$)	Biochemical oxygen demand (ppm)
Cobden Bridge	85	39	210	16	5.3
Fairthorne Manor	87	33	190	21	4.6
Fareham Town Quay	78	67	117	15	5.8
Lymington Town Quay	97	6	26	3	2.7

The Hamble Estuary

The distribution of dissolved oxygen in this estuary has been described by Wright and Barnard (1964). In 1968 the Water Pollution Research Laboratory (now the Stevenage Laboratory of the Water Research Centre) carried out a survey to calibrate a mathematical model of the estuary (Ministry of Technology, 1969). Additional salinity data are given by Collins (1967). The Southern Water Authority's routine sampling point is at Fairthorne Manor where saline conditions probably only exist around high water. Long-term averages for several water quality parameters at this point are shown in Table 6. A number of dissolved oxygen surveys have revealed concentrations ranging from 60 to 165% saturation in recent years, indicating a moderate degree of pollution. The Authority undertook a more intensive programme of surveys from 1975 to 1978. Burton *et al.* (1970) found a relationship between salinity and silicate concentration similar to that in the Test Estuary and Mayo (1970) detected a high level of over 6 mg l⁻¹ for dissolved organic carbon at the mouth of the estuary in September. Otherwise, there is little published information on this part of the system (see Table 3).

The Wallington Estuary

This estuary is surveyed as part of Portsmouth Harbour and the only chemical data are those collected by the Southern Water Authority. Salinities generally exceed 20‰ at Fareham Town Quay, the Southern Water Authority's routine sampling point, and water quality measurements are summarised in Table 6. More recent data have been reported by Soulsby *et al.* (1978). The estuary is polluted by sewage effluent at a point downstream of the town quay, a situation confirmed by the Authority's dissolved oxygen surveys which have detected concentrations as low as 15% saturation. Matters improved significantly with the commissioning of extensions to the sewage treatment works in 1976. Earlier information on dissolved oxygen in the estuary was discussed by Wright and Barnard (1964) who specifically included an example of its sag curve to illustrate adverse conditions.

Portsmouth Harbour

Since April 1973 the Southern Water Authority has been co-ordinating a programme of surveys in Portsmouth Harbour which currently involves the collection of surface water samples from twelve stations at quarterly intervals. Additional samples were collected from 1974-76 as part of the Authority's biological investigations (Soulsby *et al.* 1978). These surveys have revealed a wide range of conditions between the polluted Wallington Estuary in the harbour's north-western corner and the relatively clean waters near its entrance. From the annual means for dissolved oxygen, nutrients and biochemical oxygen demand in 1973-74 (Fig. 4), a pollution gradient, bearing an inverse relationship to salinity, is clearly visible. By comparison, seasonal variations were not very marked.

Trace metal analyses were carried out by atomic absorption spectrophotometry after preconcentration of the samples which were initially unfiltered. No obvious trends emerged from these data. Concentrations of iron and zinc were extremely variable, cadmium and cobalt concentrations were relatively stable and intermediate behaviour was displayed by nickel and copper (Table 7). On three occasions Soulsby *et al.* (1978) measured the concentrations of seven trace metals (Cd, Cr, Cu, Mn, Ni, Pb, Zn) in sediments from four

Table 7: Average concentrations ($\mu\text{g l}^{-1}$) of trace metals in unfiltered samples.

	Portsmouth Harbour 1973-74	Langstone Harbour 1974-75
Iron	130	55
Zinc	22	20
Copper	9	9
Nickel	6	2.5
Cobalt	2	1.5
Cadmium	1	0.5

sites in the harbour. A detailed investigation of the distribution of copper in water, suspended material and sediments, particularly in the neighbourhood of the dockyard, has been carried out by Ellis-Evans (1975).

Langstone Harbour

This is one of the more intensively studied parts of the system. Soon after World War II, Dr J H Oliver, a consulting industrial chemist, began to analyse water samples from near the harbour entrance. By the time of his death in 1960 he had compiled a great deal of valuable information, including pioneer studies of interstitial water chemistry. This work has never been fully published. In 1957 the Admiralty established its Exposure Trials Station at Eastney to undertake marine fouling investigations. Routine surface samples were taken from rafts moored about 1 km inside the harbour at weekly intervals over the period 1958-69 and this programme still continues on a reduced scale. Many of the data for salinity, dissolved oxygen and pH have been published (OECD, 1966). Samples taken from Sinah Lake at low water in 1969 and 1970 have been analysed by Askew (1976). Much of the above information was reviewed by Dunn (1972) as the baseline for a study sponsored by the Hampshire River Authority to assess the ecological consequences of increasing the discharge of sewage effluent from a treatment works on the harbour's northern shore (Portsmouth Polytechnic, 1976). In the course of this work, a large number of chemical surveys including some sediment analyses were carried out and a simple formula to predict nutrient distributions under conditions of increased sewage flow was developed. The sediment analyses included measurements of phosphate in interstitial water, total nitrogen and total phosphorus in the solid phase and the pH and sulphide content of whole samples.

