COPPER MINE TAILING DISPOSAL IN NORTHERN CHILE ROCKY SHORES: ENTEROMORPHA COMPRESSA (CHLOROPHYTA) AS A SENTINEL SPECIES

JUAN C. CASTILLA

Estaci6n Costera de Investigaciones Marinas, Las Cruces, Facultad de Ciencias Biol6gicas, P. Universidad Cat6lica de Chile, Casilla 114, D. Santiago, Chile

(Received: June 1995; revised: July 1995)

Abstract. The study assesses the ecological impact caused by the El Salvador untreated (1975-1990) and treated (1991-1994) copper mine tailings on rocky intertidal communities in and around the dumping site at Caleta Palito, northern Chile. Ecological changes are monitored for 16 years in polluted and unpolluted sites within a geographical area of 90 km. Copper concentration levels in water and the intertidal Chlorophyta *E. compressa are* presented. The results confirm a notorious reduction in the number of species and significant differences between polluted and unpolluted intertidal communities. At polluted sites, following the initiation of the disposal, all species of invertebrates and algae disappeared and primary space (rock) was partially or completely dominated by *E. compressa* along more than a decade. Its persistence in these sites supports the view that this taxon is a sentinel species resisting high levels of copper pollution. During the past four years, following the steps given to treat the tallings, at polluted sites there are preliminary indications showing increases in the number of species of algae and invertebrate. The need for future monitoring to elucidate ecosystem restoration processes is discussed.

Introduction

In Chile most of the copper mines are located in the central and northern Andes mountains. Ore extraction, milling, processing and tailing dumping operations normally take place around the mine pits. Exceptionally, however, copper tailing disposal occurs in coastal areas. This was the case of Potrerillos (1938-1958) and E1 Salvador (1959-1975) copper mines, located in the Third Region of Chile. E1 Salvador (26 $^{\circ}$ 14' S; 69 $^{\circ}$ 37' W) operates at 2400-2600 m above sea level and is located 120 km east of the coastal city of Chafiaral (Castilla, 1975; Castilla and Nealler, 1978). For 32 years (1938–1975) the untreated copper mine tailings (solids, water and chemicals) were routed to the Salado River bed and disposed directly onto the sandy beach of Chañaral Bay (26° 15' S; 69° 34' W). The river received an additional series of industrial (small-scale copper and gold operations) and urban waste waters.

In February 1975 the disposal sea site at Chafiaral was moved about 8 km North, to a rocky beach known as Caleta Palito (Castilla and Nealler, 1978). This site received the copper tailings directly onto the rocky intertidal and operated until February 1990. Based on the values for daily solid dumpings reported by Castilla (1983) 126- 150 million tons of solids were discharged at Caleta Palito between 1975-1990. According to unpublished information (CODELCO 1985), the tailing water contained 6000-7000 μ g L⁻¹ of total copper.

In March 1990, and as a consequence of an Appeal for Protection, the Chilean Supreme Court (Asenjo 1989, Appeal for Protection, July 28, 1988), ruled against the El Salvador mine and the disposal of untreated tailing wastes was banned. E1 Salvador was compelled to build a tailing settling pond. This was done at Pampa Austral, a deserted area near the town of Diego de Almagro (26° $23'$ S; 70° $02'$ W). The so-called "aguas claras de relave" or "clear tailing water" originated at the settling pond has been legally channeled back to the bed of the Salado River and disposed at Caleta Palito since 1991. According to the present regulations "clear water" must contain less than 2000 μ g L⁻¹ of total copper.

