



Effects of a small seagull colony on trophic status and primary production in a Mediterranean coastal system (Marinello ponds, Italy)

Geraldina Signa*, Antonio Mazzola, Salvatrice Vizzini

Department of Earth and Marine Sciences, University of Palermo, CoNISMa, via Archirafi 18, 90123 Palermo, Italy

ARTICLE INFO

Article history:

Received 21 September 2011

Accepted 15 June 2012

Available online 14 July 2012

Keywords:

transitional environments

yellow-legged gull

seabird

trophic status

primary production

stable isotopes

ABSTRACT

Colonies of seabirds have been shown to influence nutrient cycling and primary production of coastal areas, but knowledge is still limited above all for smaller colonies. This study evaluates the influence of a small resident seagull colony (*Larus michahellis* Naumann, 1840) on a Mediterranean coastal system (Marinello ponds, Sicily, Italy). The presence of ornithogenic organic matter from seagull guano was first assessed at increasing distances from the colony using $\delta^{15}\text{N}$ to indicate the effects of guano on the trophic status and primary production. The pond directly affected by guano deposition showed an anomalous water and sediment chemistry, especially regarding physico-chemical variables (pH), nitrogen isotopic signature, nutrient balance and phytoplankton biomass. These effects were not observed in the adjacent ponds, highlighting pronounced, small spatial-scale variability. Given the worldwide presence of seabird colonies and the scarcity of research on their effect on coastal marine areas, the study shows that seabird-mediated input may be important in influencing ecosystem dynamics of coastal areas, even where both the system in question and the colony are small.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Transitional environments are unstable and sensitive coastal systems, owing to their interface location and consequent variable morpho- and trophodynamic regime. Major features are their shallow waters, limited surface area and variable degree of confinement, depending on the number and width of connections with the adjacent sea and their freshwater input (McLusky and Elliot, 2007). In this context, while many factors influence both estuarine/coastal trophic status and primary production, the rates of nutrient supply and the balance between internal and external load are of the utmost importance in regulating these processes.

Allochthonous nutrients and organic matter can reach transitional environments in two ways: carried passively by abiotic factors (watershed runoff, riverine and tidal inflow) and actively by biotic vectors (Dame and Allen, 1996). While the role of abiotic drivers in influencing ecosystem dynamics and functioning in coastal areas is well-studied and documented (e.g. Sarà, 2006; Como et al., 2007), little is known about the role of biotic vectors in moving and redistributing resources across coastal landscape boundaries, especially in transitional environments.

Amongst the biotic allochthonous nutrient sources that greatly influence aquatic ecosystems, seabirds are among the most important, and are often underestimated in transitional environments. It is well known that avian populations may affect nutrient and organic matter processing by moving nutrients and organic matter between ecosystems, with birds feeding in one area and roosting or nesting in another (Bildstein et al., 1992; Polis and Hurd, 1996). Because of this widespread phenomenon, several seabirds have been labelled as biovectors, introducing large amounts of marine-derived nutrients to land (e.g. Loder et al., 1996; Polis and Hurd, 1996; Anderson and Polis, 2004; Ellis et al., 2006). Due to their recent very large demographic increase (Vidal et al., 1998; Duhem et al., 2008) and their opportunistic feeding behaviour (Payne and Moore, 2006; Ramos et al., 2009; Moreno et al., 2010), seagulls also move nutrients in the opposite direction as they feed mainly on terrestrial resources in urbanised areas and live and nest in aquatic ecosystems (e.g. Marion et al., 1994; Hahn et al., 2007).

Seabird guano has been recognised globally as an important fertiliser (e.g. Bosman and Hockey, 1986), being rich in organic and inorganic nutrients, especially nitrogen and phosphorus. Its primary effect, as observed in the most widely studied aquatic systems that feature large colonies (i.e. freshwater, marine pelagic and, in particular Arctic and Antarctic), is enhancement of local nutrient availability (e.g. Sanchez-Piñero and Polis, 2000; Ellis et al., 2006; Keatley et al., 2009). Other direct and indirect effects often

* Corresponding author.

E-mail addresses: geraldina.signa@unipa.it, geraldinasigna@yahoo.it (G. Signa).

associated with bird guano deposition are alterations of physico-chemical variables and trophic status (e.g. Manny et al., 1994; Marion et al., 1994; Loder et al., 1996; Brimble et al., 2009), an increase in nutrient uptake by primary producers and phytoplankton biomass (e.g. Bosman and Hockey, 1986; Payne and Moore, 2006; Brimble et al., 2009; Gwiazda et al., 2010) as well as an increase in zooplankton and zoobenthos density (Wootton, 1991; Palomo et al., 1999; Kolb et al., 2010).

Stable nitrogen isotope ratios (^{15}N ; ^{14}N ; $\delta^{15}\text{N}$) are widely used as a proxy for the ornithogenic influence on ecosystems (e.g. Wainright et al., 1998; Blais et al., 2005; Keatley et al., 2009). Many studies have showed that sediments and water close to bird colonies are ^{15}N -enriched, exhibiting a distinctive isotopic signature that is valuable for demonstrating bird-derived input to aquatic systems. This enrichment results from the ^{15}N enrichment along marine food chains and the isotopic fractionation occurring during volatilisation of the ammonia from seabird products (Mizutani and Wada, 1988). Since most research on the effects of avian input in aquatic systems has been carried out in lotic systems characterised by large colonies and high hydrodynamism, there is a need for studies in lentic systems such as transitional environments, where bird colonies are smaller and the limited size and scarce connections with the sea and rivers can magnify effects.

This study assessed the effects of avian allochthonous input from a small seagull colony on trophic status and primary production in a Mediterranean coastal system. The purpose of this study was firstly to detect the presence of avian allochthonous input in the system at increasing distances from the colony, using $\delta^{15}\text{N}$ in sedimentary and particulate organic matter. Once the isotopic influence of guano was ascertained, we evaluated the effect on the trophic status and primary production using nutrient concentrations in surface water and sediment and Chl-*a* concentration in the surface water.

2. Materials and methods

2.1. Study area

The Marinello coastal system is in the Gulf of Patti (Messina, Italy) on the Tyrrhenian coast of Sicily (Italy, Mediterranean) (Fig. 1) and is characterised by rapid geomorphological evolution and high structural and hydrobiological complexity. The particular anemological and hydrological regime formed littoral bars, delimiting 5 small coastal ponds (Verde, Fondo Porto, Porto Vecchio, Mergolo and Marinello). These are characterised by a dynamic shape and size due to rapid evolution of the coastal morphology (Crisafi et al., 1981). The ponds are affected by different water inflows. The outermost ponds are mainly influenced by seawater inflows, through infiltration or direct contribution during storms. In contrast, the most significant input to the three inner ponds is surface runoff, carrying dissolved and particulate matter from surrounding land (Leonardi et al., 2005).

Of these five ponds, three were sampled in this study: Verde, Fondo Porto and Mergolo, selected according to their increasing distance from a resident seagull colony. Verde is small (1.7 Ha; 3.0 m max depth) and directly affected by a colony of yellow-legged gulls (*Larus michahellis* Naumann, 1840) living on the cliff of Tindari behind (Mazzola et al., 2010, Fig. 1). The adjacent ponds, Fondo Porto (1.3 Ha, 2.0 m max depth) and Mergolo (2.5 Ha, 3.5 m max depth), around 200 m and 600 m respectively from the colony, completely lack gulls (Mazzola et al., 2010, personal observation).

