



CHEMICAL POLLUTION FROM URBAN AND INDUSTRIAL SEWAGES IN AUGUSTA BAY (SICILY)

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ABSTRACT

The Augusta Bay is a complex area where heavy industrialization and dense urbanization have promoted a very high state of degradation. This basin has already been studied for several years because of various eutrophication phenomena which induced a massive fish mortality.

In order to deepen our knowledge on the state of chemical pollution due to Dissolved/Dispersed Petroleum Hydrocarbons (DDPH), detergents and N- and P-salts as well as on the eutrophication of the bay, three campaigns have been carried out. The results (from 0.0 to 96.6 µg/l in chrysene equivalents) have indicated that the distribution of DDPH is characterized by an extreme spatial and temporal variability linked to occasional localized spills and to the wind's action which influences the surface water circulation in the bay.

The concentration of non ionic (BiAS) and ionic (ABS) detergents averages respectively 63 and 55 µg/l with a predominance of BiAS in the waters affected by the urban discharges, while high ABS values have been also measured in correspondence of a cooling water effluent.

Finally, the PO₄ (max 0.3 µ/l) and NO₂ + NO₃ (max 4 µl) levels were relatively low and constant in comparison with previous results, while NH₄ remains at a high level (max 14.6 µ/l) with supplies located in the urban discharge as well as in the industrial ones, indicating that both types of effluents are equally responsible for eutrophication and the dystrophic crisis observed in the bay.

KEYWORDS

Chemical pollution; nutrients; industrial and urban sewage.

INTRODUCTION

The "Rada di Augusta" is a wide natural bay which occupies about 30 km of the eastern coast of the Sicily. In the past years, a part of the bay has been walled up with breakwaters to form a vast harbour basin communicating with the sea through two narrow inlets (east and south, Fig. 1).

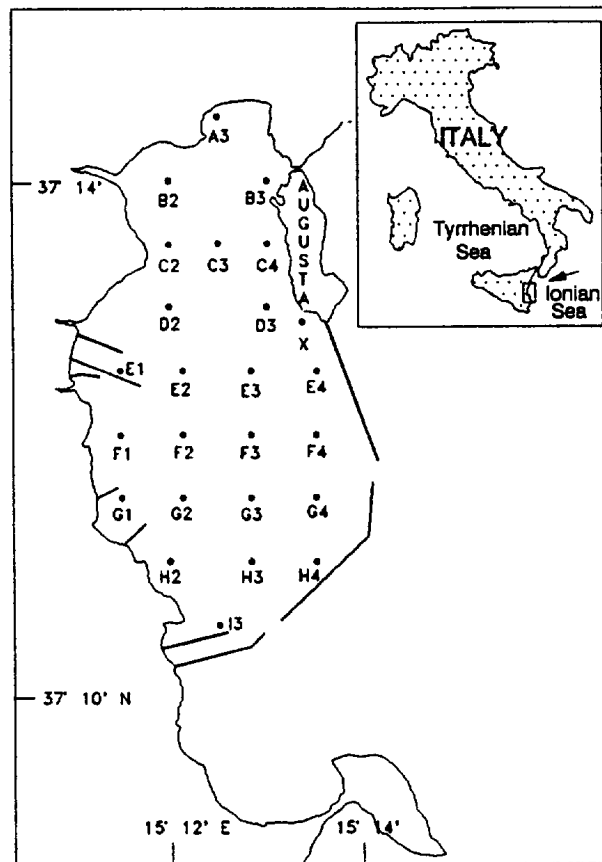


Figure 1. Map of the studied area and location of sampling stations.

Owing to its nature, a coastal marine environment with a low water turnover, and to the intense human activities, the Augusta bay is a complex area, where heavy industrialization and urbanization have promoted a very high state of degradation which can be essentially ascribed to these two activities.

