

Dissolved fluxes of nutrients and carbon at the sediment-water interface in the Adriatic Sea: review of early data and methods from the Italian National Research Council (CNR)

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ABSTRACT

We report the measurement of the Fluxes of Dissolved Compounds at the Sediment-Water Interface (DFSWis), obtained by analyzing data collected in the Italian Exclusive Economic Zone (EEZ) of the Northern and Central Adriatic Sea from 1982. We also describe the methods, honed by Italy's Consiglio Nazionale delle Ricerche (CNR), employed to measure and calculate DFSWis, including benthic chambers and landers, sediment-water interface micro-profiling, on-board incubation, and pore water modeling. Data analysis demonstrated that *in situ* measurements are the most reliable approaches, but that on-board collected data also supply interesting results. The DFSWI data allowed to divide the Adriatic seafloor into areas with similar DFSWI types and intensities and to define the role of sediments as sources or sinks of chemicals such as nutrients, Dissolved Inorganic Carbon (DIC), and metals. DFSWis mainly depend on dissolved and solid river inputs, Marine Organic Matter (mOM) production, and sediment reworking. They show a seasonal temperature-related trend, which in summer induces increased chemical reaction kinetics and microbial activity. DFSWis decline from the Po River mouths southward, along the Holocene mud wedge. North of the Po River Delta, the DFSWis are weaker and confined to the areas in front of the major river mouths, due to poor Organic Matter (OM) inputs and strong reworking of bottom sediments. The area south of the Po Delta cusp is characterized by strong DFSWis, due to the high deposition of solid inputs from the Po River, strong primary production, and protection from the Western Adriatic Current and Bora storms; in summer, higher temperatures, and calm hydrodynamic conditions generate near-bottom hypoxic to anoxic environments in this area. In Northern and Central Adriatic offshore areas, negative DIC and phosphate fluxes are due to poorly reactive OM reaching this area and to the mainly carbonate composition and oxic environment of local bottom sediments. DFSWI data analysis highlighted the important contribution of sediments to marine carbon and nutrient cycles. This is particularly important for carbon, which plays a major role in seawater acidification and global climate change. The study also provides average DFSWI data for each diagenetic area, which allow calculating the carbon and nutrient budgets in the Adriatic Sea.

Introduction

In marine environments, the Fluxes of Dissolved Substances at the Sediment-Water Interface (DFSWIs) can be due to three main factors: i) early diagenesis processes; ii) fluids coming from deeper sub-bottom layers; iii) volcanic and hydrothermal processes.

Early diagenesis refers to the biogeochemical processes taking place in the top centimeters of sediments (Berner, 1980), where the presence of Reactive Organic Matter (rOM) provides sufficient energy for elevated microbial activity. These processes produce or consume chemicals found in Pore Waters (PWs), thus generating concentration gradients at the sediment water-interface that result in fluxes in or out of the sediments (*Figure S1*). rOM settling from the water column concentrates in sediment. It consists of authigenic Marine Particulate Organic Matter (mPOM) and Terrestrial Particulate Organic Matter (tPOM) as well as of flocs, formed by the aggregation of Dissolved Organic Matter (DOM) upon contact with the saline environment. The Particulate Organic Matter (POM) is degraded or mineralized by microbial activity that disrupts the original POM to high molecular weight DOM, which, in anaerobic environments, is in turn further hydrolyzed and fermented to monomeric low molecular weight DOM (Weston *et al.*, 2006). This latter is mainly measured as Dissolved Organic Carbon (DOC). To a lesser extent, early diagenesis is also affected by processes involving the Inorganic Matter (IM) reaching the seafloor, which consists of carbonate and silicate biogenic or lithogenic particles as well as of trace elements, pollutants, and other anthropogenic inputs (*i.e.* black carbon).

The mineralization of POM and DOM is achieved by the final electron acceptors, acting in decreasing order of free energy as follows (*Figure S2*): dissolved oxygen (O_2), nitrate (NO_3^-), iron and manganese oxyhydroxides ($Fe_nO_x(OH)_y$, $Mn_nO_x(OH)_y$), and sulfate (SO_4^{2-}). The rOM mineralization induces the accumulation in PWs of organic matter (OM) degradation products, *i.e.* dissolved inorganic carbon (DIC), ammonium (NH_4^+), phosphate (PO_4^{3-}), and methane (CH_4), as well as the reduced forms of the electron acceptors, *i.e.* reduced iron and manganese (Fe^{2+} and Mn^{2+}), dinitrogen gas (N_2), and hydrogen sulfide (H_2S).

The intensity and type of the early diagenesis processes mainly depend on the following key factors:

- **Reactive Organic Matter (rOM) content.** High amounts of rOM, which is strongly affected by the presence of fresh OM, increase the intensity of early diagenesis processes. The high reactivity of rOM is due to its easy mineralization, which is particularly strong in recently produced (fresh) OM, especially near the Sediment-Water Interface (SWI), where aerobic degradation is more efficient (Westrich and Berner, 1984). The formation of rOM is favored by nutrient inputs from land, which increase primary production; high nutrient inputs are possible near the continental borders, particularly at the mouths of major rivers, which, in turn, also release large OM amounts of continental origin.
- **Fe and Mn oxyhydroxides.** Fe and Mn oxyhydroxides are important chemicals in early diagenesis processes because they can undergo dissolution or precipitation at the oxic-anoxic interface in sediments. In reducing environments, Fe and Mn tend to dissolve from the insoluble oxidized form (Fe^{3+} , Mn^{4+}) to the soluble reduced form (Fe^{2+} , Mn^{2+}), whereas

in oxidizing environments, they tend to precipitate as oxyhydroxides (*Figure S2*, enlargement). These reactions induce an accumulation of Fe and Mn oxyhydroxides at the oxic-anoxic interface, albeit with a slight discrepancy between Fe and Mn due to their different free energy. The process is more intense where the initial amount of the oxyhydroxides of these two metals is greater and where the stability of the oxic-anoxic interface is higher, *i.e.* in the areas facing large river estuaries and on sea bottoms characterized by low sedimentation rates (Lalond *et al.*, 2012).

