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Gull-derived trace elements trigger small-scale contamination in a remote Mediterranean nature reserve

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ABSTRACT

The role of a yellow-legged gull (*Larus michahellis*) small colony in conveying trace elements (As, Cd, Cr, Cu, Ni, Pb, THg, V, Zn) was assessed in a Mediterranean nature reserve (Marinello ponds) at various spatial and temporal scales. Trace element concentrations in guano were high and seasonally variable. In contrast, contamination in the ponds was not influenced by season but showed strong spatial variability among ponds, according to the different guano input. Biogenic enrichment factor B confirmed the role of gulls in the release of trace elements through guano subsidies. In addition, comparing trace element pond concentrations to the US NOAA's SQGs, As, Cu and Ni showed contamination levels associated with possible negative biological effects. Thus, this study reflects the need to take seabirds into account as key factors influencing ecological processes and contamination levels even in remote areas, especially around the Mediterranean, where these birds are abundant but overlooked.

1. Introduction

Seabirds are exposed to a wide range of chemicals. As ingested food and water are the main routes of contaminant exposure (Burger and Gochfeld, 2004), trophic position, feeding habit and foraging range are the main factors influencing their contaminant level (Anderson et al., 2009; Michelutti et al., 2010). Seabirds spend a considerable part of their lives in coastal and marine environments and represent a well-known biological vector, hereafter biovector, moving and redistributing nutrients, organic matter and pollutants across coastal boundaries, from marine to terrestrial habitats (e.g. Brimble et al., 2009a; Choy et al., 2010) and vice versa (e.g. Ellis et al., 2006; Hahn et al., 2007; Signa et al., 2012) at various spatial scales. Seabird biovector transport consists of three crucial stages: (i) contaminant collection from the environment, (ii) contaminant transport, (iii) contaminant deposition, release or transfer at a receptor site (Blais et al., 2007). Being at the top of food chains, many seabirds are exposed to high levels of contaminants through their prey due to biomagnification and thus represent useful bioindicators of coastal and marine pollution (Furness and Camphuysen, 1997; Burger and Gochfeld, 2004; Yin et al., 2008). The trophic plasticity of some seabirds, among which gulls are a striking example, allows them to benefit from anthropogenic food resources, e.g. fishery discards and/or refuse (Duhem et al., 2008; Ramos et al., 2009; Navarro et al., 2010) with an important influence on contaminant exposure and accumulation.

Bird feathers and eggs are common routes of pollutant elimination (e.g. Furness and Camphuysen, 1997; Burger et al., 2009) and for this reason are widely recognised as biomonitoring tools of bird pollutant bioaccumulation. Less attention has been given to bird guano, although it is the most direct source of allochthonous avian input in areas surrounding bird colonies. Due to the physiological mechanisms of organism self-purification and homeostatic mechanisms modulating the body content of some elements, bird excreta can exhibit the highest element contents (Metcheva et al., 2011). Indeed, only recently a number of reviews confirmed the important role of avian excreta as contaminant biomonitoring tool providing a continuous and long-term record of environmental metal contamination history (Yin et al., 2008; Joshi et al., 2013). When mediated by guano, contaminant release and accumulation at receptor sites can be even higher than abiotic transport (i.e. atmospheric and oceanic) as observed in migratory seabirds, which are able to concentrate contaminants following a period of wide dispersal (Wania, 1998). While the role of migratory species in the transport of mercury and persistent organic pollutants around the globe has been widely studied (e.g. Evenset et al., 2007; Blais et al., 2005, 2007), small-scale biovector transport, from feeding to nesting areas, deserves more attention. Many nature reserves are in remote areas which are far from direct anthropogenic impact and commonly believed to be unpolluted and pristine. Instead, high ecological connectivity, a distinctive feature of coastal transitional environments, facilitates the transport and accumulation of pollutants in these areas. In addition to abiotic factors, the presence of seabird colonies can provide an additional contaminant source. Further, despite the abundance of birds in Mediterranean

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lagoon-like systems, they are rarely seen as an important link between the terrestrial and marine domains, potentially influencing ecological processes.