The first kind of pollution is principally attributable to the oil hydrocarbons coming from the petrochemical refining plants, situated outside and inside the "Rada", which involve about 10,000 operators. A further contribution is supplied by the intense harbour activities especially imputable to the loading of crude and refined oil.

The second kind of pollution that leads to a semipermanent condition of eutrophication is related to urban waste waters (70,000 inhabitants) which reach the bay after only a partial treatment. A high contribution of N and P can be also charged to industrial (production of fertilizers) and agricultural activities (Marsili, 1982; Azzaro, 1993).

The basin has already been studied for several years to evaluate the relationship between the pollution and the very frequent problems of water eutrophication (Magazzù, 1977; Andreoli *et al.*, 1986-87).

More recently, since 1989, in the frame of the strategic project named "Monitoring of Marine pollution in the South Italian Seas" executed by the C.N.R. - Talassografico Institute (Messina) and the Biology Department of the University of Lecce, an intense research programme started, with the installation of a

buoy net for the automatic monitoring of environmental parameters (Crisafi, 1993), chemical (Azzaro, 1993) and biological (Decembrini *et al.*, 1993) characteristics.

These researches have been carried out for one year with monthly samplings. Oil pollution has been studied either by traditional methods, (Crisafi *et al.*, 1993) either by remote sensing (De Domenico *et al.*, 1994).

The present study has been planned within the frame of a global programme for the improvement of the environmental conditions of the bay as foreseen by recent legislative regulations of the Regional and Central governments. The objective is the definition, immediately before any intervention, of the present trophic level, through the revision of nutrients distribution, and of the degree of the chemical pollution, through the study of diffusion and concentration of synthetic surfactants and oil hydrocarbons, on the basis of the consideration that in the past studies these substances have appeared as being highly responsible for the degradation of the bay.

MATERIAL AND METHODS

Samples have been collected, on the surface of the bay, with 5 l Niskin bottles in 25 stations, during three cruises held respectively on March 8 and 24 and April 6, 1994. For oil hydrocarbons glass bottles, mounted on a weighted frame have been used, according to the procedure adopted for the IGOSS Project (IOC, 1976).

Pretreatment of samples has been effected on board immediately after the drawing. Nutrients: filtration on Whatman GF/F filters and freezing at -20°C ; surfactants: addition of 1 ml of a 10% solution of HgCl_2 ; aromatic hydrocarbons: pre-extractions with 50 ml of $\text{CH}_2\text{Cl}_2/4\text{l}$ of sample. Analytical determinations have been performed according to literature procedures (Strickland and Parsons, 1972; De Domenico *et al.*, 1994; IRSA-CNR, 1973; 1979).

Table 1. Chemico-physical parameters, nutrients and chemical pollutants in Augusta Bay (N/P = inorganic N-PO₄ ratio; B/A = BiAS/ABS ratio)