2.2. Field activities

To estimate nutrient load from the yellow-legged gulls of the Marinello colony, birds sitting on the cliff, moving around the shore

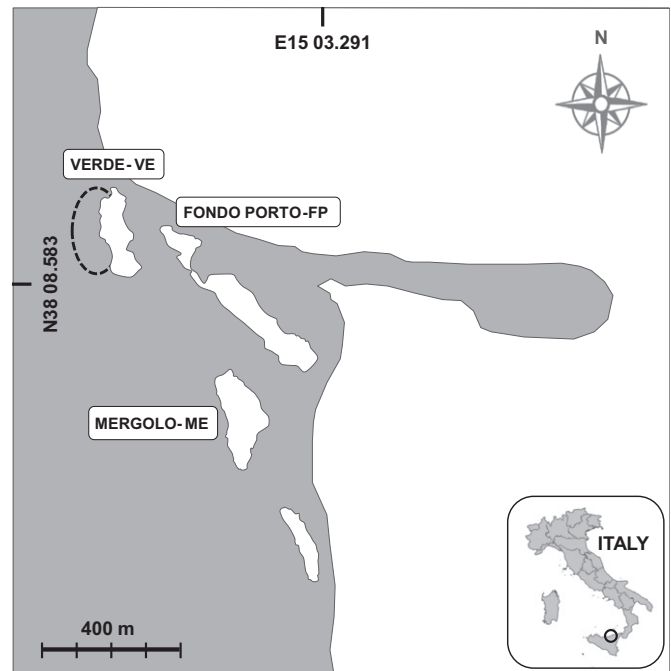


Fig. 1. Map of the study area with sampling ponds. The dotted oval indicates the seagull colony location.

and flying over Verde pond were counted seasonally using binoculars (10 × 50) from three points equidistant from the cliff and by three observers contemporaneously. Diurnal estimates were representative of the 24-h period and seasonal estimates representative of the entire season considering the resident habit of the Marinello seagulls (Perco et al., 1986).

From September 2008 to August 2009, surface water and sediment were collected monthly from the three ponds (Fig. 1) and seagull guano was carefully scraped from the sandy shores of Verde. Surface water was collected from each basin using 5 l bottles; physico-chemical variables of surface water were measured in an YSI 556 Multiprobe System. Hand corers (inner diameter: 4 cm) were used to collect surface sediment from the bottom of each pond. Both surface water and sediment were sampled in triplicate. All samples were kept cool and dark upon arrival at the laboratory.

2.3. Laboratory analyses

Surface water was filtered through a 200 μm mesh net to obtain the particulate fraction, and then onto precombusted (450 °C, 4 h) Whatman GF/F filters for analysis of particulate organic matter (POM) $\delta^{15}\text{N}$, particulate nitrogen and phosphorus (PN and PP) and Chlorophyll-*a* (Chl-*a*). Filtered water was kept for dissolved nitrogen and phosphorus (DN and DP) analyses and then, as for filters, sediment and guano were frozen at –20 °C until analysis.

Before analysis, guano was wet sieved at 200 μm to eliminate sand and coarse residuals, while sediment was sieved at 63 μm to select the bioavailable fraction of sedimentary organic matter (SOM). Samples of filters, guano and sediments previously oven-dried (60 °C) and ground to a fine powder, were analysed for $\delta^{15}\text{N}$ in an Isotope Ratio Mass Spectrometer (Thermo Scientific Delta Plus XP) connected to an Elemental Analyser (Thermo Scientific Flash EA 1112). Isotopic values were expressed in conventional δ unit notation as parts per mil deviations from the international standard, atmospheric nitrogen (N_2), following the

formula: $\delta X = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3$, where X is ^{15}N and R is the corresponding $^{15}\text{N}/^{14}\text{N}$ ratio. Analytical precision based on the standard deviation of replicates of internal standards was 0.2‰.

Both dissolved and particulate nitrogen (DN and PN) and phosphorus (DP and PP) were determined according to the persulfate digestion procedure proposed by Koroleff–Valderrama (Valderrama, 1981; Koroleff, 1983a,b), with consecutive determination of nitrate and phosphate based on colorimetric methods (cf. Grasshoff, 1983). Guano and sediment nitrogen (SN) were measured according to Hedges and Stern (1984) in an Elemental Analyser (Thermo Scientific Flash EA 1112). Acetanilide was used as standard to calculate the K -factor. Guano and sediment phosphorus (SP) was measured after hot digestion with nitric and perchloric acids (IRSA, 1985). The determinations were carried out using ascorbic acid as a reducing agent (Murphy and Riley, 1962; Jones and Spencer, 1963), followed by the determination of phosphate based on colorimetric methods. Chlorophyll- a (Chl- a) was extracted in the dark using 90% acetone overnight (4 °C) (Morabito, 1997) and determined spectrophotometrically (Jeffrey and Humphrey, 1975; Lorenzen and Jeffrey, 1980).

2.4. Data elaboration

Mean loading rate of N and P by seagulls to Verde was derived as the product of seagull excretion rate, mean concentration of N and P in seagull guano and mean numbers of seagulls counted on the Verde cliff according to the modification of the approach indicated by Manny et al. (1994). Bird excretion rate was based on literature estimates for the herring gull *Larus argentatus*, reviewed by Hahn et al. (2007), the closest related species to the yellow-legged gull in the Mediterranean area. N:P molar ratios were calculated for guano and surface water from total nitrogen TN and total phosphorus TP data transformed on molar basis.

Data were found to be heteroscedastic even when transformed, so nonparametric Kruskal–Wallis ANOVA on ranks (Zar, 1999) was carried out, using the Statistica 8.0 package, to test differences in $\delta^{15}\text{N}$ and concentration of nutrients and Chl- a between ponds. Analyses were followed by post-hoc multiple comparison tests of mean ranks. Principal coordinates analysis (PCO) was performed using the Primer 6.0 package to assess the main directions of variation in the dataset, based on $\delta^{15}\text{N}$, nutrients and Chl- a data. Physico-chemical variables were superimposed onto the graph to detect their correspondence with the ordination obtained.

3. Results

3.1. Ornithogenic input

The highest numbers of seagulls were recorded in summer and autumn (125 and 105 ind. respectively). This agrees with the post-reproductive coastal aggregation habits of Italian yellow-legged gulls due to post-natal dispersion (Brichetti and Fracasso, 2006). In contrast, the lowest numbers found in winter and spring (80 and 90 ind. respectively) may correspond to adult individuals comprising the resident colony. Throughout the study period, high variation in guano nitrogen content was observed, ranging from 18.3 to 96.5 mg/g (mean: 44.2 ± 25.7 mg/g), while phosphorus content was less variable and appreciably lower, ranging from 3.1 to 20.4 mg/g (mean: 7.3 ± 4.1 mg/g). Consequently, analysis of nutrients in guano, associated with estimates of total numbers and defecation rate of seagulls, suggested that nutrient load in Verde from seagulls was seasonally variable, ranging from 31.4 to 49.1 kg/year, with a mean value of 39.3 ± 7.7 kg/year for nitrogen, and from 5.2 to 8.1 kg/year, with a mean value of 6.5 ± 1.3 kg/year for phosphorus.