The Marinello coastal system in the Gulf of Patti, north-eastern Sicily (Italy, South-Tyrrhenian, Mediterranean) (Fig. 1), represents a model area for investigating bird-mediated connectivity. Marinello is a Nature Reserve composed of several small ponds subject to differing guano input from a colony of yellow-legged gulls, *Larus michahellis*. This is a good example of an opportunistic species that exhibits clear plasticity in its diet, usually feeding on waste landfills (Ramos et al., 2009; Navarro et al., 2010). Previous research on bird-mediated ecological processes in the Marinello ponds revealed strong influences from bird-derived nutrients on trophic status and productivity (Signa et al., 2012). Bird-mediated contamination (As, Cd, Pb, THg) was also assessed in the system, with its consequent trophic transfer to the biota (Signa et al., 2013), but this research was restricted to a single season. Thus, in light of these results, our study investigated bird-mediated contamination dynamics further by increasing the temporal and spatial resolution of the analysis and including additional trace elements.

The main objective was thus to assess the role of a small yellow-legged gull colony in conveying trace elements (As, Cd, Cr, Cu, Ni, Pb, THg, V, Zn) in the Mediterranean coastal system of Marinello, examining the temporal and spatial dynamics. To achieve our aims, we analysed seasonal and small-scale spatial variations in guano and surface sediment contamination. The biogenic enrichment factor B (Brimble et al., 2009a) was applied to evaluate the likelihood that surface sediments are enriched by guano subsidies. Further, trace element data were compared with limits specified in the US NOAA's sediment quality guidelines (SQGs) (Long et al., 1995; Macdonald et al., 1996) to assess the environmental quality of the study area.

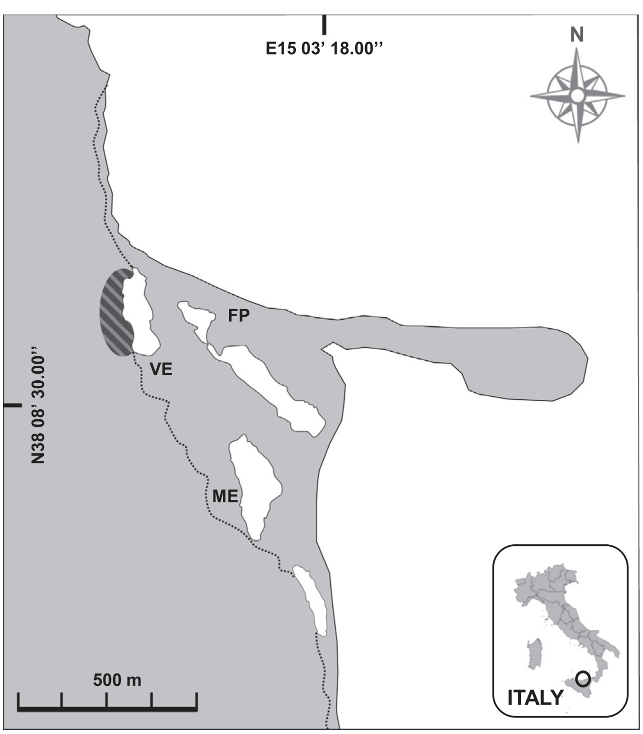

Fig. 1. Map of the study area with sampling ponds: Verde (VE), Fondo Porto (FP) Mergolo (ME). Dotted lines indicate the edge of the promontory of Tindari. The grey striped oval indicates the gull colony site on the Tindari cliff.

