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An operative definition of alkalinity in interstitial waters

A. Gómez-Parra[a], J.M. Forja[b]
[a]*Instituto de Ciencias Marinas de Andalucía, C.S.I.C., Apartado Oficial, 11510 Puerto Real, Cádiz, Spain*
[b]*Dpto. Química–Física, Facultad de Ciencias del Mar, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Cádiz, Spain*

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Abstract

Vertical profiles of total alkalinity, pH, and salinity, as well as ammonia, silicate, sulphate, sulphur and borate concentration in the interstitial water of sediments from the Bay of Cadiz were measured. The results established which of those chemical species included in Dickson's (1981) definition have an influence on total alkalinity above the limits of accuracy of the analytical method. This enables an operative definition of alkalinity in interstitial waters to be proposed:

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [HS^-] + [NH_3]$$

The main advantage is that with only a moderate amount of analytical work, the speciation of inorganic C in the interstitial water can be accurately determined.

At the same time, the analytical method proposed by Van den Berg and Rogers (1987) for estuarine waters has been revised and adapted for the measurement of alkalinity in interstitial waters.

1. Introduction

The study of chemistry in interstitial waters plays an important role in our knowledge of the marine environment, especially in coastal ecosystems. In fact, most natural and anthropogenic chemical species which can affect physicochemical conditions throughout whole ecosystems are transported from the sediment to the water column through the interstitial water.

The alkalinity of interstitial waters is normally high (e.g. Aller, 1980; Berelson et al., 1987). This is due to the presence of CO_2 produced in the degradative processes of sedimentary organic matter (Froelich et al., 1979), to the dissolution of biogenic carbonates (Sayles, 1985), and to the presence of several protolytic materials generated during the early diagenesis of organic matter. The speed at which these degradative processes proceed causes the concentration of some chemical species in the interstitial waters to be up to four orders of magnitude higher than that existing in the water column (Klump and Martens, 1983).

Simple definitions of alkalinity have been used for sea water (e.g. Riley and Chester, 1971). They allow the calculation of carbonate alkalinity with sufficient accuracy. However, none of them are applicable to interstitial waters. Starting from the "exact definition" proposed by Dickson (1981), the influence of all the chemical species involved in the alkalinity of interstitial waters was determined in the present study. The results enable an operative definition of total alkalinity to be given, one which might be applicable to many marine ecosystems. The analytical method used was that proposed by Van den Berg and Rogers (1987), adapted for the determination of total alkalinity in interstitial water.

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2. Experimental

2.1 Characteristics of sediments

Sediment cores were sampled at two stations located in the Bay of Cadiz, a shallow water temperate ecosystem. The area is at a latitude of 30°31′N and a longitude of 6°15′W. Primary productivity is high as a consequence of the great inputs of organic matter and the high rate of benthic nutrient regeneration (Gómez-Parra and Forja, 1991). Approximately a quarter of the area (10 km^2) has a water depth of less than 3 m and has stagnant conditions. For these reasons, physicochemical conditions in the water column are largely conditioned by the processes of matter transfer across the water–sediment interface. The two stations studied (PR and LC) were chosen as good representatives of the two main sedimentary environments of the Bay. Some of their characteristics, including sediment composition, are shown in Table 1.

Table 1
Characteristics of sampling stations and the studied sediments

Station	PR	LC
Temperature[a] (°C)	24.7 ± 0.4	25.9 ± 0.7
Salinity[a]	36.54 ± 0.06	37.56 ± 0.35
Macrofaunal density[b] (individuals m^{-2})	1132 ± 448	1512 ± 315
Mean depth (m)	2.7	8.5
Mean current speed near the bottom (m s^{-1})	0.12	0.30
Granulometry[c] (%)		
Sand (> 20 μm)	9	4
Silt (20–2 μm)	11	26
Clay (< 2 μm)	79	70
Heavy metals[c]		
Fe (%)	3.31	2.73
Mn (ppm)	340	356
Cu (ppm)	40	41
Pb (ppm)	71	74
Zn (ppm)	163	247
Cd (ppm)	1.5	1.9
Organic matter[c] (%)		
Organic carbon	2.84	2.72
Organic nitrogen	0.34	0.207

[a] At the time of sampling.
[b] Annual average.
[c] At surface.

Sediments were sampled by means of a 45 mm i.d. gravity core. They were sliced at 1 cm intervals and the sections thus obtained were centrifuged at 24,000 *g* for 30 min. This process allows 70 to 80% (3 to 5 cm^3) of the total water contained in the samples to be obtained. Handling of sediment cores and subsequent analysis of interstitial waters were performed under an inert atmosphere.

3. Analytical methods

pH (SWS) (Hansson, 1973) and alkalinity were measured with an ion analyzer (Radiometer, ION85) using combined glass electrodes (GK2401G), and supplied with a temperature compensation probe (T801). Alkalinity was determined by means of potentiometric microtitration using 0.1 M HCl, after a modification of the method of Van den Berg and Rogers (1987), discussed below. The titration was performed over a thermostated 2 cm^3 sample. The precision of the analytical techniques are: pH (±0.001), total alkalinity (±0.003 mM), and carbonate alkalinity (±0.007 mM).

