Biogeochemical Processes in Coastal Lagoons: from Chemical Reactions to Ecosystem Functions and Properties

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Anthropogenic disturbances and natural factors often cause unpredictable non-linear responses in coastal lagoons. Important changes include the shift from seagrass to ephemeral seaweed communities, especially in sheltered habitats (Castel *et al.*, 1996). Here, biogeochemical reactions are related to primary production and decomposition processes and depend upon bioturbation by benthic fauna. Scaling up, the network of these components and reactions can be regarded as an ecosystem property which accounts for oxygen availability and for potential buffering functions - e.g. phosphate retention within the sediment, immobilisation of sulphides into the insoluble iron mono-sulphide and release of molecular nitrogen to the atmosphere (Golterman, 1995; de Wit *et al.*, 2001).

The net ecosystem metabolism basically results from primary production and microbial processes. At a first glance, it can be estimated with a simple mass balance of water, C, N and P and stoichiometric relationships, e.g. with the LOICZ biogeochemical model (Gordon *et al.*, 1996). Suitable descriptions of the ecosystem metabolism and its consequences are usually achieved with measurements of oxygen fluxes and processing over time and space (Viaroli & Christian, 2003 and references therein). Furthermore, the extent of oxygen production and consumption is given by an index resulting from the relationship between net maximum productivity, measured at saturating light, and dark respiration of the community (Fig. 1). The categorical classification of this index from autotrophy to heterotrophy provides a rapid assessment of the potential oxygen balance. It can also discriminate among different photoautotrophic conditions, including hyperautotrophy, as an abnormal oxygen production with respect to the biomass build up, and dystrophy, as the subsequent abnormal oxygen deficit which causes prolonged anoxia and the onset of anaerobic metabolism.

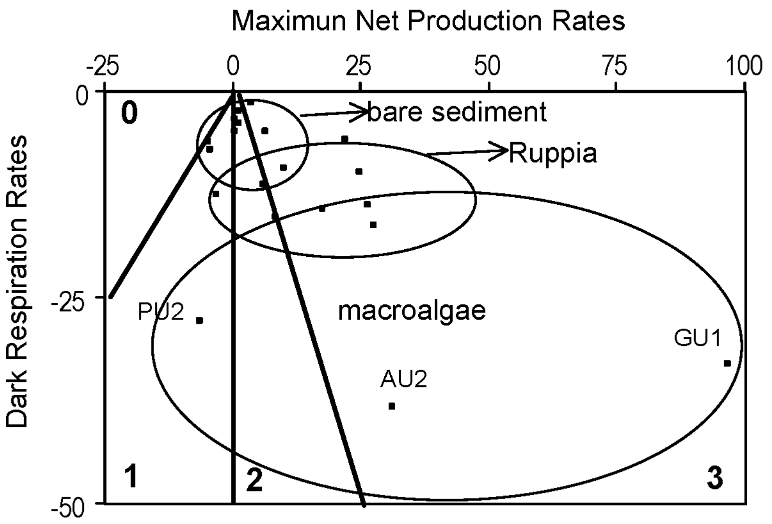

Figure 1. *Representation of ecosystem metabolism with a trophic oxygen status index for lagoon with different benthic vegetation communities. Numbers represent the ecosystem metabolism categories with 0 = totally heterotrophic, 1 = net heterotrophic, 2 = net autotrophic, 3 = totally autotrophic. Units: mmol* O_2 *m^{-2} h^{-1}. For more details see Viaroli & Christian (2003).*

The presence of labile organic matter combined with anoxia stimulates bacterial sulfate reduction, resulting in the production of toxic sulphide. Reactions of sulphide with iron represent an efficient buffering mechanism, which removes sulphide as insoluble FeS and FeS_2 (Heijs *et al.*, 2000; Azzoni *et al.* 2001; de Wit *et al.* 2001). The potential sedimentary buffering capacity of iron is usually assessed by determining reactive iron and its degree of pyritisation (Rozan *et al.*, 2002). To a first approximation, the buffering capacity of iron can be also estimated with the reactive Fe(II) to AVS ratio, with AVS (acid volatile sulphide) representing the iron quota precipitated as FeS (Viaroli *et al.*, 2004).

