as a banner at the top of the search results screen. Sponsors can also have a hypertext link to their own home page from a chosen word in any of the journal articles. In addition, sponsors can choose to place an advert which appears only to members with a particular specialisation.

7. Summary

In the words of Sir John Maddox, former editor of *Nature*, "ChemWeb promises to provide the interlocking data, journals and search services that are only possible in a well-designed electronic medium" [1]. It is, however, first and foremost a club for chemists who not only have access to a vast collection of information, but also have easy contact with thousands of fellow chemists, many of whom will be working in a similar area of specialisation.

References

[1] Information Today, October 1996, p. 48.
[2] Developed by Andrew Witbrock at Electronic Press Ltd.
[3] W.A. Warr, 'Focus', Web offerings: hype or hope? Inf. World Rev. June 1997.

case study

Identifying the processes involved in the hydrochemistry and environmental quality of a littoral system (Bay of Cadiz, Spain): a case study using factor analysis

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A factor analysis was carried out to interpret the variability observed in the data obtained for a salt-marsh area to the south of the Bay of Cadiz in the southwest of Spain. A case involving the quantitation of 15 variables in 273 water samples of the Sancti Petri Channel has been selected for examination. An overall synthesis of all the information obtained from the factor analysis establishes five processes that determine the hydrochemistry of the zone: mineralisation, influence of urban effluents, seasonality, degree of agitation and action of the tides. Of all the processes, the mineralisation of the organic matter stands out as the main process determining the hydrochemistry of the zone. ©1998 Elsevier Science B.V.

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Keywords: Hydrochemistry; Factor analysis; Environmental case study

1. Introduction

In aquatic ecosystems, a number of processes take place that affect their hydrochemistry and their environmental quality. Whether these processes are caused by human activity (contamination, dredging, etc.), or originate naturally (the mineralisation of organic matter, consumption of nutrients by phytoplankton, etc.), the fact that they occur simultaneously makes it difficult to characterise the role played by each process in the environmental condition of the particular ecosystem at any particular point in time.

In environmental fieldwork studies, it is common to use statistical techniques to interpret the variability observed in the data obtained. Among these techniques, factor analysis is one of the most frequently employed, as it allows the simple and graphical

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explanation of the relationships observed between a number of important variables [1–4]. This technique also enables the determination of the relative importance of those processes affecting environmental quality, together with their spatial and temporal variations, if there is found to be an ecological significance in the new variables (defined as linear combinations of the variables measured in such studies). This is valuable knowledge, since the measurement of these many interacting processes is considerably more complex than the mere monitoring of the environmental variables of any system.

With this objective, this article discusses the application of factor analysis to a typical set of data (4000), in this case obtained from an arm of the sea that links the Bay of Cadiz with the Atlantic.

This ecosystem is interesting for its complexity, derived from the following circumstances: (i) there is regular discharge of untreated sewage from an urban area with a population of some 100 000; (ii) it is subject to a complex hydrodynamic regime; (iii) as a function of the tidal condition, this marine channel exchanges water by means of sluice gates with a large adjacent area of commercial salt ponds, but the quantities of these exchanges cannot be determined; and (iv) its sediments show high spatial heterogeneity with respect to granulometry, thus producing great variability in their capacity for exchange of matter with the overlying masses of water.

2. Sampling

The Bay of Cadiz is a shallow littoral ecosystem, with an area of 33.6 km^2 and an average depth of 3 m. It is subjected to a moderate tidal regime, with the result that approximately 20% has an inter-tidal character. Within the Bay, there is a significant zone of salt marshes (6000 ha) supplied with water by an arm of the sea (the Sancti Petri Channel) that links the Bay with the Atlantic, in the south (Fig. 1). The Channel is 18 km long and receives the untreated urban effluent waters from a population of more than 100 000 inhabitants. Tidal flows from the Atlantic Ocean and from within the bay enter by both mouths of the channel.

A total of 21 sampling stations was established along the length of the Channel and, during the course of 1991 and 1992, 13 samplings were conducted at each station.

The 15 variables recorded at each station, and the abbreviations employed in the statistical analysis were: tidal condition (TC); temperature (T); dissolved

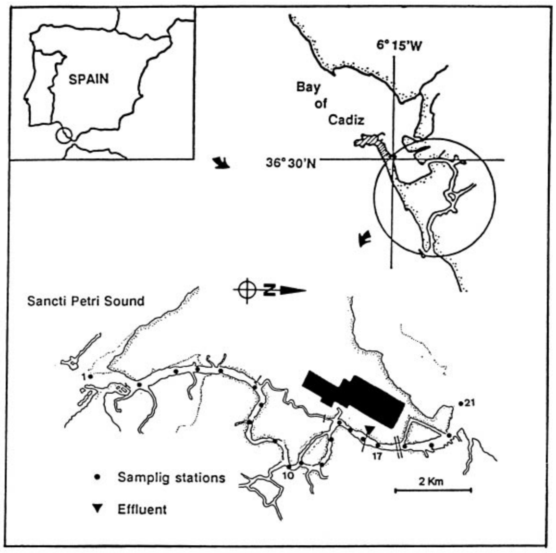

Fig. 1. Schematic of the Bay of Cadiz showing the positions of the sampling stations.

oxygen (DO); salinity (SAL); pH; alkalinity (ALK); ammonia content (NH_4^+); nitrite content (NO_2^-); nitrate content (NO_3^-); phosphate content (HPO_4^{2-}); silicate content (SiO_2); solids in suspension (SS); volatile solids (VS); linear alkylbenzene sulphonates (LAS); and distance from the effluent discharge outlet (DDO). The data base covered the seasonal variations and the influence of the hydrodynamic regime in this zone. For this, the samplings were conducted under four different tidal conditions, and with the following coefficients: low (0.3–0.5), moderate (0.65–0.85) and high (0.9–1.1).

Sample collection was carried out over a maximum period of 1 h and samples were preserved (in cold and darkness and, where necessary, with the addition of formaldehyde) until their analysis in the laboratory.

3. Analytical methods

The tidal condition was established by taking the product of the tidal coefficient and the difference between the sampling time and the time of high or low tide, whichever was nearer.

The variable DDO is the distance in km of each sampling station from the point of discharge of the untreated waste waters from the town of San Fernando.