Nutrient analyses (ammonia, phosphate, nitrate and silicate) were carried out in a TRACCS 800 Technicon autoanalyzer. Borate was determined using the method of Grasshoff et al. (1983). Sulphate concentration was gravimetrically measured in 2 cm^3 aliquots, using AP40 Millipore fiber glass filters. Total sulphur ($H_2S + HS^- + S^{2-}$) was potentiometrically analyzed with an ion analyzer (Radiometer, ION-85), using a specific electrode (F1212S) and a calomel reference electrode (K401). For this, samples had been buffered to pH = 11.5 with 15 cm^3 of a solution containing 0.20 mM of $Na_2PO_4\ 2H_2O$, 0.45 mM of $NaNO_3$, and 0.10 mM of NaOH. Chloride concentration was measured by microtitration with $AgNO_3$, using phenozafranine as an indicator. According to Charnock and Crease (UNESCO, 1966) an estimation of salinity was ontained fron chlorinity using the equation: $S(‰) = 1.80655 \cdot Cl(‰)$. Potential differing ionic ratios between seawater and interstitial waters belonging to the major elements are not extremely high (Manheim and Sayles, 1974; Millero, 1974), and that is the reason why this relation between chlorinity and salinity can be approximately used. Sediment porosity was calculated by determining the weight loss after 72 h at 80°C. Granulometry was determined by the chain hydrometer method (De Leenheer et al., 1965), while heavy metals were analyzed by AAS after sample digestion with 10:1 $HCl:HNO_3$ (Arjonilla et al., 1987).

4. Results and discussion

4.1 Measurement of alkalinity in interstitial waters

Normally, alkalinity is determined by means of a linear transformation of the titration curve in the region of excess acid using the Gran function, the expression being:

$$F = (v_0 + v) \cdot [H^+]_T / C_A$$

where v_0 is the sample volume, v the volume of added acid, C_A its concentration, and $[H^+]_T$ the total concentration of hydrogen ions.

Assuming the appropriate zero level of protons proposed by Dickson (1981) for the equivalence point, the total concentration of protons will be given by the following expression:

$$\begin{aligned}[H^+]_T = {} & [H^+] + [HSO_4^-] + [HF] + [H_3PO_4] \\ & - [HCO_3^-] - 2[CO_3^{2-}] - [B(OH)_4^-] \\ & - [OH^-] - [HPO_4^{2-}] - 2[PO_4^{3-}] \\ & - [NH_3] - [SiO(OH)_3^-] - [HS^-] \\ & - 2[S^{2-}]\end{aligned}$$

Concentrations of all protolytic species can be a function of the total analytic concentration together with pH, using the dissociation constants shown in Table 2:

$$\begin{aligned}[H^+]_T = {} & [H^+] + S_T \cdot \frac{[H^+]}{[H^+] + K_{2,S}} + F_T \cdot \frac{[H^+]}{[H^+] + K_F} \\ & - B_T \cdot \frac{K_B}{[H^+] + K_B} \\ & - Si_T \cdot \frac{K_{Si}}{[H^+] + K_{Si}} \\ & + P_T \cdot ([H^+]^3 - K_{1,P} \cdot K_{2,P} \cdot [H^+] \\ & - 2 \cdot K_{1,P} \cdot K_{2,P} \cdot K_{3,P}) / ([H^+]^3 \\ & + K_{1,P} \cdot [H^+]^2 + K_{1,P} \cdot K_{2,P} \cdot [H^+] \\ & + K_{1,P} \cdot K_{2,P} \cdot K_{3,P}) \\ & - C_T \cdot \frac{K_{1,C} \cdot [H^+] + 2 \cdot K_{1,C} \cdot K_{2,C}}{[H^+]^2 + K_{1,C} \cdot [H^+] + K_{1,C} \cdot K_{2,C}} \\ & - N_T \cdot \frac{K_N}{[H^+] + K_N} \\ & - Su_T \cdot (K_{1,Su} \cdot [H^+] \\ & + 2 \cdot K_{1,Su} \cdot K_{2,Su}) / ([H^+]^2 + K_{1,Su} \cdot [H^+] \\ & + K_{1,Su} \cdot K_{2,Su}) - \frac{K_W}{[H^+]}\end{aligned}$$

where $[H^+]$ is the free hydrogen ion concentration in solution, and can be calculated from pH (SWS) (see e.g. UNESCO, 1987). S_T, F_T, B_T, Si_T, P_T, C_T, N_T and Su_T are concentrations during titration of total sulphate, fluoride, borate, silicate, phosphate, carbonate, ammonia and sulphur, respectively. They are calculated according to the expression:

$$C_T = C_0 \frac{v_0}{v_0 + v}$$

where C_T is the concentration during titration and C_0 is the initial analytical concentration.