- **Sedimentation rates.** High sedimentation rates favor the incorporation of both more and less reactive OM, since they result in a shorter stay of OM in the oxic environment, where mineralization is faster and stronger than in anoxic environments. OM preservation at greater depths induces a deepening of early diagenesis processes and a thinning of oxic and suboxic environments (*Figure S2*).
- **Grain size.** Fine grain sizes prevent oxygen penetration into sediment and promote OM preservation, as do high sedimentation rates. In contrast, coarse sediments favor oxygen penetration and increase OM mineralization close to the SWI.
- **Sediment reworking.** The reworking of surface sediment, due to resuspension and bioturbation, plays a significant role in early diagenesis processes. An intense reworking process results in faster and stronger OM decomposition; in particular, repeated OM contacts with the oxidizing environment of the water column, due to resuspension, makes mineralization more efficient.

Moreover, DFSWIs can also be generated by seeps of fluids and gases, whether focused or diffused (Price *et al.*, 2015; Spagnoli *et al.*, 2020), due to hydrothermal and diagenetic processes, including low-grade metamorphism, taking place at greater sub-bottom depths (Esposito *et al.*, 2018, Rovere *et al.*, 2020).

This paper addresses the DFSWIs in marine environments, the processes by which they are generated, and the methods by which they can be measured or calculated. It presents data regarding the DFSWIs measured *in situ* and calculated from PWs in the Adriatic Sea, mainly by the Italian Consiglio Nazionale delle Ricerche (CNR), the University of Trieste, and the Slovenian Marine Biology Station. The study focuses on research carried out from 1982 on the Italian side of the Central and Northern Adriatic Sea (Barbanti *et al.*, 1995; Bertuzzi *et al.*, 1996; Bertuzzi *et al.*, 1997; Cermelj *et al.* 1997; Cermelj *et al.*, 2001; Frascari *et al.*, 1995; Giordani and Hammond, 1985; Giordani *et al.*, 1992; Giordani *et al.*, 1994; Giordani *et al.*, 1996; Hammond *et al.*, 1999; Spagnoli and Bergamini 1997; Tahey *et al.*, 1996; Spagnoli *et al.*, 2010) (*Figure S3*, *Table S1*). Previous papers on dissolved benthic fluxes in the Adriatic basin have addressed transitional ecosystems (Covelli *et al.*, 1999; Covelli *et al.*, 2011; De Vittor *et al.*, 2012; Petranich *et al.*, 2018; Petranich *et al.*, 2021), specific elements (Ciceri *et al.*, 1992; Covelli *et al.*, 2008; Emili *et al.*, 2011; Emili *et al.*, 2014; Epping and Helder, 1997; Zago *et al.*, 2000), or else have reworked previous data (Cermelj *et al.*, 1997, Ogrinc and Faganeli, 2006; Testa *et al.*, 2020) or examined other areas of the Adriatic Sea not considered in this paper (Baric *et al.*, 2006; Giordani *et al.*, 2002). This work addresses nutrients and DIC as well as iron and manganese fluxes at the SWI in the Northern and Central-

Western Adriatic Sea. We present the results obtained by the analysis of DFSWIs, measured *in situ* by benthic chamber deployments and on board by core incubations, and calculated from PW chemical profiles (Figure S3, Table S1).

Materials and Methods

Benthic flux measurement

DFSWIs can be determined in three ways (Hammond *et al.*, 1985): i) by *in situ* measurements using benthic chambers or eddy covariance systems; ii) by sediment core incubation in the laboratory; or iii) by modeling PW chemical composition. In particular, PW chemical concentrations can be obtained on board by PW extraction from sediment cores and subsequent microanalysis; by on-board or *in situ* passive sampling or micro-profiling at the SWI (Berg *et al.*, 2009; Berner, 1980; Boudreau B.P., 1996; Brand *et al.*, 2018; Burdige, 2006; Hammond *et al.*, 1996; Hammond *et al.*, 1999; Hammond *et al.*, 2004; Tengberg *et al.*, 1995; Viollier *et al.*, 2003; Webster *et al.*, 1998). At present, the most reliable DFSWI values are provided by the eddy covariance (an *in situ* approach), which integrates the DFSWI over an infinite area (Berg *et al.*, 2009), whereas benthic chamber and core incubation methods measure fluxes over more limited areas and micro-profiling examines only the diffusive component of the flux at a specific point.

Some of these methods, as adopted and implemented by the Italian CNR to measure or calculate DFSWIs, are described below. They include the construction and *in situ* deployments of benthic chambers, on-board measurements by core incubations (Spagnoli F., 1994), calculation from PW chemical profiles in PW extracted on board and subsequently analyzed, and on-board micro-profiling at the SWI (Bergamini *et al.*, 1997a and b; Spagnoli and Bergamini 1997).

Direct *in situ* measurement using benthic chambers and eddy covariance systems

A benthic chamber is a device for measuring the DFSWIs. Roughly, it is a box with a sealed top and an open bottom placed on the seafloor (Figure S4a). Benthic chambers range from very simple designs such as a plastic box placed on the sea or freshwater bottom environments, where water samples are collected manually, to very complex devices equipped with automatic sampling and control tools for shallow and deep aquatic environments (Figure S4b-g).

In Italy, *in situ* measurements using a benthic chamber began at CNR in 1984, with a collaboration between IGM-CNR (Bologna, Italy) and the University of Southern California at Los Angeles (USA). This joint effort produced the first *in situ* measurement of DFSWIs in the Adriatic Sea (Giordani and Hammond *et al.*, 1985; Figure S4b). Then, IGM-CNR went on to build the first Italian semiautomated chamber (Bergamini *et al.*, 1997 a and b; Figure S4c). Further research by the CNR resulted in the construction of the first Italian automatic chamber (Masini *et al.*, 2001; Figure S4d) and finally in the realization of the current benthic chambers and landers, respectively the AdaN (Figure S4e) and the Amerigo (Spagnoli *et al.*, 2018, 2019; Figure S4f and g). Benthic flux incubation experiments – by means of laboratory incubations (Bertuzzi *et al.*, 1996; Bertuzzi *et al.*, 1997)

as well as *in situ* deployments (Covelli *et al.*, 1999) – were also carried out in the 1990s by the University of Trieste in the Gulf of Trieste.