	March 3, 1994				March 24, 1994				April 6, 1994			
	Temp. °C	Sal. psu	O ₂ ml/l	O ₂ ‰	Temp. °C	Sal. psu	O ₂ ml/l	O ₂ ‰	Temp. °C	Sal. psu	O ₂ ml/l	O ₂ ‰
<i>Min.</i>	15.45	37.93	4.68	86.55	16.65	38.00	5.03	93.46	15.25	38.14	4.55	82.85
<i>Max.</i>	16.67	38.07	5.16	93.89	18.20	38.54	5.66	105.9	15.76	39.04	5.34	96.62
<i>Aver.</i>	15.87	38.00	5.00	91.13	17.05	38.10	5.41	100.9	15.48	38.21	4.91	88.89
<i>S.D.</i>	0.282	0.032	0.11	1.684	0.308	0.094	0.12	2.241	0.108	0.170	0.22	3.742
	$\mu\text{M/l}$				$\mu\text{M/l}$				$\mu\text{M/l}$			
	PO ₄	NO ₂ +NO ₃	NH ₄	N/P	PO ₄	NO ₂ +NO ₃	NH ₄	N/P	PO ₄	NO ₂ +NO ₃	NH ₄	N/P
<i>Min.</i>	0.02	0.03	0.10	1.9	0.00	1.39	0.23	46.2	0.00	0.21	0.21	13.5
<i>Max.</i>	0.11	1.49	2.50	76.0	0.07	4.12	14.60	583.7	0.26	3.00	2.83	322.0
<i>Aver.</i>	0.07	0.22	0.91	18.52	0.02	2.54	4.27	225.7	0.04	1.86	1.30	106.8
<i>S.D.</i>	0.02	0.30	0.62	17.35	0.03	0.62	4.66	136.8	0.05	0.64	0.77	99.76
	$\mu\text{g/l}$				$\mu\text{g/l}$				$\mu\text{g/l}$			
	ABS	BiAS	B/A	DDPH	ABS	BiAS	B/A	DDPH	ABS	BiAS	B/A	DDPH
<i>Min.</i>	15.13	16	0.16	0.36	13.76	35	0.28	0.00	11.00	22	0.34	0.00
<i>Max.</i>	189.81	88	5.82	57.52	130.67	92	4.94	96.61	179.8	150	13.63	77.90
<i>Aver.</i>	53.57	49	1.42	7.08	57.46	67	1.63	15.29	56.27	76	2.36	10.03
<i>S.D.</i>	37.191	16	1.31	11.26	30.17	21	1.21	23.70	39.34	27	2.70	20.41

RESULTS AND DISCUSSION

Chemical and physico-chemical parameters: T, S, O₂ (Table 1). Water temperature shows modest variations, linked to the meteorological conditions, ranging from 15.9 (8 March cruise) to 17.0°C (6 April cruise). In the stations I-3, G-1 and the H transect the observed higher temperatures are imputable to the

cooling water coming from a petrochemical plant located in the south-west coast of the bay. The same temperature increment had been already observed during the 1989-90 cruises, with a ΔT between northern and southern waters of 2°C.

Salinity appears constant with a high increment from March to April of 0.2 psu, caused by superficial evaporation. As reported (Talassographic Reports, 1992), the maximum value is normally attained in August (38.5 psu).

Dissolved oxygen ranges between 4.5 (6 April cruise) and 5.7 ml/l (24 March cruise), corresponding to a saturation of 83 and 106% respectively. Even if these values have been measured in the surface layer which equilibrate with atmospheric oxygen, we have not observed any phenomena linked to strong biological activities as hypoxia and supersaturation previously reported (Genovese, 1974; Magazzù, 1977).

Nutrients: NH_4 , NO_2 , NO_3 , PO_4 (Table 1). Concentration of nutrients, particularly of PO_4 , appears quite low and comparable to the levels normally registered in Sicilian coast waters. The comparison with the most recent data (Azzaro, 1993) confirms the trend observed in recent years, i.e. a drastic reduction of the PO_4 load present in the "Rada". The highest value, 0.26 $\mu\text{M/l}$ P- PO_4 , has been measured in the zone influenced by urban waste waters, while in the areas affected by the industrial sewages (south and west coast of the bay) the concentration of PO_4 appears very limited (0.1 $\mu\text{M/l}$ or less).

The principal mechanism of soluble PO_4 removal is probably represented by autotrophic processes, promoted by a phytoplankton biomass reaching, in this period (March-April), 2.5 $\mu\text{g/l}$ Chl α (Decembrini *et al.*, 1993). A further contribution to the lowering of the PO_4 level in the Rada (22 $\mu\text{M/l}$ in 1971, 12 $\mu\text{M/l}$ in 1982, 2 $\mu\text{M/l}$ in 1983, 1 $\mu\text{M/l}$ 1989) originates from the industrial waters treatments which have been applied beginning from 1982.