Although there are several unpublished reports related to the embankments and navigational problems caused by the E1 Salvador tailings dumped at Chafiaral Bay (Mission Laboratoire Central d'Hidaulique de France, 1962; Beauchesne, 1963; Rubio, 1968, 1970; Corniquel, 1969; Asenjo, 1989), only five studies have dealt with the environmental coastal impact produced by these gigantic disposals. Castilla and Nealler (1978) highlighted their ecological effects on marine (i.e. benthos and fish) subtidal nearshore coastal communities. Castilla (1983) and Paskoff and Petiet (1990) reported about the ecological impact of the tailings on the invertebrate macrofauna inhabiting sandy beaches and on coastal progradation (i.e. the creation of artificial sandy-copper tailing beaches) at Chafiaral Bay and Caleta Palito. Vermeer and Castilla (1989, 1991) reported on copper and cadmium residues found on beach deposits, marine intertidal (rocky and sandy beaches) biota and marine birds, both at impacted coastal sites, as well as distant or less impacted localities.

In spite of the existing literature, published information regarding heavy metal concentrations in coastal or oceanic waters in the geographical area impacted by the El Salvador tailing disposal is scarce (but see: Comité Ciudadano de Chañaral 1993). Therefore, chemical aspects of pollution and the degree and extension of impacted coastal areas or oceanic waters can not be thoroughly assessed. So far, most of the environmental impact reported, as due to the copper tailing disposal, is referred to the solid coastal deposits (Castilla 1983) or focused on the contents of copper residues found in beach deposits and coastal biota (Vermeer and Castilla, 1989, 1991).

The aim of this paper is to assess the ecological impact observed in rocky intertidal environments in and around Caleta Palito along nearly 16 years (1975- 1990) during which the dumping of untreated copper tailings of E1 Salvador and other waste water occurred. Changes will be compared to those observed in the past 4 years (1991-1994) following the cessation of E1 Salvador untreated waste dumping and the beginning of the "clear tailing water" disposal.

The study focuses mainly on the monitoring of the intertidal alga *Enteromorpha compressa* (Chlorophyta) at rocky intertidal, impacted and non-impacted (= control), sites within a geographical coastal area extending about 90 km. Different

Fig. 1. Shoreline sampling sites between Puerto Pan de Azúcar and Caleta Zenteno.

species of the genus *Enteromorpha* have been singled out as sentinels or indicator organisms for qualitative and quantitative studies related to copper and other heavy metal coastal pollution (Seeliger and Cordazzo, 1982; Kapraun, 1970; Wallner *et al.,* 1986 a,b; Francke and Hillbrand, 1980; Seeliger and Wallner, 1988). Contrary to other sentinel species, *Enteromorpha* shows high resistance to copper pollution (Foster, 1977; Reed and Moffat, 1983; Vermeer and Castilla, 1989, 1991).

Material and **Methods**

STUDY SITES AND FIELD OBSERVATIONS

In January 1975, following the initiation of El Salvador copper tailing dumping at Caleta Palito (Castilla and Nealler, 1978), 4 rocky intertidal sites (Figure 1, sites 1-4) exposed directly to wave action were selected to monitor changes associated with the dumping. Three to four vertical intertidal walls, 70° to 85° steep and 2.5-3.0 m in height, were selected at each site. These walls were marked and the occurring communities characterized. Three intertidal fringes (Castilla, 1981) were distinguished: a) a lower fringe, comprising 60-70 cm at the bottom of the walls, b) a mid-fringe 150-160 cm in width and c) and upper fringe, 80-100 cm in width. These habitats, specially the mid-fringe, were monitored 12 times between January 1975 and July 1994, usually during summer and early autumn (December-April). In 1985 a fifth site was incorporated to the program (Figure 1, site 5) and monitored 6 times between 1985 and 1994.

Puerto Pan de Azúcar (site 1), Caleta La Lancha (site 2) and Caleta Agua Hedionda (site 3) are 24, 7 and 2,5 km north from the disposal point at Caleta Palito (site 4) respectively. Caleta Zenteno (site 5), is 68 km south from Caleta Palito. The polluted sites 2, 3 and 4 are located in an open natural bay, between Cerro Castilla in the north and Punta Achurra in the south (Figure 1). Sites 1 and 5 were considered as control due to the distance from the disposal site and to evidences from the literature indicating absence or reduced copper enrichment (Vermeer and Castilla, 1989, 1991).

