NUTRIENT AND METAL BEHAVIOUR IN THE MEDITERRANEAN SEA, DEDUCED FROM BOX-MODEL

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In the Mediterranean Sea, the succession of deep inner basins, filled with homogeneous dense waters, facilitates budgets of chemical elements, including natural and anthropogenic inputs from Atlantic, atmospheric and terrestrial sources and transfer processes. In the frame of GECDYME (GEOchemistry and DYnamics of the MEditerranean, a Mast II/MTP sub-project) and of its preliminary studies, box-models were used to quantify the external inputs of nutrients and trace-metal and the marine transfers via biological activity: marine dynamics and cedimentation. The the marine transfers via biological activity, marine dynamics and sedimentation. The used circulation scheme was based on heat, water and salt budgets (BETHOUX, 1980) and improved by results from geochemical tracers such as tritium, oxygen and trace metal (BETHOUX, 1989; RUIZ-PINO *et al.*, 1990, 1991). At a basin scale, it gives horizontal and vertical motions which are not open to direct measurement and not yet estimated by general circulation models (GCM). In winter, vertical transfers are increased by dense water formations in the Levantine Basin, Aegean and Adriatic Seas and in the northern part of the Western Basin. In other seasons, biological activity is the main factor influencing the vertical transfer of matter from the surface to the deep waters. At a basin scale, new production may be estimated from nutrient or oxygen budgets (e.g. BETHOUX, 1989) or from satellite imagery when sea surface colour is converted into biological production and when the f ratio (new versus total production ratio) is known (e.g. MOREL and ANDRE, 1991). Dense water formation and intense horizontal and vertical circulations give a quite short recidence time of done water in the Alexen economic horizon (bet 10 to 15 mm). residence time of deep water in the Algero-provençal basin (about 10 to 15 years) and, in the surface layer, water movements and biological transfers give a residence time of a few years. These short residence times favor the detection of changes in the physical and chemical characteristics of sea water and the monitoring of the environmental changes. Effectively, in the Western Mediterranean, evolutions of deep-water concentrations (phosphate and nitrate data) or comparison of surface and deep comparison of surface and the monitoring of the environmental transmission (phosphate and nitrate data) or comparison of surface and the environmental deep comparison of surface and the environmental data and the environmental d deep concentrations (trace metal), quite different from those encountered in the great oceans, obliged to consider non-steady-state behaviour and allowed to quantify changes in the Mediterranean environment, at yearly time scale and basin scale. Such a monitoring, from marine measurements, of an evolutive environment is quite a peculiarity and an advantage of the Mediterranean Sea.

The increases of deep-water concentrations prove that the anthropogenic inputs from terrestrial and atmospheric sources definitively exceed the Antlantic and natural inputs. As a result from a six-box model, the measured increases of phosphate and nitrate in deep western water, at rates of about 0.5% a year since the early sixties, is converted into an increase of anthropogenic inputs at a rate of about 3% a year. The probable consequences are: i) an increase of biological production in surface and probable consequences are: i) an increase of biological production in surface and coastal waters, ii) an increase of oxygen consumption in deep water for the remineralization of the settling organic matter. From trace metal data, input increasing rates were estimated equal to about 6% a year for zinc and 2% a year for cadmium and copper (BETHOUX *et al.*, 1990; 1992; RUIZ-PINO *et al.*, 1991). Such environmental changes of inputs may be compared with some socio-economic data of the known evolution of the Mediterranean countries (increases in inhabitants, in mean gross national product, in energy consumption, as compiled by UNEP, 1988). Moreover, the six-box model allowed to simulate the surface water change of lead concentration from 1983 to 1993. The simulation of atmospheric input of lead was provided by lead consumption in gazoline, the biological transfer was summarized by new production and trace metal concentration in phytoplankton, the residence time of lead in the surface layer (0-100m depth) was about 1 year, and the sedimentation buried about 50% of the incoming lead (NICOLAS *et al.*, 1994). From phosphate and nitrate budgets at basin scale, three questions are arising, concerning processes at biological cell or molecular scales. The first one concerns

the phosphate input, as riverine input of phosphate only represents about 25% of the the phosphate input, as riverine input of phosphate only represents about 25% of the estimated terrestrial inputs. Consequently, the major input of useful phosphorus is the particulate fraction which is dissolved as emphasized by FROELICH (1988) in the estuaries or in the plume rivers. But redissolution processes are badly known at the land-river-sea interfaces. The second question concerns the nitrate budget, the main input of nitrate probably comes from the biological uptake of atmospheric nitrogen, a non quantified process from quite unknown bacterioplankton species (BETHOUX *et al.*, 1992). The third question is the use of the specific signature of N/P molar ratio of about 22 in the Mediterranean, instead of about 16 (the so-called "REDFIELD ratio") in the great oceans, which may be a constraint for the Mediterranean ecosystem. New technics such as organic pigments and flow cytometry may give a new picture of the ecosystem and new constraints for the modelling of biogeochemical cycles.