The effect of dilution on ionic strength was taken into account to calculate the dissociation constants. During titration, ionic strength (I) is:

$$I = \frac{I_0 v_0 + 0.1 v}{v_0 + v}$$

where I_0 is the initial ionic strength in the sample

Table 2
Set of dissociation constants in seawater media

		Reference
H_2CO_3	$pK_{1,C} = (-840.39/T + 19.894 - 3.0189 \cdot \ln T) \cdot S^{1/2} + 0.00668 \cdot S + 6320.81/T - 126.3405 + 19.568 \cdot \ln T$ $pK_{2,C} = (-690.59/T + 17.176 - 2.6719 \cdot \ln T) \cdot S^{1/2} + 0.0217 \cdot S + 5143.69/T - 90.1833 + 14.613 \cdot \ln T$	Dickson and Millero (1987)
$H_2SO_4^a$	$pK_{2,S} = 647.59/T - 6.3451 + 0.019085T - 0.5208 \cdot I^{1/2}$	Khoo et al. (1977)
$B(OH)_3$	$pK_B = (8966.90 + 2890.53 \cdot S^{1/2} + 77.942 \cdot S + 1.728 \cdot S^{3/2} + 0.0996 \cdot S^2)/T + (-148.0248 - 137.1942 \cdot S^{1/2} - 1.62142 \cdot S)$ $+(24.4344 + 25.085 \cdot S^{1/2} + 0.2474 \cdot S) \cdot \ln T - (0.053105 \cdot S^{1/2}) \cdot T$	Dickson (1990)
HF^a	$pK_F = (-1590.2/T + 12.641 - 1.525 \cdot I^{1/2})/2.303$	Dickson and Riley (1979)
H_2S	$pK_{1,Su} = -98.080 + 5765.4/T + 15.0455 \cdot \ln T - 0.1570 \cdot S^{1/2} + 0.0135 \cdot S$ $pK_{2,Su} = 17.1$	Millero et al. (1988) Giggenbach (1971)
H_3PO_4	$pK_{1,P} = 1.62$ $pK_{2,P} = 620.53/T + 4.5038 - 0.030075 \cdot S + 3.3984 \cdot 10^{-4} \cdot S^2$ $pK_{3,P} = 1903.2/T + 6.06551 - 0.03377 \cdot S + 3.5776 \cdot 10^{-4} \cdot S^2$	Johansson and Wedborg (1982)
NH_4^+	$pK_N = 9.3$	Dickson (1981)
$Si(OH)_4$	$pK_{Si} = 9.5$	Johansson and Wedborg (1982)
H_2O	$pK_w = 3418.5/T + 2.0735 - 0.012756 \cdot S + 7.8097 \cdot 10^{-5} \cdot S^2$	Johansson and Wedborg (1982)

T is the absolute temperature and S is the salinity.

[a] Ionic stregth is calculated using the expression: $I = \frac{19.919 \cdot S}{1000 - 1.00198 \cdot S}$.

(see Table 2 for the relation between salinity and ionic strength).

If α_1 is the association coefficient of hydrogen ions taking into consideration all protolytic species included in Dickson's (1981) definition, $\alpha_1 = [H^+]_T/[H^+]$, the Gran function would be as follows:

$$F = (v_0 + v)\cdot\alpha_1\cdot[H^+]/C_A$$

allowing an exact calculation of alkalinity.

Van den Berg and Rogers (1987) proposed a method, based on that of Dyrssen (1965), for the measurement of alkalinity in estuarine waters. The method is based on a modified Gran function:

$$F' = (v_0 + v)\cdot 10^{E/K}\cdot\alpha_2/C_A$$

where E is the potential measured with the glass electrode, $K = 2.303RT/F$, and α_2 is the association coefficient for hydrogen ions considering only the formation of HSO_4^- and HF ionic pairs.

Wedborg (1988) reviewed the method of Van den Berg and Rogers (1987), highlighting, amongst others, the following defects:

(1) The effect of dilution and the modification of ionic strength produced by the added acid were not taken into account. This fact is of special relevance when the method is attempted for the analysis of interstitial waters since, due to the elevated alkalinity, the addition of 0.1 mol L^{-1} HCl may account for more than 30% of the initial volume of the sample.

(2) Small errors in the measurement of the potential E may exert a noticeable effect on apparent alkalinity, since the method only uses two preestablished additions of acid.

(3) The utilization of the F function assumes that variation in the liquid junction potential in the glass electrode during titration is negligible.

Titration curves of two synthetic interstitial water samples with 0.1 M HCl at 25°C, are depicted in Fig. 1A. Both samples had a salinity of 35.8 and total concentrations of 25.0 mM sulphate, $7\cdot10^{-2}$ mM fluoride, 0.50 mM ammonia, 0.25 mM sulphur, borate and silicate, and 0.10 mM phosphate. These concentrations are similar to those found for interstitial waters in the Bay of Cádiz (see Figs. 2 and 3). Total carbonate concentration was 4.75 mmol L^{-1} for sample 1 and 12.0 mmol L^{-1} for sample 2, corresponding approximately to the mean and maximum values found in the analyzed cores. Initial pH values were 7.945 and 7.920 for

