

Biogeochemical indicators as tools for assessing sediment quality/vulnerability in transitional aquatic ecosystems

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ABSTRACT

1. We review the major variables that can be used to monitor sediment characteristics and benthic processes in transitional water bodies with respect to ecological significance, cost/time demands, method consensus, and uncertainty of the current techniques.

2. Most of the state variables, namely organic matter, total nitrogen and phosphorus contents, are easily determined at low monetary/time cost using standardized techniques. However, they are not sufficiently informative to be used as individual-specific indicators.

3. The speciation analysis of nitrogen, phosphorus, iron and reduced sulphur provides much more precise information on the sedimentary buffering capacity. However, analytical techniques are cost/time expensive and often present some critical step, which biases their generalized application.

4. A good understanding of sedimentary processes can also be achieved by measuring benthic fluxes and process rates, but analytical techniques are too expensive to be applied in conventional monitoring programmes.

5. A tentative integrated index, based on a few low-cost simple measures of sediment characteristics (granulometry, organic matter, carbonates, reactive iron and acid volatile sulphides) is proposed, which, in parallel with the water retention time, could provide a rapid assessment of sediment vulnerability status.

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KEY WORDS: sediment monitoring; state variables; benthic fluxes; process rates; integrated index

INTRODUCTION AND AIMS

Transitional waters suffer a number of environmental problems that primarily can be attributed to an excess of organic matter and nutrient inputs from the watershed (National Research Council, 2000). Further impacts are related to the human exploitation of the aquatic environment (e.g. such as tourism,

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waterways and ports) and of biological resources (e.g. aquaculture and fish farming) (Karakassis *et al.*, 2000).

Transitional aquatic ecosystems are generally shallow and have high sediment-surface-area to water-volume ratios. Therefore, processes occurring within the sediment and at the water-sediment interface can strongly influence both water quality and the biota (Borum, 1996; Castel *et al.*, 1996; Jørgensen, 1996). Consequently, coastal sediments can play an important regulatory function for the whole ecosystem, through their storage and renewal capacity for organic matter (OM) and nutrients, and the reactivity of biogeochemical buffers, such as the iron-iron monosulphide-pyrite and the calcium-carbonate-phosphate systems (Golterman, 1995; Jørgensen, 1996; De Wit *et al.*, 2001). OM enrichment affects nutrient fluxes and the balance between oxic and anoxic metabolisms, resulting in the migration of the oxic-anoxic interface towards the sediment surface (Santschi *et al.*, 1990). Therefore, the sediments and their resident benthic communities can be considered as the most sensitive part of the transitional aquatic environment and as triggers for processes in the water column. Nevertheless, despite the importance of the sediment compartment, the monitoring efforts of national and local administrations are mostly targeted on water quality and specific aquatic populations/taxa, whilst sediment characteristics and benthic biological variables and processes are mostly neglected. Even when considered, sediment monitoring is often focused on simple variables that are not always best suited for addressing key issues. Often, only certain specific pollutants are considered in order to assess the ecotoxicological risk. For example, the Italian law on water protection (Dlgs. 152/99) focuses mostly on indicators of water quality; sediment analyses are proposed only as additional or optional measures to detect specific contaminants, which are supposed to occur due to human activities. Specific programmes addressing the need to develop recommendations for potentially useful indicators of benthic health have recently been initiated by the Intergovernmental Oceanographic Commission (IOC) of UNESCO with the formation of the IOC Study Group on Benthic Indicators (<http://www.ioc.unesco.org/benthicindicators>), and a preliminary list of indicators for assessing the state (or 'health') of benthic communities has been proposed (Hyland *et al.*, 2000). In addition, test data sets containing synoptic information on benthic faunal condition (e.g. measures of community composition), controlling natural abiotic factors (e.g. sediment OM), and levels of contaminants and other anthropogenic stressors in sediments have been obtained for coastal regions worldwide to look for consistent patterns of response in selected indicators.

Tentative guidelines have also been proposed in the frameworks of national programmes (e.g. MacDonald *et al.*, 1996; Christensen, 1998) and detailed studies on sedimentary biogeochemical processes and related indicators conducted within the European Land Ocean Interactions Studies (ELOISE) Network (e.g. Dalsgaard *et al.*, 2000; De Wit *et al.*, 2001; Herman *et al.*, 2001).

