POTENTIAL ENVIRONMENTAL HAZARDS FROM THE VOLATILE ORGANIC EMISSIONS OF THE GREEN ALGAE *ULVA RIGIDA* AND *ENTEROMORPHA INTESTINALIS*

Vassilios ROUSSIS[1], Heleni CABERI[2], Michael SCOULLOS[2]

[1] NCSR "Demokritos", Institute of Biology, Agh. Paraskevi, 153 10, Greece
[2] University of Athens, Department of Chemistry, Environmental Chemistry and Chemical Oceanography, Panepistimiopolis Athens, 157 01, Greece

The oceans, besides their most important function which is the regulation of the global climate through both physicochemical and biological processes, produce a third to half of the global oxygen supply and help in the regulation of the primary greenhouse gas, carbon dioxide, by the mechanism known as the biological pump (WEBER, 1994). Scientific interest has increasingly been turning to the sea in search for medical cures and unique compounds. Marine life, a relatively unstudied frontier, has produced antileukemia drugs from sea sponges, bone graft material from corals, diagnostic chemicals from red algae and many other useful agents (KHOL, 1993; HODGSON, 1991). But the treasury of the oceans might never been fully exploited since the flow of nutrients into oceans has at least doubled since prehistoric times and sediments have nearly tripled as a result of human activity (UNEP, 1992). The recently introduced pollutants degrade estuaries and coastal waters by blocking sunlight, suffocating fish and coastal habitats and importing pathogens and toxins. They have also contributed to the increased incidence of algal blooms that release deadly toxicants into the surrounding waters (YASUMOTO & MURATA, 1993).

The cosmopolitan green algae *Ulva rigida* and *Enteromorpha intestinalis* are among the most commonly found marine organisms in polluted and eutrophicated ecosystems. The population density of these aggressive macroalgae can reach excessive levels especially during the summer months (HO, 1981). All around the Mediterranean basin the wave-protected coastal areas are facing seasonal blooms of these intertidal species. In continuation of our program aiming at the evaluation of the impact these algal blooms might have at their immediate habitat, we focused our recent efforts on the identification of the volatile secondary metabolites produced by *U. rigida* and *E. intestinalis*. In the past we studied the composition of the non-volatile metabolites of *U. rigida*, as well as the variation of the chemical profile when the organism is stressed, exposed to increased concentrations of heavy metals (SCOULLOS *et al.*, 1992).

The intense odour of *U. rigida* and *E. intestinalis* and the precedence of harmful volatile emissions from other marine organisms (MANLEY *et al.*, 1992; GSCHWEND *et al.*,1985) were the main reasons that intrigued us to analyze the composition of the volatile chemicals of these macroalgae. Both species were collected from the gulf of Elefsis and the experiments were performed in the laboratory under simulated natural conditions (temperature, photoperiod, medium). The algae were placed in air-tight fiberglass containers and the air of the system was recycled for 24 hrs via a membrane pump. The volatile organic metabolites were trapped in glass traps loaded with surface active polymers. The experiment was repeated with sea water from the same area in the absence of algae, to determine whether the detected chemicals were true volatile metabolites of the algae or contaminants of the water. The quantification and identification of the volatile constituents were performed by Gas Chromatography and Gas Chromatography-Mass Spectrometry analyses. The results of the experiments revealed that significant amounts of low molecular weight halogenated and non halogenated hydrocarbons are produced and liberated, by the algae, at the atmosphere during their life cycle. Besides the head-space analyses, quantities of the algae were subjected to steam distillation-extraction (Likens Nickerson method) (GODEFROOT *et al.*, 1981) for the quantitative determination of the total volatile chemical content of the organisms. Many of these chemicals were found to be oxygenated water-soluble hydrocarbons, that most probably are liberated from the algae in the water. Eventhough the percentages of the most harmful secondary metabolites within the total emitted chemicals have been determined, precise calculation of the actual amounts of these metabolites per Kg of biomass need to be performed so that it would be possible to assess if these notorious to the stratospheric ozone layer chemicals constitute an alarming factor.

Some Volatile Metabolites of *U. rigida* and *E. intestinalis*.

Hydrocarbons :
Pentane Octane 1,2 Dimethyl cyclopentane Decane
Oxygenated Hydrocarbons :
Hexanal Heptanol 2-Ethyl hexanol Nonanal
Aromatic Hydrocarbons :
Toluene Benzaldehyde
Halogenated Hydrocarbons :
Dichloromethane Tribromomethane
Sulfur containing Metabolites :
Dimethyl sulfide

ACKNOWLEDGMENTS

The financial support of the project was provided from the Ministry of Research and Technology under the form of a PENED programme

REFERENCES

WEBER P., State of the World 1994 (Safeguarding Oceans) 1994, p. 41, Earthscan Publications Ltd, London.

KOHL J. The Ocean's Bounty : Untapped Pharmacy, Currents (Woods Hole Oceanographic Institution, Woods Hole Mass.) Spring 1993.

HODGSON G., Drugs from the Sea, 1991, *Far Eastern Economic Review*, 11.

Marine Pollution from Land-based Sources : Facts and Figures (January/June 1992), UNEP Industry and Environment.

YASUMOTO T., MURATA M., 1993, Marine toxins. *Chem. Rev.*, 93 :1897.

HO Y.B., 1981, Mineral element content in *Ulva lactuca* with reference to eutrophication in the Hong Kong coastal waters, *Hydrobiologia*, 77 : 43.

SCOULLOS M.J., CABERI H., ROUSSIS V., 1992, Effects of cadmium on the physiology and chemical composition of the green algae *Ulva rigida* (C. Ag.), *Rapp. Comm. Int. Me Medit.*, 33 : 183.

MANLEY S.L., GOODWIN K., NORTH W.J., Laboratory production of bromoform, methylene bromide and methyl iodide by macroalgae and distribution in nearshore southern California waters. *Limnol. Oceanog.*, 37 : 1652.

GSCHWEND P.M., MACFARLANE J.K., NEWMAN K.A., 1985, Volatile halogenated organic compounds released to seawater from temperate marine macroalgae, *Science*, 227 : 1033.

GODEFROOT M., SANDRA P., VERZELE., 1981, New method for quantitative essential oil.