2. Materials and methods

2.1. Study area and sampling

Marinello ponds constitute a very small coastal transitional system (≈50 ha) located on the north-eastern coast of Sicily (Italy, South-Tyrrhenian, Mediterranean) (Fig. 1). The ponds, five at present (Verde, Fondo Porto, Porto Vecchio, Mergolo and Marinello), form part of the Marinello Nature Reserve (≈440 ha), which is located in a fairly remote coastal area far from urban centres and other direct anthropic input. The coastal area is affected by a moderate influx of visitors during the summer season. The particular hydrogeomorphological features of the whole coastal area, which contributed to the formation of the ponds in the last century, determine the remarkable geomorphologic dynamic and high structural and hydrobiological complexity of the ponds (Mazzola et al., 2010). For example, despite their common origin and proximity and the small size of the whole area, the ponds are affected differently by abiotic and biotic input. As regards the abiotic input sources, the innermost ponds are mainly influenced by surface run-off, while the outermost ones are affected by indirect seawater inflows through infiltration by sand bars and high waves during storms (Mazzola et al., 2010). As for biotic input sources, the ponds are located at increasing distance from a small colony of yellow-legged gulls (*L. michahellis,* 80–125 ind.) (Signa et al., 2012) and only one of the ponds, Verde, which is adjacent to the cliff where the gulls reside, is affected by direct guano input. Indeed, Signa et al. (2012, 2013) showed that seabird allochthonous input influences trophic status, primary production and non-essential trace metal (As, Cd, Pb and THg) background contamination in the system.

In this study, three ponds were sampled, Verde (VE), Fondo Porto (FP) and Mergolo (ME), chosen for their increasing distance from the gull colony (0, 200 and 600 m respectively). Seasonally, from autumn 2008 to summer 2009, guano was carefully scraped from the shores of VE and from the adjacent cliff and pooled. PVC cores (inner diameter: 4 cm) were used to collect surface sediment in two sites in triplicate (shore: depth 0.1 m; bottom: depth 3.0, 2.0 and 3.5 m for VE, FP and ME respectively) (Fig. 1) for trace element, $\delta^{15}N$, TOC and carbonate analysis. Contextually, physico-chemical variables (Temperature *T*, Salinity *S*, and Dissolved Oxygen LDO) of the bottom water were measured using a YSI 556 Multiprobe System, and pH and Eh at the water/sediment interface with a B&C Electronics 152.2 pH/ORP portable meter.

2.2. Laboratory activities

In the laboratory, the first centimetre of sediment was carefully sliced from each core. Due to the presence of coarse residuals in guano and surface sediment, both were wet sieved at 1000 μm before analysis. Guano and sediment for trace element analysis were oven dried (40 °C) and ground to a fine powder. The trace elements analysed were arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), total mercury (THg), vanadium (V) and zinc (Zn). Guano was mineralised in Teflon digestion vessels with HNO_3, H_2O_2 and MilliQ deionized water at a ratio of 5:1:4, while sediment was mineralised with HNO_3, HF, H_2O_2, and MilliQ deionised water at 18:6:1:5. The analytical procedure was checked using a standard reference material *Lagarosiphon major* BCR-060 (Community Bureau of Reference B.C.R.) for guano and Marine Sediment MESS-3 (National Research Council of Canada) for sediment. Recovery of reference standards was between 90% and 98%. An inductively coupled plasma optical emission spectrometer (ICP-OES, Varian Vista MPX) was used to analyse the digested samples. Concentrations of As and THg were determined using a hydride generation system (VGA-77) linked to the ICP-OES. Analysis was carried out in triplicate and all reagents were Suprapur.

Before stable isotope analysis, sediment was oven-dried (60 °C), ground to a fine powder and analysed for $\delta^{15}N$ 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: $\delta X = [(R_{sample}/R_{standard}) - 1] \times 10^3$, where X is ^{15}N and R is the corresponding $^{15}N/^{14}N$ ratio. Analytical precision based on the standard deviation of replicates of internal standards was 0.2‰.

Sediment carbonate content was estimated according to the loss on ignition (LOI) method (Heiri et al., 2001) based on sequential weightings of samples before and after heating at 105 °C, 550 °C and 950 °C. Bulk sediment for TOC analysis was oven dried (60 °C) in aluminium capsules, ground and weighed in silver capsules. Carbonates were eliminated by three acidification steps according to Nieuwenhuize et al. (1994). Samples were then analysed in an Elemental Analyser (Thermo Scientific Flash EA 1112) using Acetanilide as a standard.

