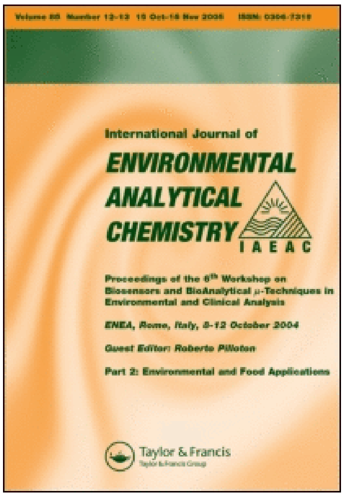

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Application of Non-Destructive X-Ray Fluorescence Spectrometry to the Analysis of Suspended Matter in Sea Water

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Application of Non-Destructive X-Ray Fluorescence Spectrometry to the Analysis of Suspended Matter in Sea Water†

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In the framework of remote sensing studies concerning coastal transport of pollution in the Northern Adriatic Sea, a method has been developed for the quantitative determination of sulphur, iron, titanium, calcium, phosphorus, silicon, aluminium, magnesium in suspended matter of sea water.

The suspended material was collected by filtering on millipore membrane filters with pore width of 0.45 μ and directly analysed by X-ray spectroscopy. For calibration dried solution and particulate standard samples were used. Limits of sensitivity and precision of the method are reported.

Correlations between the concentration of these elements and the total suspended matter/chlorophyll are discussed.

The aim is to study the geochemical composition of particulate matter and its variations within the geographical site of the sea basin and the seasonal conditions. The approach is to consider aluminium and the other elements normalized on Al. On the basis of a matrix correlation analyses of some sets of data chosen in the restricted area for investigation, some hypothesis on superficial distribution of clay, carbonate, iron hydrous oxides and other mineral detrites, are taken into account. The results confirm the complex situation existing in the offshore area of the Venice lagoon from a geochemical point of view.

The suspended matter seem to be argillaceous in the Southern part of the investigated area and semi-argillaceous with hydrous oxides and carbonates in the Northern part which is influenced by the Piave river.

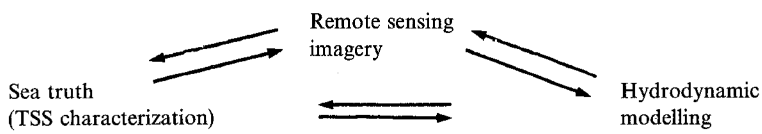
†Presented at the 14th annual symposium on the analytical chemistry of pollutants. Barcelona, November 21–23, 1984.

KEY WORDS: RS Remote Sensing, CZCS Coastal Zone Colour Scanner, spectral sensor on Nimbus-7 satellite, CNR (Italian) National Council of Research, TSS Total Suspended Solids, PCB PoliChlorinated Biphenyles.

1. INTRODUCTION

Remote sensing techniques can be an important tool in the multidisciplinary study of the marine environment. Total suspended matter (TSS) in the sea water is a carrier for pollutants such as heavy metals, pesticides, PCB and nutrients. It interacts with the incoming sunlight and is then reponsible, with the phytoplankton, for the amount of reflected light which can be detected by remote sensors (CZCS on Nimbus 7 satellite). The spectral signals collected are transformed in synoptic thematic maps through interpretation algorithms.[1]

The aim of our study is the characterization of TSS from the geochemical point of view, determining some trace elements such as: Si, Al, Ti, Fe, Ca, K, P, Mg, in order to obtain a complete "Sea Truth" which is involved in this multiple scheme:



2. TEST SITE (Fig. 1)

The Northern Adriatic Sea is the shallowest area of the whole Mediterranean. Large river run-offs, an extended lagoon system and the seasonally variable heat-exchange at the surface, give rise to relatively large levels and gradients of phytoplankton and TSS concentrations while urban and industrial wastes are responsible for the pollutants in the sea. The Po river has a mean annual outflow of $47.10^9\,m^3$ equivalent to 7.3% of the northern part of the basin delimited by a transversal line from Ancona to Zadar in Jugoslavia.[2] Because of tidal movement, an average of about $3.10^8\,m^3$ of water is exchanged daily between the Adriatic and the Venice lagoon.[3] The sedimentation is mainly due to the terrigenous load of the river Po:

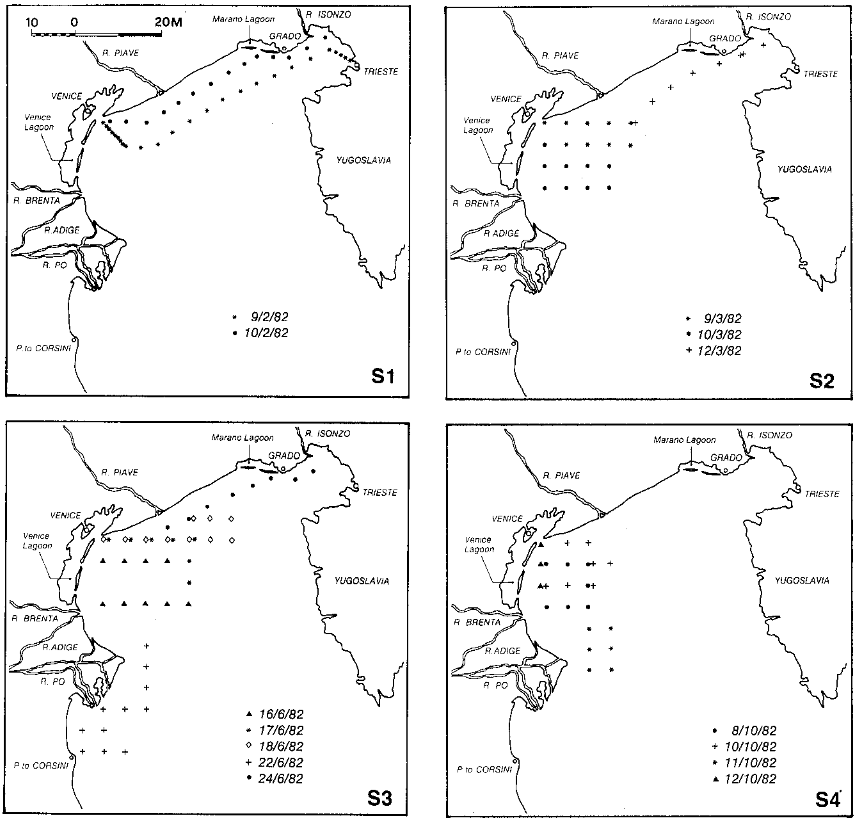


FIGURE 1 Test area and point stations.

10 to 20.10^6 tons/year, and to the Venetian and Apennine rivers which are responsible for 5.10^6 tons/year of sediment into the entire Adriatic Sea.[4]

The composition of the terrigenous load of the river Po varies because its drainage basin is made up of many geological districts: Apennine, Central and Western Alps. On the other hand, the drainage basin of Venetian rivers like the Adige, Brenta, Piave, Livenza, Tagliamento and Isonzo is chiefly composed of mesozaic limestone, dolomite and a small volcanic area (Alto Adige).

3. ANALYTICAL PROCEDURES

Samples of surface water to a depth of 20 m were collected during the R.S. cruises in the Northern Adriatic Sea in 1982, 1983 and 1984. The geographical location of the collecting sites of the sea water samples is shown in Figure 1. The water samples were filtered under pressure (3 atm max) on cellulose millipore filters with a pore width of 0.45 μ by means of the system shown in Figure 2.

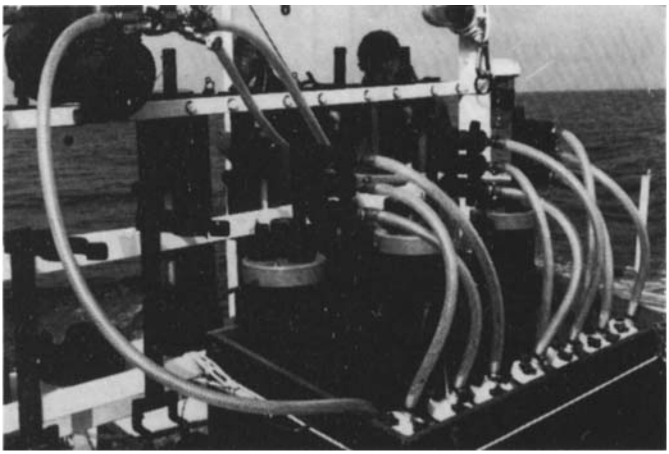


FIGURE 2 Sampling Apparatus on oceanographic ship U. D'Ancona (It. Reas. Nat. Counc.).