AdaN is an automatic benthic chamber consisting of a polymethyl methacrylate cylinder (internal diameter, 80 cm; height, 33 cm) (Figure S4e). The water sampler is managed by a commercially available tool to collect samples inside and outside the chamber or to inject tracers. The chamber is equipped with an internal rotating paddle and a multiparameter probe to measure pH, oxygen, oxidation-reduction potential, temperature, conductivity, and pressure. AdaN can operate on the continental shelf (down to 200 m depth) and is deployed on the seafloor through a cable to which is attached a flashing buoy for signaling and recovery.

Amerigo is a lander (Figure S4f), that it is deployed on the bottom, operates on the seafloor, and then returns to the surface without the need for a cable, tether, or propeller. For this reason, it is equipped with ballast and buoy arrays for controlled falling, landing, and surfacing, as well as a radio, flashing light, and GPS tracker for recovery. Amerigo has a wide depth range, from the continental shelf to the abyssal plains (down to 6000 m depth). Although its current configuration is designed to measure DFSWIs by means of three benthic chambers, it can also be equipped with instruments for different monitoring and measurement tasks, such as water column sensors (oxygen, pH, methane, PAHs, pCO₂, H₂S, turbidity, fluorescence) and instrumentation for seafloor measurements (micro-profilers, penetrometers, gravimeters, wave, and current meters, corers). Each benthic chamber is a polymethyl methacrylate cylinder (internal diameter, 37.5 cm; height, 15 cm) with a closing lid, a rotating paddle, a device for collecting water samples inside and outside the chamber and to inject tracers in the chamber, and an OXISTAT device to replace oxygen in the chamber (Morse *et al.*, 1999). The hardware and software are developed in-house.

Once on board, the water samples collected by the AdaN or the Amerigo are processed in an inert gas glove box and stored for subsequent analyses, which may be performed directly on board or later in the laboratory. Chemical and downloaded sensor data are then used for DFSWI calculation.

Sediment core incubation

For on-board incubation, core sediments collected from the sea bottom are placed in a thermostatic bath at a constant temperature. The core tops are sealed with a lid fitted with a rotating paddle, to preserve the homogeneity of the seawater above the sediment and the thickness of the benthic boundary layer. As in a benthic chamber, water samples are collected at predetermined time intervals while physicochemical parameters are monitored by sensors (Figure S4h).

Calculation of sediment-water interface dissolved fluxes by benthic chambers and core incubations

Dissolved fluxes at the SWI are calculated in different ways, depending on whether they are measured by sediment incubations or calculated by modeling PW chemical composition profile.

The DFSWIs measured by benthic chambers or core incubations are calculated by (1):

1. dividing the sample concentration of each chemical by the sample collection time t ;
 2. multiplying this gradient by the volume of the incubation and dividing it by the bottom area of the incubation chamber.
- Namely:

$$J_i = \frac{(\partial C_i)}{\partial t} (VA) \quad (1)$$

where:

J_i = flux of chemical compound i^{th} at SWI;

C_i = concentration of chemical compound i^{th} ;

t = time of sample collection or sensor measurement;

V = actual volume of the incubation chamber;

A = bottom area of the incubation chamber.

If multiple samples have been collected inside the chamber at different times, a regression line needs to be calculated, and (1) becomes:

$$J_i = m_i * h \quad (2)$$

where:

m_i = angular coefficient or slope of the regression line between C_i/A and t_i (Figure S5);

h = height of the incubation chamber.

Calculation of sediment-water interface dissolved fluxes from pore water chemical profiles

Pore water concentration profiles for DFSWI calculation can be obtained in two ways: i) by on board extraction and analysis of PW from sediment cores or measured *in situ* by passive sampling or ii) by direct concentration measurements by a microprofiler, either *in situ* or on board.

CNR has honed PW extraction and analysis methods, on-board micro-profiling, and *in situ* dialyzers.

Pore water extraction and analysis

Pore waters are extracted from a sediment core collected by a specially built corer (SW104, Magagnoli & Mengoli, 1995). On deck, the internal liner of the SW104 corer is placed in the extrusion frame (Figure S6a). After the top of the liner has been placed in a nitrogen-filled glove box, the sediment is pushed up and cut into slices of different thicknesses (thinner near the interface and thicker at greater depths; Figure S6b). After the determination of pH, redox potential, and temperature in the slices with punch-in electrodes, each slice is placed in a vessel, centrifuged (Figure S6c), and then returned to the nitrogen-filled glove box. The supernatant of each slice is filtered and the resulting PW is split into aliquots, poisoned or acidified, and then stored for subsequent analyses. All operations are conducted at the same temperature as the *in situ* environment.

For PW micro-profiling, the sediment core is placed on the micro-profiling frame; the microelectrodes (oxygen, pH, and resistivity) are lowered by a micro-manipulator (Figure S7a) to obtain measurements at steps of a few microns (Figure S7b), with higher resolution at the SWI, which is identified by the resistivity measurements.

IGM-CNR has also honed a method for chemical

determination of PW at the SWI using *in situ* dialyzers (Viel *et al.*, 1991), but in the past few years this approach has been replaced by more efficient passive samplers (Lei *et al.*, 2023).

Diffusive flux calculation

The diffusive fluxes at the SWI are calculated from PW chemical profiles, by applying Fick's first law of diffusion at the concentration gradient measured at the SWI (Berner, 1980):

$$J_i = -\varnothing D_i \left(\frac{\partial C_i}{\partial z} \right)_{z=0} \quad (3)$$

where:

\varnothing = porosity

D_i = diffusion coefficient of solute i

$\left(\frac{\partial C_i}{\partial z} \right)_{z=0}$ = concentration gradients at the SWI of solute i .

z = depth.