In this paper we review the major parameters/variables that could be used to monitor sediment characteristics and benthic processes in transitional water bodies. Measurements of state variables, speciation of the main nutrients and key elements, fluxes and rates are discussed with respect to their ecological significance, cost/time demands, method consensus and uncertainty of the current techniques. Finally, we present a tentative integrated index, based on a few low-cost simple measures of sediment characteristics, that could provide a rapid assessment of sediment vulnerability status. Here, we do not implicitly consider specific impacts of organic and inorganic pollutants, as such studies belong to the field ecotoxicology.

STATE VARIABLES

A list of the major state variables that can be considered for sediment monitoring is given in Table 1.

Variable	C	C/ TC	U/ MC	Ecological significance
Granulometry	H	L	L/H	Sediment structure
Water content	H	L	L/H	Sediment structure
Porosity	L	L	L/H	Sediment packing, influence on diffusion
Bulk density	L	L	L/H	Sediment age, packing, influence on diffusion
pH	H	L	I/H	Acid-base equilibria in the aqueous solution
Redox potential	H	L	I/H	Equilibria of the redox pairs
Oxygen profiles	L	H/I	I/H	Oxygen availability for chemical and biological reactions. Oxic-anoxic gradients
OM	H	L	L/H	Organic enrichment
	L	H	H/L	Potentially high biodegradability, high SOD
	L	H	H/L	Potentially low biodegradability, sediment stability, low SOD
Nitrogen	H	L	L/H	Total storage
	H	L	L/H	Organic N deposition/burial
	L	H	H/I	Potential N availability to the water
Exchangeable NH ₄	L	H	I/I	Oxidation status of the N compounds, N availability to the water column,
Pore water:				potential occurrence of microbial processes, e.g. nitrification, denitrification
Nitrate				
Nitrite				
Ammonium				
DON				
Phosphorus	H	L	L/H	Total storage
	H	L	L/H	Organic P deposition/burial
	L	H	H/L	Strong retention of P by sediments
	L	H	H/L	Weak retention of P by sediments
	L	H	I/I	Potential P availability to the water
	L	H	I/I	P availability to the water
SRP				
DOP				
	L	H	L/H	Redox conditions, potential sedimentary buffering capacity against sulphides,
Iron				regulation of the P cycling
	L	H	L/H	
	L	H	L/H	Reducing power, sulphide trapped by iron (weak)
Sulphur	L	H	L/H	Reducing power, sulphide trapped by iron (strong)
	L	H	I/H	Potential risk for the aquatic biota, potential dystrophy

Sediment structure and general characteristics

Granulometry, bulk density, dry matter, water content and porosity provide basic information on sediment composition. They are important determinants of diffusive properties and, therefore, of exchanges of oxygen and nutrients with the water column. Sediment composition also influences the capacity of the sediment to retain inorganic ammonium and phosphate within exchangeable pools associated with ion-exchange sites on the particle surfaces. Simple and standardized techniques are available (see Dalsgaard *et al.* (2000) and references cited therein) and adopted with a general consensus; they are not expensive, even though they are relatively time consuming.

OM and nutrients

The OM content of the sediment results from the difference between inputs (benthic primary production and sedimentation) and community respiration. Analytical methods for determining sediment total OM content are based on both wet and dry oxidative techniques (see Froelich (1980) and references cited therein). Since sediment OM is the fuel for both aerobic and anaerobic metabolisms, total OM can be thought of as representing potential metabolism; however, the degree to which this potential is realized depends upon the composition of the OM pool, as this determines both the nutritive quality of OM for the benthic fauna and the degradability of the OM for microorganisms (Mann, 1988). The overall degradability of sedimentary OM can be assessed directly by respirometric techniques, by determining benthic dark oxygen or CO₂ fluxes (see below), or indirectly by molecular analyses of the OM pools (Fabiano *et al.*, 1995) or its elemental (C:N:P) ratio (Enriquez *et al.*, 1993). Similarly, modelling studies have emphasized the role of OM quality and its depth distribution in the sediment as major factors regulating overall benthic metabolism and nutrient cycling (Fenchel *et al.*, 1998). The use of OM levels in the surface sediments as an indicator of the risk of species diversity reduction in benthic macrofaunal communities has recently been assessed by the IOC Study Group on Benthic Indicators. As a general pattern, OM at low concentrations can be a limiting resource for benthic animal communities. Increasing sedimentary OM content supplies more energy to benthic consumers, but also stimulates sediment oxygen demand (SOD). Above certain OM thresholds, the oxygen demand for bacterial respiration and the reoxidation of the products of anaerobic respiration become critical. These induce hypoxia or anoxia at the water–sediment interface and/or the accumulation of toxic reduced compounds in the surficial sediments, which negatively affect benthic animal communities (Figure 1). Thus, as described in a recent review (Gray *et al.*, 2002), the lability of the OM is of crucial importance: it is the degree to which OM stimulates microbial metabolism, rather than the quantity of OM *per se*, that induces hypoxia or the accumulation of reduced compounds and, thereby, impacts on the macrofaunal community.