3.1 Non-destructive analysis

A Siemens SRS 300 sequential X-ray spectrometer was utilized for this analysis and operated under the instrumental parameters as listed in Table I.

Dried solution standards used for the determination of Fe and Ti cannot be used for the light elements without self-absorption corrections which are very large for Si, Al and Mg. These correction factors for a homogeneous dried solution standard are due to self-absorption in the cellulose acetate/cellulose nitrate fibre material. Calculated self-absorption factors for silicon and aluminium, assuming a 5.9 KeV excitation energy are given in Table II.

TABLE I

Operating parameters for suspended matter analysis

X-ray tube	rhodium end-window
Anode voltage	55 kV
Anode current	45 mA
Counting rate	40 sec
Collimator	0.4° aperture
	LiF 100 = Fe-Ti-Ca
Analyser crystals	PET = Al-Si-S
	T1AP = Mg
	Ge = P

TABLE II

Self-absorption factors for Si and Al dried solution standards

	Si	Al
Millipore	2.9	4.0
Whatman 541	6.4	9.2

Thus, for the determination of Si, Al, Mg, S and Ca we have used particulate standards.† Large errors which are made in the determination of the light elements using dried solution standards without self-absorption corrections are demonstrated in Figure 3, where calibration curves for Al of dried solution and particulate standards are compared together with suspended matter filters analysed after measurement of the X-ray intensities by chemical methods.

Finally, limits of sensitivity for the various analysed elements are presented in Table III.

4. RESULTS

In this study, multivariate analysis was chosen as a statistical approach for treatment of the sea-truth data. A preliminary examination of the correlations between the values collected at sea, such as

†Delivered by CSI (Columbia Scientific Industries, P.O. Box, Austin, Texas, U.S.A.

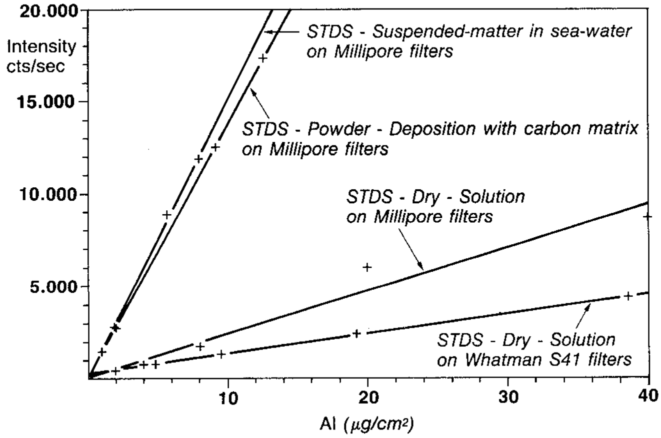


FIGURE 3 Calibration curves for Aluminium determination.

TABLE III
Limits of detection for the various analysed elements

Element	Limit of detection ($\mu g/cm^2$)
Fe	7.10^{-3}
Ti	8.10^{-3}
Ca	2.10^{-3}
K	$4.5.10^{-3}$
S	$1.5.10^{-3}$
P	$0.8.10^{-3}$
Si	$1.4.10^{-3}$
Al	$1.1.10^{-3}$
Mg	$1.4.10^{-3}$

chlorophyll, TSS and the above mentioned trace elements analysed by X-ray fluorescence, can be envisaged for a suspended matter pattern recognition in given seasonal and geographical conditions. The marine measurements were carried out during the four 1982 campaigns which took place in different seasons. In the first 1982 campaign, three sets of data were taken into account. The first nine stations were situated between the entrance of the port of Venice and the CNR (Italian National Council of Research) platform (9 miles offshore) (Figure 1). The indices of determination matrices (Figure 4) allow us to show a good correlation with TSS for the Ca, Ti and Fe. Si correlates with Al but not with TSS. We can suppose a balanced composition of TSS between clay materials, Ca carbonate, the hydrous metal oxides and/or phosphates. The high correlation coefficient of Ca and Fe between TSS allows us to suppose a prevalent carbonate and hydrous metal oxides TSS composition.