3.2. Stable nitrogen isotopes

$\delta^{15}\text{N}$ for yellow-legged gull guano collected from the shores of Verde showed a wide range, varying from 6.0 to 14.7‰ (mean: 9.8 ± 2.3 ‰) (Fig. 2). The $\delta^{15}\text{N}$ of SOM from VE, the pond closest to the gull colony, fell precisely inside the range for guano, varying from 6.6 to 11.3‰ (mean: 9.6 ± 1.1 ‰), while in the other ponds SOM was significantly depleted in ^{15}N (Table 1), ranging from 1.4 to 7.6‰ (mean: 4.8 ± 1.6 ‰) and from 3.9 to 7.6‰ (mean: 4.8 ± 0.7 ‰) in FP and ME ponds respectively (Fig. 2). The $\delta^{15}\text{N}$ of POM showed a similar trend, the samples from VE pond being highly enriched in ^{15}N (range: 8.8–16.8‰; mean: 11.6 ± 2.0 ‰), followed by FP pond (range: 4.1–9.0‰; mean: 6.6 ± 1.4 ‰) and ME pond (range: 0.8–7.4‰; mean: 4.7 ± 1.6 ‰). Kruskal–Wallis ANOVA showed a highly significant difference between the POM $\delta^{15}\text{N}$ signature from the three ponds (Table 1) and the multiple comparisons highlighted the following ordination: VE > FP > ME, corresponding to increasing distance from the seabird colony.

3.3. Trophic status

During the sampling period, physico-chemical variables of surface water were as follows: pH varied from 7.8 to 8.8 (mean: 8.5 ± 0.2 units) in Verde, VE from 7.8 to 8.5 (mean: 8.1 ± 0.2 units) in Fondo Porto, FP and from 7.7 to 8.2 (mean: 7.9 ± 0.2 units) in Mergolo, ME. Dissolved oxygen, DO, varied from 36.6 to 135.7% (mean: 106.9 ± 25.0 %) in VE, from 44.7 to 146.1% (mean: 100.1 ± 23.2 %) in FP and from 48.3 to 133.9% (mean: 98.4 ± 19.5 %) in ME.

Nitrogen and phosphorus concentrations, both in the particulate and dissolved compartment, as well as Chl- a concentration, were higher overall in Verde, VE, than in the other ponds (Figs. 3 and 4) as shown by Kruskal–Wallis analysis and multiple comparisons (Table 1). Both particulate nitrogen and phosphorus, PN and PP, from VE showed a clear seasonal trend, with two major peaks in October and July, corresponding respectively to 2265.4 and 1206.4 $\mu\text{g/l}$ for PN, and 443.9 and 409.3 $\mu\text{g/l}$ for PP (Fig. 3a and b). A similar seasonal trend was observed for Chl- a and dissolved

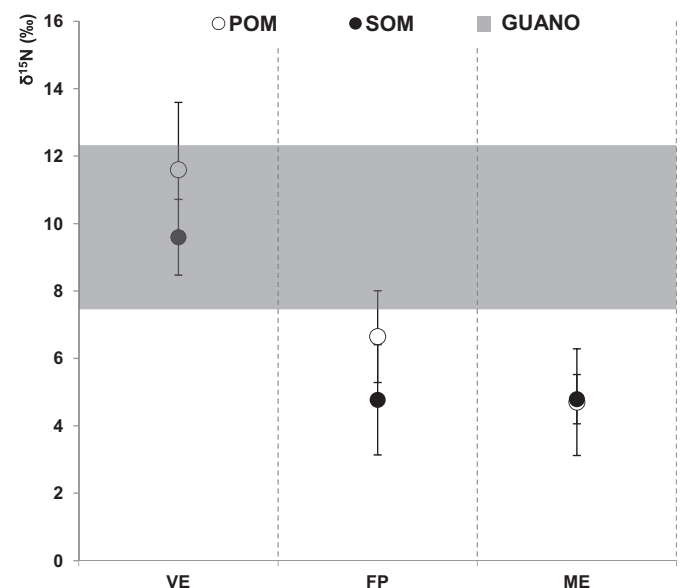


Fig. 2. Annual mean $\delta^{15}\text{N}$ (‰) \pm st. dev. of POM and SOM in the three ponds: Verde (VE), Fondo Porto (FP) and Mergolo (ME). Annual mean $\delta^{15}\text{N}$ (‰) \pm st. dev. of guano is superimposed onto the graph.

Table 1
Summary of Kruskal–Wallis ANOVA on ranks and post-hoc multiple comparison tests for $\delta^{15}\text{N}$, nutrient and Chl-*a* concentrations, N:P ratio of the three ponds: Verde (VE), Fondo Porto (FP) and Mergolo (ME).

Compartment	Variable	H	p	Multiple comparisons
Particulate	$\delta^{15}\text{N}$	80.37	***	VE > FP > ME
	PN	55.47	***	VE > ME = FP
	PP	69.63	***	VE > ME = FP
	Chl- <i>a</i>	56.77	***	VE > ME = FP
Dissolved	DN	36.34	***	VE > ME > FP
	DP	8.25	*	VE = ME > FP
Surface water	N:P	51.35	***	ME = FP > VE
Surface sediment	$\delta^{15}\text{N}$	71.00	***	VE > ME = FP
	SN	66.52	***	VE > ME > FP
	SP	50.50	***	VE > FP > ME

nitrogen, DN, from the same pond, although the summer peak shifted to August (103.2 and 792.7 $\mu\text{g/l}$ respectively for Chl-*a* and DN) (Figs. 3c and 4a). The lowest values were recorded from December to May for all these variables, followed by a sharp increase in summer (Figs. 3 and 4). This clear seasonal trend was not distinguishable in the other ponds, Fondo Porto, FP, and Mergolo, ME, for any of the above-mentioned variables (Figs. 3 and 4). Differences in dissolved phosphorus concentration, DP, between

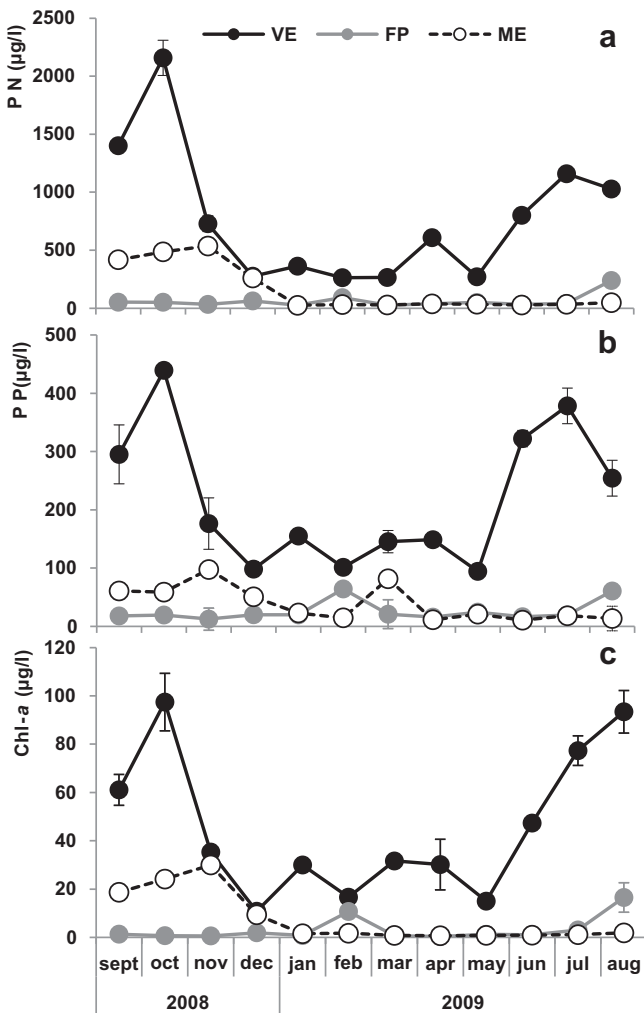


Fig. 3. Mean particulate nitrogen (a), phosphorus (b) and Chl-*a* concentrations (c) ($\mu\text{g/l}$) \pm st. dev. throughout the sampling period in surface water of the three ponds: Verde (VE), Fondo Porto (FP) and Mergolo (ME).