In addition to sediment OM, information on nutrient stocks and their composition is also important. Sediment total nitrogen and phosphorus contents are usually determined using automated elemental analysers, or the Kjeldahl technique for nitrogen and acid extraction of ashed samples followed by conventional spectrophotometry for phosphorus. However, whilst measurements of standing stocks gives a snapshot of the total nutrients stored in the sediment at a given time, it is the speciation of these stocks and the residence times within the various pools that controls the sedimentary storage capacity and exchange rates with the water column. Therefore, the size of a standing stock of OM or nutrients is not necessarily predictive of the net effect on water quality. Fluxes of nitrogen and phosphorus from the sediment to the water column are highly dependent on speciation, since the different nutrient species are more or less strongly retained, follow different pathways and have different fates.

Inorganic nitrogen that is potentially available to the water column in the short-term can be determined as KCl-extractable (pore water plus exchangeable) ammonium (Laima, 1992). Parallel determination of pore-water ammonium concentrations allows both estimation of fluxes from the ammonium profile and the ratio of this pool to the KCl-extractable pool, which gives an indication of the sediment capacity to retain

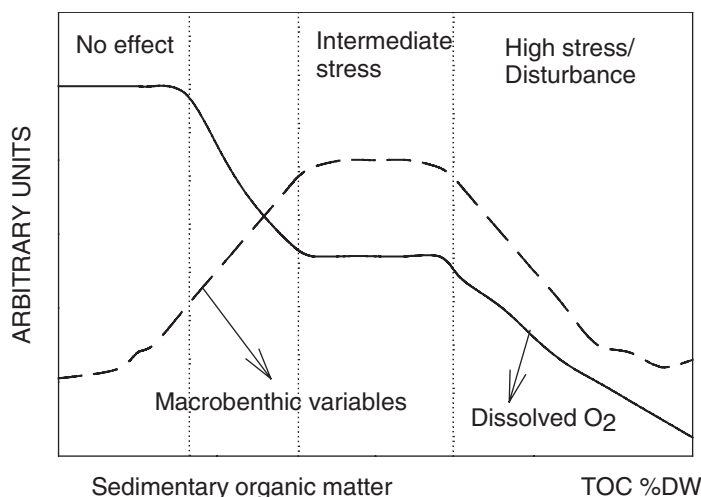


Figure 1. Conceptual model of the relationships among sedimentary organic matter and benthic characteristics (e.g. responses of macrofaunal communities, dissolved oxygen, etc.). The figure was modified from Pearson and Rosenberg (1978), according to Hyland *et al.* (2000) and De Wit *et al.* (2001).

ammonium in exchangeable pools. The form in which nitrogen is returned to the water column is highly dependent upon oxygen availability since, under oxic conditions, ammonium can be oxidized to nitrate through bacterial nitrification. Part of this nitrate diffuses to anoxic zones, where it can be reduced back to ammonium (dissimilatory nitrate reduction to ammonium; DNRA) or denitrified to gaseous end-products (N_2O , N_2) and eliminated from the system (Fenchel *et al.*, 1998; Herbert, 1999 and references cited therein). In eutrophic environments, oxygen penetration is limited to the upper few millimetres. Therefore, nitrogen oxidation and reduction often occur in a microscopic sediment layer. Their dynamics are now better understood due to a novel generation of microelectrodes that are commercially available (for updated references see Dalsgaard *et al.* (2000)).