The temperature was determined using mercury thermometers of 0–50°C, graduated in tenths of a degree. The dissolved oxygen was measured using

Table 1
Average values and standard deviations of each variable for the set of samplings made

Station	DDO (km)	Tidal condition	Temperature (°C)	DO (μM)	Salinity	Suspended solids (mg/l)	Volatile solids (mg/l)
1	13.36	−0.153 ± 1.434	17.9 ± 2.7	232.9 ± 23.1	36.170 ± 0.704	108 ± 28	16 ± 4
2	12.57	−0.064 ± 1.360	18.6 ± 3.1	228.7 ± 17.4	36.166 ± 1.286	108 ± 32	15 ± 4
3	10.79	−0.038 ± 1.384	18.8 ± 3.3	216.1 ± 30.5	36.419 ± 1.477	103 ± 32	15 ± 4
4	10.14	−0.023 ± 1.410	18.9 ± 3.5	206.6 ± 34.6	36.518 ± 1.644	107 ± 36	16 ± 5
5	8.89	−0.007 ± 1.421	18.9 ± 3.8	192.8 ± 37.1	36.617 ± 1.845	110 ± 30	16 ± 5
6	8.00	−0.002 ± 1.412	19.1 ± 3.9	180.2 ± 39.8	36.660 ± 2.171	126 ± 57	18 ± 8
7	7.10	−0.002 ± 1.386	19.1 ± 4.1	168.5 ± 40.5	36.703 ± 2.590	127 ± 31	17 ± 4
8	6.40	−0.010 ± 1.362	19.1 ± 4.2	167.2 ± 36.1	36.687 ± 2.916	139 ± 72	21 ± 11
9	5.55	−0.012 ± 1.334	19.2 ± 4.3	158.0 ± 34.4	36.795 ± 3.231	121 ± 27	16 ± 4
10	4.33	−0.005 ± 1.303	19.4 ± 4.4	139.9 ± 35.4	36.571 ± 3.981	130 ± 28	18 ± 4
11	3.68	−0.053 ± 1.279	18.0 ± 4.0	153.9 ± 34.0	36.887 ± 3.543	146 ± 46	18 ± 4
12	2.93	−0.051 ± 1.295	18.0 ± 4.0	150.3 ± 37.0	37.005 ± 3.728	144 ± 33	18 ± 3
13	1.96	−0.050 ± 1.319	18.9 ± 4.4	147.7 ± 46.2	36.602 ± 4.014	155 ± 72	21 ± 10
14	1.09	−0.039 ± 1.360	18.9 ± 4.4	135.0 ± 47.2	35.841 ± 4.255	129 ± 29	19 ± 5
15	0.62	−0.027 ± 1.376	18.2 ± 4.4	141.5 ± 44.9	36.215 ± 3.262	125 ± 30	19 ± 4
16	0.10	−0.021 ± 1.385	18.8 ± 4.4	142.9 ± 47.0	35.898 ± 3.246	123 ± 27	20 ± 8
17	0.50	−0.005 ± 1.413	18.9 ± 4.5	140.1 ± 62.0	35.849 ± 2.406	122 ± 32	20 ± 4
18	1.37	0.008 ± 1.418	18.8 ± 4.4	156.0 ± 51.8	36.150 ± 1.946	112 ± 31	16 ± 5
19	2.32	0.016 ± 1.404	18.8 ± 4.5	168.7 ± 57.3	36.410 ± 1.514	126 ± 34	22 ± 9
20	3.07	0.102 ± 1.408	18.8 ± 4.6	177.3 ± 59.8	36.462 ± 1.336	109 ± 34	17 ± 6
21	4.09	0.081 ± 1.443	18.2 ± 4.4	231.8 ± 34.2	36.178 ± 1.046	105 ± 37	21 ± 7