The first visit to the sites was in March 1975, one week after the dumping started at Caleta Palito. Subsequently, eight visits were made between 1976 and 1988, during the period of untreated cooper mine tailing disposal. The last three visits occurred between 1990 and 1994, during the period of"clear tailing water" disposal. Data acquisition was achieved mainly by color slide photographing (Foster *et al.,* 1991) of the whole intertidal vertical extension of each monitored wall during low spring neap diurnal tides. In northern Chile tides are semi diurnal and show a maximum range of 1.8 m. For quantification the slides were projected and the total surface covered by either organisms or bare rock was estimated by drawings followed by the use of a planimeter (Ushikata, model 220 L). A particular effort was placed in the mid-intertidal fringe (Castilla, 1981), where the percentage cover of sessile organisms present in a 1 m^2 was determined. A two-way Analysis of Variance (ANOVA) and an *a posteriori* Bonferroni test ($\alpha = 0.05$) were used to assess differences between polluted and control sites regarding both sessile communities and primary space. The analysis was done using a SAS statistical package (version 6.1).

When more than 50% of the intertidal fringe under analysis was covered by *Enteromorpha compressa* it was considered that the algae had formed an "intertidal band" and its vertical extension was measured to the nearest centimeter.

TABLE I

Beach deposits, *Enteromorpha compressa* and copper concentrations according to Vermeer and Castilla (1989, 1991) and present study

(1) Samples collected in 1981 and 1982. Flameless Atomic Absorption analytical method. Vermeer and Castilla (1989, 1991).

(2) Samples collected in August 1994; Anodic Stripping Voltametry analytical method. (3) Samples collected in August 1994, filtered through 0.45 μ (dissolved copper); Anodic Stripping Voltametry analytical method.

(4) Concentration of dissolved copper at the mouth of the Salado River disposal canal reaching Caleta Palito: 2410; 2390 μ g L⁻¹. Samples collected in August 1994 and filtered through 0.45 μ (dissolved copper). Anodic Stripping Voltametry analytical method.

Based on *in situ* observations, a list was made containing all sessile and mobile species found at each wall along the study sites. For the purpose of this study a species was considered "present" if it was observed at least in 5 opportunities during the 12 visits (1975-1994); otherwise it was considered "absent".

SAMPLING AND ANALYTICAL METHODS

 $(\mu \varrho \varrho^{-1})$, wet weight) (1) *Enteromorpha compressa* $(\mu g g^{-1}, dry weight)$ (2)

Intertidal seawater μ g L⁻¹ (3, 4)

In August 1994 water samples were collected for analysis of dissolved copper at the mouth of the Salado River disposal canal reaching Caleta Palito $(N = 2)$; from the intertidal, 50 m south from the disposal canal $(N = 2)$ and from the intertidal at Caleta Zenteno $(N = 2)$. Samples were collected in 1 liter non-scrap plastic bottles treated with nitric acid (EPA 1976), filtered through 0.45 μ m Sartorius membrane filters and fixed by adding 0.5 mL of concentrated nitric acid (Merck supra pur) to 500 mL of the filtered fraction. Dissolved copper was quantified by Potentiometric Stripping analysis in stationary solution, using a computerized Radiometer ISS 820 analyzer.

Simultaneously, samples of *E. compressa* were collected in acid-clean plastic bags and treated with nitric acid. Copper was quantified based on dry material

71.8 2.1 54.9 1.9

31.8 3.4 26.8 2.9

(UNEP, 1984) in a GBC 909 PBT Atomic Absorption Spectrophotometer. An atom trap mode was used to improve the sensitivity when metal concentrations were low. Copper certified standards were run simultaneously to the water and tissue samples. Standards were CASS-2 for water and DOLT-1 for algal tissue. The standards were provided by the National Research Council of Canada, Division of Chemistry, Marine Analytical Chemistry Standards Program.