Generally, measurements of the SWI concentration gradient are not very accurate, being affected by technical errors that vary depending on the method used. In particular, in the PW extraction and passive sampler methods, it is difficult to sample PW and bottom water very close to the SWI, whereas in the micro-profiling method the actual extension and position of the interface is difficult to determine.

Furthermore, DFSWIs include other components, besides the diffusive one, which cannot be calculated by Fick's first law due to the contribution of the biogenic irrigation and sedimentation rate (4).

$$F_{\text{total}} = F_{\text{diff}} + F_{\text{irr}} + F_{\text{adv}} \quad (4)$$

where:

F_{total} = total dissolved flux at the SWI;

F_{diff} = dissolved flux due to molecular diffusion;

F_{irr} = dissolved flux due to irrigation;

F_{adv} = advection of the sediment with respect to the SWI.

For this reason, mathematical procedures are used to calculate the interface gradient and the irrigation component, while the advective component is generally neglected (Berner 1980, Boudreau, 1997). From the general diagenetic equation (5):

$$\frac{\delta C_i}{\delta t} = D_s \left(\frac{\delta^2 C_i}{\delta z^2} \right) - w(1+K) \left(\frac{\partial C_i}{\partial z} \right) + R_z + I_z = 0 \quad (5)$$

C_i = concentration of the solute i

z = depth

R = adsorption or desorption constant or equation;

I = irrigation constant or equation (non-local transport);

w = burial rate

K = constant

As regards (5), the solution must be found on the basis of PW best fitting among the following methods (Hammond *et al.*, 1996)

$$R_z = \text{constant} \quad C = C_0 + a_1 z \quad (6)$$

$$R_z = \text{quadratic} \quad C = C_0 + a_1 z + a_2 z^2 \quad (7)$$

$$R_z = \text{exponential} \quad C = C_\infty(1 - e^{-bz}) + C_0e^{-bz} \quad (8)$$

The equation that best approximates the PW profile is used to compute the gradient at the SWI by calculating the first derivative at $z = 0$. Alternatively, as a first approximation and raw calculation, the gradient can be obtained by (9) which provides difference between the concentration in the bottom water column and the concentration in the first slice (*Figure S8*).

Early or raw approach:

$$\frac{C_{i(bw)}}{C_{i(z_1)}} \quad (9)$$

where:

$C_{i(bw)}$ = concentration of chemical compound i^{th} in the water sample collected as close as possible to the sea bottom, or considering as bottom water the supernatant of the sediment core extruded in the nitrogen-filled glove box;

$C_{i(z_1)}$ = concentration of chemical compound i^{th} in the first, near surface sediment core slice.

Comparison of measured and calculated benthic fluxes

Comparing measured and calculated DFSWIs is useful when both are available. The comparison allows to identify processes due to non-local transport or taking place at the seafloor, as well as to evaluate the accuracy of the calculation in relation to the PW analysis method applied (see section 2.5.2).

Comparisons of the values obtained by *in situ* incubation in the benthic chamber, on-board core incubation, and PW modeling at the same station in the same season usually show that the *in situ* method yields systematically higher fluxes than laboratory incubation, and that the latter method yields higher fluxes than PW modeling (Berg *et al.*, 2009; Hammond *et al.*, 2004). The different values produced by the three methods, particularly at the station facing the Po Delta mouths (station 17) are shown in *Figure S9*.

The considerable and systematically lower fluxes obtained by on-board core incubation compared with the *in situ* benthic chamber (*Figure S9*, blue and light blue sticks, respectively) are attributable to the smaller area of incubated sediment core over which the fluxes are measured (Berg *et al.*, 2009; Hammond *et al.*, 2004). The smaller area limits the lateral variability of the fluxes, due particularly to the irrigation component, which increases with sediment area due to the increase of the benthic community. The fluxes determined by PW chemical profile modeling are even lower owing to two limitations: the difficulty to measure the concentration gradient as close to the SWI as possible and the fact that the mathematical models applied, which consider only the diffusive component. Specifically, according to the CNR approach, the gradient is calculated from the concentration in the extruded core supernatant water or in the very-near-bottom water collected by a modified Niskin bottle to the concentration in the PW extracted from the first sediment core slice. These two concentrations are very close, but not precisely above and below the SWI. Furthermore, the concentration in the first sediment core slice is an average of the top 0.5 cm of the sediment rather than the concentration immediately below the SWI, and the dz is set at 0.25 cm (the half thickness of the first sediment core slice) rather than the theoretical distance of $l \rightarrow 0$.

Based on the technical limitations detailed above, *in situ*-measured DFSWIs should be preferred to core incubation and PW modeling. The *in situ* approaches are easy to apply in shallow and very shallow marine and continental environments, because, in these conditions, deployment and recovery can be made using a cable, and the water in the chambers can be sampled using a miniature connected to a syringe, or by divers. However, the use of divers is hampered by safety restrictions, high costs as well as technical difficulties as depth increases, and becomes very problematic beyond 20-25 m. Tube sampling also becomes more difficult as depth increases. On the other hand, *in situ* incubation at greater depths is burdened by the high costs of the instruments and the ships. This is why modeling is often preferred.

Results

DFSWI measurements taken in different seasons highlighted a variance between summer and late winter-spring (*Figure S10*). DFSWIs were generally lower in winter and spring, due to both lower temperatures near the bottom and to rare primary production blooms. In summer, as temperatures rises, so do the kinetics of the biogeochemical reactions and microbial activity (Hopkinson and Smith, 2005; Li and Gregory, 1974; Price and Sowers, 2004; Westrich and Berner, 1988), therefore OM mineralization and the consequent DFSWIs increase (Westrich and Berner, 1988). The same process affects primary production, which increases in spring and summer, providing further rOM to the seafloor (Giani *et al.*, 2005; Pugnetti *et al.*, 2004).