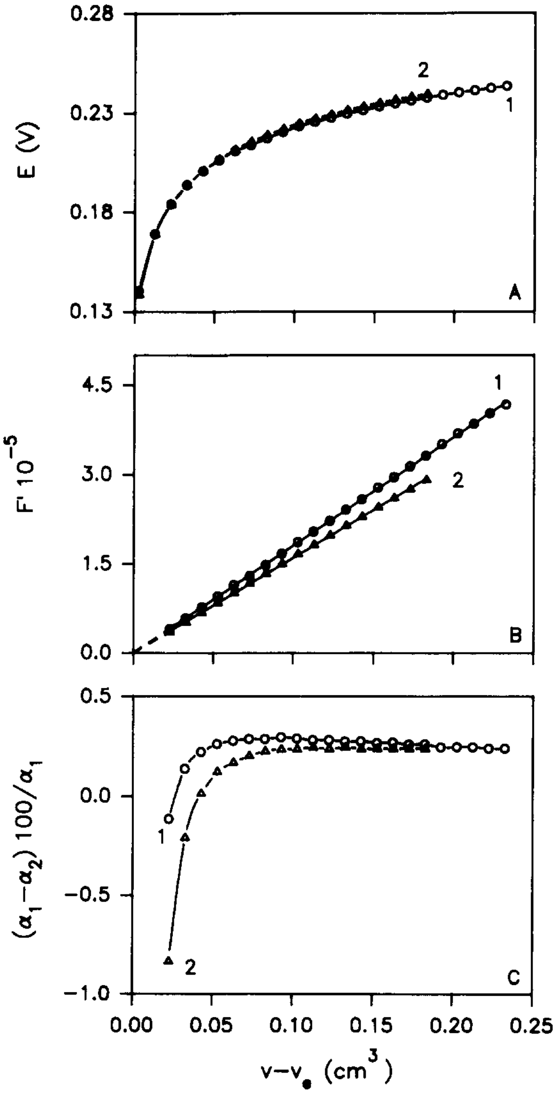

Fig. 1. (A) Titration curve with 0.1 mol l^{-1} HCl of two 2-cm^3 samples of synthetic interstitial water (sample composition given in the text). (B) Linearization of the same titration curves using Gran function. (C) Relative error of the hydrogen ion association coefficient (α_2) proposed by Van den Berg and Rogers (1987), with respect to the value (α_1) based on the proton zero level proposed by Dickson (1981).

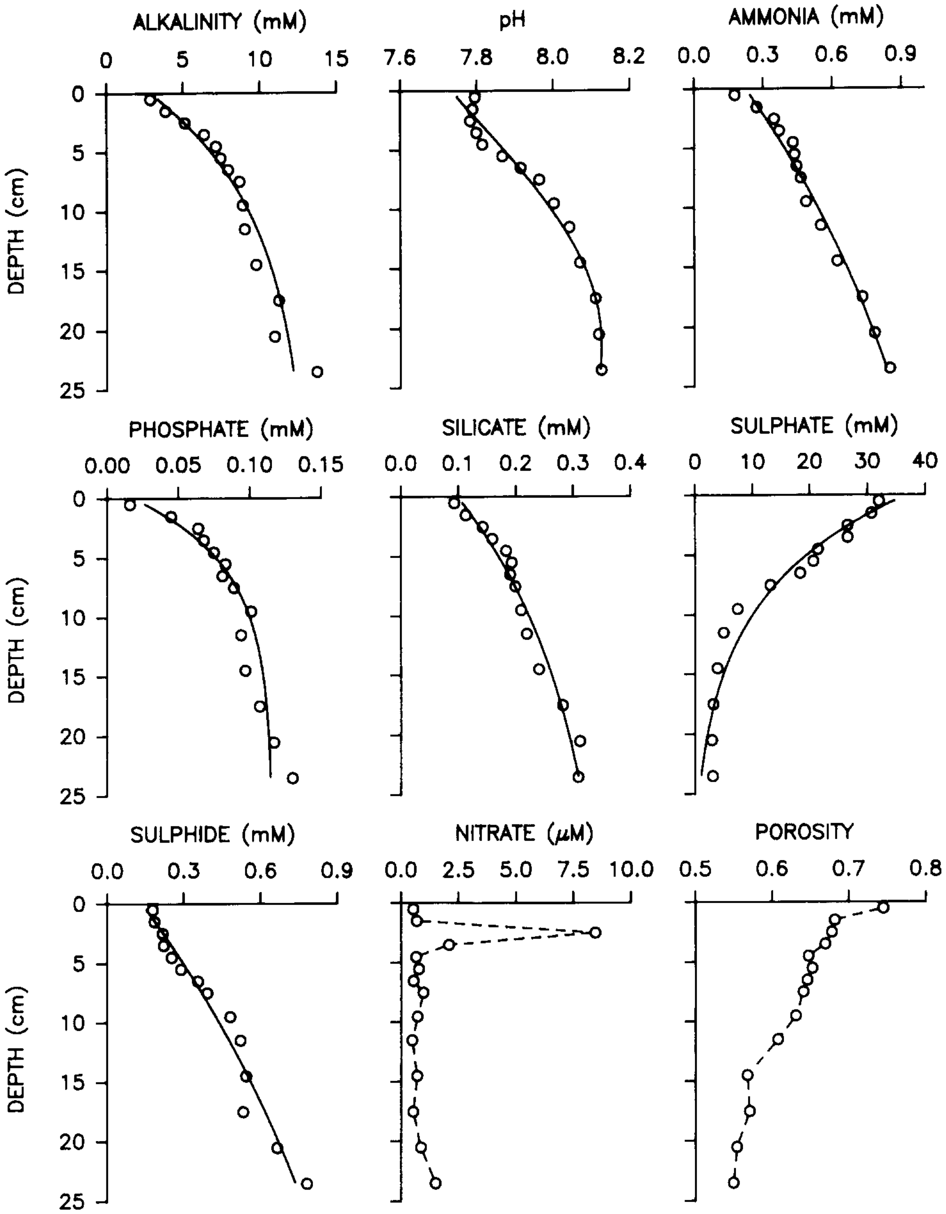

Fig. 2. Vertical profiles of alkalinity, pH, porosity, and concentration of ammonia, phosphate, silicate, sulphate, sulphide and nitrate in the interstitial water of station PR.

samples 1 and 2, respectively.