Phosphorus speciation depends mostly on geochemical reactions with calcium, carbonates, iron, aluminium, and humic compounds. The common techniques are based on sequential extraction, which present several critical steps and are time-expensive (De Groot and Golterman, 1990; Ruttemberg, 1992; Barbanti *et al.*, 1994; Anderson and Delaney, 2000). Moreover, there are different points of view on how best to extract the different phosphorus pools; therefore, at present, there is no universally accepted method for analyses of sediment phosphorus speciation. As in the case of nitrogen, available phosphorus, comprising the pore-water and exchangeable fractions, can be assessed by simple extraction, in this case with MgCl_2 . Phosphate can also be precipitated as apatite; this calcium-bound phosphate is strongly retained by the sediment. The metal-bound (mostly iron-bound) phosphate is more weakly trapped and its availability depends on changes in microbial activity and redox potential. Phosphorus speciation also depends on acid–base equilibria, and can be influenced by pH variations. The calcium–carbonate–phosphate and the iron hydroxide–phosphate–sulphide systems have also been proposed as potential buffers that control phosphorus and sulphur reactivity and mobility (Golterman, 1995; Jensen *et al.*, 1998; Heijs *et al.*, 2000). Therefore, the integrated analysis of different phosphorus, sulphur and iron species is an interesting tool to assess the sediment tendency to release/retain phosphorus and control sulphide mobility.

In general, pools of organic nitrogen and phosphorus are calculated by difference between total nitrogen or phosphorus and the sum of the individual inorganic pools. Knowledge of these pools is extremely useful, as it allows calculation of the average C:N:P ratio of the sediment OM pool, which in turn is a good indicator of OM lability (Enriquez *et al.*, 1993).

Iron and sulphur

In coastal areas, the biogeochemical interactions between iron and sulphide play a major role in regulating sulphur speciation and retention of phosphate in the iron-bound pool (Howarth and Stewart, 1992; Fenchel *et al.*, 1998). Via a suite of redox reactions, sedimentary reactive iron immobilizes sulphides as highly insoluble FeS and FeS₂. Therefore, reaction with iron represents a potent mechanism for the efficient removal of toxic hydrogen sulphide and can buffer periods of excess sulphide production. The potential sedimentary buffering capacity can be assessed by determining the sediment content of reactive iron (Table 1). A first approximation of the actual sedimentary buffering capacity to sulphide can be estimated by determining acid-volatile sulphide (AVS), which approximates to the pool of iron already precipitated as FeS. Therefore, the ratio of AVS to reactive iron (II) represents the saturation state of the buffer. When AVS/iron(II) = 1, all the available iron is bound as FeS, and sulphide produced by bacterial sulphate reduction cannot be buffered. This is the case for the Étang du Prévost, where an excess of free sulphide is released in the water column (Figure 2). By contrast, in the Sacca di Goro lagoon the AVS/iron(II) ratio is low and a high residual buffer capacity is potentially available. However, several studies indicate that the acid extraction used to determine reactive iron overestimates the true buffering capacity against sulphide (Azzoni *et al.*, 2001). Recently, a biological oxygen and sulphide monitor (BOSM) has been developed for monitoring the sediment capacity to trap sulphide (Heijs *et al.*, 1999). BOSM experiments have confirmed previous observations showing that the sedimentary buffering capacity against sulphides is not a simple function of the reactive iron concentration, since not all of the iron is available to react with sulphide.

Overall determination of sediment stocks/pools provides only a snapshot of the current status. Although repeated measures give information on changes in pool sizes, only the determination of process rates and fluxes can provide details of the exchanges between pools, pool turnover rates and the transfer of energy and materials between the sediment and water column.

FLUXES AND RATES

Measurements of net fluxes of oxygen, inorganic carbon, soluble reactive phosphorus (SRP) and nitrogen, dissolved reactive silica (DRSi) are usually performed in dark and light conditions in order to discriminate

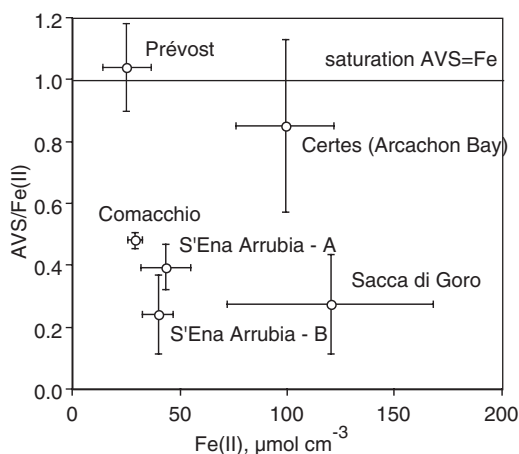


Figure 2. Relationship between iron and AVS in five transitional aquatic ecosystems. Bars represent the annual variation range (redrawn from Giordani *et al.* (1996) and Viaroli *et al.* (1999)).

the role of photosynthetic primary producers (Table 2). Fluxes are determined during *in situ* benthic chamber or laboratory core incubations. Actual incubation techniques are mostly dependent upon the primary producer community structure, e.g. bare sediments, microphytobenthic systems and macrophyte beds (see Dalsgaard *et al.* (2000) for an updated review).