Station	pH (NBS)	Alkalinity (mM)	NH_4^+ (μM)	NO_2^- (μM)	NO_3^- (μM)	HPO_4^{2-} (μM)	SiO_2 (μM)	LAS (μg/l)
1	8.00 ± 0.08	2.595 ± 0.149	3.3 ± 2.8	0.3 ± 0.2	1.3 ± 1.7	0.4 ± 0.3	3.5 ± 3.8	26.2 ± 32.2
2	7.99 ± 0.10	2.627 ± 0.141	6.9 ± 8.5	0.6 ± 0.4	2.0 ± 2.3	0.6 ± 0.4	4.3 ± 4.1	16.6 ± 16.5
3	7.98 ± 0.11	2.664 ± 1.169	7.0 ± 5.9	1.0 ± 0.8	2.1 ± 2.0	1.1 ± 1.0	6.2 ± 5.1	12.4 ± 8.5
4	7.95 ± 0.11	2.682 ± 0.187	12.3 ± 8.8	1.4 ± 1.0	2.8 ± 2.2	1.7 ± 1.2	7.6 ± 5.5	27.1 ± 47.0
5	7.93 ± 0.11	2.760 ± 0.228	14.1 ± 9.2	1.9 ± 1.1	3.4 ± 1.9	2.2 ± 1.4	8.2 ± 4.9	26.9 ± 39.1
6	7.91 ± 0.13	2.782 ± 0.222	19.2 ± 10.0	2.4 ± 1.1	4.4 ± 1.9	2.9 ± 1.3	10.5 ± 6.3	31.3 ± 56.2
7	7.89 ± 0.13	2.922 ± 0.204	22.1 ± 9.6	3.1 ± 1.4	5.6 ± 2.2	3.5 ± 1.3	11.9 ± 7.8	24.0 ± 41.7
8	7.87 ± 0.14	2.974 ± 0.216	28.0 ± 10.2	3.8 ± 1.5	6.4 ± 3.3	4.4 ± 1.4	13.1 ± 7.1	24.0 ± 42.7
9	7.87 ± 0.18	3.039 ± 0.229	33.2 ± 9.2	4.6 ± 1.8	7.1 ± 2.8	5.4 ± 1.8	14.6 ± 8.4	7.9 ± 4.8
10	7.83 ± 0.16	3.214 ± 0.378	43.2 ± 15.8	5.4 ± 2.5	9.6 ± 12.8	7.1 ± 2.8	16.7 ± 10.2	15.3 ± 20.9
11	7.87 ± 0.14	3.131 ± 0.243	36.6 ± 6.9	5.5 ± 2.8	7.2 ± 6.1	6.0 ± 1.6	14.9 ± 7.5	8.2 ± 4.3
12	7.88 ± 0.16	3.261 ± 0.256	39.2 ± 6.7	6.6 ± 2.3	7.1 ± 2.8	6.2 ± 1.4	15.6 ± 7.1	9.4 ± 4.2
13	7.91 ± 0.13	3.236 ± 0.541	34.7 ± 11.0	4.6 ± 2.8	6.1 ± 3.5	5.5 ± 1.8	15.0 ± 8.8	16.3 ± 16.0
14	7.86 ± 0.22	3.205 ± 0.421	75.7 ± 109.2	7.4 ± 9.5	15.2 ± 31.7	9.1 ± 10.4	18.5 ± 13.4	56.4 ± 130.9
15	7.90 ± 0.14	3.090 ± 0.380	37.2 ± 23.7	3.5 ± 2.3	5.7 ± 5.1	5.5 ± 2.0	14.1 ± 7.9	44.5 ± 83.7
16	7.87 ± 0.18	3.177 ± 0.488	48.7 ± 68.3	2.7 ± 1.7	4.1 ± 2.4	6.0 ± 5.4	13.2 ± 7.8	43.0 ± 50.7
17	7.89 ± 0.20	2.975 ± 0.221	48.3 ± 58.8	2.2 ± 1.3	10.6 ± 16.5	5.7 ± 5.1	12.9 ± 7.4	112.5 ± 150.8
18	7.95 ± 0.16	2.897 ± 0.096	32.7 ± 31.2	1.3 ± 0.7	4.4 ± 3.8	4.2 ± 3.0	10.4 ± 7.6	64.9 ± 81.4
19	7.98 ± 0.16	2.813 ± 0.106	14.2 ± 8.0	0.9 ± 0.4	1.8 ± 1.3	2.6 ± 1.1	8.3 ± 5.5	21.1 ± 15.9
20	8.06 ± 0.13	2.779 ± 0.183	6.5 ± 3.3	0.5 ± 0.3	1.2 ± 0.9	1.6 ± 0.5	6.7 ± 4.6	14.9 ± 9.0
21	8.06 ± 0.14	2.698 ± 0.081	3.3 ± 3.4	0.4 ± 0.4	0.8 ± 1.1	1.0 ± 0.4	6.7 ± 6.5	12.8 ± 9.3

the Winkler method [5], which gives an accuracy of ±0.03 mg/l. The instrument used to determine salinity was a Beckman induction salinometer, model RS-10, with automatic temperature compensator, the accuracy of which is ±0.001. The pH measurement was according to the NBS scale using an ION-85 pH meter, by Radiometer, Copenhagen, and combined glass electrodes of Ag/AgCl (Radiometer, model GK2401), with an accuracy of ±0.001 units. The total alkalinity was measured by potentiometric titration [6], with an accuracy of ±5 μ*M*. The suspended solids were measured by filtering a set volume of water, usually between 150 and 300 ml, using depth filters of glass microfibre (Millipore, AP40), then drying the material retained for 1 h at 105°C and weighing it. The content of volatile solids was quantified by calcifying at 450°C for 30 min the filters in which the suspended solids had previously been determined; the accuracy in both cases is ±0.1 mg/l.

The nutrients were analysed spectrophotometrically with a segmented continuous flow autoanalyser (Technicon, TRAACS 800, Bran Luebbe). The analytical methods employed are a modification of those described by Grasshoff et al. [5], as described in detail by Forja [7]. For the range of concentrations found, the accuracy in the determination of NH_4^+, NO_2^-, NO_3^- and HPO_4^{2-} is ±0.02 μ*M* and ±0.2 μ*M* in the case of SiO_2.

LAS, which are widely used anionic surfactants, have been proposed as a molecular marker of domestic wastes [8,9]. Quantification of LAS was performed by reversed-phase liquid chromatography with fluorescence detector, the samples being previously concentrated and purified by solid-phase extraction, following the procedure described by Gonzalez-Mazo et al. [10].

4. Statistical analysis

The BMDP package of statistical programs was used for the multivariate analyses [11], run on the VAX system of the Calculation Centre of the University of Cadiz. The total space across which the statistical analysis was applied consisted of 4095 separate data (21 stations × 13 samplings × 15 variables).

In the first place, the analysis was applied to the set of stations, numbered 01–21, along the Sancti Petri Channel. Subsequently, with the aim of getting more homogeneous systems, the Channel was divided into several different zones, which were subjected to a discriminant analysis to find out which variables best delimit these zones. Specifically, the Channel was divided into three large zones: the southern zone (stations 01–09) influenced by the provision of oceanic water; the central zone (stations 10–16) which represents the most stagnant part of the Channel; and the northern zone (stations 17–21) which is more influenced by water inflow from the Bay.

Table 2
Classification matrix

	% agreement	Southern	Central	Northern
Southern	79.5	70	10	8
Central	73.7	6	56	14
Northern	80.6	6	1	29
Total	77.5	82	67	51

Table 3
Result of the factor analysis: southern zone

Variable	Factor 1	Factor 2	Factor 3	Factor 4
NO_2^-	0.956	0	0	0
NO_3^-	0.950	0	0	0
HPO_4^{2-}	0.925	0	0	0
NH_4^+	0.876	0	0	0
DDO	−0.827	0	0	0
ALK	0.826	0	0	0
DO	−0.757	−0.261	−0.293	0
SS	0	0.934	0	0
VS	0	0.895	0	0
SiO_2	0.412	0	0.854	0
pH	−0.293	0	−0.750	0
T	0	0.383	0.734	0
TC	0	0	0	0.857
SAL	0.256	0.425	0.273	−0.736
LAS	0	0	−0.256	−0.426
% Variance	42.47	17.1	11.49	8.17

Values $< 0.250 = 0$.

The discriminant analysis was performed in steps, adding at each step the variable that produces a linear function giving the best differentiation between the groups [11].