2.3. Data elaboration and statistical analysis

1-way ANOVA was performed to test differences among seasons in trace element content of guano, while Pearson linear correlations were carried out to assess the occurrence of common trends. Relationships between sediment trace element concentrations and both the distance of ponds from the gull colony and the physico-chemical variables (bottom water: T, S and LDO; interface water/sediment: pH and Eh; surface sediment: $\delta^{15}N$, TOC and carbonates) were analysed by non-linear models. Quadratic regression was the most appropriate model for describing the relationships among variables. Due to the strength of the correlation with trace elements (Table 1) and the highly significant difference among ponds (1-way ANOVA: df: 2; MS: 33.6; F: 618.9; $p < 0.001$), carbonate content was used as a geochemical normalisation factor. Indeed, carbonates are considered to be among the most influential factors in trace element chemical partitioning, enhancing direct precipitation in sediment (Horowitz, 1985). Further both trace elements and environmental datasets were standardised by normalisation according to Clarke and Warwick (2001) to make data scales comparable. Differences in sediment trace element concentrations between ponds, sites and seasons were tested at multivariate level with permutational analysis of variance (PERMANOVA). Principal component analysis (PCA) on trace element data was performed to assess the main direction of variation in the dataset. All statistical analysis was performed using the software packages Statistica 8.0 and Primer 6.0.

Biogenic enrichment factor B (Brimble et al., 2009a) was calculated to assess the likelihood that guano represents trace element allochthonous input in the Marinello ponds, as follows:

$$B = \frac{\text{Mean concentration of trace element in seagull guano}}{\text{Mean concentration of trace element in control pond}}$$

ME was selected as control pond, in accordance with its greater distance from the colony and low background contamination (Signa et al., 2013).

3. Results

3.1. Guano and sediment trace elements

Trace element content of guano collected along the shores of pond VE and on the adjacent cliff is shown in Table 2. A significant seasonal trend is evident for all the elements studied, showing overall the lowest concentrations in winter (except for THg) and the highest in spring (Cd, Cr, Cu, Ni, V, Zn) and autumn (As, Pb, THg). Among others, the Zn range was very wide, while the Cr, Cu and V ranges were narrower and comparable. As and Ni also showed comparable ranges but concentrations were lower, while Pb, Cd and THg showed the narrowest ranges. Cd, Cr, Cu, Ni, V and Zn all showed mutual highly significant positive correlations ($p < 0.01$), with high correlation coefficients ($r > 0.7$) and coefficients of determination ($R^2 > 0.5$).

Concentrations of trace elements in sediment showed important spatial variations at both pond and site scale (Fig. 2). Overall, trace elements showed the highest concentrations in the ponds close to the gull colony (VE and FP). A different trend was evident for THg, which also showed high sediment enrichment in ME (Fig. 2g). Regarding small-scale spatial variations, trace element concentrations were higher in the bottom sites than in the shore sites. PERMANOVA confirmed the significance of spatial variation at both spatial scales (factor pond: df: 3; MS: 171.8; Pseudo-F: 439.5; $p < 0.001$; factor site: df: 1; MS: 93.5; Pseudo-F: 239.3; $p < 0.001$). In contrast, as for seasonal variations, it was not possible to identify a unequivocal trend, the trace elements showing different behaviours both between and within ponds. PCA revealed that ponds in the multivariate space distributed along the first axis (total variation explained: 62.8%) according to the degree of ornithogenic input (Fig. 3). While FP and ME grouped in the centre and the right part of the graph respectively, VE spread along the graph with a clear separation of samples based on the factor site: bottom samples grouped on the left and shore samples in the central part of the graph, together with FP. Clusters superimposed on the PCA projection (distance: 3.4) confirmed the separation among VE bottom, FP and VE shore, and ME. The second axis explained 23.4% of the total variation, with a total explained variation of 86.1%. Among the variables studied, only distance from the colony, $\delta^{15}N$, TOC, carbonate content and redox potential were correlated with trace elements (Pearson correlation coefficient $r > 0.5$).

3.2. Biogenic enrichment factor, B

Biogenic enrichment factor B, calculated seasonally for each trace element studied, is shown in Table 3. B was characterised by a clear seasonal trend according to the patterns highlighted in

Table 1
Coefficients of quadratic correlations (r) between sediment trace element concentrations and both the distance of ponds from the gull colony and the physico-chemical variables. Correlations marked in bold are significant at $p < 0.001$.