The level of inorganic N is much more consistent and is related to the NH_4 concentration ranging from 0.1 to 14.6 $\mu\text{M/l}$ N- NH_4 , while NO_2 and NO_3 distribution does not exceed the value of 4 $\mu\text{M/l}$ with an average value for the three cruise of 1.5 $\mu\text{M/l}$.

The lack of balance in the concentration of N and P salts is evidenced by the very high values of N/P ratio (Table 1), which in the last two cruises averaged 200. This result is not attributable to biological activity or to the modest reduction of PO_4 in the last two cruises, but is essentially due to the increment of NH_4 salts. Figures 2, 3 and 4 show localized increments in the proximity of the industrial areas and in zones subjected to urban wastes.

Indexes of chemical pollution: ABS, BiAS, DDPH (Table 1). Ionic synthetic detergents show a high level of concentration with a minimum of 11 $\mu\text{g/l}$ and maximum of 190 $\mu\text{g/l}$ for ABS.

The highest concentration for all the cruise has been measured in the C, D, and H transects, the first two situated around the town of Augusta and the third one located in the meridional part of the bay (Figs 2, 3 and 4), corresponding to the cooling water effluent coming from a big petrochemical plant. The BiAS level appears relatively high, principally in the northern area of the bay which is influenced by urban waste waters (Figs 2, 3 and 4).

The BiAS/ABS ratio points out that the highest contribution of non ionic detergents derives from urban activities: in fact their distribution in the southern part of the bay, particularly influenced by industrial discharges, is characterized by a BiAS/ABS ratio < 1.

The concentration of aromatic hydrocarbons ranges from 0 to 96.6 $\mu\text{g/l}$ with an average of 10.8 $\mu\text{g/l}$ as chrysene equivalents. The patterns of distribution, reproduced in Figs 2, 3 and 4, show the highest concentrations, characterized by strong gradients, in the central and the southern areas (E, H, transects), along the west coast (III cruise) and in front of Augusta town (II cruise).