5. Results and discussion

Table 1 shows the average values and standard deviations of each variable for the set of samplings made. The high standard deviations are the result of intense seasonal variations, the influence of the tides on the physico-chemical characteristics of the zone, and the effect produced by the discharge of urban wastes on the environmental quality of the waters.

In the statistical analysis performed for the Channel as a whole, six factors are identified that together explain 74.2% of the variance observed. Each variable is not associated with a single factor; rather, their contribution is shared between two or three factors, and their interpretation is not simple. Overall, the Channel of Sancti Petri constitutes a heterogeneous space, due mainly to the following features: the sharp incidence of various points of waste discharge in certain zones, whose effect is fortuitous in nature, with varying intensities between them; the differences in depth of the Channel's course; the existence of stagnant sections where the flow backs up, in contrast to other zones of fast-flowing currents; the provision of oceanic waters mainly from one end, and of Bay waters mainly from the other, with significant differences in water characteristics between them.

The result of the discriminant analysis for the three basic zones into which the Channel is divided gives the following combination of variables that best discriminate between them: alkalinity, dissolved oxygen, pH, salinity, silicates and nitrites. Table 2 shows the classification matrix with the percentage of agreement for each zone. The number of variables that differentiate the three zones, together with the agreement percentage for the total number of samples, confirm that the division of the sampling zone into three subzones is appropriate from the point of view of the homogeneity of each one. The results cannot be improved by modifying the groups of stations assigned to the various zones.

The factor analysis was performed separately for each zone and a smaller number of factors explaining a greater percentage of the variance was obtained. For the three cases, the first factor has a much greater eigenvalue than the rest. These are the characteristics that define a homogeneous space.

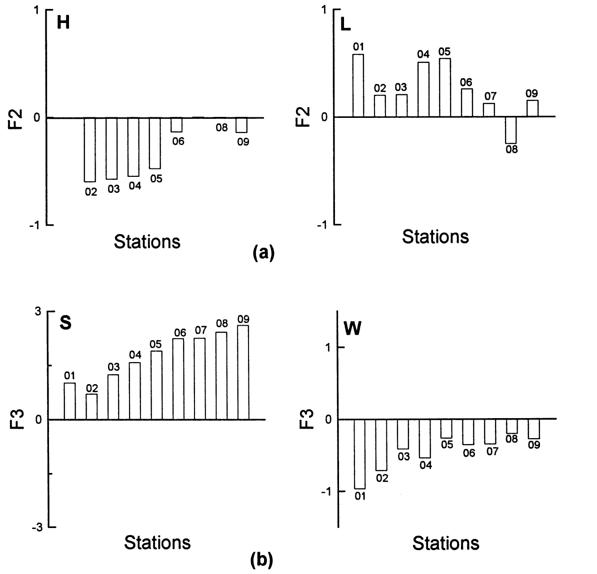

Fig. 3. Graphical representation of factors 2 and 3 in the southern zone. a: Factor 2 for the different cases grouped by tidal conditions H and L. b: Factor 3 for the different cases grouped by samplings conducted in summer (S) and winter (W).

5.1. Southern zone (stations 01–09)

In the factorial analysis applied to the 15 variables measured at these nine stations, four factors were obtained that account for 79.23% of the total variance of the data (Table 3). The sequence of the factors is according to the percentage score of the variance explained, and therefore according to how representative the set of original data comprising the factor is. It is important to note that the variables associated with each factor are very well defined, and contribute very little to the other factors, which helps in the interpretation of the results.

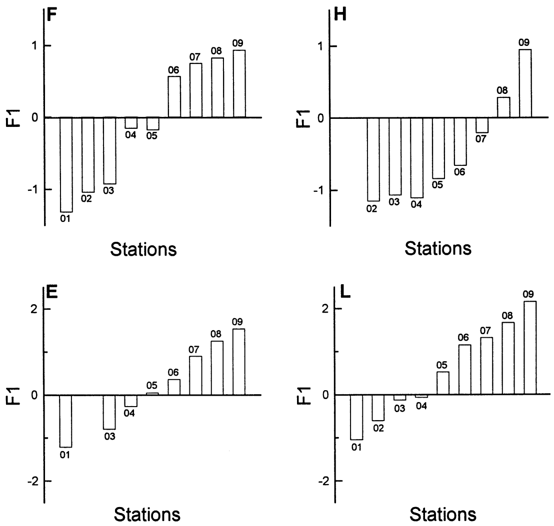

Fig. 2. Graphical representation of the value of factor 1 in the southern zone, for the different cases grouped by tidal condition (F = flowing; H = high; E = ebbing; L = low tide).

Factor 1 accounts for 42.47% of the variance, and includes, in order of importance, the following variables: nitrite, nitrate, phosphate, ammonia, distance from the discharge point, alkalinity and dissolved oxygen. All these variables, except dissolved oxygen and distance from discharge point, have an inverse relationship with the factor. The masses of water rich in nutrients, of high alkalinity and depleted of dissolved oxygen, are typical of the more interior stations. Overall, it can be stated that this factor characterises the processes of mineralisation of organic matter which on its own explains almost half of the hydrochemical phenomena of this zone. The closer the stations are to the central section of the Channel, the greater the influence of the process of benthic regeneration, as a result of the increasing stagnation of the waters.

A graphical representation of the weight of the factor for the various cases (a case being the set of variables for a particular station in a particular sampling), grouped by four tidal conditions, is shown as Fig. 2.

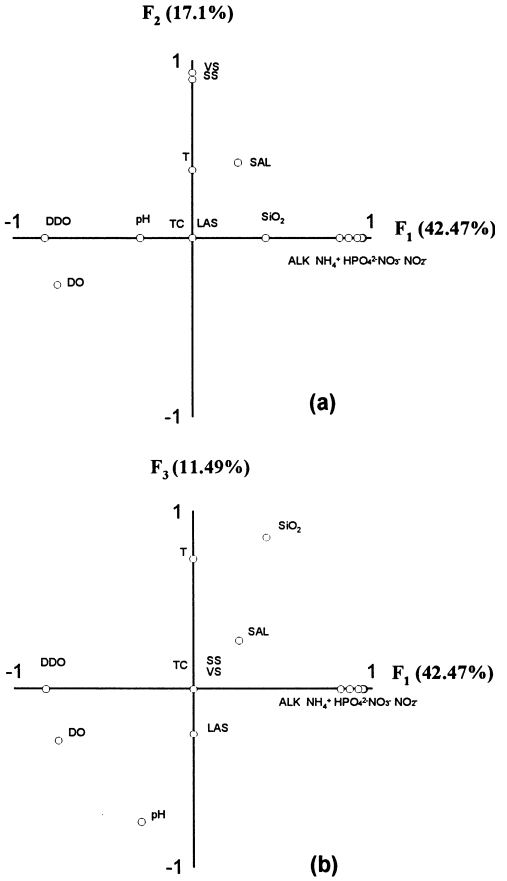

Fig. 4. Distribution of the variables in the factor space in the southern zone. a: Factor 1 against factor 2. b: Factor 1 against factor 3.