	Distance (m)	Temp. (°C)	Sal. (ppt)	LDO% (Sat)	pH (units)	Eh (mV)	TOC (%)	Carbonates (%)	$\delta^{15}N$ (‰)
As	0.35	0.19	−0.18	0.08	0.14	−0.34	0.25	−0.13	0.41
Cd	**−0.84**	−0.42	0.32	0.06	0.36	0.26	−0.19	**−0.86**	**0.51**
Cr	**−0.90**	0.08	**0.10**	−0.24	0.30	−0.21	0.49	**−0.94**	**0.55**
Cu	**−0.46**	0.11	0.25	−0.27	−0.30	**−0.45**	**0.57**	−0.26	0.38
Ni	**−0.90**	−0.48	**0.43**	0.36	**0.38**	0.52	**−0.49**	**−0.98**	**0.54**
Pb	**−0.78**	0.10	0.41	−0.19	0.13	**−0.43**	**0.62**	**−0.72**	**0.51**
THg	**0.61**	0.35	−0.17	−0.26	−0.36	−0.43	0.40	**0.70**	**−0.56**
V	**−0.87**	0.25	**0.32**	−0.21	0.19	−0.24	0.52	**−0.72**	**0.50**
Zn	**−0.82**	0.18	0.38	−0.17	0.13	−0.34	0.68	**−0.82**	**0.60**

Table 2
Averaged trace element concentration (mg kg^{-1} d.w.) of guano collected from Autumn 2008 to Summer 2009 in VE. Results of 1-way ANOVA to test seasonal differences are also showed.

	Autumn		Winter		Spring		Summer		1 way ANOVA (df = 3)		
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	MS	*F*	*P*
As	19.07	0.04	5.06	0.07	7.59	0.46	8.32	1.03	115.36	362.70	<0.001
Cd	0.15	0.01	0.02	0.01	0.62	0.01	0.52	0.01	0.25	2115.05	<0.001
Cr	18.82	0.50	6.11	0.17	47.71	0.10	37.98	0.39	1051.12	9530.49	<0.001
Cu	25.92	0.86	10.30	0.09	41.76	0.57	35.49	0.30	562.48	1935.71	<0.001
Ni	20.92	1.87	12.08	1.57	21.82	1.00	18.97	1.16	58.25	28.12	<0.001
Pb	7.24	0.28	1.20	0.14	5.81	0.38	4.56	0.26	19.97	262.83	<0.001
THg	1.02	0.10	0.83	0.00	0.92	0.15	0.80	0.10	0.03	2.75	n.s.
V	19.81	1.18	6.13	0.04	43.77	0.33	37.68	0.99	882.38	1424.08	<0.001
Zn	149.55	7.76	46.86	1.27	273.76	4.13	216.24	2.73	28477.47	333.60	<0.001

n.s. = not significant.