The Southern Water Authority has undertaken a considerable amount of monitoring in Langstone Harbour during recent years. The basic programme is similar to that in Portsmouth Harbour, but following publication of the Polytechnic's report the Authority established a comprehensive programme of surveys largely designed to detect changes in the harbour's nutrient regime that may result from altered sewage management practices, including nutrient removal. Existing chemical data on Langstone Harbour are summarised in Figure 5.

Langstone Harbour is a shallow, almost land-locked bay receiving little freshwater runoff. Consequently salinities are high throughout the harbour. Dissolved oxygen concentrations usually lie within $\pm 20\%$ of saturation (Southern Water Authority data), but the annual mean has dropped by about 15% over the years (Exposure Trials Station data).

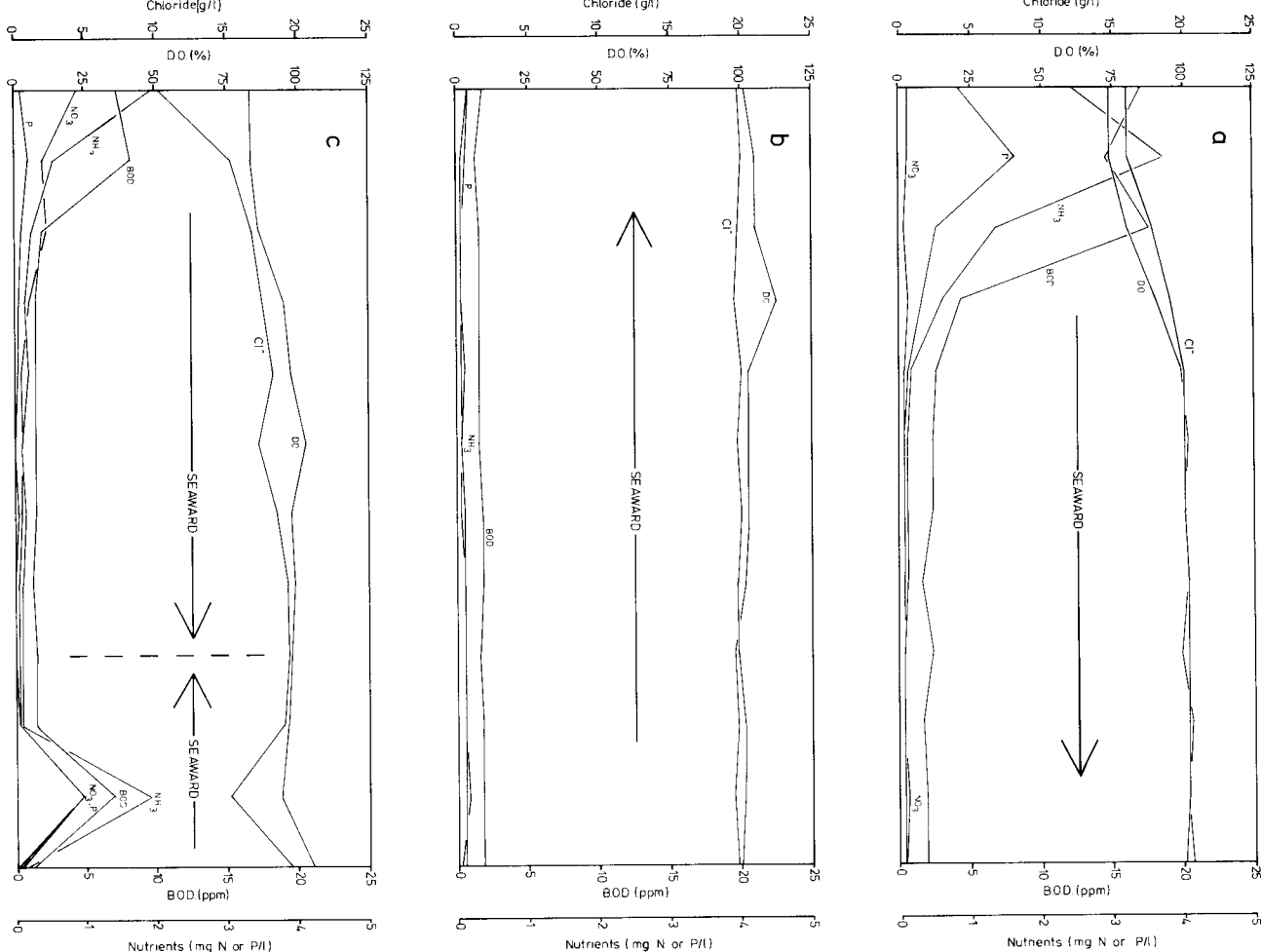


Fig. 4 Average distributions of various parameters in (a) Portsmouth Harbour, (b) Langstone Harbour, (c) Chichester Harbour, during the early 1970s. Based on data supplied by The Southern Water Authority.

Marked seasonal cycles are evident in nutrient concentrations, as shown by Table 8, which illustrates the general situation in 1973-74 (Portsmouth Polytechnic, 1976). The nutrient data available for the years up to 1970 relate to fixed stations in the harbour's seaward channels. Since 1970, information has been obtained from surveys extending across the harbour towards the mainland shore where seasonal cycles become less distinct as a result of local influences and much higher concentrations are often encountered. Despite these variations, annual mean distributions of dissolved oxygen, nutrients and biochemical oxygen demanded in 1973-74 were fairly uniform (Fig 4). There is strong evidence for an upward trend in phosphate concentration which has apparently doubled between the mid 1950s