Phosphorus speciation depends mostly on reactions with calcium, carbonates, iron, aluminium, and humic compounds. Reactions of the calcium-carbonate-phosphate system control the formation of stable P-species and their strong retention within the sediment, whilst the iron hydroxide-phosphate-sulphide system has a weaker buffering capacity and regulates the short term cycling of phosphates (Golterman, 1995, Heijs *et al.*, 2000; Rozan *et al.*, 2002). Under oxic conditions reactive phosphorus is sequestered in different ways by ferric iron, e.g. through adsorption onto FeOOH, as Fe-P complexes, etc. Under persistent anoxic conditions the reduction of ferric iron favours Fe solubilisation with the concurrent phosphate release. The formation of the insoluble FeS and FeS_2 results in a drastic decrease of the P-retention capacity. Overall, iron-sulphur-phosphorus interactions may determine positive feedbacks for benthic vegetation, favouring the disappearance of phanerogams and the development of bloom forming macroalgae (see Heijs *et al.*, 2000; Rozan *et al.*, 2002 and references therein).

Nitrogen transformations within the lagoon ecosystems are primarily processed by benthic vegetation and microbial processes (Bartoli *et al.*, 2001), but are highly dependent on the element speciation (Herbert, 1999). In turn, nitrogen speciation is controlled by oxygen availability, and the different nitrogen species have different fates and follow different biogeochemical pathways. Benthic macrophytes take up and retain nitrogen at different degrees, depending on their life cycles and tissue recalcitrance. Usually, seagrass species tend to store nitrogen keeping at low levels benthic fluxes of ammonium and nitrate, as well as denitrification rates. By contrast, bloom forming seaweeds can induce wide pulses in nitrogen fluxes within the lagoon ecosystem. Benthic microalgae have a great influence on oxygen penetration and nitrogen transformations at the sediment-water interface, within a submillimetric sedimentary horizon. Here, the form in which N is returned to the water column is highly dependent upon oxygen availability.

Under oxic conditions ammonium can be oxidised to nitrate through bacterial nitrification. Part of this nitrate which diffuses to anoxic zones can be reduced to ammonium (dissimilatory nitrate reduction to ammonium-DNRA) or denitrified to gaseous N_2 and N_2O, which are eliminated from the system (Herbert, 1999 and reference therein).

A tentative summary of essential elements and components, and associated properties and functions is reported in Table 1 (for details see Viaroli *et al.*, 2004 and references cited therein). A synthetic description of the most relevant properties depending on the different benthic vegetation types is also given in Table 2. Overall, we suggest that benthic vegetation, oxygen metabolism and coarse sedimentary biogeochemical indicators are sufficiently informative to be used for assessing environmental quality and to identify ecosystem properties and functions of coastal lagoons.

Table 1. *Identification of essential quality elements and associated ecosystem properties and function for coastal lagoons. OM: organic matter, NP: net production rates of oxygen at saturating light (ecosystem level); DR: dark respiration rates of oxygen (ecosystem level); AVS: acid volatile sulphides (FeS and dissolved sulphides).*

Quality element	**Associated properties/functions**
Benthic vegetation	Oxygen release, OM production, nutrient sink, sediment stability
NP versus DR	Ecosystem metabolism and stability
Sedimentary OM	Tendency of the system to consume oxygen and produce sulphides. Rates of oxygen uptake and sulphide production will depend upon OM lability
Sedimentary Reactive Iron	Buffering capacity towards sulphide and phosphate (weak)
Sedimentary AVS	Saturation degree of the buffering capacity towards sulphides
Sedimentary Carbonates	Buffering capacity towards phosphorus (strong)

Table 2. *Ecosystem properties and functions associated to the different benthic vegetation types of coastal lagoons*

	Microphytobenthos	**Seaweeds**	**Seagrasses**
Oxygen	Diffusion in the water mass and in the sediment	Stratification with surface rich water and bottom deficit. Pulsed availability	Oxygenation of the water mass. Radial loss by roots (ROL) in the sediment
Sulphide	Accumulation in the sediment	Production during biomass decomposing. Release into the water mass, dystrophy	Well buffered (depends on health status of vegetation)
Nitrogen	Losses due to coupled nitrification-denitrification	Pulsed assimilation and sudden release. Low denitrification	Retention by macrophyte biomass. Negligible denitrification

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