Organic matter degradation products

The DFSWIs of the OM degradation products (NH_4^+ , DIC, PO_4^{3-}) declined south of the Po River mouth and as far as the Mid-Adriatic Depression (*Figure S11*) along the Holocene mud wedge (Spagnoli *et al.*, 2014). The DFSWIs were highest in front of the Po River, close to the main mouth (*Po di Pila*, station 17), and just south of the Po Delta (stations 18, 24, 32, and E1). Then they gradually declined in southward direction, at stations sharing a similar depth and distance from the coast (stations 39, 40, E3, 47) and were lowest in the MAD (station 52). To the north of the Po Delta and in areas farther offshore with respect to the Holocene muddy wedge, the fluxes were much lower than at the Po mouths, except at station AA1 (in the Gulf of Trieste) and station 13 (facing the Adige River mouth, just to the north of the Po Delta), where the DFSWIs were significantly lower than at the Po River mouths (*Figure S12*). The other open sea stations (stations 4 and 10) did not show a general trend: here, the fluxes were strongly site-dependent, low at station 4 and anomalous, even negative, at station 10 (*Figure S12*).

Final electron acceptors: oxygen, nitrate, iron and manganese

With regard to the final electron acceptors, DFSWIs showed negative values for oxygen and positive values as regard iron and manganese (*Figure S13*). The oxygen fluxes were stronger at the stations off the Po River Delta, and lower southward (station 28) and in the Central Adriatic (station 10). Nitrate DFSWIs were negative at all stations south of the Po and positive to the north of the Delta (station 13) and in the Central Adriatic (station 10). Iron

and manganese DFSWIs declined from the Po River mouths both southward and northward, although the Manganese fluxes remained high to the south.

Discussion

The strong DFSWIs of the OM degradation products and the final electron acceptors, close to the main Po River mouth (station 17), depend on the fact that this is the first deposition area of large amounts of OM both of continental and marine origin (Boldrin *et al.*, 2015; Frascari *et al.*, 2006; Tesi *et al.*, 2006). This OM contains highly reactive components consisting mainly of marine organisms, which proliferate in the nutrient-rich coastal waters, particularly those affected by the Po River inputs. The continental OM includes large amounts of low-reactive components – due to its content in OM that has already undergone decomposition processes and in OM from higher organisms – as well as a high rOM component, consisting of recent primary production organisms from lagoons, rivers, and canals near the coast. In addition, the OM settling in these areas is highly reactive because these are the first deposition areas: thus, this OM has not undergone significant resuspension, which would involve some degree of mineralization and consequent loss of reactivity. Another factor that contributes to the strong DFSWIs of the OM degradation products and, to a lesser extent, of the final electron acceptors in this area, is the high sedimentation rate. This results in fast incorporation in the sediment of rOM and of Fe and Mn-oxyhydroxides, which rapidly sink to greater depths to an anoxic environment. Furthermore, anoxic conditions slow down OM degradation (Westrich and Berner 1984), enhancing its incorporation at greater depths. Therefore, in this area, the DFSWIs of the OM degradation products increased due to mineralization processes both close to the SWI and to mineralization at a greater depth. This explains why the benthic fluxes were highest close to the main Po River mouth (Po di Pila), where particle and nutrient inputs and the sedimentation rate were also highest (Frignani *et al.*, 2005). DFSWIs plummet a few miles offshore (Figure S12, Figure S13), where the Western Adriatic Current (WAC), combined with resuspension processes, removes fine sediments and rOM (Frascari *et al.*, 2006).

The DFSWIs of the OM degradation products, particularly NH_4^+ and PO_4^{3-} , and of the final electron acceptors (oxygen, iron and manganese) were also high south of the Po Delta (Figure S11, Figure S13). Here, the cusp of the Po River Delta protects the sea bottom sediments from resuspension and removal by the WAC and the Bora storms. As a result, rOM-rich sediments settle over a wider first deposition area south of the Po Delta and are subject to more limited reworking. In this protected area, the high nutrient content of the Po River waters also remains confined nearshore, further contributing to primary production and rOM inputs to sediments. In addition, the high temperatures, calm sea, and the water column stratification characterizing this coastal area in summer, associated with high oxygen consumption, often lead to hypoxic and even anoxic conditions near the bottom (Alvisi *et al.*, 2013; Djakovac *et al.*, 2015). Such conditions induce a further increase in the release of NH_4^+ and PO_4^{3-} , which do not undergo oxidation, and of Fe and Mn, which are subject to stronger dissolution processes also above the SWI.

At the southernmost stations, the DFSWIs of the OM

degradation products declined (Figure S11), due to the limited rOM inputs (Spagnoli *et al.*, 2014). Notably, the OM reaching this area has already undergone extensive transport as well as several reworking processes, which result in its being largely mineralized and less reactive. In addition, in this area, smaller amounts of nutrients limit primary production and rOM deposition on the bottom. Clearly, in the presence of weaker degradation processes, the final electron acceptors are less involved in the reactions, and their DFSWIs are also weaker.

The lowest DFSWI values were found in the MAD. This is easily explained by the poorly reactive nature of the OM reaching this area, which has largely been mineralized. This factor, combined with a lower sedimentation rate, gives rise to the set-up of a plain aerobic environment in the upper few centimeters of sediment that greatly reduces the NH_4^+ and PO_4^{3-} DFSWIs compared with the DIC DFSWIs. This is due to the fact that NH_4^+ oxidizes to N_2 and NO_3^- , while PO_4^{3-} precipitates with the Fe-oxyhydroxides. In contrast, the PO_4^{3-} DFSWIs are strongest close to the Po River Delta mouths, where the redox conditions promote the reduction of Fe-oxyhydroxides and phosphate release.