The entry of oceanic water generates a dilution phenomenon and thus represents a negative contribution against this factor's effect, which is clear as far as station 07. In contrast, when the tide is ebbing and low, the mineralisation process extends from the interior towards the Channel's mouth, presenting a positive contribution as far as station 05. The maximum values for this factor are produced at low tide.

Factor 2 accounts for 17.1% of the variance and therefore its importance in this zone of the Channel is considerably less than that of factor 1. The variables associated with this second factor are solids in suspension and volatile solids, both positively. This factor reflects the phenomena of agitation in the water column. Its evolution at high and low tide is shown in Fig. 3a. At low tide, its positive contribution indicates the influence of the phenomenon of disturbance of the bottom when the volume of water is relatively small. At high tide, the reverse effect is seen.

The third factor accounts for 11.49% of the total variance. The variables with significant weight in factor 3 are the temperature and silicate content, positively, and pH, negatively. This factor represents the seasonal variations, as seen in its evolution in summer and winter. (Fig. 3b). As the temperature increases, the oxidation of organic matter increases, which produces the observed reduction in pH. Silica dissolution and release from the cores of sediment accelerate rapidly with increase in temperature [12]. Previous studies made of this zone show that there is a marked seasonal variation of the benthic fluxes of silica

Table 4
Result of the statistical analysis: central zone

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
NO_3^-	0.937	0	0	0	0
HPO_4^{2-}	0.928	0	0	0	0
NO_2^-	0.914	0	0	0	0
NH_4^+	0.893	0	0	0	0
SAL	−0.714	0	0.433	0	−0.359
pH	−0.576	−0.491	0	0	0
ALK	0.567	0	0	−0.318	−0.271
DO	0	−0.877	0	0	0
T	−0.306	0.696	0.278	0	0
SiO_2	0.595	0.649	0	0.297	0.253
DDO	0	0	0.766	0	0
LAS	0	0	−0.737	0	0
VS	0.406	0	0	0.837	0
SS	0	0.318	0.427	0.636	0
TC	0	0	0	0	0.939
% Variance	36.4	17.17	10.2	8.77	7.14

Values $< 0.250 = 0$.

[13]. The samplings performed in summer show a positive contribution to this factor, which increases in line with the distance from the Channel's mouth; the reverse happens in winter.

The fourth and last factor accounts for 8.17% of the variance. The variable of tidal condition is directly related, while conversely salinity shows a negative contribution. This factor represents the action of the tides. The highest values correspond to the flowing tide. The entry of water into the Channel diminishes the salinity by dilution. Here the presence of LAS is important, although with a relatively small contribution to the factor. The high rate of renovation of these waters together with their distance from the effluent discharge point explain why the influence of LAS on this factor is small.

The relationships between the various factors is obtained from plotting the distribution of the variables in the factor space, using as coordinates the correlations between the variables and the axes. Hence, the variables associated with a particular factor make no contribution to the other factors (these variables are plotted along the line of the axes), apart from certain exceptions that are discussed below.

When factor 1 (mineralisation) is plotted against factor 2 (agitation) (Fig. 4a), it can be observed that only two variables share their contribution between the two axes, salinity and dissolved oxygen. The phenomena of agitation and mineralisation are greater at low tide, just when the salinity is higher, giving its positive correlation with the two factors. In the same way, mineralisation causes the dissolved oxygen to be consumed, a process accentuated by greater agitation, giving its negative correlation with the two factors. It should, however, be borne in mind that these variable shared between both factors are relatively unimportant (low values), compared with the variables strongly associated with a single factor (with values around 1). The variables of tidal condition and LAS concentration make no contribution to either factor. Taking into account that together these two factors account for about 60% of the total variance, it can be concluded that this zone is not very influenced by the urban waste discharges containing LAS in the form of detergents.

When factor 1 is plotted against factor 3 (seasonal variations) (Fig. 4b), there are four variables shown to participate in both factors. Salinity shows a positive correlation with both factors, in a situation similar to the previous case. On the other hand, the reduction in pH that occurs when mineralisation is greater explains the negative contribution of this variable to factor 1. Dissolved oxygen shows a similar behaviour to that in

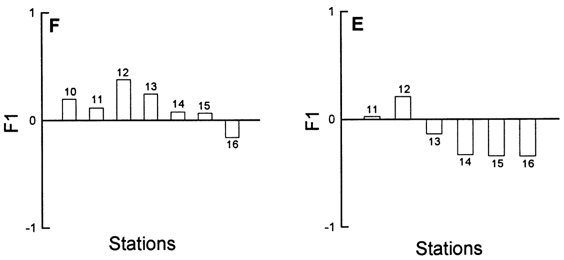

Fig. 5. Graphical representation of the value of factor 1 in the central zone, for the different cases grouped by tidal conditions F and E.

Fig. 4a, because an increase in temperature causes an increase in oxygen consumption through the acceleration of microbial metabolism. The variables of tidal condition, suspended and volatile solids make no contribution to these factors. In the rest of the factor-factor plots (F1–F4, F2–F3, F2–F4 and F3–F4) not shown, only salinity shows a contribution shared between factors.

It may be concluded that mineralisation is the main process explaining the hydrochemical processes in this zone. On its own it explains 42.47% of the total variance and it is seen to be influenced by the Channel's inflow and outflow of water. The rest of the variance is explained by the phenomena of agitation (17.1%), seasonal variations (11.49%), and, lastly, the action of the tides (8.17%).