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra
Si	100	77	64	81	88	33	53	32
Ca		100	77	92	88	68	79	60
Ti			100	88	81	28	64	45
Fe				100	89	51	74	57
Al					100	38	58	40
Chl						100	59	72
TSS							100	64
Or.Fra								100

S1 campaign 1-9 station

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra
Si	100	66	78	35	56	56	73	87
Ca		100	75	21	17	46	34	64
Ti			100	50	25	63	46	88
Fe				100	36	21	40	91
Al					100	6	62	49
Chl						100	33	82
TSS							100	65
Or.Fra								100

S1 campaign 10-23 station

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra
Si	100	27	43	6	73	16	49	39
Ca		100	8	6	37	1	16	1
Ti			100	5	73	6	0	2
Fe				100	7	5	4	4
Al					100	14	13	6
Chl						100	4	17
TSS							100	35
Or.Fra								100

S1 campaign 26-39 station

FIGURE 4 Correlation matrices derived from S1 (March 1982) campaign data.

In the second set of stations taken between the CNR platform and Trieste, silicon shows a good correlation with TSS, the organic fraction and chlorophyll, while Al (alumino-silicate trace element) does not correlate with the other parameters. This suggests a non-argillaceous but biogenous matrix of the particulate. Figure 5 represents a multiparametric horizontal profile along the track from the CNR platform to Trieste during the S1 campaign (9.2.1982). The peaks at stations 11, 12 and 14 seem to represent a resuspension from the bottom as indicated by high salinity conditions.

In the second campaign (S2 = March 1982), the correlation matrices (Figure 6) represent three data sets which were supposed to be homogeneous. The first was collected in the northern part of the Gulf of Venice, the second in the southern part of the Gulf of Venice, and the last along the track from the Piave river mouth to the Gulf of Trieste. In the first 10 stations the particulate matter seems to be mainly influenced by oxides/carbonates where the clay component is nevertheless important.