and the late 1960s and again since then. The data are insufficient to determine whether a similar rise has occurred in ammonium concentration although there appears to have been a less pronounced rise by a factor of 1.5 in winter nitrate concentrations. Silicate concentrations have remained approximately constant.

Oliver measured several other forms of phosphorus and nitrogen in Langstone Harbour and found that the average levels of particulate phosphorus and dissolved organic phosphorus were comparable with that of phosphate. Although dissolved organic phosphorus showed little variation, particulate phosphorus fluctuated widely with higher levels coinciding with gales. 'Albuminoid nitrogen', a labile fraction of organic nitrogen, amounted to approximately $7 \mu\text{g-atoms l}^{-1}$, about one third of which was retained on a filter, and showed a weak seasonal cycle, with maximum concentrations in the summer months. Total organic nitrogen concentrations, measured by Kjeldahl digestion, were three times greater than those of 'albuminoid nitrogen'.

The first measurements of total iron in Langstone Harbour waters were also made by Oliver and ranged from $50\text{-}4000 \mu\text{g l}^{-1}$, with a mean of $550 \mu\text{g l}^{-1}$. Elevated levels of iron were associated with high values of particulate phosphorus, suggesting a common origin in resuspended sedimentary material. Some trace metal results obtained by the Southern Water Authority are listed in Table 7.

Table 8: Average nutrient concentrations in Langstone Harbour ($\mu\text{g-atoms l}^{-1}$).

	Summer	Winter
Phosphate	1.9	1.6
Ammonia	4	8
Nitrite	0.4	1.0
Nitrate	2.5	25
Silicate	4	12