5.2. Central zone (stations 10–16)

The factor analysis for this zone leads to the determination of five factors that together explain 79.68% of the total variance of the data (Table 4). As with the southern zone, the variables are almost exclusively associated with one single factor.

Factor 1 represents 36.4% of the total variance; the variable with greater weight for this axis are, in order of importance, NO_3^-, HPO_4^{2-}, NO_2^-, NH_4^+, salinity, pH, alkalinity, and SiO_2. In comparison with factor 1 for the southern zone, it includes two new variables: salinity and pH. Both these are in inverse relationship to the factor, and show the importance of the effect of the nearby discharge of urban waste waters on the process of mineralisation. The high content of organic matter of the waters near the discharge point intensifies the mineralisation process. Therefore, it could be stated that this factor represents generically the process of mineralisation which, in turn, is influenced by introduction of quantities of fresh water through the discharges.

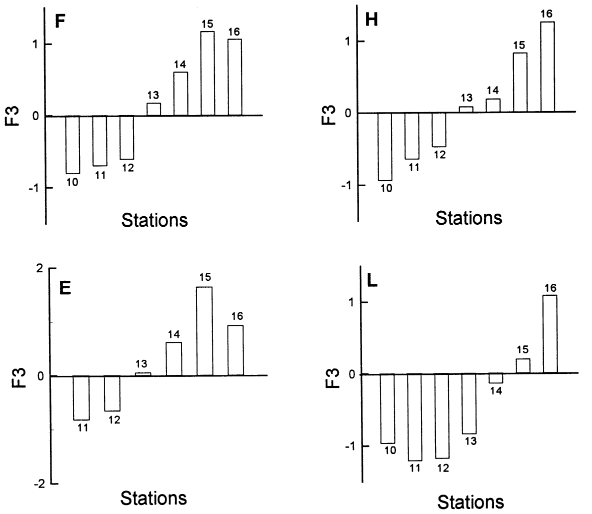

Fig. 6. Graphical representation of the value of factor 3 in the central zone, for the different cases grouped by tidal conditions F, H, E, and L.

In Fig. 5 the value of this factor is shown for the distinct cases grouped under flowing and ebbing tides. When the tide is flowing, stations 10–15 show a positive contribution for this factor, whereas when ebbing only stations 10–12 are positive. At the more interior stations (10–12), the processes of mineralisation are more intense, mainly due to the greater stagnation of the waters. The variability found for the more external stations (13–15) is, depending on the tidal condition considered, due to the influence of the waters rich in organic matter near the waste discharge point, rather than the mineralisation process, as previously commented. When the tide is flowing, the mass of incoming water is displaced towards the middle part of the Channel, and stations 13, 14 and 15 show a positive contribution. At ebbing tide, the contribution of these stations is negative and, in addition, the interior stations show lower values than at flowing tide.

Factor 2 accounts for 17.17% of the variance. The significant variables associated with this factor are: dissolved oxygen, negatively, and temperature and silicates, positively. The pH is also associated with this factor but with a lower negative contribution. This axis appears very similar to factor 3 (seasonal variations) for the southern zone, although here the percentage of variance explained is higher. In summer the factor shows positive values and in winter negative, as occurs in the southern zone.

The variables with significant weight in factor 3 are the distance from the waste discharge point and LAS concentration, both inversely related. This factor explains 10.2% of the variance. Also showing a positive correlation are salinity and solids in suspension, although both with small values. Logically, the LAS concentration is seen to increase closer to the discharge point. This factor clearly represents the contamination of urban origin. The input of fresh water produces a reduction in salinity at stations closest to the discharge point.

The values for factor 3 for the cases of the four different tidal conditions is shown in Fig. 6. It can be observed that the tidal wave coming into the Channel from within the Bay (at station 21) extends the influ-

Table 5
Result of the statistical analysis: northern zone

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
NH_4^+	0.956	0	0	0	0
HPO_4^{2-}	0.956	0	0	0	0
LAS	0.931	0	0	0	0
NO_2^-	0.763	0.492	0	0	0
pH	−0.690	−0.290	0	−0.430	0
DO	−0.569	0	0	0	0.487
NO_3^-	0	0.843	0	0	0
DDO	−0.341	−0.724	0	0	0
ALK	0.436	0.705	0	0	0
T	0	0	0.915	0	0
SiO_2	0.442	0	0.582	0.495	0
SS	0	0	0.337	0.823	0
VS	0	0	−0.451	0.783	0
TC	0	0	0	0	0.931
SAL	−0.383	0	0.578	0	−0.635
% Variance	40.75	15.43	11.03	9.67	7.06

Values $< 0.250 = 0$.

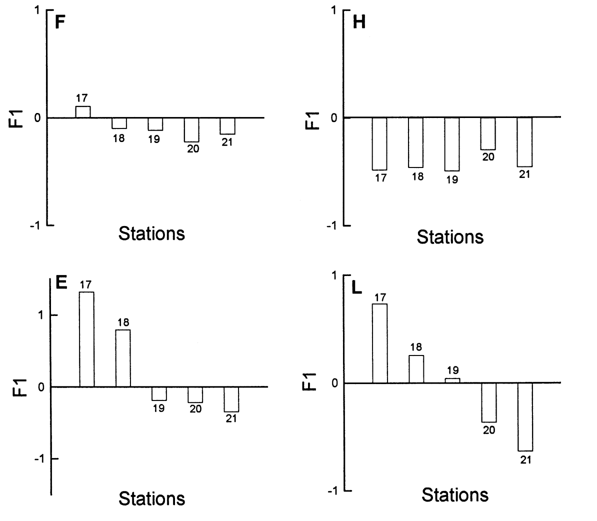

Fig. 7. Graphical representation of the value of factor 1 in the northern zone, for the different cases grouped by tidal conditions F, H, D, and L.

ence of the discharged waste towards the interior stations (16, 15 and 14) at flowing and high tides. At ebbing and low tides, this waste water moves away, limiting its influence to only the nearest area, station 16. It is important to note that at the central stations (10, 11 and 12), the effect of the waste discharge is not appreciated, since their values at any tidal condition are always negative. The intermediate station shows a very small contribution, positive or negative depending on the tidal condition considered.