In coastal sediments north of the Po River (stations 4a and 13), the fluxes of the OM degradation products were weaker than in the area south of the Po. This is due to low OM inputs from local rivers and to the removal of part of the settled OM by coastal currents and storms, which prevent a large accumulation. Only in the Gulf of Trieste does the protected environment enable a greater accumulation of fine and OM-rich sediment (Ogorolec *et al.*, 1991; Ogrinc *et al.*, 2005), hence stronger fluxes (Testa *et al.*, 2021).

In the Central Adriatic, south of the Po River Delta, which receives little fine sediment and OM inputs arrive (Giani *et al.*, 2003; Giani *et al.*, 2018; Spagnoli *et al.*, 2014), the DFSWIs were weak (Figure S12). Indeed, this area receives small amounts of OM, which remains largely confined nearshore by the action of the WAC. Finally, in the center of the Northern Adriatic Sea, which receives scanty amounts of fine sediment, OM, and nutrients, the DFSWIs of DIC and PO_4^{3-} were low or even negative. This is due to the predominance of PO_4^{3-} and DIC precipitation and sediment incorporation, favored by aerobic environments and the carbonate sediments, over OM degradation.

The measurement and calculation of DFSWIs allowed identifying areas sharing comparable fluxes as well as biogeochemical properties (Spagnoli *et al.*, 2010; Spagnoli *et al.*, 2013, Spagnoli *et al.*, 2015), which allowed sketching a preliminary DFSWI map (Figure S14). These areas show different sediment characteristics due to the variables affecting its biogeochemical composition, such as: i) rOM inputs (fresh marine and continental OM); ii) sedimentation rate; iii) particulate and dissolved continental inputs; iv) composition of terrigenous inputs; v) distance from the main sediment sources (mainly the Po River); vi) bottom sediment composition (carbonate or siliciclastic); vii) water column hydrodynamics; viii) oxygen content in near bottom waters; ix) depth.

In front of the Po River mouths, sediments are characterized by a diagenetic environment (type B diagenesis; Figure S14) involving a high sedimentation rate and high inputs of marine rOM, continental OM, and Fe-oxyhydroxide, which, in turn, produce high concentrations of OM degradation products in PWs and strong DFSWIs of both OM degradation products and final electron acceptors. Notably, these processes give rise to strongly

anoxic environments close to the SWI. In contrast, in the MAD, the greater depth and considerable distance from the main continental inputs induce a diagenetic environment characterized by highly reworked fine sediment, low sedimentation rate, low OM reactivity, and mixed fine carbonate and siliciclastic sediment (type E diagenesis; *Figure S14*). This setting is associated with major degradation at the SWI, low concentrations of PW OM degradation products, an oxic environment near the surface, and weak dissolved benthic fluxes.

In between these two extreme types of early diagenesis, there are several environments with intermediate reactivity (types C and D, *Figure S14*), or where coastal areas are influenced by local river inputs (type DD', *Figure S14*). In particular, in area C in summer, the presence of anoxic conditions in bottom waters favors greater NH_4^+ , PO_4^{3-} , Fe, and Mn DFSWIs.

Early diagenesis plays an important role in the Benthic-Pelagic Coupling (BPC) processes, *i.e.* sediment processes that affect the water column and water column processes that affect sediments (Testa *et al.*, 2021). In this interaction, bathymetry plays a major role in BPC, because the same amounts of a dissolved element, released or absorbed by sediments, exert very different effects on shallow and deep-water columns. Indeed, in shallow and very shallow bottoms, dissolved substances can diffuse throughout the water column up to the photic zone, thus affecting primary production; the consequent, increased nutrient supply increases the amount of rOM reaching sediment, thus inducing stronger DFSWIs and triggers an increasingly intense cycle (Joi and Anderson, 2008). In the Adriatic Sea, the BPC is clearly strongest in the areas located in front and south of the Po River Delta, which receive large amounts of nutrients and rOM (Cozzi *et al.*, 2019); indeed, in this area the BPC is so strong that it could

be described as land-benthic-pelagic coupling. In deep marine environments, BPC processes are clearly less intense, since the substances released by the SWI diffuse and dilute in a much larger volume and fail to involve the photic zone. This situation, combined with the presence in these areas of OM that has lost much of its reactivity, results in a much blander BPC. The physical structure of the water column is another major factor influencing the coupling of the benthic and pelagic systems. In fact, water column stratification favors the confinement of the substances released/absorbed by sediment to the bottom layer, particularly below the pycnocline. This, in turn, boosts OM mineralization, which as noted above, in the Adriatic Sea can induce complete anoxia of the seafloor and of bottom waters, subverting the SWI biogeochemical cycles besides hampering benthic production (Sturdivant *et al.*, 2013). Notably, P and metals are no longer trapped at the SWI with Fe and Mn hydroxide precipitates, but rather are released in the water column (Middelburg and Levin, 1999). Water column stratification also exerts effects in deeper environments, such as the MAD. In this basin, dense water standing close to the bottom for one or more years undergoes an aging process characterized by gradual loss of oxygen and nutrient enrichment due to extended OM mineralization.

The identification of areas sharing similar biogeochemical and sedimentological composition and processes (Spagnoli *et al.*, 2014), as well as DFSWIs, allows providing for the first time DFSWI values for DIC, ammonia, and phosphates on the Northern and Central Adriatic seafloor, enabling a more accurate definition of the budget of these elements in this ecosystem (Table 1).

North of the Po River Delta, some areas, facing local rivers, are characterized by diagenetic environments producing weak

Table 1. Average data of dissolved fluxes at the sediment-water interface as measured and calculated in the Northern and Central-Western Adriatic Sea (see *Figure S14* for location of the early diagenesis types).