Sampling and analytical methods to determine copper concentration in *Enteromorpha* and beach sediments in the study area during 1981-1982 were reported elsewhere (Vermeer and Castilla, 1989; 1991).

Results

Table I summarizes previous and present results on the copper levels in four of the sites studied. In 1981 and 1982, (Vermeer and Castilla, 1989; 1991) time at which the E1 Salvador untreated copper tailings were being dumped at Palito, beach deposits presented the highest copper levels (5000 μ g g⁻¹) followed by Caleta La Lancha (813 μ g g⁻¹), Puerto Pan de Azúcar (231 μ g g⁻¹) and Caleta Zenteno $(5.8 \text{ }\mu\text{g g}^{-1})$. A similar trend is observed regarding the concentration of copper in *Enteromorpha* sp.(= *E.compressa),* with the highest concentrations reported in plants from Caleta Palito (1260 μ g g⁻¹ wet weight) and from Caleta La Lancha (197 μ g g⁻¹ wet weight). The lowest value of copper was detected at Zenteno (0.8) μ g g⁻¹ wet weight), a control site.

In 1994, four years after the El Salvador untreated copper tailing dumping ended, copper concentration in *Enteromorpha* plants from Palito ranged from 54.9 to 71.8 μ g g⁻¹ dry weight and from 1.9 to 2.1 μ g g⁻¹ dry weight (about 30 times less) in plants from Caleta Zenteno.

Water samples collected in 1994 at the mouth of the disposal canal showed a dissolved copper concentration of 2390-2410 μ g L⁻¹. Intertidal water samples taken 50 m from the canal mouth showed concentrations of dissolved copper ranging from 26.8 to 31.8 μ g L⁻¹, about 10 times higher than those found at Caleta Zenteno, where values of copper were 2.9 and 3.4 μ g L⁻¹ (Table I).

Mid-intertidal sessile communities and primary space (grouped as shown in Table II) were not significantly different ($F = 1.03$, $p = 0.3871$) regarding the four sites sampled early in 1975. The barnacles *Jehlius cirratus* and *Chthamalus scabrosus* were the main sessile organisms. The Chlorophyta *E. compressa* showed cover values lower than 4% and did not form bands at any of the sampled sites. This pattern persisted throughout the study at Puerto Pan de Azúcar and Caleta Zenteno. By the contrary, the intertidal sites heavily impacted by the untreated cooper tailings showed dramatic modifications in the structure of their mid-intertidal sessile communities. In a short period of time (1 to 2 years) the species of invertebrates disappeared and the primary space was partially or completely dominated by E. *compressa.* Highly significant differences were found in the structure of the mid-

ther sessile species (= O) and rock or primary substrate (= *R*) at the five sites studied. Caleta Zenteno and Puerto Pan de Azúcar other sessile species $(= 0)$ and rock or primary substrate $(= R)$ at the five sites studied. Caleta Zenteno and Puerto Pan de Azúcar Percentage intertidal cover of *Enteromorpha compressa (= E);* barnacles (= *B: Jehlius cirratus* and *Chthamalus scabrosus);* Percentage intertidal cover of Enteromorpha compressa $(= E)$; barnacles $(= B$: Jehlius cirratus and Chthamalus scabrosus);

are control sites. Caleta Palito, Caleta Agua Hedionda and Caleta La Lancha are impacted ones are control sites. Caleta Palito, Caleta Agua Hedionda and Caleta La Lancha are impacted ones

OCKY SUODE CODDED TAILING DISDOSAL

TABLE III

List of species 'present' and 'absent'. Presence assessed at the studied sites by at least five consecutive of non/consecutive observations along the nearly 20 years monitoring period

(*) Observed in 1990, 1991, 1993 and 1994.