Factor 4 accounts for 8.77% of the variance and is positively associated with solids in suspension and volatile solids. The percentage of variance explained is less than half the value for the southern zone, which indicates that the phenomena of agitation are less important in this zone. Factor 5 explains 7.14% of the variance and is associated with the tidal condition. The relative unimportance of this factor and the lack of interaction with the rest of the variables shows the low influence exerted by the tidal condition in this central zone of the channel.

By way of summary, it is concluded that the process of mineralisation influenced by the input of water near the discharge point accounts for 36.4% of the variance. Although as a percentage this is lower than for factor 1 of the southern zone, it continues to be important in relation to the other factors. The seasonal variation is the second factor in importance for this central zone, explaining 17.17% of variance. Under flowing tidal conditions, the urban contamination from the town of San Fernando extends to stations 16, 15 and 14; at ebbing tides, the influence of the discharge is only seen at station 16. The factor of agitation, which is fairly important for the southern zone, here only explains 8.77% of variance and one can explain this finding as the reduced influence of the tides in the central zone.

5.3. Northern zone (stations 17–21)

For this zone, five factors have been determined. Together they account for 83.94% of the total variance of the data (Table 5).

Factor 1 includes the following variables, in order of importance: NH_4^+, HPO_4^{2-}, LAS, NO_2^-, pH, and dissolved oxygen; it accounts for 40.74% of the total variance. The variables pH and dissolved oxygen are in inverse relationship to this factor. It is significant that the nitrate variable is absent, in contrast with the other zones. This factor represents the effect of the urban waste discharge on the waters of this zone. If the large quantities of allochthonous organic matter

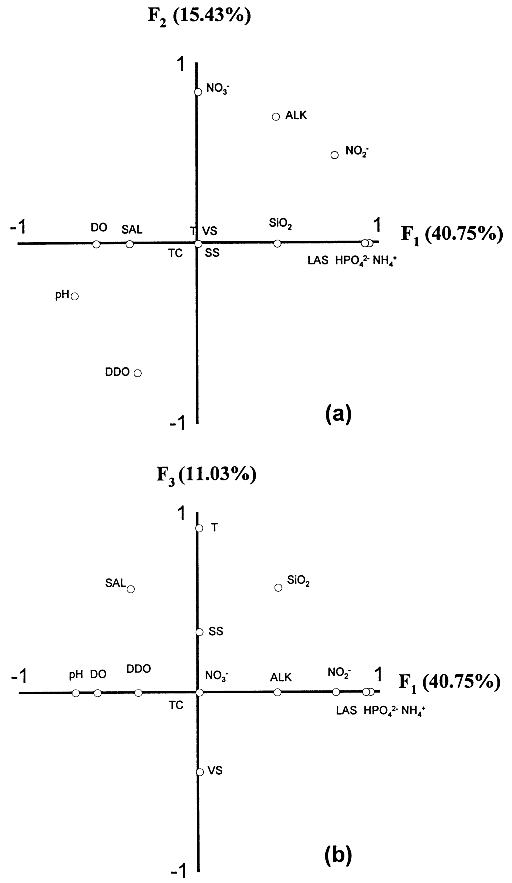

Fig. 8. Distribution of the variables in the factor space in the northern zone. a: Factor 1 against factor 2. b: Factor 1 against factor 3.

introduced into the medium close to the discharge point are considered, the inclusion in this factor of nutrient concentrations, dissolved oxygen, pH and alkalinity may be partly due to an increase in the mineralisation processes. In this respect, this factor should be interpreted in a broad form, including the direct effect of the discharge and the influence this exerts on the processes of degradation of the organic matter existing in the zone. The representation of this factor for the various cases, at different tidal conditions, is shown in Fig. 7. When the tide is flowing and at high tide, the factor shows negative values at all stations: at ebbing and low tides, the value of the factor is positive for the more interior stations. This behaviour is particularly noticeable at station 17.

The variables that correlate positively with factor 2 are nitrates and alkalinity, and negatively, distance from the discharge point. The factor explains 15.43% of the variance and could be related to the importance of the process of nitrification in the zone as a result of the high concentrations of ammonia found in the effluents [14]. The maximum values are shown at ebbing and particularly at low tide, at stations close to the discharge point. Despite the entry of clean water from the Bay, stations 17 and 18 show positive values for this factor both at flowing and at high tides.

Factor 3 accounts for 11.03% of the variance and is associated positively with the variables temperature, silicates and salinity. The contribution of this factor is positive in summer and negative in winter, and could be related to the seasonal evolution of salinity due to the processes of evaporation, and to the dissolution of biogenic silica. A similar proportion of the total variance, 9.67%, is represented by factor 4. The variables solids in suspension and volatile solids are correlated positively with the factor. This factor could be associated with the degree of agitation of the water; however, a clear sequence corresponding to the different tidal conditions considered has not been observed. Factor 5 accounts for only 7.06% of variance, and includes the variables tidal condition and salinity, inversely correlated. It represents the action of the tides when the speed of flow is slow, at high and low tide; the values of the factor are always small and in most cases negative (figure not shown).

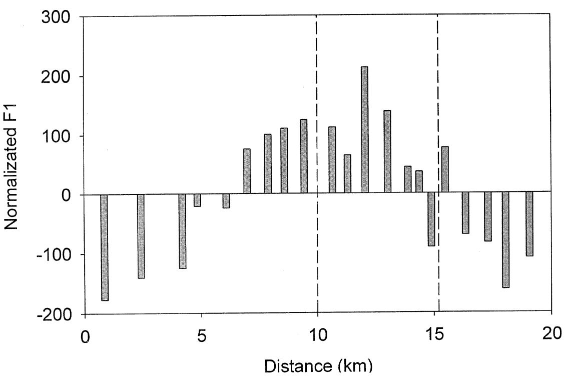

Fig. 9. Graphical representation of the value of factor 1, normalized, in the Channel of Sancti Petri, for the different cases.

The relation between factors 1 and 2, shown in Fig. 8, demonstrates that with increasing distance from the discharge point, the effect of the urban contamination and of its subsequent phases of mineralisation of organic matter diminishes. When both factors increase, there is also an increase in the alkalinity and in the concentration of nitrites, as well as a decrease in pH (Fig. 8a). This shows clearly the influence of the processes of mineralisation on both factors.