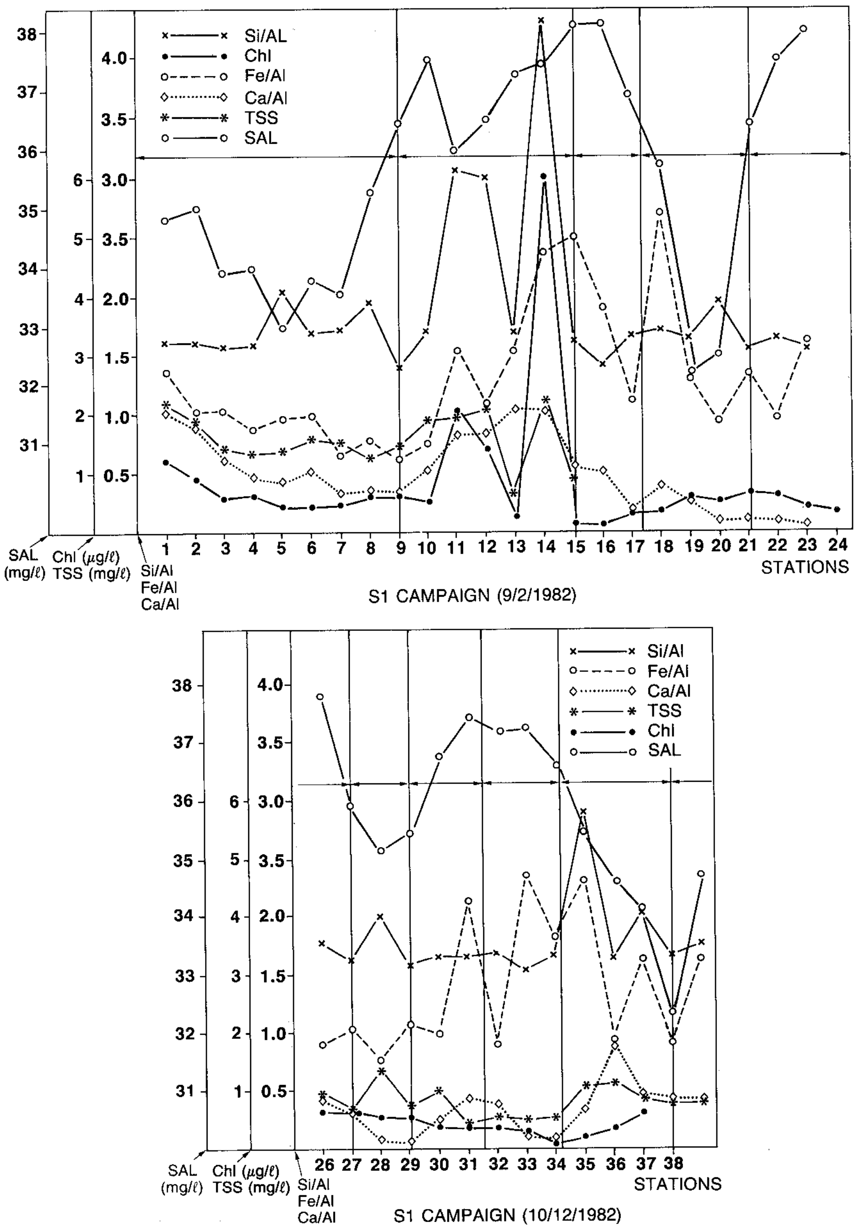


FIGURE 5 Multiparametric profiles along the track plot NCR-Gulf of Trieste 9-2-1982 tide descendent.

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra
Si	100	0	1	0	82	10	0	14
Ca		100	74	96	95	64	91	83
Ti			100	83	61	69	91	25
Fe				100	83	75	97	86
Al					100	47	78	52
Chl						100	70	67
TSS							100	75
Or.Fra								100

S2 campaign 1-10 station

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra
Si	100	88	58	87	100	33	80	70
Ca		100	87	83	89	44	74	56
Ti			100	93	95	30	73	61
Fe				100	82	48	72	65
Al					100	31	80	70
Chl						100	31	61
TSS							100	73
Or.Fra								100

S2 campaign 11-19 station

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra
Si	100	88	51	19	100	67	0	8
Ca		100	100	99	38	88	95	75
Ti			100	100	34	89	97	91
Fe				100	38	91	98	78
Al					100	63	32	38
Chl						100	89	72
TSS							100	80
Or.Fra								100

S2 campaign 20-26 station

FIGURE 6 Correlation matrices derived from S2 (March 1982) campaign data.

In the second set of stations, located in front of Chioggia and the Adige and Brenta river mouths, the clay component appears to be more important. In the last stations, along the northern coast, the clay component became less important, compared with the carbonates and the hydrous metal oxides.

Offshore of the Po delta (third data set), the particulate matrix seems to be siliceous but with a strong organic component. In the last area, along the northern coast, it appears to be completely inorganic.

In the June campaign (S3) the matrix correlation (Figure 7) does not give a clear indication of the nature of particulate matter. Therefore, in the first group, which was collected in an extended area in the central part of the Gulf of Venice, an argillaceous particulate seems to be prevalent. A mixed composition of clay, carbonate and iron hydrous metal oxides can be ascribed to TSS in the second data set collected in the northern part of the Gulf of Venice where the chlorophyll concentration shows a good correlation with TSS.

In front of the Po delta (third data set) the particulate matrix seems to be siliceous while in the last area, along the northern coast, it appears to be completely inorganic.

During the October campaign (S4) two sets of stations were taken into account. The first was represented by a large area in front of the lagoon of Venice. On the basis of matrix correlation (Figure 8), a particulate matter composition is difficult to ascertain. In the last data collected in front of the Po river mouth, the particulate matter has predominantly argillaceous composition.

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra	Si/Al	Ca/Al	Fe/Al	Ti/Al
Si	100	89	100	100	100	1	87	39	1	28	4	85
Ca		100	87	88	88	0	83	36	4	14	3	100
Ti			100	100	100	13	99	36	1	16	0	85
Fe				100	100	0	87	40	0	28	3	83
Al					100	1	88	42	0	31	4	82
Chl						100	6	32	5	47	11	38
TSS							100	69	1	45	9	81
Or.Fra								100	2	62	13	9
Si/Al									100	15	0	18
Ca/Al										100	46	0
Fe/Al											100	10
Ti/Al												100