Fig. 2. Intertidal extension of bands of *Enteromorpha compressa*, from the lower to the upper fringe, at Caleta La Lancha, between 1975 (no band formation, see arrow) and 1994.

intertidal community (Table II) between the polluted and control sites $(F = 21.94$, $p = 0.0001$ for 1981; F = 182.5, $p = 0.0001$ for 1985, and F = 6.44, $p = 0.001$ for 1994). Furthermore, *E. compressa* also dominated most of the low-intertidal fringe at the polluted sites (see Caleta La Lancha, Figure 2), a situation never observed at the control sites.

Following the cessation of dumping of untreated tailings in March 1990, a dramatic ecological change occurred at Caleta Palito. By February 1991 all the intertidal rocks (vertical walls and platforms) about 100 m around the disposal site acquired a brown-reddish coloration and the existing *E. compressa* population disappeared. The same phenomenon was observed in August 1994. A few months later, following these events, the population of E. *compressa* returned to its previous status as a dominant taxa (Figure 3).

Since 1990 and following the end of the untreated tailing dumpings at Palito, a slow re-establishment of intertidal species in the polluted sites is becoming apparent. Table HI shows a list of species "present" and "absent" from the three intertidal fringes of the monitored sites throughout the study. The control sites show a higher number of taxa $(30 - 32)$ in comparison to the few species occurring at the three polluted sites. The algal species recorded at the polluted sites include the chlorophycean *E. compressa, the* phaeophycean *Petalonia fascia and Scytosiphon lomentaria* and the rhodophycean *Hildenbrandtia lacanelleri and Ceramium* sp. *Collisella araucana* was the only invertebrate recorded during the surveys.

Fig. 3. Percentage cover of *Enteromorpha compressa,* in the mid-intertidal fringe at the three polluted sites between 1975 and 1994. 1) Initiation of untreated tailings disposal at Caleta Palito. 2) Intertidal rocks covered by tailing sediments. 3) Cessation of untreated tailings disposal at Caleta Palito. 4) Eradication of *Enteromorpha compressa* due to an extreme pollution event. Bars represent standard errors.

Discussion

Numerous marine coastal pollution effects are related to sea dumping of copper mine tailing or industrial mine wastes which may result in turbidity, smothering, coastal embankments, beach progradation and contamination of beach deposits (Ellis, 1987). In addition, fauna, flora or both can be affected by heavy metals (Ellis, 1987; Vermeer and Castilla, 1989, 1991). The occurrence of all of these effects at Chafiaral Bay and Caleta Palito, as a consequence of solid and liquid waste disposals, have been reported during the past thirty years (Mission Laboratoire d' Hidraulique de France, 1962; Castilla and Nealler, 1978; Paskoff and Petiot, 1990; present paper).

Levels of copper over 1000 μ g g⁻¹ dry weight in marine sediments are normally associated with mine waste discharges (Moore and Ramamoorthy, 1984). This is consistent with the published data (Vermeer and Castilla, 1989, 1991) from Caleta Palito. Furthermore, copper concentration in sea water from Caleta Palito detected during 1994 and compared to that of Caleta Zenteno confirm the high degree of copper enrichment still present (Table I).

Chlorophycean algae (i.e. *Ulva, Enteromorpha)* have been widely used as indicator species resisting high concentrations of heavy metals in coastal and estuarine environments (Seeliger and Cordazzo, 1982; Kapraund, 1970; Ott, 1972; Moss and Woodhead, 1975; Seeliger and Edwards, 1977; Ho, 1987, 1990). Further, it has been shown that filamentous Chlorophyta, such as *Enteromorpha,* display capabilities to exclude heavy metals, particularly copper, from their tissues (Foster, 1977; Reed and Moffat, 1983). Vermeer and Castilla (1989, 1991) reported that *Enteromorpha* sp. (= *Enteromorpha compressa)* was the only sessile aquatic alga inhabiting the copper-enriched intertidal rocky shores at Caleta Palito. They showed the existence of high concentrations of copper (1260 μ g g⁻¹ wet weight) and cadmium (Vermeer and Castilla, 1991) in *Enteromorpha* samples obtained from Palito. This copper concentration is the highest reported in the literature for the genus *Enteromor*pha (Seeliger and Cordazzo, 1982; Reed and Moffat, 1983; Castagna *et at.,* 1985; Ho, 1987; Ganesan *et al.,* 1991; Munda and Hudnik, 1991). Nevertheless, it must be pointed out that the samples of *Enteromorpha* taken from Palito by Vermeer and Castilla (1989, 1991) occurred in heavily copper (pyrite) enriched sea waters. Pyrite particles adhered to *Enteromorpha* cell walls could have accounted for the unusually high concentration of copper reported by these authors.