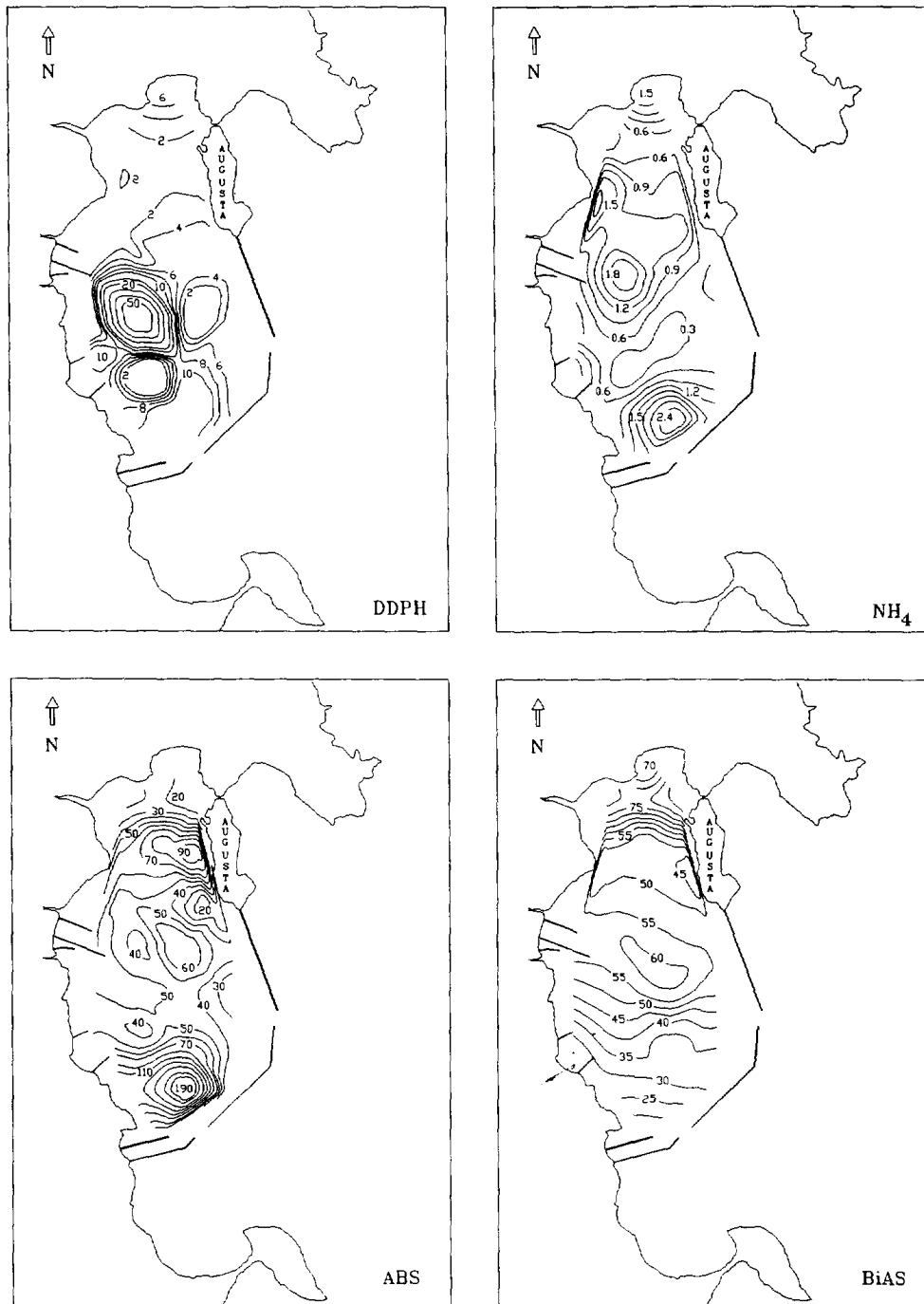


Figure 2. Distribution of NH₄ (µM/l), ABS, BiAS, DDPH (µg/l) in surface layer (03-08-94).



Figure 3. Distribution of NH₄ ($\mu\text{M/l}$), ABS, BiAS, DDPH ($\mu\text{g/l}$) in surface layer (03-24-94).