S3 campaign 2-11 station

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra	Si/Al	Ca/Al	Fe/Al	Ti/Al
Si	100	1	56	32	50	72	55	69	16	63	36	19
Ca		100	1	31	10	1	5	4	6	0	1	9
Ti			100	57	11	35	16	26	5	6	22	33
Fe				100	25	39	18	18	0	10	1	2
Al					100	40	10	21	11	34	41	19
Chl						100	33	36	10	33	15	8
TSS							100	83	17	50	21	20
Or.Fra								100	14	50	23	19
Si/Al									100	6	0	83
Ca/Al										100	84	2
Fe/Al											100	64
Ti/Al												100

S3 campaign 22-32 station

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra	Si/Al	Ca/Al	Fe/Al	Ti/Al
Si	100	48	37	77	98	61	52	43	26	33	69	99
Ca		100	84	71	39	66	67	65	16	0	31	22
Ti			100	39	19	92	92	99	2	6	8	26
Fe				100	71	77	73	64	14	12	34	99
Al					100	48	40	30	15	35	71	99
Chl						100	99	95	25	9	24	66
TSS							100	96	39	6	20	100
Or.Fra								100	27	5	13	0
Si/Al									100	20	26	100
Ca/Al										100	23	100
Fe/Al											100	100
Ti/Al												100

S3 campaign 12-21 station

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra	Si/Al	Ca/Al	Fe/Al	Ti/Al
Si	100	51	97	82	95	4	38	1	66	38	85	8
Ca		100	94	25	33	9	3	42	13	0	29	6
Ti			100	3	80	5	67	56	12	61	60	0
Fe				100	80	6	55	1	78	56	92	99
Al					100	16	35	0	76	58	91	32
Chl						100	2	3	22	58	13	84
TSS							100	2	16	24	20	49
Or.Fra								100	4	18	1	48
Si/Al									100	77	93	95
Ca/Al										100	63	42
Fe/Al											100	57
Ti/Al												100

S3 campaign 42-51 station

FIGURE 7 Correlation matrices.

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra	Si/Al	Ca/Al	Fe/Al	Ti/Al
Si	100	72	90	82	76	17	29	26	1	0	17	9
Ca		100	58	61	34	42	34	45	0	23	26	9
Ti			100	80	70	10	26	20	1	0	17	29
Fe				100	70	12	61	56	4	0	48	12
Al					100	14	17	16	16	7	8	2
Chl						100	3	15	4	38	1	1
TSS							100	85	1	0	75	10
Or.Fra								100	4	8	65	4
Si/Al									100	20	6	2
Ca/Al										100	0	0
Fe/Al											100	18
Ti/Al												100

S4 campaign 1-14 station

Index of determination r^2

	Si	Ca	Ti	Fe	Al	Chl	TSS	Or.Fra	Si/Al	Ca/Al	Fe/Al	Ti/Al
Si	100	89	92	97	92	13	75	0	3	32	27	1
Ca		100	96	96	89	21	91	5	11	10	18	13
Ti			100	99	98	15	90	1	16	22	31	4
Fe				100	97	15	86	0	10	24	29	3
Al					100	8	86	0	19	35	45	0
Chl						100	5	1	2	11	20	41
TSS							100	1	28	13	34	8
Or.Fra								100	1	52	35	95
Si/Al									100	4	42	0
Ca/Al										100	73	55
Fe/Al											100	33
Ti/Al												100

S4 campaign 15-20 station

FIGURE 8 Correlation matrices derived from S4 (October 1982) campaign data.

6. CONCLUSION

The matrix correlation analyses give an indication for improvement of the TSS characterization study. From the preliminary results we have hypothesized for instance, by means of the correlation coefficients between Si, Al, Ca, Ti and Fe, that in the southern part of the Gulf of Venice to the mouth of the Pò, argillaceous particulates prevail. In the nothern part, which is perhaps more influenced by the lagoon system, hydrous metal oxides, phosphate and/or carbonate seem to be prevalent.

Further information can be derived from analysis of the variation of other parameters. Si/Al ratios[5] are an indication of a clay material which is probably different from the geochemical point of view. The "non-fitting point" (see Figure 9) can be seen to correspond to biogeneous silica areas (phytoplankton bloom) and/or to continental terrigenous particulate areas. For the S1, S2 and S4 campaigns the Si/A1 ratio derived from the best fit line was very similar: 1.66 (S1), 1.58 (S2) and 1.53 (S4) while during the June campaign the clay material is characterized by a Si/Al ratio of 2.7.