Net oxygen fluxes give an estimate of oxygen availability resulting from production and consumption by the benthic subsystem. Benthic indicators based on these fluxes have been proposed for the classification of trophic status, total heterotrophy–total autotrophy (Rizzo *et al.*, 1996) and the temporal changes in trophic status and magnitude of the oxygen fluxes (Viarelli and Christian, 2003). The respiratory quotient (ratio of dark O₂ consumption to dark CO₂ production) has also been proposed as an indicator of the metabolic balance of the system. For example, ratios greatly above unity indicate sediment reduction, i.e. that there is significant anaerobic carbon oxidation without complete reoxidation of the reduced products, e.g. the sulphides formed.

Fluxes of inorganic nutrients result from the net balance between assimilation, transformation and regeneration processes, and thus give a rough assessment of whether the system is a sink or a source. A better understanding of nutrient cycling and sulphide production can be achieved by determination of the rates of the major sedimentary bacterial processes. Nitrogen fixation, nitrification and denitrification are critical steps of the nitrogen cycle, the first being an input and the latter a loss of nitrogen from the system (Herbert, 1999; Nedwell *et al.*, 1999; Welsh, 2000). Moreover, denitrification rates are enhanced when coupled to nitrification, which is itself dependent upon ammonium production (OM turnover) and oxygen availability. Bacterial sulphate reduction rates account for the dissimilatory production of sulphide, which is often the dominant carbon oxidation process in coastal sediments, accounting for more than 50% of OM turnover (Jørgensen, 1996). Sediment microprofiling with microelectrodes gives high-resolution analyses of sedimentary gradients of oxygen, sulphide, pH and nitrate, allowing calculation of diffusive fluxes and estimation of process rates and their depth distributions (Revsbech and Jørgensen, 1986). However, whilst

Table 2. Benthic fluxes and process rates that can be considered for sediment monitoring. C: consideration in the current monitoring programmes; C/TC: cost/time consumption; U/MC: uncertainty/method consensus; H: high; I: intermediate; L: low; DON: dissolved organic nitrogen; SRP: soluble reactive phosphorus; DRSi: dissolved reactive silica

Flux/rate	C	C/TC	U/MC	Ecological significance
Dissolved oxygen flux	L	I/I	L/I	Oxygen availability to the water, balance of respiration, oxidation and photosynthesis
Dissolved inorganic carbon flux	L	I/I	L/I	Balance of respiration and photosynthesis
SRP flux	L	I/I	L/I	Net SRP flux, internal mineral P-loading
Ammonium flux	L	I/I	L/I	Net ammonium flux, recycling, internal loading
Nitrate + nitrite flux	L	I/I	L/I	N oxidation, recycling, internal loading
DRSi flux	L	I/I	L/I	DRSi recycling, internal loading
Dissolved sulphide flux	L	L/H		Sulphide release to the water column, toxic risk
Nitrogen fixation rates	L	H/H	L/I	Biological N inputs
Potential nitrification rates	L	H/H	H/H	Potential N oxidation
Denitrification rates (isotope pairing technique)	L	H/H	L/I	N losses to the atmosphere, buffering capacity against N loading
Dw (from water)	L	H/H	L/I	
Dn (coupled with nitrification)				
Total = Dw + Dn	L	H/H	L/I	
Denitrification rates (block technique)	L	H/H	L/I	
Bacterial sulphate reduction rates	L	I/H	L/H	Sulphide production

determinations of fluxes, rates and sediment profiles provide in-depth knowledge on the status, tendency and dynamics of the system, they require sophisticated expensive equipment, are costly to perform and are time consuming. Accordingly, they are not suitable for inclusion in most monitoring programmes.

