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

J.-P. BETHOUX and D. RUIZ-PINO

LPCM, Université Paris 6, CNRS/INSU, BP8, F06230 Villefranche/Mer, France

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 GEODYME (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 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 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 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 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 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.

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 acting at small scales of time and space.

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