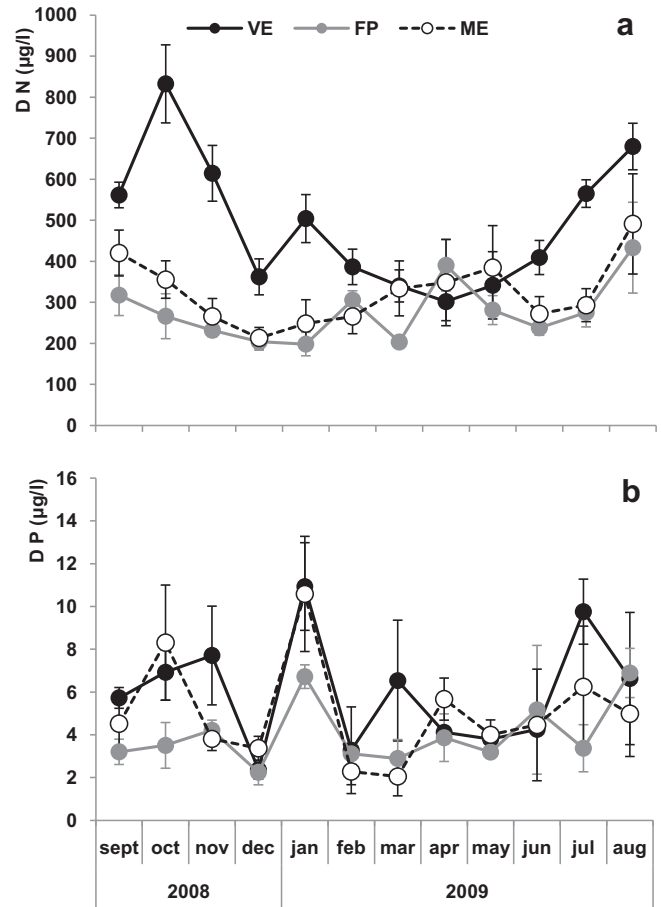


Fig. 4. Mean dissolved nitrogen (a) and phosphorus (b) concentrations ($\mu\text{g/l}$) \pm st. dev. throughout the sampling period in surface water of the three ponds: Verde (VE), Fondo Porto (FP) and Mergolo (ME).

ponds were less pronounced, although significant (Fig. 4b, Table 1). The highest concentrations were detected in January in all ponds (Fig. 4b), though VE and ME showed significantly higher values overall than FP (Table 1).

The N:P molar ratio of guano and surface water from Verde overlapped, varying respectively between 4.1 and 26.5 (mean: 14.9 ± 6.8), and between 7.8 and 21.4 (mean: 12.9 ± 3.1) (Fig. 5). Comparing the N:P ratio in surface water from the three ponds, VE showed significantly lower values and a narrower range than the other ponds (Table 1, Fig. 5).

Sedimentary nitrogen and phosphorus concentration were significantly higher in VE than in the other ponds (Table 1, Fig. 6), although post-hoc multiple comparisons did not show a unique spatial gradient for both variables, nitrogen being higher in Mergolo, ME, than Fondo Porto, FP, and vice-versa for phosphorus. Furthermore, in contrast to previous records of the particulate compartment, sedimentary nutrients did not exhibit a common temporal trend, showing the highest values in winter and summer respectively for nitrogen and phosphorus, while sedimentary nutrient dynamics were similar in the three ponds studied (Fig. 6).

Principal coordinates analysis, PCO, was performed using trophic and isotopic variables to assess similarity between ponds in multivariate space (Fig. 7). The ponds away from the direct influence of the seagull colony, FP and ME, clustered together to the left side of the graph, while the seabird-affected pond, VE, was distributed more along the right side of the graph. Even along the vertical axis, ME and FP were fairly overlapped, while VE samples

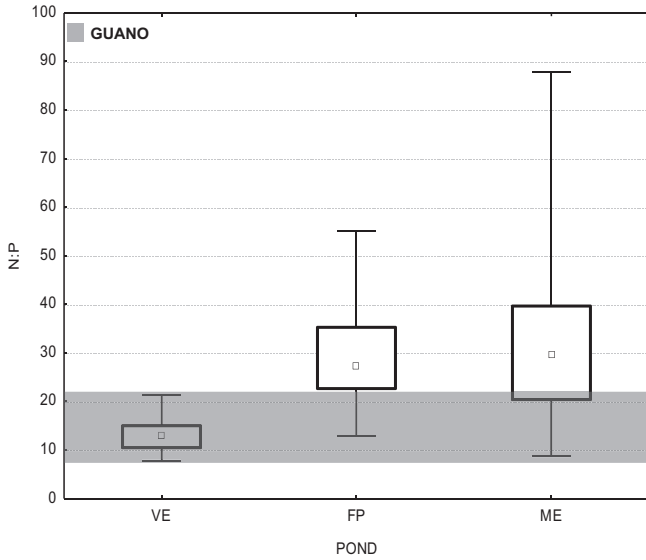


Fig. 5. Box and whisker plots of molar N:P Redfield ratio of surface water in the three ponds: Verde (VE), Fondo Porto (FP) and Mergolo (ME). Whiskers indicate the range of variation; boxes indicate the 25–75% percentiles; squares inside boxes indicate the median. Mean N:P ratio \pm st. dev. of guano is superimposed onto the graph.

were distributed on a temporal basis, with samples from July to October clustering together in the lower right part of the graph. Axis 1 explains 54.8% of total variation, while axis 2 explains only 13%. Physico-chemical variables superimposed onto the graph

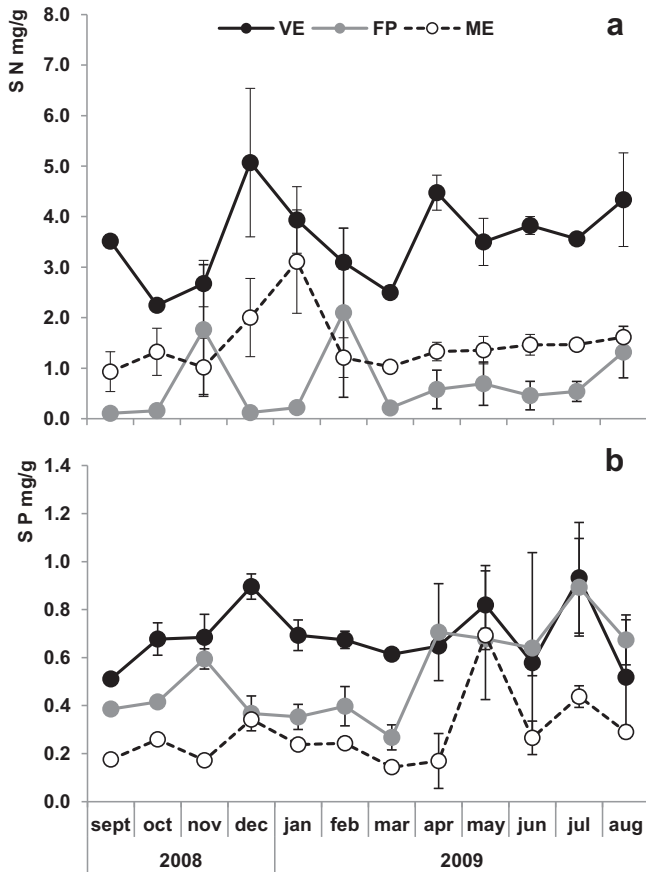


Fig. 6. Mean sedimentary nitrogen (a) and phosphorus (b) concentrations ($\mu\text{g/l}$) \pm st. dev. throughout the sampling period in the surface water of the three ponds: Verde (VE), Fondo Porto (FP) and Mergolo (ME).