On the other hand, the 1994 *E. compressa* copper concentrations values (Table I) in plants from Palito are within the higher and those in plants from Zenteno within the lower reported for that genus (Seeliger and Cordazzo, 1982; Ho 1987).

The results confirm the negative impact caused by the dumping of El Salvador tailings on the intertidal communities. The persistence and dominance at the contaminated sites of *Enteromorpha compressa* supports the view of this taxon as a sentinel species able to resist high levels of copper pollution. Under the polluted conditions in and around Caleta Palito the species not only increased in density but expanded its vertical distribution along the lower and mid-intertidal rocky shore domain (Figure 2). Further, this impact seems to persist today, in spite of the steps taken to treat the tailings.

This bears important ecological significance as the polluted intertidal sites could be considered equivalent to a long-term removal of grazer and sessile competitors. Under these circumstances *E. compressa* expanded notoriously its vertical intertidal distribution and becomes the dominant species. This occurred exclusively at the polluted sites and during more than a decade, but not at the control sites. These arguments stress the relevance of biotic factors (i.e. competition, predation) as determinants of the patterns of vertical distribution and abundance of an ephemeral species (Castilla, 1981).

In the past 4 years the E1 Salvador effluent consists mainly of the so called clear tailing waters and their solids have been almost completely eliminated. In spite of

this, the concentration of dissolved copper reaching Caleta Palito is rather high, with values around 2400 μ g L⁻¹. This is due not only to the El Salvador clear tailing water, but also to small-scale mining operation wastes draining along the Salado River. At particular times these operations can produce intensive pollution pulses, affecting the coastal communities.

The 1990-1994 scenario opens a possibility to study long-term changes in the intertidal and shallow subtidal coastal ecosystems impacted by the treated tailing and compare them with previous impacts. For example, it is encouraging to observe that during the past four years both at Caleta Palito and at La Lancha, for the first time in more than 14 years, 4 species of algae other than *Enteromorpha* have been recorded (Table III). Whether this is a first sign of the ecosystem restoration or not remains to be elucidated. Restoring damaged ecosystems is one of the modern branches of ecology, needing more detailed studies (Cairns, 1989).

Undoubtedly, in the case of Chafiaral Bay and Caleta Palito a much satisfactory scenario will be to follow coastal ecosystem restoration processes under a total lack of pollution. To achieve this a comprehensive de-contamination program, including all sources of heavy metals and domestic waste pollution sources along the Salado River, should be implemented.

Acknowledgements

The author acknowledges field assistant during the monitoring given by E. Nealler, C. Espoz, D. Oliva, S. Miethke, J. Correa, J. Mufioz and C. Pacheco. The paper was concluded in 1994 with financial support from contract Centro de Investigaciones Minero Metalúrgicas (CIMM) No 119406: COPPER-ALGAE INTERAC-TIONS, to Dr. J. Correa, Pontificia Universidad Cat61ica de Chile, Departamento de Ecologia. I also thank E. Rho, J. Correa, I. Meneses and an anonymous referee for revising early versions of the manuscript and suggesting important modifications.