The high temperatures in summer and the increase in the volume of effluent discharged cause a greater concentration of silica (Fig. 8b). The positive contribution of the concentration of silicates in factors 1 and 3 relates the high availability of nutrients to the populations of diatoms, and the effect of the temperature on the dissolution of biogenic silica. In turn, the highest levels of salinity occur in summer, in spite of the local reduction produced by the urban effluent discharge at nearby stations. The provision of dissolved oxygen through the contamination-free waters of the Bay explains the positive correlation of this variable with factor 5 (figure not shown).

It can be concluded, therefore, that as a consequence of the proximity of the discharge point for waste waters from the town of San Fernando, contamination of urban origin and the processes of mineralisation of the organic matter constitute the first factor that explains 40.75% of the variance. When Bay water enters the Channel, the influence of this factor is limited to the station closest to the discharge, No. 17, with a relatively very low value. A second phase of the regeneration process, characterised by an intense nitrification in the medium, explains 15.43% of variance. Lastly, factors 3 (seasonality), 4 (agitation) and 5 (action of the tides) explain 11.03%, 9.67% and 7.06%, respectively, of the variance.

6. Conclusions

In spite of the apparent simplicity of the ecosystem studied, a priori capable of being modelled unidimensionally, an overall synthesis of all the information obtained from the factor analysis establishes five processes that determine the hydrochemistry of the zone (mineralisation, influence of urban effluents, seasonality, degree of agitation and action of the tides). These processes are not defined in an exclusive way by the factors obtained in each zone.

Of all the processes, the mineralisation of the organic matter, either of basically autochthonous origin in the zone or with a certain participation of autochthonous matter in the central and northern zones, stands out as the main process determining the hydrochemistry of the zone, explaining around 40% of the total variance in the data. This process is in large measure influenced by the presence of urban effluents. Fig. 9 shows the evolution of factor 1, once normalised, along the length of the Channel studied. The sinusoidal shape of the graph demonstrates the importance of the processes of benthic regeneration in the chemical composition of the water, basically in the central zone of the channel, of less depth and with a longer residence time. In contrast, at the two ends of the channel, which are deeper areas where the interchange of water through the tides takes place more easily, this factor acquires negative values.

This interpretation, based solely on the results of the factor analysis, is in agreement with previously accumulated knowledge about the zone. In general, the benthic fluxes of nitrogen, phosphorus and inorganic carbons, as well as the benthic demand for oxygen, are high in this zone [13,15,16]. Furthermore, there exist clear gradients of the concentration of organic carbon in the sediment, with values up to 5% in the central zone [17], and of the granulometry, with clay fractions more abundant in the central zone and sandy fractions at the two ends [18]. Both the quantity of organic matter [13] and the granulometry of the sediment [19] have been described as determining factors in the benthic fluxes.

The influence of the urban effluent on the process of mineralisation shows an increasing trend, moving along the Channel from south to north. This phenomenon is demonstrated by the inclusion of salinity in factor 1 for the central zone or by the concentration of LAS in the northern zone. In fact, in the northern zone, the entry of residual waters with large quantities of particulate organic matter and ammonia causes the appearance of a second factor that includes alkalinity and the nitrate concentration, which may be related to those processes of mineralisation more kinetically impeded.

The third process involved, in order of relative importance, is constituted by the influence of temperature, basically on the dynamics of the diatom populations [20] and on the subsequent dissolution of the biogenic silica, which is also affected by the salinity. The inclusion of pH (factor 3, southern zone) or of the concentration of oxygen (factor 2, central zone) clearly shows the control exercised by the temperature over the benthic fluxes themselves that are responsible for the decrease in the concentration of oxygen and pH in the water column in this zone [13].

Lastly, the processes of agitation characterised by the variations in the content of solids in suspension and volatile solids, together with the action of the tides, which generally include the variables of tidal condition and salinity, appear in separate factors, due perhaps to the wind regimes in the zone, which are generally intense. These two factors between then explain only some 15–20% of the total variance for the variables studied; this would appear curious given that the Atlantic littoral of the Iberian Peninsula is subjected to a moderate tidal regime.

In summary, it can be stated that the analysis of factors allows a differentiation between zones that show a slightly different behaviour within a littoral ecosystem on the basis of the main processes that determine its hydrochemistry.

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trends

Flow injection analysis – Where are we heading?

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1. Introduction

Although conceived in Denmark, it was in Piracicaba[1] during the late 70's at the Centro de Energia Nuclear na Agricultura (CENA) where FIA was demonstrated, for the first time, to be a practical and useful analytical tool. Indeed, by 1978 50% of all the papers published world-wide originated at CENA (where at that time 40 000 samples were analyzed yearly by FIA) [1]. Since then, the scope of applications has grown world-wide (Fig. 1), and flow injection (FI) has become a major analytical technique described in over 8000 papers [2]. While this development confirms the usefulness of FI, it also poses a question as to which direction the future research should be aimed – work with any 'mature' technique tends to bring about a repetitive pattern of well trodden topics that through accumulation of trivia might lead to stagnation and even decline the quality of the research.

2. Continuous and discontinuous FI systems

While the 'classical' or *continuous* flow FI systems can operate well without the aid of a computer, they are uneconomical in terms of reagent consumption and waste generation, because all solutions are pumped continuously. In contrast, the recently designed variant of FI, sequential injection (SI) [3], is based on *discontinuous* flow and consumes reagents only when the sample is being treated by exploiting a combination of stopped, reversed as well as forward flow in the microlitre scale. Nowadays, the proliferation of PCs and the availability of dedicated and object oriented software make SI widely accessible, although SI also imposes some constraints on the versatility of operation as compared to FI. The simplicity of the SI flow channel, which comprises for a majority of applications only a single (piston) pump and a single (multi-

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[1] The Seventh International Conference on Flow Analysis, held in Piracicaba, Brazil, in August 1997, offered a vantage point to reflect on the status of Flow Injection Analysis (FIA). And for these authors, who have been engaged in the field from the start, to contemplate on the future directions of FIA. G.D. Christian will in this issue inform the readers of TrAC of the presentations made at the conference.

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