cytometry may give a new picture of the ecosystem and new constraints for the modelling of biogeochemical cycles. Concerning trace metals, progress in clear sampling and analytical method allows to propose budgets of dissolved and particulate matters. In spite of the first attempt to describe biological transfers of trace metals through new production (i.e. BETHOUX et al., 1990), respective implications for this transfer and for biological activity depend of the chemical speciation of bioactive trace-metals. All these questions are arising from box-model studies at a basin scale, but box-models cannot give solution for problems earling at small scales of time and space. for problems acting at small scales of time and space.

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The role of upper ocean biochemical processes in determining the basic trophic kinetics and distribution is deeply connected with the dynamical processes that determine the physical forcings active at the biological scales. The seasonal signal of the lower trophic level evolution in the Mediterranean Sea is reproduced by means of a trophodynamic model representing the aggregated nitrogen cycle in oligotrophic conditions. The total nitrogen, divided in inorganic nitrogen, phytoplankton and detritus, maintains the numerical conservativeness of the scheme described in CRISE *et al.* (1992), but includes exchanges at the Gibraltar Strait, because of the nitrogen and phytoplankton relaxation to climatological profiles in the transition zone between the Alboran Sea and the Atlantic Ocean all along the simulation.

between the Alboran Sea and the Atlantic Ocean all along the simulation. Limiting factors of the phytoplankton growth are the sea temperature, the irradiance and the available nutrient. The limiting factors are all considered to be depth dependent, and are respectively represented by the STEELE (1962), the EPPLEY (1972) and Michaelis-Menten uptake formulations. The hydrodinamical horizontal processes that affect the biogeochemical state variables are explicitly taken into account, as well as the vertical dynamics governed by advection- diffusion processes and the convective adjustments. For this purpose, the ecomodel is tightly coupled with the hydrodynamics simulation as developed in the frame of MERMAIDS project by PINARDI *et al.* (1993). This MOM based general circulation model has a 1/4 degree horizontal grid size and 31 vertical levels. The dynamical forcing terms used are the NMC winds, the COADS monthly mean clouds maps and the heat fluxes as in CASTELLARI *et al.* (1993). Even with a highly aggregated ecomodel, the seasonal cycle exibits a marked variability induced principally by the horizontal advective forcing. To study this effect on the ecomodel, the basic experiment considers the light as constant all over the basin varying only in time on an astronomical base. Two as constant all over the basin varying only in time on an astronomical base. Two significant examples are shown to confirm the above statements. The differences in tracer concentration are all due to the internal dynamics, because the inorganic nitrogen and phytoplankton are initialized with the same climatological profiles in the whole Mediterranean. The hydrodynamical model is spinned up for eight years and the presented results were obtained in the second year of the ecological model run.

The inorganic nitrogen (full) and the phytoplankton (dashed) concentrations, all in micromoles Nitrogen per liter, are presented in two typical stations, the first in the Catalan-Algerian Basin and the second in the Ionian Sea. Salinity (full) and temperature (dashed) variability slightly affects the inorganic nitrogen distibution below the euphotic zone,

> 0.200 1-

> > 109

250

showing instead a stronger seasonal signal in the first hundred meters. After an initial period of mixing mainly due to convective adjustment, temperature and salinity exhibit the typical late spring-summer stratification, preventing the exchange of upper layer. The phytoplankon response to the higher irradiance and relatively abundant nitrates decreases in April showing a well shaped subsurface maximum in late summer. This second maximum is enhanced by the low salinity Modified Atlantic Water. In the Ionian Sea station the wind stirring creates an homogeneous phytoplankton maximum all along the water column even below the euphotic zone. The stratification is evident during the summer and early autumn and creates an isopycnal barrier with the surface layer. The anticyclonic regime of the northern Ionian is stronger in summer affecting progressively the inorganic nitrogen concentration below 150 meters. This effect is masked in the physical tracers and the intrusion of less salty water does not seem to influence the trophic dynamics. In winter, the progressive mixing of the upper layer creates again the homogeneous conditions typical of the beginnnig of the cycle.

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In. Nitrogen-Phyto - St.6E 39N

Solinity-Temperature - St.6E 39N



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