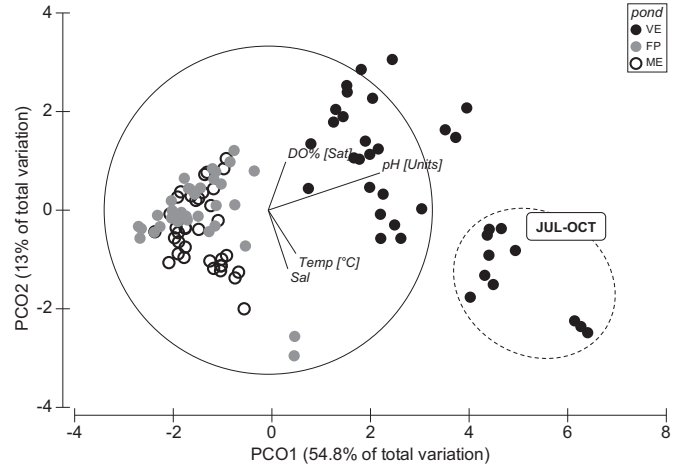


Fig. 7. PCA based on $\delta^{15}\text{N}$, nutrient and Chl-*a* concentration of the three ponds: Verde (VE), Fondo Porto (FP) and Mergolo (ME). Physico-chemical variables were superimposed onto the graph.

indicated that pH is the variable that best fits the ordination obtained, with the highest values in VE samples and the lowest in samples from the other ponds.

4. Discussion

In the Marinello coastal system, the pond directly affected by seabird guano deposition had an anomalous water and sediment chemistry, especially regarding physico-chemical variables, nitrogen isotopic signature, nutrient balance and phytoplankton biomass (Chl-*a*).

4.1. Detection of ornithogenic input

$\delta^{15}\text{N}$ of guano from Verde shores was highly comparable to the isotopic signature of seabird and other seabird guano from different areas (Mizutani and Wada, 1988; Wainright et al., 1998; Evenset et al., 2007). $\delta^{15}\text{N}$ of guano reflects the isotopic signature of the bird diet (Mizutani and Wada, 1988), thus the wide range obtained in this study mirrors the variability of the seagull diet during the sampling period. The yellow-legged gull, *Larus michahellis*, like other seagulls, has an omnivorous and scavenger trophic habit, consuming prey in proportion to its availability (Moreno et al., 2010). Studies on the seagull diet carried out using both classic and isotopic approaches identified a broad spectrum of prey of both terrestrial and marine origin but also, and often principally, various items of rubbish of anthropic origin, easily available in urbanised areas (Payne and Moore, 2006; Ramos et al., 2009; Moreno et al., 2010). Dietary changes over the reproductive and growth cycle due to varying seagull nutritional requirements (Navarro et al., 2010) may also contribute to the observed variability in nutrients and guano $\delta^{15}\text{N}$.

$\delta^{15}\text{N}$ of SOM and POM is widely used as a proxy of ornithogenic origin of organic matter in polar systems (e.g. Wainright et al., 1998; Blais et al., 2005; Keatley et al., 2009) because of the important isotopic enrichment due to guano input. As first shown by Mizutani and Wada (1988), the main mechanism responsible for this enrichment is ornithogenic nitrogen, once excreted, undergoing ammonium volatilisation and isotopic fractionation, leaving the residual pool of NH_4 enriched in ^{15}N . This mechanism was widely observed in terrestrial soils from islands (e.g. García et al., 2002; Markwell and Daugherty, 2003; Kolb et al., 2010) and polar areas (e.g. Wainright et al., 1998; Blais et al., 2005; Brimble et al., 2009).

Despite the widespread demographic increase in seagulls in the Mediterranean basin over the past 40 years (Vidal et al., 1998), almost no research has been carried out on seagull-impacted coastal systems using stable isotopes, preventing comparison with similar areas. In this study, the enriched values in Verde mirror the enriched values of guano, suggesting allochthonous input of ornithogenic origin. In fact, seagulls in the Marinello coastal system spend most of their time resting in the colony, flying over and walking along the shores of Verde, excreting directly into the water and along the shore. In contrast, in Mergolo and Fondo Porto, $\delta^{15}\text{N}$ was similar to values previously reported in other Mediterranean transitional environments unaffected by seabirds (e.g. Vizzini and Mazzola, 2008; Carlier et al., 2009; Lloret and Marin, 2009). As observed by Wainright et al. (1998) in the waters surrounding the Alaskan Pribilof islands, which are highly affected by guano deposition, similar effects were found in the $\delta^{15}\text{N}$ of phytoplankton receiving allochthonous input from bird guano. In this case, trophic enrichment seemed to be the main factor in enriching the dissolved inorganic nitrogen pool with ^{15}N , thus $\delta^{15}\text{N}$ of the nitrogen available to phytoplankton followed a gradient from higher $\delta^{15}\text{N}$ in areas of large input to lower $\delta^{15}\text{N}$ where there is less input. In agreement with these results, the highest $\delta^{15}\text{N}$ in our study was found in Verde, the lowest in Mergolo, which is furthest from the gull colony, and intermediate values in Fondo Porto, the midway station (Fig. 2).

Sedimentary $\delta^{15}\text{N}$ did not follow a similar isotopic gradient at increasing distance from the colony, being higher in Verde and comparably lower in both ponds further from the colony, probably due to the slow environmental response of the sedimentary compartment. The results of this study confirm the effectiveness of $\delta^{15}\text{N}$ as a proxy of ornithogenic origin of organic matter also in transitional environments, where the effects seem to be magnified by constrained geomorphological drivers and marked small-scale variability.

4.2. Nutrient balance and primary production

Once the presence of ornithogenic organic matter was detected using $\delta^{15}\text{N}$, nutrient balance and primary production in the three ponds were assessed. Nutrient and chlorophyll-*a* concentrations showed that Verde had the highest trophic status in the system, as previously highlighted by Leonardi et al. (2000), representing a hotspot of biological primary production. Similar fertilising effects were observed in other aquatic systems affected by bird guano influence (e.g. freshwater, Payne and Moore, 2006 and polar ecosystems, Michelutti et al., 2010).