Fig. 1B shows linearization of the titration curves in Fig. 1A using the function:

$$F' = (v_0 + v)\cdot 10^{E'/K}\cdot \alpha_1/C_A$$

in which proton associations with other species included in Dickson's (1981) definition (α_1), as well as the corrections of Wedborg (1988) have been taken into account. Thus, the measured potential (E) was corrected according to the variation in the liquid junction potential during titration:

$$E' = E + j_H\cdot[H^+]$$

The value $j_H = -40.2 \pm 1.7$ mV M^{-1} was experimentally determined for the electrodes

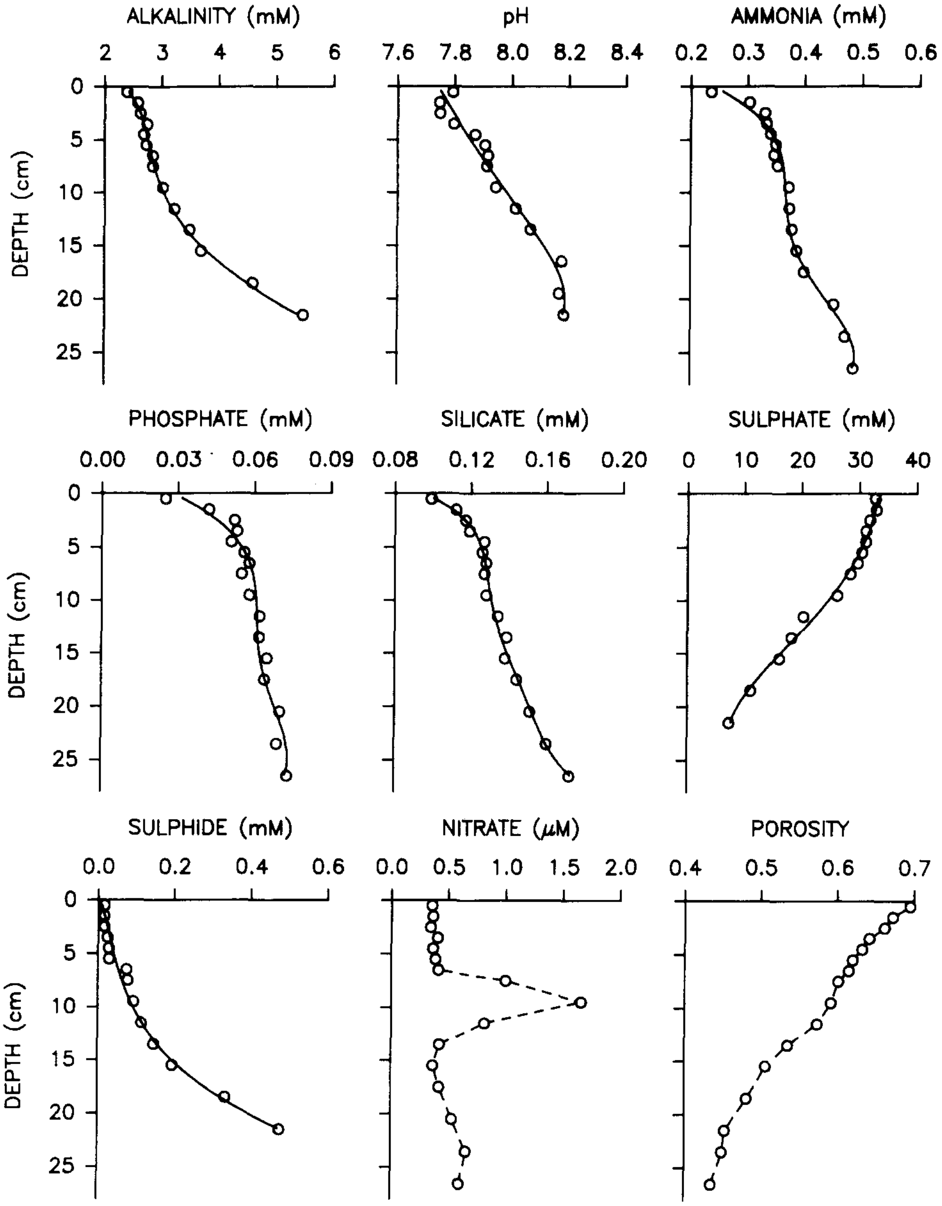

Fig. 3. Vertical profiles of alkalinity, pH, porosity, and concentration of ammonia, phosphate, silicate, sulphate, sulphide and nitrate in the interstitial water of station LC.

according to Dickson and Riley (1979). The corrections made by variations in the union liquid potential during titration did increase when the value of alkalinity diminished, and their values oscillated between 0.2 and 0.6% for the studied samples (12.0 mM$\leqslant A_T \leqslant$2.5 mM).