References

- Appeal for Protection. Supreme Court, Chile: 1988, 'Pedro Flores et al. v. CODELCO, División Salvador'. vol 12, 753. (Translated: *George Town International Environment Law Review* 1989. 2: 251-269).
- Asenjo, R.: 1989, 'Innovative Environmental Litigation in Chile: The Case of Chafiaral', *George Town International Environmental Law Review* 2, 99-110.
- Beauchesne, P.: 1963, 'Estudios en Chañaral de las Animas'. Santiago, Dirección de Obras Portuarias.
- Cairns, J.C.: 1989, 'Restoring Damaged Ecosystems: Is Predisturbance Condition a Viable Option'? *The Environmental Professional* 11, 152-159.
- Castagna, A., Sinatra, F., Castagna, G., Stoli, A. and Zafarana, S.: 1985, 'Trace Elements Evaluations in Marine Organisms', *Marine Pollution Bull.* 16(10), 416-419.
- Castilla, J.C.: 1975, 'Problemática General de la Contaminación Marina en Chile: Evaluación, Estudios y Perspectivas', Primer Congreso Iberoamericano del Medio Ambiente, Centro de Estudios del Medio Ambiente, 12-18 Octubre, Madrid, España, pp. 724-6748.
- Castilla, J.C.: 1981, 'Perspectivas de Investigación en Estructura y Dinámica de Comunidades Intermareales Rocosas de Chile Central. II Depredadores de Alto Nivel Tr6fico', *Medio Ambiente 5,* 190-215.
- Castilla, J.C.: 1983, 'Environmental Impact in Sandy Beaches of Copper Mine Tailings at Chafiaral, Chile', *Marine Pollution Bull.* 14(12), 459-464.
- Castilla, J.C. and Nealler, E.: 1978, 'Marine Environmental Impact Due to Mining Activities of E1 Salvador Copper Mine, Chile', *Marine Pollution Bull.* 9(3), 67-70.
- Comit6 Ciudadano de Chafiaral: 1993, 'La Contaminaci6n de Chafiaral: Chafiaral, Lecci6n de Nunca Más'.Téngase Presente, Corte de Apelaciones de Copiapó, Chile, Agosto 1993, 32pp.
- Corniquel, L.: 1969, 'Embancamiento Puerto de Chafiaral', Unpublished report.
- Ellis, D.W.:1987, 'A Decade of Environmental Impact Assessment at Marine and Coastal Mines', *Marine Pollution Bull.* 6, 385-417.
- EPA: 1976, 'Manual de Métodos para el Análisis Químico de Agua y Desechos. EPA Report/625/6-76/003a. 434pp.
- Foster, EL.: 1977, 'Copper Exclusion as a Mechanism of Heavy Metal Tolerance in a Green Algae', *Nature* 269, 322-323.
- Foster, M.S., Harrold, C. and Hardin, D.D.: 1991, 'Point vs. Photo Quadrant on the Cover of Sessile Marine Organisms', J. *exp. Mar. Biol. Ecol.* 146, 193-203.
- Francke, J.A. and Hillbrand, H.: 1980, 'Effects of Copper on Some Filamentous Chlorophyta', *Aquatic Biology* 285-289.
- Ganesan, M., Kannan, R., Rajendran, K., Govindasamy, C., Sampathkumar, E and Kannan, L.: 1991, 'Trace Metals Distribution in Seaweeds of the Gulf of Mannar, Bay of Bengal', *Marine Pollution Bull.* 22(4), 205-207.
- Ho, Y.B.: 1987, 'Metals in 19 Intertidal Macroalgae in Hong Kong Waters', *Marine Pollution Bull.* 18(10), 564-566.
- Ho, Y.B.: 1990, *'Ulva lactuca* as Bioindicator of Metal Contamination in Intertidal Waters in Hong Kong', *Hydrobiologia* 203, 73-81.