Seabird guano is typically rich in nitrogen, phosphorus and potassium (Wootton, 1991) and mainly composed of uric acid (Lindeboom, 1984). Once guano is excreted, uric acid is mineralised into ammonia by aerobic and anaerobic bacteria (Loder et al., 1996; Wainright et al., 1998), becoming directly available to primary producers. Although some of the ammonia subsequently volatilises, much is rapidly converted into nitrite and nitrate by nitrifying bacteria (Bosman and Hockey, 1986). The availability of nitrogen and phosphorus is particularly important for marine primary production as marine algae absorb nitrogen and phosphorus mainly in their inorganic forms (de Boer, 1982; Middelburg and Nieuwenhuize, 2000). Furthermore, experimental approaches have shown that especially nitrate, ammonium and phosphate enhance the growth rate of phytoplankton (Örnólfsson et al., 2004) and of both benthic and turf algae (e.g. Kuffner and Paul, 2001).

Due to the small size of the Marinello seagull colony, the estimated phosphorus and nitrogen load from seabird input to Verde was very small compared to other areas with larger seabird colonies (e.g. Manny et al., 1994; Marion et al., 1994; Post et al., 1998;

Palomo et al., 1999). Despite this, the consequences for nutrient status and primary production of Verde were marked. Annual mean particulate nitrogen and phosphorus concentrations were respectively 13 and 8 times higher in Verde than in Fondo Porto and respectively 5 and 6 times higher than in Mergolo. Annual mean Chl-*a* concentration, a proxy of phytoplankton biomass and estuarine/coastal eutrophication (Paerl et al., 2003), was 14 and 5 times higher in Verde than in Fondo Porto and Mergolo respectively. Ecosystem responses depend on nutrient load but also on several critical physico-chemical characteristics and processes (Pinckney et al., 2001). Small pond size and scarce water exchange in Verde due to the absence of direct marine influence definitely contributed to magnifying the expected effect on trophic status and primary production, while greater water exchange in Fondo Porto probably reduced the expected indirect effect due to its proximity to Verde.

pH and dissolved oxygen are the physico-chemical variables of surface water that give the best indication of trophic status, as they depend mainly on the photosynthetic activity of aquatic organisms (Giordani et al., 2009). These were higher in Verde than in the other ponds. Accordingly, supersaturation and alkalinity conditions associated with Verde are basically attributable to phytoplanktonic primary production enhanced by high nutrient availability, completing the altered picture emerging from Verde.

Differences between the ponds were more pronounced for the particulate compartment than the dissolved one. Although in coastal areas the former is mainly composed of phytoplankton and detritus due to primary production and resuspension phenomena (Pinckney et al., 2001), very high Chl-*a* concentrations and microtidal features of Verde suggest a dominance of phytoplankton. After experimental pulse nutrient enrichments in tidepools, Methratta (2004) observed that dissolved nutrient concentration increased initially but the effect rapidly diminished, indicating that the nutrients pulsed were rapidly taken up by algae and retained in the algal biomass. Hence, differences between particulate and dissolved nutrients in Verde may be attributable to the rapid uptake of dissolved nutrients by phytoplankton. The striking correspondence between particulate nutrients and Chl-*a* concentration seasonal trends in Verde (Fig. 3) confirms the previous hypothesis, providing evidence of the rapid response of phytoplankton biomass to allochthonous nutrient load, due to the capacity of algal cells to divide daily under optimal conditions (Cloern and Jassby, 2008). Furthermore, under phytoplankton bloom conditions, large amounts of phytoplankton detritus can be deposited onto the sediment (Fisher et al., 1998) and the nutrients released again, leading to a positive feedback loop that perpetuates blooms and high particulate and sedimentary nutrient concentration (Pinckney et al., 2001), as observed in Verde.

As confirmation of the non-canonical trends observed in Verde, recent reviews show a broad spectrum of seasonal phytoplankton patterns in nearshore waters, providing strong evidence that site-specific, local-scale processes are the dominant drivers at the land–sea interface (Cloern and Jassby, 2008). Local processes and marked small-scale variability are also responsible for the mean N:P ratio observed in the ponds of the Marinello coastal system. The narrow range of N:P in Verde surface waters and the strong correspondence with guano N:P (Fig. 5) show scarce temporal variability due to the strong and constant influence of guano nutrients, as observed in coastal rockpools by Loder et al. (1996). A stoichiometric molar ratio of 16 N:1 P (Redfield, 1958) is accepted as the “ideal” ratio for phytoplankton growth and is often used to describe the cycling and limitations of nutrients in sea water (Geider and La Roche, 2002). Changes in nutrient supply are often reflected in their ratios (Yin et al., 2001), thus significant deviations from the typical ratio may signal nutrient limitation (Dorth and Whitedge, 1992). Therefore, the wider N:P range from Mergolo

and Fondo Porto may be attributable to the strong seasonality in nutrient limitation or co-limitation in coastal and transitional systems widely discussed in the literature (e.g. Fisher et al., 1998; Pinckney et al., 2001; Arrigo, 2005).

5. Conclusions

Stable isotope signatures, trophic status, primary production and related seasonal trends were significantly different in one pond of the Marinello coastal system, Verde, corresponding to the allochthonous input of guano from a small seagull colony inhabiting the adjacent cliff. Geomorphological and hydrological features, mainly the small size and scarce water exchange of the impacted pond, magnified this effect, highlighting that even a small bird colony can represent an important impact source in coastal systems. Furthermore, despite the proximity of the ponds, the highly pronounced ecological response of Verde to guano input was reduced in the adjacent pond (200 m away) and totally absent in the pond furthest from the source of impact (600 m away), showing that there is sharp small-scale variability in this coastal system.

Considering the recent massive geographic expansion and demographic proliferation of seagulls in the Mediterranean area (Vidal et al., 1998) in correspondence with human activities (Duhem et al., 2008), we suggest that the seagull transport pathway, until now described only from sea to land (e.g. Anderson and Polis, 2004; Ellis et al., 2006), should also be considered in the opposite direction, with seabirds feeding mainly in urbanised areas and living in coastal areas, as in the present study. Thus, among coastal systems, transitional environments are worthy of special attention because of their sensitivity and fragility.

The effects of prolonged eutrophication on both food web structure and biogeochemical cycling (Pinckney et al., 2001) as well as the greater environmental contamination level of impacted ecosystems due to the seagull's acknowledged role as contaminant biovector (e.g. Blais et al., 2005; Evenset et al., 2007) indicate potential directions for future research.

Acknowledgements

The authors are grateful to M. Lo Valvo and M. Bartoli for their suggestions during various stages of this work, A. Savona for assistance during field work and C. Tramati, E.A. Aleo and V.A. Tumbarello for help with laboratory analysis. Many thanks are due to the Director, M.L. Molino, and staff of the Nature Reserve "Laghetto di Marinello" for permission to work in the Reserve and the support provided. This study was funded by PRIN 2008 and University of Palermo.

References

Anderson, W.B., Polis, G.A., 2004. Allochthonous nutrient and food inputs: consequences for temporal stability. In: Polis, G.A., Power, M.E., Huxel, G.R. (Eds.), *Food Webs at the Landscape Level*. University of Chicago Press, Chicago, Illinois, USA, pp. 82–95.

Arrigo, K.R., 2005. Marine microorganisms and global nutrient cycles. *Nature* 437, 349–355.

Bildstein, K., Blood, E., Frederick, P., 1992. The relative importance of biotic and abiotic vectors in nutrient transport. *Estuaries and Coasts* 15, 147–157.

Blais, J.M., Kimpe, L.E., McMahon, D., Keatley, B.E., Mattory, M.L., Douglas, M.S.V., Smol, J.P., 2005. Arctic seabirds transport marine-derived contaminants. *Science* 309, 445.