Of particular interest when using Van den Berg and Rogers' method for interstitial waters, is the determination of the error that would be obtained if only the formation of HSO_4^- and HF(α_2) ionic pairs were considered. Fig. 1C shows the relative error during titration for the two samples described above. Underestimation errors are important at potentials close to that obtained with the first addition proposed by Van den Berg and Rogers ($E \approx 180$ mV). This is due to the formation of HCO_3^-, the errors being nearly −0.5 and −1.2% for samples 1 and 2, respectively. Close to the equivalence point, the formation of HS^- also leads to a small underestimation error (−0.01% for both samples). The contribution to the error in the determination of alkalinity of HCO_3^- and HS^- ions decreases throughout titration until it reaches insignificant values ($< |-0.015|\%$). The formation of H_3PO_4 contributes to α_1 with errors of the order of 0.4% close to the equivalence point, decreasing to 0.25% at the end of the titration. All other protolytic species considered contribute an error of less than ±0.005%.

These results lead to the conclusion that Van den Berg and Rogers' method is applicable to interstitial water samples, provided the corrections of Wedborg (1988) are taken into account and the following modifications introduced:

(1) Increasing the frequency of acid addition so as to use 5 points to linearize the titration in the region of excess acid. Our routine experience with this number of additions demonstrates an acceptable level of accuracy in the determination of the titration equivalence point.

(2) The first acid addition has to be adjusted to reach a potential higher than 185 mV, equivalent to pH = 3.05, in order to minimize the influence of HCO_3^- formation on the association coefficient for hydrogen ions. Due to the great variability in alkalinity in interstitial waters, the volume of acid to be added initially cannot be established "a priori".

The application of the function F' proposed by Van den Berg and Rogers (using α_2), with all the introduced modifications, produced a maximum error of 0.1% in the alkalinity of the samples analyzed.

4.2 Chemical composition of interstitial water

Figs. 2 and 3 show vertical profiles of parameters analyzed in the interstitial waters at stations PR and LC, respectively. Best exponential or polynomial fit have been superimposed for patterns of vertical variations in total alkalinity, pH, ammonia, phosphate, silicate, sulphate and sulphide. Fig. 4 shows vertical profiles of salinity and borate concentration for both stations. The expressions obtained were subsequently used to evaluate the influence of the species on the total alkalinity value.

Generally it can be observed that, within the depth range studied (0–25 cm), there exists a progressive increase of alkalinity, ammonia, phosphate, and silicate concentrations with depth. Vertical gradients of sulphate and

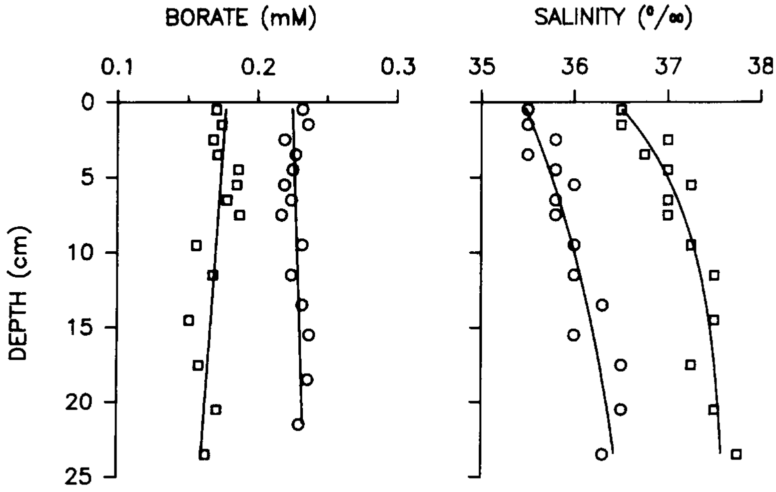

Fig. 4. Vertical profiles of borate concentration and salinity at stations PR(○) and LC(□).

sulphur suggest that sulphate reduction is the principal anaerobic process by which organic matter is being degraded in the area. This is in accordance with the high level of sulphate reduction activity found in the Bay of Cadiz (Blasco, 1985).

Vertical variation of nitrate concentration is noticeably different at the two stations: the maximum concentrations, defining the lower limit of the oxic zone, are at 2.5 cm depth at station PR and at 10 cm at station LC. Such a difference might be caused by a stronger contribution of bioturbation processes at station LC where the macrofauna is appreciably more abundant ($\sim$ 1500 individuals m^{-2}). The presence of subtantial amounts of gravel and broken bivalve shells between 3 and 9 cm below the surface could also be a contributory factor. The presence of an oxic environment at relatively large depths at station LC causes vertical profiles of parameters to be weakly marked between 0 and 10 cm. Below that depth, besides a marked decrease of porosity and sulphate, an increase in vertical gradients of alkalinity and sulphur occurs. Relatively too high nitrate concentration values were found below its maximum of concentration, particulary in station LC. According to Christensen and Rowe (1984) this could be due to the fact that about 0.5 μmol l^{-1} were indistinguishable from background.

Borate concentrations in the interstitial waters are lower than those reported by Wilson (1975) for sea water, although they fall within the range of variation found in the Deep Sea Drilling Project (Presley et al., 1970; Presley and Kaplan, 1971; Manheim and Sayles, 1974). Concentrations varied little over the depth range studied, thus the values of 0.18 and 0.22 mM were adopted for further calculations for stations PR and LC, respectively.