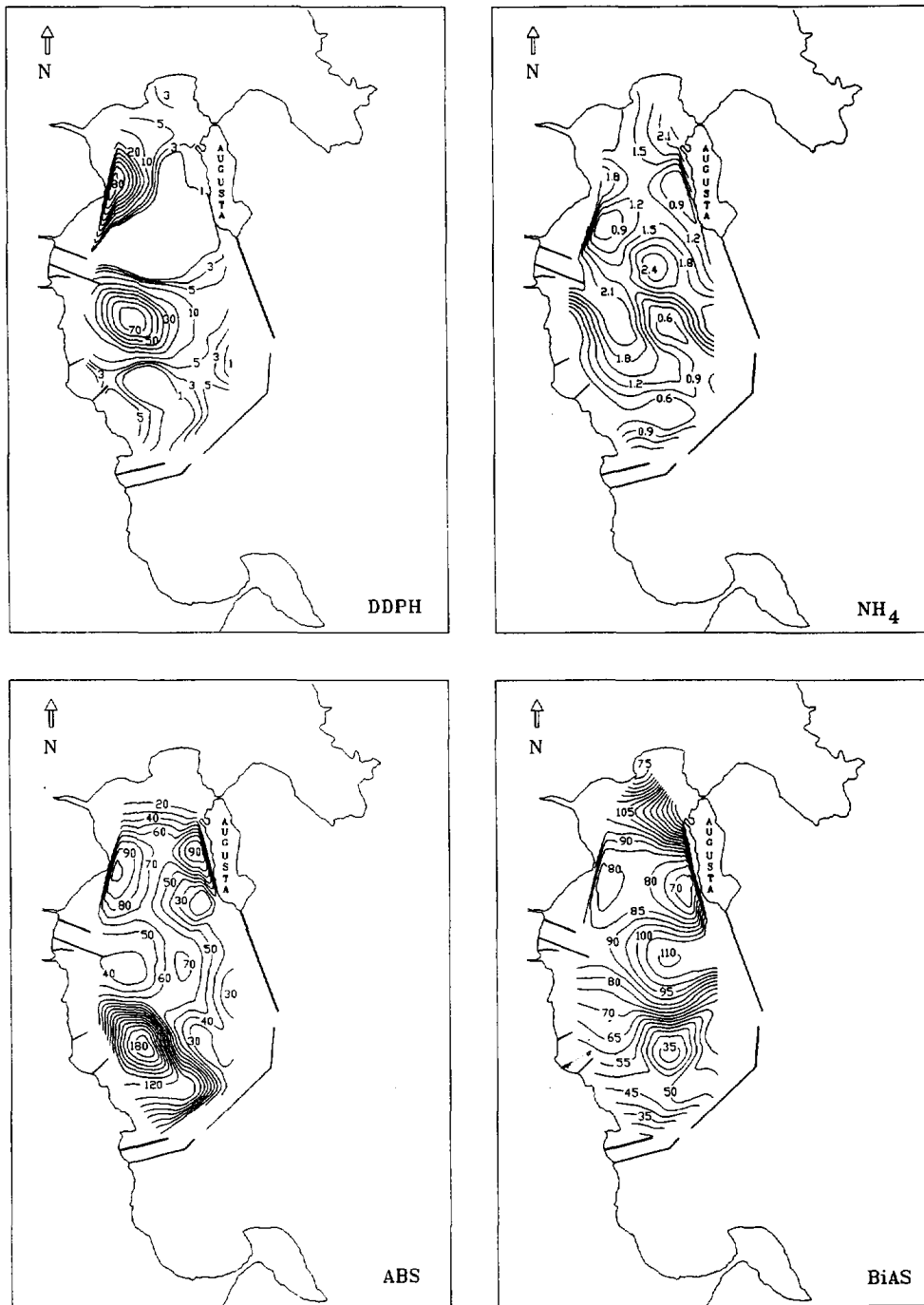


Figure 4. Distribution of NH_4 ($\mu\text{M/l}$), ABS, BiAS, DDPH ($\mu\text{g/l}$) in surface layer (04-06-94).

The comparison with the already reported data (Crisafi *et al.*, 1993), collected in 1990-91, actually indicates a big increment of DDPH which exceeds by more than 5 times the concentration level observed in those years: the previously determined maximum value (20 µg/l) is now dramatically increased to 96.6 µg/l.

The obtained results clearly indicate that the aromatic hydrocarbons distribution is characterized by an extreme spatial and temporal variability. These features are linked to localized spills and to the prevalent winds which determine surface currents and the consequent transport of the oil residues towards the meridional part of the bay.

It is important to point out that through the small southern opening off the bay only little water can flow out and oil therefore remains enclosed within the artificial barrier.

CONCLUSIONS

All the measured parameters, compared with the literature data for the last 5 years, are clear evidence that the waters of the "Rada di Augusta" had undergone a sharp improvement concerning the trophic levels.

Since 1985, in fact, the eutrophication phenomena, which in the seventies and early eighties caused frequent dystrophic crises and fish deaths, have not been observed.

The PO₄ load of the last 5 years has remained very low as well as the NO₂ and NO₃. However, NH₄ concentrations remain at a high level with supplies located in the urban discharges (northern part of the bay) as well as in the industrial ones (west coast, southern area).

The obtained results can be rationalized on the basis of the consideration that the improvement of the trophic conditions, such as the dramatic lowering of PO₄ from 22 to 0.1-0.2 µM/l, can be essentially ascribed both to the working (starting from 1982) of urban and industrial sewage plants and of a submarine outfall.