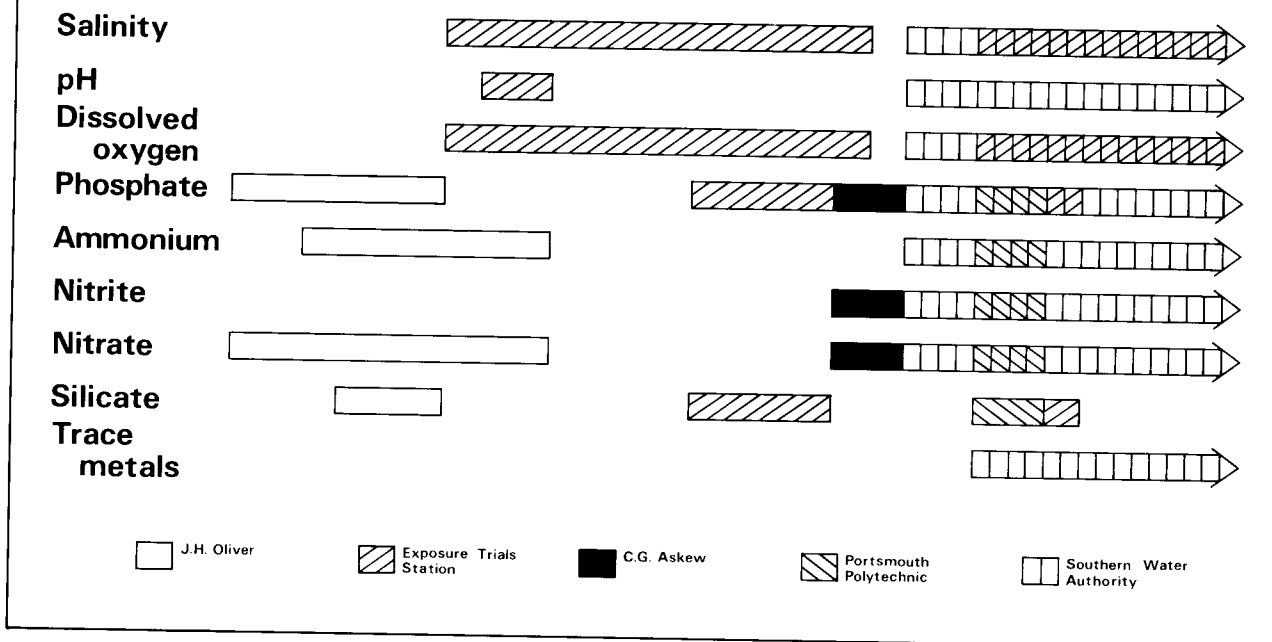


Fig. 5 A summary of chemical work carried out in Langstone Harbour, after Dunn 1972.

Chichester Harbour

The Admiralty was responsible for early work in this area. Hendey (1951) considered the distribution of salinity, phosphate and silicate in Emsworth Channel in 1948-50 and described the seasonal cycles of these two nutrients. Higher levels of both were found in water draining from the mud banks at low tide and interstitial water contained as much as 20 and 180 $\mu\text{g-atoms l}^{-1}$ of phosphate and silicate respectively. Stubbings and Houghton (1964) extended the nutrient data up to 1956 and discussed salinity conditions in more detail. At the entrance to Emsworth Channel, where stratification is slight and salinities rarely fall below 33‰, the mean annual ranges at the surface within 3h of high water were 0.2-0.6 $\mu\text{g-atoms P l}^{-1}$ and 5-14 $\mu\text{g-atoms Si l}^{-1}$. Further salinity data have been collected by Askew (1972). From 1971 to 1973 the Sussex River Authority carried out five surface water surveys around low water to the east of Thorney Island (Fig. 4). The high values at either end corresponded to areas influenced by sewage treatment works near the heads of Chichester and Thorney Channels. No significant change in phosphate concentrations were noted from the earlier work. The present survey programme includes occasional analyses for trace metals and pesticides.

The Beaulieu Estuary

Wright and Barnard (1964) reported uniformly high levels of dissolved oxygen in this estuary and there is no reason to think that the situation has changed since then. The estuary has been the subject of several investigations into the behaviour of dissolved constituents during the mixing of river and sea water. Leatherland (1969) restricted his work to silicate while Coles (1977) included other nutrients and measurements of ultra-violet absorbance as an index of dissolved organic matter. In general, nitrate and silicate concentrations varied inversely with salinity. However, variability

increased in the upper reaches of the estuary which are influenced by the brackish pond at its tidal limit, and the concentration of phosphate displayed a variety of patterns, the reason for which is uncertain (Fig. 6). Dissolved organic carbon showed essentially conservative behaviour, with the highest concentrations of about 5mg l^{-1} in fresh water (Moore *et al.*, 1979). Its composition at intermediate salinities, as indicated by ultrafiltration, was similar to that of dissolved organic carbon from river waters and unlike that found at Calshot.

The same approach was extended to trace elements by Holliday and Liss (1976), who concluded that most of the iron present in fresh water was removed from solution at salinities below 10‰, while the distribution of manganese and zinc was largely governed by processes of dilution. The average concentrations found at either end of the salinity range are listed in Table 9. Neither total dissolved copper, measured after ultraviolet photolysis, nor its chloroform-extractable fraction, showed a regular trend in the estuary. The former averaged about 0.7 $\mu\text{g l}^{-1}$, of which the latter fraction amounted to less than 10% (Moore, 1978). Measures and Burton (1978) found levels of total dissolved selenium ranging from about 0.14 $\mu\text{g l}^{-1}$ at a salinity of 15‰ to about 0.09 $\mu\text{g l}^{-1}$ at 30‰.

