

## Seasonal cycles of pH and carbonate system parameters in the southern Adriatic Sea during one year of VECTOR project

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Within the VECTOR project (activity 8.1.2) the pH and other physical chemical parameters were acquired as seasonal time series from September 2007 to June 2008, at the AM1 station (in the centre of the Southern Adriatic Pit). The pH was measured by the spectrophotometric method (precision  $\pm$  0.003) and the results expressed on "total scale" at 25°C (pH<sub>T</sub>@25°C). In a few seasons also the total alkalinity  $(A_T)$  was measured by potentiometric titration at 25°C (precision  $\pm 3$ µmol/kg) and the results were checked against sea water certified as reference material (by dr. A.G. Dickson). The other derived parameters of the carbonate system (pCO<sub>2</sub>, DIC,  $\Omega_{Ar}$ ,  $\Omega_{Ca}$ ) were computed from pH, TA, salinity, temperature, SiO<sub>2</sub>, PO<sub>4</sub> according to Lewis and Wallace 98.

The pH seasonal variability was the highest in the upper layer (0-100 m), as clearly recognizable in fig 1a, b being the pH value mainly driven by biology during the productive seasons (from spring to late summer) or by mixing with deeper waters and exchange processes with atmosphere in winter. In the deeper layers (intermediate and bottom) the seasonal variability was lower but not negligible, probably driven by remineralization processes of dissolved and particulate organic matter locally produced, as suggested by Apparent Oxygen Utilization (AOU) and nitrate seasonal variabilities (fig. 1c, d, e, f).

Generally, the highest differences of physical and biogeochemical properties can be observed in both the upper (0-100m) and the intermediate (100-800 m) layers in September and June whereas during wintry season (January and February) variabilities were much lower. Through early to late summer season, the nutrients pH and dissolved inorganic

carbon (TCO<sub>2</sub>) all suggest that both layers are strongly affected by biology (quite active primary production in the upper layer although in general the region has to be considered oligotrophic, and remineralisation processes in the intermediate layer). As confirmed by the good correlation with AOU and fluorescence. The vertical variabilities of such parameters are large, representing the 28 %, 0.4 %, -115 % of the total amount. Narrower changes can be observed passing from the intermediate to the bottom layer (800 - bottom) in January, February and June. A good correlation between changes of nutrients, pH, carbonate system and AOU is still observed, indicating the significant contribution of remineralisation processes to the final values.

The physical and biogeochemical differences between the intermediate and the bottom layer further suggest that water masses of different origin filled these two layers. The persistence of inter layers variability through the year might suggest the absence of any abrupt change in the circulation scheme.

The three forms of carbon dioxide in seawater  $(TCO_2 \text{ aq}, HCO_3, CO_3^{=})$  and the saturation states of calcite and aragonite were computed, from the experimental measures of pH and total alkalinity (reported in table 1) along the water column, in February June and October 2008. Values at surface show to be higher than the surface values of other oceanic regions, this is due to the higher alkalinity of the Mediterranean Sea, thus confirming peculiar characteristics of the carbonate system and the good saturation states of the Med Sea and southern Adriatic sea in particular.