4.3 Significance of alkalinity in interstitial waters

A general definition of total alkalinity could be as follows:

$$A_T = [\text{weak acid}] + [OH^-] - [\text{protonated weak acid}] - [H^+]$$

Considering those weak acids with dissociation constants greater than $10^{-4.5}$ as proton donors, Dickson (1981) proposed an exact definition of total alkalinity in sea water:

$$\begin{aligned} A_T = {} & [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] \\ & + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] \\ & + [SiO(OH)_3^-] + [HS^-] + 2[S^{2-}] \\ & + [NH_3] - [H^+] - [HSO_4^-] - [HF] \\ & - [H_3PO_4] \end{aligned}$$

For the purposes of the present study, the concentrations of all species involved in the above definition were obtained from the results of the analysis (Figs. 2 to 4), and the set of constants shown in Table 2. These constants were originally established for seawater, but had to be used in this study is due to a lack of specific equations for the interstitial waters. Total concentration of fluoride (mM) was obtained from $[F]_T = 0.0035 \cdot Cl(‰)$ (Millero, 1974). Using empirical fits of parameters in vertical profiles, the relative contribution of these species to total alkalinity, together with their variation with respect to depth, was evaluated. Results at 25°C are shown in Fig. 5. Contributions are arranged in decreasing order of influence on total alkalinity.

Assuming an accuracy of ±0.1% in the measurement of total alkalinity (Ben-Yaakov and Lorch, 1983; Van den Berg and Rogers, 1987; Bradshaw and Brewer, 1988a), those species having a detectable influence on total alkalinity can be identified.

The concentrations of H^+, HSO_4^- and HF contribute at a level far below the accuracy of the analytic method. Consequently, they can be ignored in the formulation of an expression for alkalinity of interstitial waters. Due to high pK_2 of H_2S, the concentration of S^{2-} within the

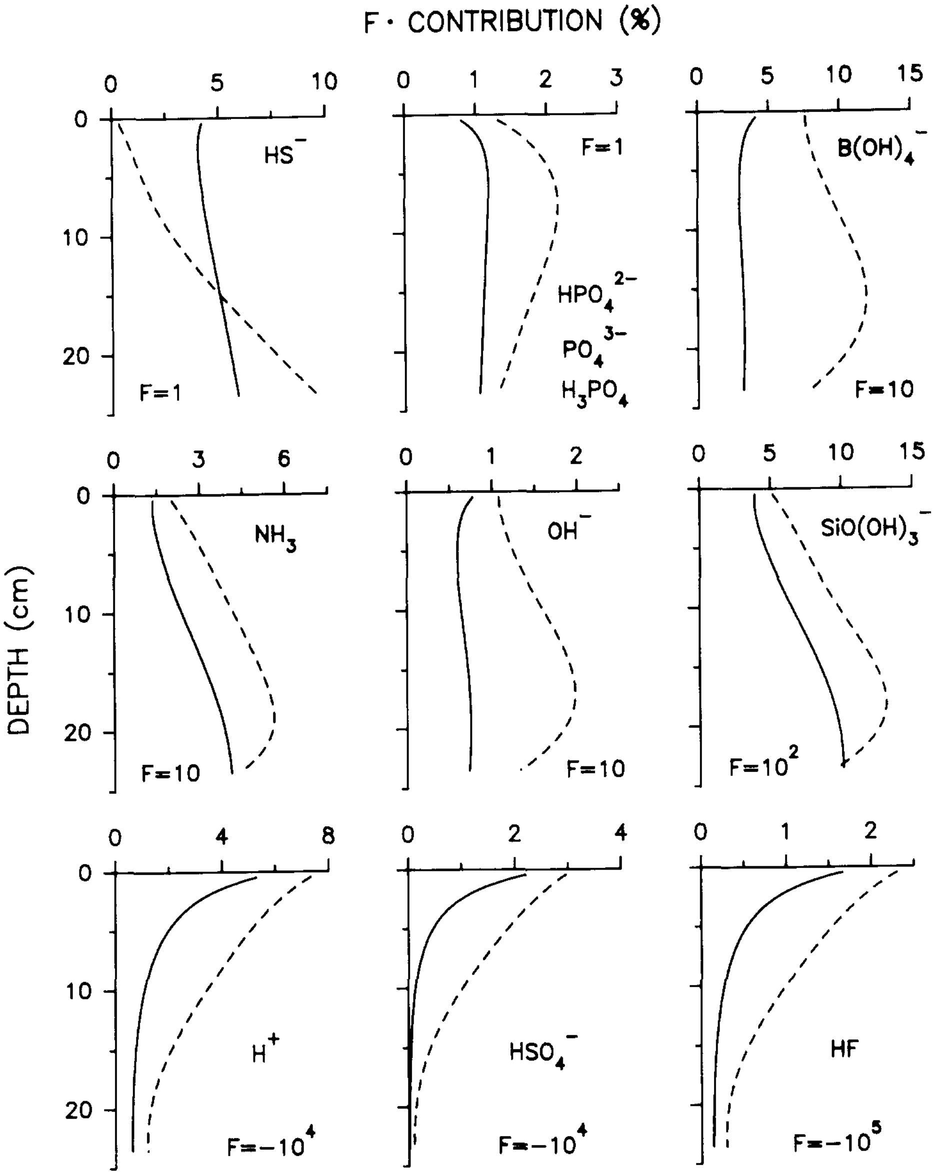

Fig. 5. Variation with depth in the contribution to total alkalinity of analyzed species at stations PR (—) and LC (- -).

observed pH and salinity range is negligible, and is also below the limits of accuracy of the analytical method.