Bosman, A.L., Hockey, P.A.R., 1986. Seabird guano as a determinant of rocky intertidal community structure. *Marine Ecology – Progress Series* 32, 247–257.

Brichetti, P., Fracasso, G., 2006. *Ornitologia Italiana* 3. Stercorariidae—Caprimulgidae. Alberto Perdisa Editore, Bologna, 438 pp.

Brimble, S.K., Blais, J.M., Kimpe, L.E., Mallory, M.L., Keatley, B.E., Douglas, M.S.V., Smol, J.P., 2009. Bioenrichment of trace elements in a series of ponds near a northern fulmar (*Fulmarus glacialis*) colony at Cape Vera, Devon Island. *Canadian Journal of Fisheries and Aquatic Sciences* 66, 949–958.

Carrier, A.P., Riera, P., Amouroux, J.M., Bodiou, J.Y., Desmalades, M., Grémare, A., 2009. Spatial heterogeneity in the food web of a heavily modified Mediterranean coastal lagoon: stable isotope evidence. *Aquatic Biology* 5 (3), 167–179.

Cloern, J.E., Jassby, A.D., 2008. Complex seasonal patterns of primary producers at the land–sea interface. *Ecology Letters* 11, 1294–1303.

Como, S., Magni, P., Casu, D., Floris, A., Giordani, G., Natale, S., Fenzi, G.A., Signa, G., De Falco, G., 2007. Sediment characteristics and macrofauna distribution along a human-modified inlet in the Gulf of Oristano (Sardinia, Italy). *Marine Pollution Bulletin* 54, 733–744.

Crisafi, E., Giacobbe, S., Leonardi, M., 1981. Nuove ricerche idrobiologiche nell'area lagunare di Oliveri-Tindari (Messina). I. Morfologia dei bacini e caratteristiche chimico-fisiche delle acque e dei sedimenti. *Memorie di Biologia Marina e di Oceanografia* IV, 139–186.

Dame, R.F., Allen, D.M., 1996. Between estuaries and the sea. *Journal of Experimental Marine Biology and Ecology* 200, 169–185.

de Boer, J.A., 1982. Nutrients. In: Lobban, C.S., Wynne, M.J. (Eds.), *The Biology of Seaweeds*. Blackwell, Oxford, pp. 356–365.

Dorth, Q., Whitley, T.E., 1992. Does nitrogen or silicon limit phytoplankton production in the Mississippi River plume and nearby regions? *Continental Shelf Research* 12 (11), 1293–1309.

Duhem, C., Roche, P., Vidal, E., Taton, T., 2008. Effects of anthropogenic food resources on yellow-legged gull colony size on Mediterranean islands. *Population Ecology* 50, 91–100.

Ellis, J.C., Fariña, J.M., Witman, J.D., 2006. Nutrient transfer from sea to land: the case of gulls and cormorants in the Gulf of Maine. *Journal of Animal Ecology* 75, 565–574.

Evenset, A., Carroll, J., Christensen, G.N., Kallenborn, R., Gregor, D., Gabrielsen, G.W., 2007. Seabird guano is an efficient conveyor of persistent organic pollutants (POPs) to Arctic lake ecosystems. *Environmental Science & Technology* 41, 1173–1179.

Fisher, T.R., Hagy, J.D., Rochelle-Newall, E., 1998. Dissolved and particulate organic carbon in Chesapeake Bay. *Estuaries* 21, 215–229.

García, L.V., Marañón, T., Ojeda, F., Clemente, L., Redondo, R., 2002. Seagull influence on soil properties, chenopod shrub distribution, and leaf nutrient status in semi-arid Mediterranean islands. *Oikos* 98, 75–86.

Geider, R.J., La Roche, J., 2002. Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis. *European Journal of Phycology* 37, 1–17.

Giordani, G., Zaldivar, J.M., Viaroli, P., 2009. Simple tools for assessing water quality and trophic status in transitional water ecosystems. *Ecological Indicators* 9, 982–991.

Grasshoff, K., 1983. Determination of nitrate. In: Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, pp. 143–150.

Gwiazda, R., Jarocha, K., Szarek-Gwiazda, E., 2010. Impact of a small cormorant (*Phalacrocorax carbo sinensis*) roost on nutrients and phytoplankton assemblages in the littoral regions of a submontane reservoir. *Biologia* 65, 742–748.

Hahn, S., Bauer, S., Klaassen, M., 2007. Estimating the contribution of carnivorous waterbirds to nutrient loading in freshwater habitats. *Freshwater Biology* 52, 2421–2433.

Hedges, J.I., Stern, J.H., 1984. Carbon and nitrogen determinations of carbonate-containing solids. *Limnology and Oceanography* 29 (3), 657–663.

IRSA, 1985. *Metodi analitici per i fanghi*. Parametri chimico-fisici, vol. 64 (3). Quaderni dell'Istituto di Ricerca Sulle Acque, Consiglio Nazionale delle Ricerche, pp. 9.1–9.3.

Jeffrey, S.W., Humphrey, G.F., 1975. New spectrophotometric equations for determining chlorophylls *a*, *b*, *c1*, and *c2* in higher plants, algae and natural phytoplankton. *Biochimie und Physiologie der Pflanzen* 167, 191–194.

Jones, P.G.W., Spencer, C.P., 1963. Comparison of several methods of determining inorganic phosphate in sea water. *Journal of the Marine Biological Association of the United Kingdom* 43, 251–273.

Keatley, B., Douglas, M., Blais, J., Mallory, M., Smol, J., 2009. Impacts of seabird-derived nutrients on water quality and diatom assemblages from Cape Vera, Devon Island, Canadian High Arctic. *Hydrobiologia* 621, 191–205.

Kolb, G.S., Ekholm, J., Hambäck, P.A., 2010. Effects of seabird nesting colonies on algae and aquatic invertebrates in coastal waters. *Marine Ecology – Progress Series* 417, 287–300.

Koroleff, F., 1983a. Determination of phosphorus. In: Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, pp. 125–139.

Koroleff, F., 1983b. Total and organic nitrogen. In: Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, pp. 162–173.

Kuffner, I.B., Paul, V.J., 2001. Effects of nitrate, phosphate and iron on the growth of macroalgae and benthic cyanobacteria from Cocos Lagoon, Guam. *Marine Ecology – Progress Series* 222, 63–72.

Leonardi, M., Azzaro, F., Azzaro, M., Decembrini, F., Monticelli, L.S., 2000. Ciclo della sostanza organica nell'ecosistema lagunare di Tindari (ME). *Biologia Marina Mediterranea* 7 (1), 222–232.

Leonardi, M., Azzaro, F., Azzaro, M., Bergamasco, A., Decembrini, F., 2005. Marinello coastal system, north-eastern Sicily. In: Giordani, G., Viaroli, P., Swaney, D.P., Murray, C.N., Zaldivar, J.M., Marshall Crossland, J.I. (Eds.), *Nutrient Fluxes in Transitional Zones of the Italian Coast*. LOICZ Reports & Studies, vol. 28, pp. 95–102. Texel.

Lindeboom, H.J., 1984. The nitrogen pathway in a penguin rookery. *Ecology* 65, 269–277.