Another conclusion can be derived considering the availability of CZCS data to map the chlorophyll production and TSS deposition areas. A correlation test between the data derived from CZCS imagery and some geochemical characteristics of TSS has been carried out.

Figure 10 shows the excellent correlation which exists between TSS/CZCS derived data and silicon in the first nine stations of the S1 campaign. Ca and Fe, present as hydrous oxides and/or phosphate and carbonate, correlate with weighed TSS in those areas where the suspended particulate is under the direct influence of the lagoon system. The good correlation with silicon seems to show a tendency of CZCS imagery to underestimate TSS in this area where the clay components are important but not predominant. As a conclusion it can be said that a recognition of suspended matter classes, based on their geochemical characteristics, is possible; seasonal maps of particulate species in these coastal zones could also be produced. This suggests a new physical approach to the measurement *in situ* of their optical behaviour to improve interpretation algorithms.

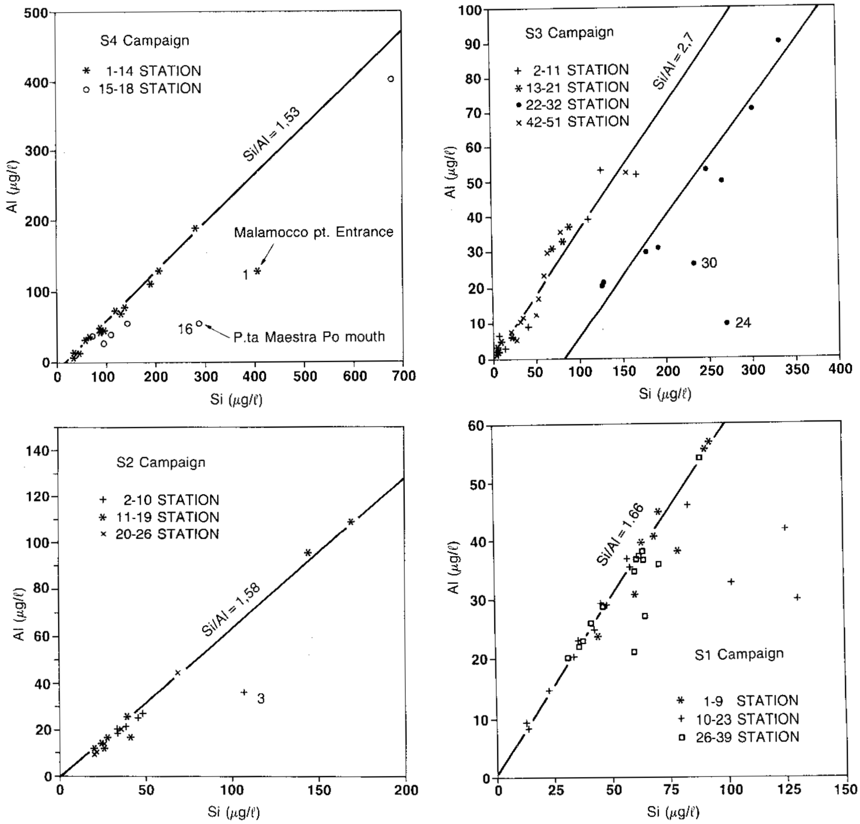


FIGURE 9 Correlation curves between Silicon and Aluminium in the northern Adriatic 1982 campaign.

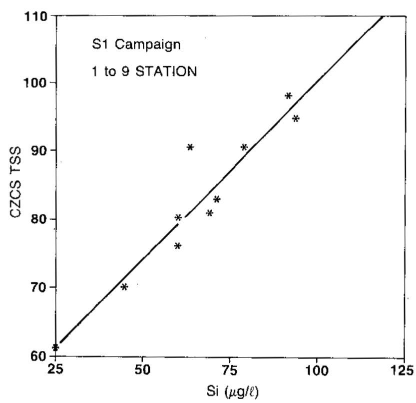


FIGURE 10 Correlation between the TSS derived from CZCS Nimbus 7 data (relative units) and measured Silicon.

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