Early diagenesis types	Average DIC benthic flux	Standard deviation	NH_4^+	Standard deviation	PO_4^{3-}	Standard deviation
	$\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$					
Type A (1)	3.09		0.59		0.03	
Type A (2)	19.61	16.51	0.50	0.42	0.12	0.08
Type B	55.96		13.62	19.98	0.31	0.29
Type C	5.66	10.89	8.06	21.87	0.09	0.09
Type D1 (north of Ancona)	7.89	6.91	3.70	3.55	0.01	0.01
Type D2a (from Ancona to Giulianova)	22.06		0.92		0.00	
Type D2b (from Giulianova to Ortona)			1.75	2.13	0.21	0.45
Type DD'			0.77		0.01	0.01
Type D'			2.22	0.54	0.01	
Type E	6.05	2.90	1.34	2.44	0.01	0.00
Type F1	-59.37		0.27		-0.02	
Type F2	9.15		0.17		0.00	
Type G	6.29	1.80	0.84	0.91	0.02	0.05

DFSWIs, due to solid and dissolved inputs from the local rivers and to water column hydrodynamics, which remove and redistribute OM and fine sediments along the coast and offshore (type A diagenesis; *Figure S14*). In the Gulf of Trieste, bottom sediment deposition is less affected by hydrodynamic conditions (Cosoli *et al.*, 2013; Pavoni *et al.*, 2023). This results in the buildup of fine sediments and OM inputs from the local rivers (Ogrinc *et al.*, 2005) and in benthic fluxes comparable to those measured south of the Po River Delta (type G diagenesis; *Figure S14*). In the Central Adriatic the DFSWIs are almost null (type F diagenesis, *Figure S14*); in some cases, where sediments are predominantly carbonate, phosphate, and DIC DFSWIs may be negative (type F1 diagenesis; *Figure S14*). However, since in some areas of the Adriatic Sea DFSWI measurements have not yet been performed, the insufficient data prevent classification (*Figure S14*: question dots).

The above findings highlight the role of bottom Adriatic sediments as sinks or sources of nutrients and carbon, especially as regards their contribution to the marine carbon budget. In particular, the bottom sediments in the Northern and Central Adriatic play a large role as carbon and phosphate sinks, whereas the rest of the Adriatic seafloor is a major source of nutrients, particularly of essential elements such as nitrogen and phosphorous, which control the primary production, and metals such as iron and manganese. In contrast, the coastal and fine sediments of the Western Adriatic are major DIC sources. This dual role of bottom sediments as carbon sources and sinks should be carefully examined and considered when formulating marine carbon budgets. Table 1 provides data that can be used for this purpose as well as to identify areas where data are still insufficient.

Another important finding regards the regeneration of nitrogen, carbon and phosphorous, which in sediments depends chiefly on OM degradation and – where N and P are concerned – also on iron and oxygen. Accordingly, the contribution of the bottom sediment to the recycling of these elements is the function of the main OM and particulate sources.

Notably, among the electron acceptors, oxygen always showed negative values, thus favoring eutrophication and the setup of anoxic emergencies in the offshore areas of Emilia Romagna and northern Marche. Finally, nitrate showed both negative and positive, but altogether negligible DFSWIs in terms of its contribution to the water column.

Conclusions

From 1982, several researches have been carried out in the Adriatic Sea by Italy's CNR and in the Gulf of Trieste by other research bodies. These activities allowed to develop and hone a number of approaches and methods to measure and calculate DFSWIs, which are described in detail in the paper. These methods include the construction and deployment of a benthic chamber, the AdaN, and of a lander, the Amerigo, for *in situ* measurements; the laboratory core incubation, as well as on-board PW extraction or micro-measurements at SWI, for laboratory measurements. Taking measurements using these methods allowed collecting data on DFSWIs in the Northern and Central Western Adriatic Sea and identifying the more reliable and appropriate approaches.

Although *in situ* measurements are more reliable, because of

the wider area measured and of the minimal modification of the environment under measurement, laboratory core incubation, PW modeling and on-board micro-profiling are often preferred as they involve lower costs and fewer technical challenges.

DFSWIs generally showed a seasonal trend, they are stronger in late summer and weaker in late winter, due to different near-bottom temperatures and primary production. The DFSWIs of the OM degradation products and of the final electron acceptors commonly declined from the Po River mouths southward along the Holocene mud wedge. This is due to a combination of two factors: i) the increasing distance from the main particulate and nutrient sources (the Po River mouths), with consequent weakening of the primary production, which is the main contributor of the highly rOM to the sediment, and ii) continuous and repeated bottom sediment reworking, which reduces the rOM content in surface sediments through the faster and stronger mineralization active in the aerobic water column. DFSWIs were weakest in the MAD, where low sedimentation rate and low rOM content favor the formation, near the SWI, of an aerobic environment where iron, manganese and phosphorous sink into sediment.

In summer, the DFSWIs of iron, manganese, and phosphorous were especially high in the nearshore area south of the Po River Delta, which is the first deposition area of the Po River particulate. This process is related to the presence of calm sea conditions, water column stratification, and high oxygen consumption on the seafloor, which induce anoxic conditions hence the reduction and release of iron, manganese, and phosphates. This environmental set up highlighted the high sensitivity of the phosphorous DFSWIs to changes in bottom physicochemical conditions, since phosphate regeneration is strongly affected by the reduction of Fe-oxyhydroxides, together with which the phosphate precipitates in oxidizing conditions.

In the coastal areas to the north of the Po River Delta, the DFSWIs were weak and determined by local conditions. In particular, scarce particulate and solute inputs from the local northern rivers combined with coastal hydrodynamics, which tend to remove fine sediments and rOM, result in OM accumulation only in limited areas in front of the mouths of the northern rivers.

In the center of the Northern Adriatic, DFSWIs were almost null and DIC and phosphate DFSWIs were sometimes negative. This is due to the predominant carbonate and aerobic environments on the seafloor, which favors the DIC and phosphorous precipitation into sediment.

In the offshore areas of the Central Adriatic, south of the Po River Delta, DFSWIs were weak due to the poor amount of rOM and fine sediments, which are confined by the WAC to nearshore areas. In the nearshore areas south of the Po River Delta, DFSWIs were always considerable and were influenced by the inputs from the minor rivers.