- Kapraun, D.E: 1970, 'Field and Cultural Studies of *Ulva* and *Enteromorpha* in the Vicinity of Port Aransas, Texas', *Contr. Mar. Sci. Univ. Tex.* 15, 206-285.
- Mission Laboratoire d' Hidraulique de France: 1962, 'Embancamiento de la Bahia de Chafiaral', unpublished Report.
- Moore, J.W. and Ramamoorthy, S.: 1984, 'Heavy Metals in Natural Waters', Springer-Verlag.
- Moss, B. and Woodhead, E: 1975, 'The Effect of Two Commercial Herbicides on the Settlement, Germination and Growth of *Enteromorpha', Marine Pollution Bulletin* 6, 189-192.
- Munda, I.M. and Hudnik, V.: 1991, 'Trace Metals Content in Some Seaweeds from Northern Adriatic',Botanica *Marina 34,* 241-249.
- Ott, ED.: 1972, 'Macroalgae of Chesapeake Bay', *Chesapeake Sci. Supp.* 13, 83-84.
- Paskoff, R. and Petiot, R.: 1990, 'Coastal Progradation as a By-product of Human Activity: An Example from Chafiaral Bay, Atacama Desert, Chile', J. *Coastal Research* Special Issue 6, 91-102.
- Reed, R.H. and Moffat, L.: 1983, 'Copper Toxicity and Copper Tolerance in *Enteromorpha compressa* (L.) Gev', J. *Exp. MarBiol. Ecol.* 69, 85-103.
- Rubio, H.: 1968, ' Embancamiento de la Bahia de Chafiaral', unpublished Report.
- Rubio, H.: 1970, ' Embancamiento de la Bahia de Chafiaral. Proyecto Nuevo Canal de Relave', unpublished Report.
- Seeliger, U. and Wallner, M.: 1988, 'Multispecies Metal Monitoring in Tropical Brazilian Estuaries', in: U. Seeliger, L.D. Lacerda and S.R. Patchineelam (eds.), *Metals in Coastal Environments of* Latin America, Springer-Verlag.
- Seeliger, U. and Cordazzo, C.: 1982 'Field and Experimental Evaluation of *Enteromorpha* as a Quali-quantitative Monitoring Organism for Copper and Mercury in Estuaries', *Environmental Pollution* 29, 197-206.
- Seeliger, U. and Edwards, E: 1977, 'Correlation Coefficients and Concentration Factors of Copper and Lead in Seawater and Benthic Algae', *Marine Pollution Bull* 8, 16-9.
- UNEP: 1984, 'Sampling of Selected Marine Organisms and Sample Preparation for Trace Metals Analysis', *Reference Methods for Marine Pollution Studies* 7, Rev. 2.
- Vermeer, K. and Castilla, J.C.: 1989, 'Trace Metals in the Marine Bird Food Chain Downstream from the E1 Salvador Copper Mine, Chile', *Technical Report Series* No. 83, Canadian Wildlife Service, Pacific and Yukon Region, British Columbia.
- Vermeer, K. and Castilla, J.C.: 1991, 'High Cadmium Residues Observed During a Pilot Study in Shorebirds and Their Prey Downstream from E1 Salvador Copper Mine, Chile', *Bull Environ. Contam. Toxicol.* 46, 242-248.
- Wallner, M. Seeliger, U. and Liberal da Silva, R.: 1986a, 'Monitoramento de Metais Pesados Cu, Zn, Cd, e Pb, no Canal de Santa Cruz, Utilizando a Macroalga *Enteromorpha* sp.', *Ciencia e Cultura* 38(11), 1884-1889.
- Wallner, M. Seeliger, U., Texeira, V.L., Joventino, EP. and Silva S.C.: 1986b, 'Variacioes Regionais na Concentracao de Metais Pesados na Macroalga *Enteromorpha* sp. dos Estuarios do Rio Ceará (Ceará), Lagoa de Mundaú (Alagoas) e Lagoa da Tijuca (Rio de Janeiro)', *Arq. Cien. Mar.* 25, 41-50.