The suspended material has been investigated by Moore *et al.* (1979). Although the concentration of lattice-held iron and manganese remained essentially constant, the non lattice-held fractions decreased with increasing salinity. In the case of manganese the decrease was approximately linear and could be accounted for by mixing between particles of marine and freshwater origin. However, the concentration of non lattice-held iron fell more rapidly, suggesting accumulation of iron from the dissolved fraction at low salinities. Wilson (1976) measured total and non-lithogenous cadmium,

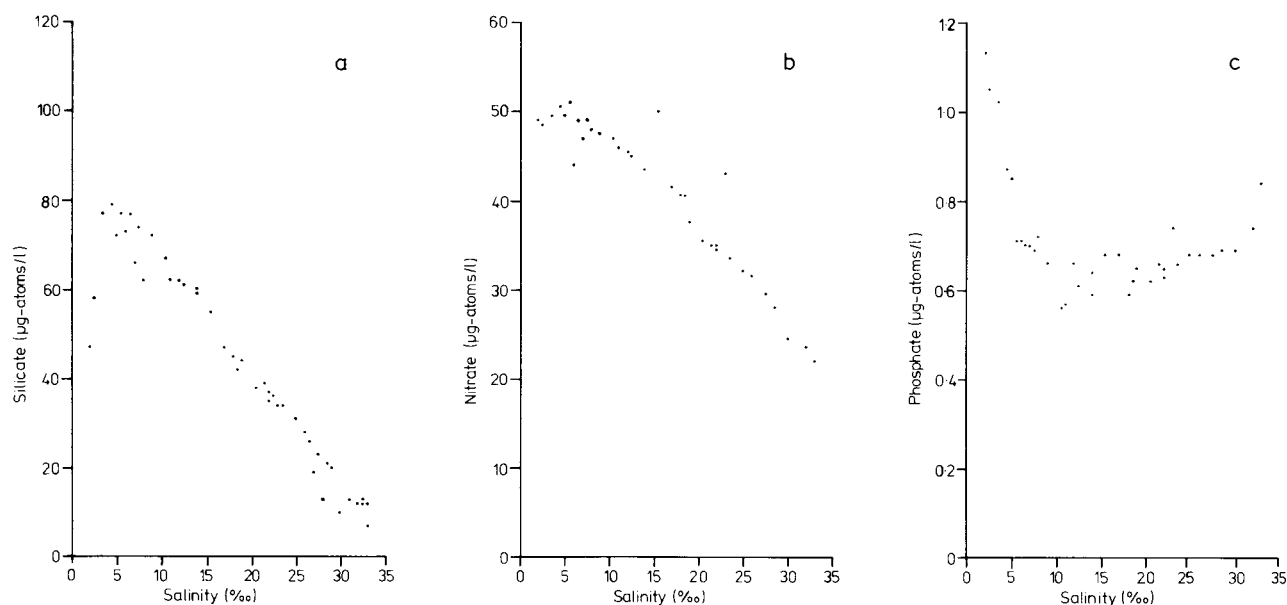


Fig. 6 Graphs of (a) silicate, (b) nitrate and (c) phosphate against salinity for The Beaulieu Estuary on 27th February 1970.

cobalt, copper, iron, nickel and zinc in surface sediments from the upper estuary and Mierzejewski (1977) extended this work by measuring cobalt, copper, nickel and zinc in samples collected further downstream with emphasis on the organic fraction. Studies on the dissolved and particulate materials of the river input and their behaviour during estuarine mixing is continuing at the Department of Oceanography, Southampton University, especially on the possible effects of iron removal on levels of dissolved silicon and phosphorus and the trace metal composition of particulates.

The Lymington Estuary

The situation at Lymington Town Quay, the Southern Water Authority's routine sampling point, is summarised in Table 6. The average salinity is about 30‰ and dissolved oxygen surveys throughout the estuary are similar to those found at Town Quay indicating that the region is substantially free of pollution. In 1969, Askew (1976) recorded phosphate values of 0.1-0.6 µg-atoms l⁻¹ depending on the state of the tide, in water entering the nearby Salterns Pool.