However, parallel improvement has been not verified for chemical pollutants, particularly DDPH, whose distribution is increasing mainly because of the localized spills and the action of the winds which determine water circulation inside the bay and the observed superficial distribution.

Surfactants come both from the urban and industrial wastes (ABS), while BiAS predominates in the northern part of the bay as a consequence of urban loads. This trend confirms the present important role of BiAS in urban effluents with respect to the traditionally used ABS.

REFERENCES

- Andreoli, C., Ferlito, V., Geraci, C., Guglielmo, L., Magazzù, G., Nicoletti, G. and Zerbo, G. (1986-87). Ciclo annuale di osservazioni chimico-fisiche e biologiche in un ambiente costiero eutrofizzato. *Mem. Biol. Mar. Ocean*, **16**, 49-77.
- Azzaro, F. (1993). Concentrazione di nutrienti nella Rada di Augusta (Sicilia). *Atti I Workshop. Risorsa mare: un progetto per il Mezzogiorno. Salvaguardia e valorizzazione delle acque costiere del Salento*. Lecce 8 Luglio 1991, 93-108.
- Crisafi, E. (1993). Esperienze di monitoraggio della qualità delle acque della Rada di Augusta. *Atti I Workshop. Risorsa Mare: un progetto per il Mezzogiorno. Salvaguardia e valorizzazione delle acque costiere del Salento*. Lecce 8 Luglio 1991, 75-91.
- Crisafi, E., De Domenico, L., Magazzù, G. and Puglisi, A. (1993). Pollution by hydrocarbons and monitoring in the Augusta Bay. *Conference proceedings. Clean Seas 93*. 9-11 November 1993, Valletta, Malta.
- Decembrini, F., Azzaro, F. and Magazzù, G. (1993). Studio delle condizioni trofiche della Rada di Augusta per il monitoraggio automatico dei fenomeni di eutrofizzazione. *Atti I Workshop. Risorsa mare: un progetto per il Mezzogiorno. Salvaguardia e valorizzazione delle acque costiere del Salento*. Lecce 8 Luglio 1991, 109-127.
- De Domenico, L., Crisafi, E., Magazzù, G., Puglisi, A. and La Rosa, A. (1994). Monitoring of Petroleum hydrocarbon pollution in surface waters by a direct comparison of fluorescence spectroscopy and remote sensing techniques. *Mar. Pollut. Bull.*, **10**, 587-591.
- Genovese, S. (1974). Relazione su un fenomeno di mare sporco verificatosi nel settembre del 1974 nello specchio d'acqua antistante lo stabilimento petrolchimico SINCAT di Priolo (Augusta). Unpublished ms.
- IRSA-CNR (1973). Metodi analitici per le acque, 11, II.
- IRSA-CNR (1979). Tensioattivi non ionici etossilati, E-013.

- IRSA-CNR (1983). Metodi di analisi per acque di mare. *Quaderni*, 59.
- Magazzù, G. (1977). Rapporti sui risultati delle ricerche svolte nella Rada di Augusta in occasione dei fenomeni verificatosi nel settembre 1977. Technical Report, *Staz. Biol. Mar. Univ. Messina* Unpublished ms.
- Marsili, M. (1982). Conoscenza e prevenzione dell'inquinamento nella Rada di Augusta e nelle coste della Sicilia sud-orientale. *Inquinamento*, 5, 73-78.
- Strickland, J. F. H. and Parsons, T. R. (1972). A practical handbook of sea water analysis. *Bull. Fish Res. Bd. Can.*, 167, 1-311.
- Talassographic Reports (1992). Sistema integrato per il monitoraggio automatico della Rada di Augusta, 6, 1-120.
- UNESCO-IOC (1976). Guide to operational Procedures for the IGOSS Pilot Project on Marine Pollution (Petroleum) Monitoring. *Manuals and Guides*, 7, Paris.