AN INTEGRATED APPROACH TO MONITORING

The design of monitoring programmes for transitional waters should consider how best to address the relevant issues and specific controversial problems (National Research Council, 2000). Most often, the issues to be analysed are complex and cannot be resolved by considering only simple variables and linear relationships (De Wit *et al.*, 2001). To be suited to monitoring programmes, indicators should be: quantitative, based on scientific consensus and sound methodologies; sensitive to changes in time and space, and the appropriate scale; cost effective and user friendly. From the variables listed in Tables 1 and 2, it can be seen that most of the state variables are easily determined at low monetary/time cost using standardized techniques. However, alone they give only a coarse description of the general sedimentary features; therefore, they are not sufficiently informative to be used as individual-specific indicators. By contrast, most of the analytical techniques for measuring fluxes and rates provide a better understanding of sedimentary processes, but are too expensive to be applied in conventional monitoring programmes. Thus, no single parameter fulfils all the requirements listed previously, and individual determinations of single parameters will always be ambiguous. Therefore, integrated approaches may be more useful than mechanistic design for analysing such complex systems that have a high level of uncertainty and are characterized by non-linear responses (Holling, 1998). Adaptive strategies are also useful in order to assess ecosystem responses to forcing factors.

We propose to integrate the simple, easily measured state variables into a synthetic index, as shown in Table 3, to provide a rapid assessment of the potential vulnerability level (PVL) for the identification of sensitive sites, thereby allowing agencies to focus their monitoring efforts better. This index combines the water retention time (WRT) in the aquatic ecosystem with five sedimentary variables, namely granulometry, sedimentary OM, carbonates, reactive iron and AVS. These state variables have been chosen because they represent the potential capacity of the ecosystem to react against specific pollutants and other forcing factors. Granulometry and sedimentary OM provide basic information on sediment composition and are important determinants of exchanges of oxygen and nutrients with the water column. The sedimentary carbonate content can be used to assess the capacity of the sediment to retain phosphate through the calcium–carbonate–phosphate system (Lapointe *et al.*, 1992; Golterman, 1995). Reactive iron provides an indication of the sediment's capacity to buffer against sulphides, whilst the AVS/reactive-iron

Table 3. Tentative assessment of the potential vulnerability level (PVL) of transitional waters throughout the integrated measurement of status variables in the surficial sediment horizon (upper 5 cm)

Vulnerability	Low	Moderate	High	Excessive
Individual rank	3	2	1	0
PVL	18	12	6	0
Water retention time (WRT, days)	< 1	1–7	7–15	> 15
Granulometry (G)	Sand	Sand-silt	Silt-clay	Clay
Total organic carbon (TOC, % dw) upper 5 cm ^a	< 0.5	0.5–2.5	2.5–5	> 5
Carbonate (CaCO ₃ , % dw)	> 40	20–40	5–20	< 5
Reactive Fe (µmol cm ⁻³)	> 200	100–200	50–100	< 50
(AVS, µmol cm ⁻³)	< 50	50–100	100–150	> 150

^a Modified from Hyland *et al.* (2000).

ratio is an index of the buffer saturation (De Wit *et al.*, 2001). WRT is the ratio of the recipient volume to the water flux through the system. Ecosystems with low WRT undergo rapid flushing, whereas a high WRT is an index of potential water stagnation. In turn, water stagnation can increase the retention of pollutants within the system and increase the risk of water deoxygenation. WRT can be easily estimated with water mass balances (Gordon *et al.*, 1996).

The synthetic index combines the status variables and WRT into a matrix, where each cell corresponds to a level from low to excessive vulnerability potential and scores from 3 (best) to 0 (worst). The resulting PVL is the sum of the individual values, and varies from 18 (best) to 0 (worst). For example, considering a hypothetical lagoon with WRT = 3 days, G = silt–clay, TOC = 4% (dry weight), CaCO_3 = 7% (dry weight), $[\text{Fe}] = 150 \mu\text{mol cm}^{-3}$, $[\text{AVS}] = 109 \mu\text{mol cm}^{-3}$, the sum of the individual scores is PVL = 8, which represents a vulnerability level from moderate to high.

Since oxygen availability is critical in the management of coastal systems, data in Table 3 should be integrated with an assessment of oxygen metabolism and the amplitude of its variation with time. A benthic trophic status index (BTSI) based on oxygen metabolism has been proposed for this purpose (Rizzo *et al.*, 1996) and recently extended to take into account temporal variations and extreme excursions in oxygen fluxes (Viaroli and Christian, 2003). All the data listed in Table 3 and for BTSI and TOSI calculations could readily be collected by technical staff of the relevant public environmental agency. Therefore, we consider that these approaches represent promising diagnostic tools for the analysis, comparison and classification of transitional water bodies. Moreover, the simple sediment and biogeochemical indicators proposed here could easily be combined with indices based on the plant and macrozoobenthos (e.g. Fano *et al.*, 2003; and papers in this issue), to provide a true ecosystem-based indicator.

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