- Lloret, J., Marin, A., 2009. The role of benthic macrophytes and their associated macroinvertebrate community in coastal lagoon resistance to eutrophication. *Marine Pollution Bulletin* 58 (12), 1827–1834.
- Loder, T.C., Ganning, B., Love, J.A., 1996. Ammonia nitrogen dynamics in coastal rockpools affected by gull guano. *Journal of Experimental Marine Biology and Ecology* 196, 113–129.
- Lorenzen, C.J., Jeffrey, S.W., 1980. Determination of chlorophyll in sea water. *Unesco Technical Paper Marine Science* 35, 1–20.
- Manny, B.A., Johnson, W.C., Wetzel, R.G., 1994. Nutrient additions by waterfowl to lakes and reservoirs – predicting their effects on productivity and water-quality. *Hydrobiologia* 280, 121–132.
- Marion, L., Clergeau, P., Briant, L., Bertru, G., 1994. The importance of avian-contributed nitrogen (N) and phosphorus (P) to Lake Grand-Lieu, France. *Hydrobiologia* 279–280 (1), 133–147.
- Markwell, T.J., Daugherty, C.H., 2003. Variability in delta N-15, delta C-13 and Kjeldahl nitrogen of soils from islands with and without seabirds in the Marlborough Sounds, New Zealand. *New Zealand Journal of Ecology* 27, 25–30.
- Mazzola, A., Bergamasco, A., Calvo, S., Caruso, G., Chemello, R., Colombo, F., Giaccone, G., Gianguzza, P., Guglielmo, L., Leonardi, M., Riggio, S., Sara, G., Signa, G., Tomasello, A., Vizzini, S., 2010. Sicilian transitional waters: current status and future development. *Chemistry and Ecology* 26, 267–283.
- McLusky, D.S., Elliot, M., 2007. Transitional waters: a new approach, semantics or just muddying the waters? *Estuarine, Coastal and Shelf Science* 71, 359–363.
- Methratta, E.T., 2004. Top-down and bottom-up factors in tidepool communities. *Journal of Experimental Marine Biology and Ecology* 299, 77–96.
- Michelutti, N., Blais, J.M., Mallory, M.L., Brash, J., Thienpont, J., Kimpe, L.E., Douglas, M.S.V., Smol, J.P., 2010. Trophic position influences the efficacy of seabirds as metal biovectors. *Proceedings of the National Academy of Sciences of the United States of America* 107, 10543–10548.
- Middelburg, J.J., Nieuwenhuize, J., 2000. Uptake of dissolved inorganic nitrogen in turbid, tidal estuaries. *Marine Ecology – Progress Series* 192, 79–88.
- Mizutani, H., Wada, E., 1988. Nitrogen and carbon isotope ratios in seabird rookeries and their ecological implications. *Ecology* 69, 340–349.
- Morabito, G., 1997. Dinamica stagionale delle comunità algali e analisi microscopica del fitoplancton. In: *Proceedings of Criteri e metodologie per lo studio e il controllo delle alghe in acque destinate alla potabilizzazione*. AGAC, Reggio Emilia, Italy, pp. 3–18.
- Moreno, R., Jover, L., Munilla, I., Velando, A., Sanpera, C., 2010. A three-isotope approach to disentangling the diet of a generalist consumer: the yellow-legged gull in northwest Spain. *Marine Biology* 157, 545–553.
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27, 1–36.
- Navarro, J., Oro, D., Bertolero, A., Genovart, M., Delgado, A., Forero, M.G., 2010. Age and sexual differences in the exploitation of two anthropogenic food resources for an opportunistic seabird. *Marine Biology* 157, 2453–2459.
- Örnólfsson, E.B., Lumsden, S.E., Pinckney, J.L., 2004. Phytoplankton community growth-rate response to nutrient pulses in a shallow turbid estuary, Galveston Bay, Texas. *Journal of Plankton Research* 26, 325–339.
- Paerl, H.W., Valdes, L.M., Pinckney, J.L., Piehler, M.F., Dyble, J., Moisander, P.H., 2003. Phytoplankton photopigments as indicators of estuarine and coastal eutrophication. *Bioscience* 53, 953–964.
- Palomo, G., Iribarne, O., Martinez, M.M., 1999. The effect of migratory seabirds guano on the soft bottom community of a SW Atlantic coastal lagoon. *Bulletin of Marine Science* 65, 119–128.
- Payne, X.L., Moore, J.W., 2006. Mobile scavengers create hotspots of freshwater productivity. *Oikos* 115, 69–80.
- Perco, F., Lambertini, M., Lo Valvo, M., Milone, M., 1986. Gabbiano reale *Larus cachinnans* Pallas 1811. In: Fasola, M. (Ed.), *Distribuzione e popolazione dei Laridi e sternidi nidificanti in Italia*. Supplemento *Ricerca Biologica Selvaggina*, vol. XI, pp. 53–71.
- Pinckney, J.L., Paerl, H.W., Tester, P., Richardson, T.L., 2001. The role of nutrient loading and eutrophication in estuarine ecology. *Environmental Health Perspectives* 109, 699–706.
- Polis, G.A., Hurd, S.D., 1996. Linking marine and terrestrial food webs: allochthonous input from the ocean supports high secondary productivity on small islands and coastal land communities. *American Naturalist* 147, 396–423.
- Post, D.M., Taylor, J.P., Kitchell, J.F., Olson, M.H., Schindler, D.E., Herwig, B.R., 1998. The role of migratory waterfowl as nutrient vectors in a managed wetland. *Conservation Biology* 12, 910–920.
- Ramos, R., Ramirez, F., Sanpera, C., Jover, L., Ruiz, X., 2009. Feeding ecology of yellow-legged gulls *Larus michahellis* in the western Mediterranean: a comparative assessment using conventional and isotopic methods. *Marine Ecology – Progress Series* 377, 289–297.
- Redfield, A.C., 1958. The biological control of chemical factors in the environment. *American Science* 46, 205–221.
- Sanchez-Piñero, F., Polis, G.A., 2000. Bottom-up dynamics of allochthonous input: direct and indirect effects of seabirds on islands. *Ecology* 81, 3117–3132.
- Sarà, G., 2006. Hydrodynamic effects on the origin and quality of organic matter for bivalves: an integrated isotopic, biochemical and transplant study. *Marine Ecology – Progress Series* 328, 65–73.
- Valderrama, J.C., 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Marine Chemistry* 10, 109–122.
- Vidal, E., Medail, F., Taton, T., 1998. Is the yellow-legged gull a superabundant bird species in the Mediterranean? Impact on fauna and flora, conservation measures and research priorities. *Biodiversity and Conservation* 7, 1013–1026.
- Vizzini, S., Mazzola, A., 2008. The fate of organic matter sources in coastal environments: a comparison of three Mediterranean lagoons. *Hydrobiologia* 611, 67–79.
- Wainright, S.C., Haney, J.C., Kerr, C., Golovkin, A.N., Flint, M.V., 1998. Utilization of nitrogen derived from seabird guano by terrestrial and marine plants at St. Paul, Pribilof Islands, Bering sea, Alaska. *Marine Biology* 131, 63–71.
- Wootton, J.T., 1991. Direct and indirect effects of nutrients on intertidal community structure: variable consequences of seabird guano. *Journal of Experimental Marine Biology and Ecology* 151, 139–153.
- Yin, K., Quian, P.Y., Wu, M.C.S., Chen, J.C., Huang, L.M., Song, X., Jian, W.J., 2001. Shift from P to N limitation of phyto-plankton biomass across the Pearl River estuarine plume during summer. *Marine Ecology – Progress Series* 221, 17–28.
- Zar, J.H., 1999. *Biostatistical Analysis*. Prentice Hall, Upper Saddle River, NJ, 929 pp.