DFSWIs measurements and calculations in various areas of the Adriatic Sea allowed to identify biogeochemical facies (Spagnoli *et al.*, 2014) with comparable DFSWIs and to map the seafloor according to flux type and intensity. However, some areas for which data are yet to be collected remain to be classified. These findings allowed to provide, for the first time, a DFSWI value that can be used for carbon and nutrient budget calculations in the Adriatic Sea.

Finally, a greater knowledge of Adriatic DFSWIs highlighted the important role of sediments in water column

processes. In particular, in summer, bottom sediments play a non-negligible role in the development of hypoxic or anoxic conditions in the bottom waters of the Emilia-Romagna and northern Marche. This is due to high oxygen consumption determined by the mineralization of the OM deposited in the superficial sediments of these areas, coupled with the high water temperatures and water column stratification. Furthermore, bottom sediments in the central areas of the Northern Adriatic Sea play an important role as DIC and phosphate sinks, while in the areas close to the coast, they behave like sources of carbon and phosphorous. This dual role of the Adriatic Sea sediments should be carefully considered in carbon and nutrient budget modeling, especially when assessing the contribution of DIC to carbon fluxes at the atmosphere-sea interface and to seawater acidification. In this context, additional data about DFSWIs are needed to assess in greater detail the contribution of sediments to the marine budget of the main chemical compounds that play a role in global climate and marine cycles changes.

Finally, as noted by Testa *et al.* (2021), most recent efforts directed at the quantification of the nutrient and carbon budgets in the Adriatic Sea have been devoted to developing numerical modeling, not collecting fresh data (Alvarez *et al.*, 2022). Yet, new information would be extremely useful, especially at a time when far-reaching global changes – particularly increased temperature and solid and liquid riverine variations of contributions – are affecting marine biogeochemical cycles in the Adriatic Sea.

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Online supplementary material:

Figure S1. Schematic view of early diagenesis processes.

Figure S2. Early diagenesis processes. a) Schematic drawing of dissolved ions produced and/or consumed in pore waters by early diagenesis processes (modified from Froelich et al., 1979; Milucka et al., 2012). Enlargement: Fe and Mn oxyhydroxide cycles; b) biogeochemical reactions taking place in the top few centimeters of sediment (Blue: final electron acceptors; Red: organic matter degradation products).

Figure S3. Stations in the Central and Northern Adriatic Sea where in situ measurements, on-board core incubations, and pore water chemical profile modeling were conducted from 1982. Symbols, season, and depth color codes are reported in the legend, stations are listed in Table S1.

Figure S4. a) Schematic drawing of a benthic chamber (Spagnoli et al., 2018, 2019). BC, Benthic Chamber: 1) Device for collecting water samples inside and outside the chamber or to inject tracers into the chamber (Vampire); 2) multiparameter probe (Hydrolab MSS) to measure oxygen, pH, Eh, temperature, conductivity (i.e. salinity) and pressure (depth) in the chamber; 3) housing of the electronics (Idec MicroSmart FC6A PLC); 4) housings of batteries; 5) rotating paddle; 6) motors. b-g) Evolution of the benthic chamber technology at the Italian CNR: b) Benthic lander deployed on the Adriatic seafloor in 1982 (Berelson and Hammond, 1986) (credit, Gabriele Marozzi); c) first manual benthic chambers involving sampling by divers; d) first automatic benthic chamber developed at IGM-CNR of Bologna (Masini et al., 2001); e) the AdaN chamber (Spagnoli et al., 2018, 2019). f) the Amerigo lander on deck (Spagnoli et al., 2018, 2019); g) the Amerigo deployed on the seafloor. h) incubation of cores for the measurement of dissolved fluxes at the sediment-water interface in a thermostatic box (Spagnoli F., 1994).

Figure S5. Concentrations of chemical compound i^{th} versus time; m is the angular coefficient of the straight line calculated by the minimum square method.

Figure S6. Pictures of some steps of the collection of pore waters from sediment cores by the SW104 corer. a) the sediment core mounted on the extrusion frame with its top in the inert gas glove box; b) subsampling of the sediment core slices; c) centrifugation of sediment slices d) pore water filtration, aliquot preparation poisoning and acidification in the inert gas glove box.

Figure S7. On-board profiling at the sediment-water interface on a core by a microelectrode (CNR, Cruise Vector 632). a) micro-profiling apparatus; b) drawing of the results (O_2 concentrations).

Figure S8. Pore water and bottom water concentration profile of chemical compound i^{th} obtained from pore water extraction.

Figure S9. DFSWIs of NH_4^+ and PO_4^{3-} measured by in situ benthic chamber deployments (blue), by on-board core incubation (clear blue), and by pore water modeling (grey) at the same station in the same season. See Figure S3 for station locations.

Figure S10. Variability of NH_4^+ and PO_4^{3-} DFSWIs in different seasons (summer and spring) at stations located in the same area (in this case, facing the Po di Pila mouth). See Figure S3 for station locations.

Figure S11. DFSWIs of organic matter degradation products (NH_4^+ , DIC, PO_4^{3-}) at stations located along the Holocene mud wedge on the Adriatic seafloor, between the Po River Delta and the MAD, in late summer. Blue: in situ deployments, light blue: on-board incubations, grey: pore water calculations. PW, Pore Water.

Figure S12. DFSWIs of organic matter degradation products (NH_4^+ , DIC, PO_4^{3-}) on the Adriatic seafloor north of the Po Delta and offshore in the Central Adriatic. PW, Pore Water.

Figure S13. DFSWIs of the final electron acceptors (O_2 , NO_3^- , Fe, Mn) at the station established on the Adriatic seafloor. PW, Pore Water.

Figure S14. Areas characterized by different early diagenesis processes and flux intensities at the water-sediment interface in the Adriatic Sea. Question marks indicate areas where the available data are insufficient for classification.

Table S1. Dissolved fluxes at the sediment-water interface as measured and calculated from pore water profiles in the Northern and Central-Western Adriatic Sea. Units: $mmol \cdot m^{-2} \cdot d^{-1}$.