The contribution of inorganic phosphate to alkalinity is important. Both PO_4^{3-} and HPO_4^{2-} species must be included in the definition of alkalinity in interstitial waters, since they account for 8.5–14.5% and 85.5–91.5% of total phosphate concentration, respectively. In contrast, H_3PO_4 concentration only represents $3.7\cdot10^{-6}$% of total concentration, and can thus be eliminated from Dickson's (1981) expression.

Using these results, total alkalinity in interstitial waters can be formulated as follows:

$$\begin{aligned} A_T = {} & [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] \\ & + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] \\ & + [SiO(OH)_3^-] + [HS^-] + [NH_3] \end{aligned}$$

This definition is mainly operative and is based on the vertical profiles of parameters in interstitial waters from the Bay of Cadiz. It could, however, be applied to other coastal ecosystems showing similar vertical profiles. There are very few accounts in the literature where alkalinity, pH, salinity, and the concentration of ammonia, phosphate, silicate, sulphate and borate from interstitial waters have been simultaneously determined. From the profiles reported here, the present definition of alkalinity would be of application in ecosystems such as Long Island Sound (Aller, 1980; Boudreau and Canfield, 1988), Cape Lookout Bight (Klump and Martens, 1981, 1989), Saanich Inlet (Murray et al., 1978), Georgia Bight (Hopkinson and Wetzel, 1982), Chesapeake Bay (Callender and Hammond, 1982), Southern California Borderland (Berelson et al., 1987).

In addition, carbonate alkalinity can also be calculated with this definition, and thus it is possible to perform an inorganic carbon speciation (e.g. Skirrow, 1975) without any other sources of error than those arising from the analytical methods and the constants used. As an example, vertical profiles of carbonate alkalinity, together with carbonate and bicarbonate concentrations, are shown in Fig. 6.

5. Concluding remarks

The complete potentiometric titration of a sample, determining the two equivalence points, and further linearization (e.g. Hansson and Jagner, 1973; Bradshaw et al., 1981) or non-linear curve-fitting (e.g. Dickson, 1981; Johansson and Wedborg, 1982), are the best procedures to determine alkalinity in interstitial waters. Nevertheless, the method proposed by Van den Berg and Rogers (1987), including the modifications suggested by Wedborg (1988) and those from the present work, enables a sufficiently accurate measurement of alkalinity. The method is inexpensive, quick and does not need complex equipment. For these reasons it can be used to analyze large number of samples, both in coastal laboratories and on board of ships.

The definition proposed for total alkalinity in interstitial waters allows the calculation of carbonate alkalinity with a reasonable degree of analytical effort. This allows, among other things, the quantification of diffusive fluxes of ΣCO_2 through the water-sediment interface, which can be used as an estimation of benthic organic matter oxidation (Anderson et al., 1986).

Although Dickson's (1981) definition, on which the present work is based, includes all inorganic ions of potential influence on total

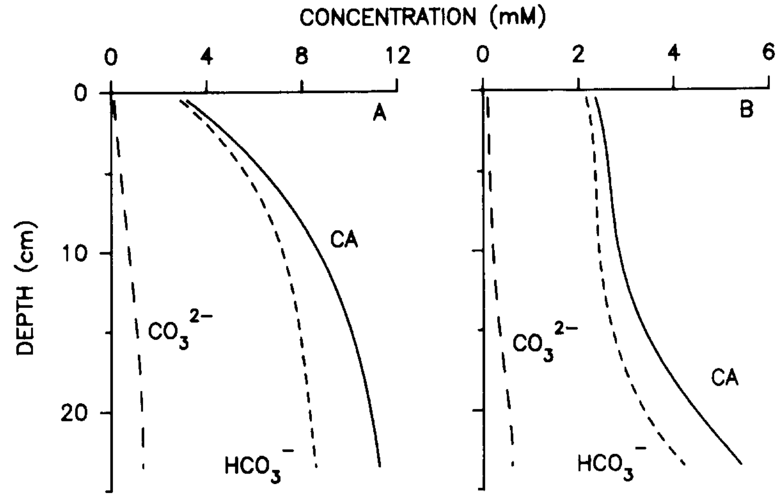

Fig. 6. Vertical profiles of carbonate alkalinity (*CA*) and the concentration of bicarbonate and carbonate in the interstitial water of stations PR (A) and LC (B).

alkalinity, the effect of certain organic substances should not be underestimated (Bradshaw and Brewer, 1988a,b). With respect to interstitial waters, the quantification of some metal hidroxide complexes, principally of Fe(II) and Mn (II), and protolytic organic species, whose concentrations may be high, and the measurement of their respective dissociation constants, will be of particular interest when proposing a more complete definition of total alkalinity.

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