The Medina Estuary

Six surveys were carried out by the Isle of Wight River and Water Authority during 1971. They revealed high salinities on spring tides as far inland as Newport, where a wide range of values from almost zero to 30‰ was observed over the tidal cycle in October. In February the water column at Newport was stratified at high water springs to the extent of a 25‰ difference in salinity in a total depth of 2m.

Dissolved oxygen concentrations were normally 80-110% saturation during the winter, increasing sea-

wards, but concentrations outside this range were not uncommon. Much higher values, some approaching 200%, were found to be widespread on a neap tide in May, presumably due to photosynthesis, and values down to 40% were found near Newport during warm weather in October. Although levels of biochemical oxygen demand were generally less than 5mg l⁻¹ they occasionally exceeded 20mg l⁻¹ in the upper reaches of the estuary. However, there are plans to improve the sewage treatment works serving Newport, which discharges to this area. A more intensive survey programme including analyses for trace metals in sediments was undertaken from 1976 to 1978.

Conclusions

The River Pollution Survey of England and Wales (Department of the Environment, 1971) classified rivers based on measurements of dissolved oxygen and biochemical oxygen demand, and took no direct account of nutrient levels. With the exception of the estuaries of the Itchen, the Test downstream of Redbridge and the Hamble upstream of Hound which were graded Class 2, the Medina Estuary (Class 3 to Fairlee and Class 2 seawards) and the Wallington Estuary (Class 4), the areas covered by this review were accorded Class 1 status (Table 10). The Solent itself, being essentially marine, was not classified. No changes were reported up to the end of 1975 (Department of the Environment, 1978) although the Wallington Estuary is likely to be upgraded at the next revision.

Sewage effluents are the major source of biochemical oxygen demand in the region but their effects on dissolved oxygen concentration depend to a considerable extent on the physical characteristics of the various estuaries involved, as well as the siting of outfalls and the volumes discharged. Similarly, although the oil refinery at Fawley is much the largest single source of biochemical oxygen demand, its impact is reduced by the fact that it discharges to relatively open water. Although this discharge is also an important source of nitrogen, mainly in the form of ammonium, and a similar amount comes from sewage effluent, the major supply results from the rivers in the form of nitrate. Most of the phosphorus enters the system in sewage effluent. These generally enhanced

Table 9: Summary of trace metal concentrations (µg l⁻¹) in the Beaulieu Estuary on 5 February, 1974 (Holliday and Liss, 1976).

Salinity (‰)	Iron	Manganese	Zinc
0.1	400	110	45
25	10	20	5

Table 10: A summary of the present situation.

Area	DoE class	Coverage	General reference
The Solent	—	Fair	South Hampshire Plan Advisory Committee 1972
Southampton Water	1	Good	Raymont 1972
Test	1/2	Good	Woolley 1973
Itchen	2	Fair	Snell 1972
Hamble	1/2	Poor	—
Wallington	(4)	Fair	Soulsby <i>et al.</i>
Portsmouth	1	Fair	(1978)
Langstone	1	Good	Portsmouth Polytechnic 1976
Chichester	1	Poor	—
Beaulieu	1	Fair	—
Lymington	1	Poor	—
Medina	2/3	Poor	—

nutrient inputs support high levels of primary production in suitable areas, notably Langstone Harbour which suffers from heavy growths of seaweed, and

Southampton Water where 'red tides' have occurred in several recent years.

Although pollution by trace metals is not a major problem in the region, the oil refinery appears to be a significant source of dissolved copper (Matharu, 1975) and of copper, cadmium and zinc in sediments (Armannsson, 1979). Relatively high levels of trace metals have also been found in the sediments of the Itchen Estuary. Hydrocarbons are more abundant in both water and sediment near the refinery than elsewhere (Knap, 1979).

An analysis of the adequacy of the present chemical knowledge of the Solent estuarine system has been summarised in Table 10. In view of the contrasting developments of their similar natural regimes, it is unfortunate that the Itchen Estuary has received less attention than the Test. Similarly, more information is required from Chichester Harbour for comparison with the more highly developed Portsmouth and Langstone Harbours. In general, more information has been collected during the summer months whereas winter conditions of high freshwater flow and levels of suspended matter are often more important in terms of chemical fluxes. Likewise, conditions around low water are less well known, particularly in Southampton Water where workers try to take advantage of the relatively stable situation provided by the double high water phenomenon. Nocturnal samples are also a rarity.

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● See over for Appendix