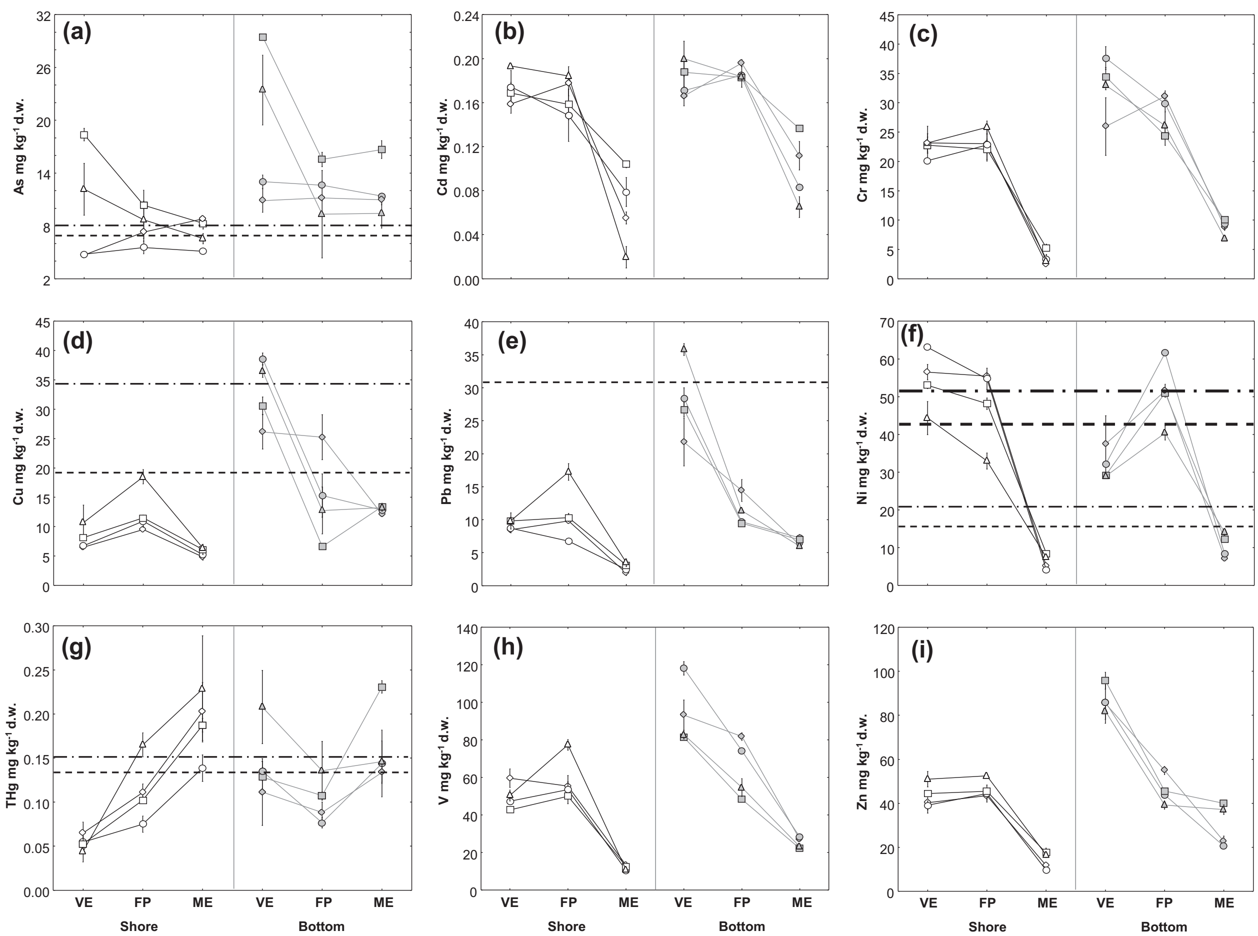

Fig. 2. Trace element concentrations in surface sediment in the sites shore (left) and bottom (right) of Verde (VE), Fondo Porto (FP) and Mergolo (ME) in the four sampling seasons: autumn (rhombus), winter (circle), spring (square), summer (triangle). SQGs thresholds are superimposed on each trace element panel when comprised in the concentration range. ERM (▬▬ ▪ ▬), ERL (— · — · — ·), PEL (▬ ▬ ▬), TEL (– – – – – – ·).

guano, with lower values overall in winter (except As, Ni and THg) and higher values in autumn (As, Ni, Pb, THg), spring (Cu, V, Zn) and summer (Cd, Cr). Overall B was >1 for all trace elements; the highest values were recorded for Cd, Cr, THg and Zn, followed by Cu, Ni and V and then As and Pb.

4. Discussion

4.1. Trace elements in gull guano

In the Marinello area, both essential and non-essential trace elements were recorded in the gull guano. Comparison with gull guano from other Mediterranean and polar areas revealed similar or higher concentrations in the Marinello colony, such as for Cr, Cu, Ni, THg and Zn (Headley, 1996; Otero, 1998; Yin et al., 2008). In contrast, Cd and Pb concentrations were appreciably lower. Cd and Pb, as well as As and V, were higher than in the excreta of other bird species such as boobies, penguins and fulmars (Bargagli et al., 1998; Liu et al., 2006; Brimble et al., 2009a; Metcheva et al., 2011). Although comparison among different bird species demands caution because of differing feeding habits and life spans, as well as physiology and biochemical characteristics (Savinov et al., 2003), diet represents the major intake route (Norheim, 1987; Yin et al., 2008). Thus, the seasonal variability observed in the gull guano

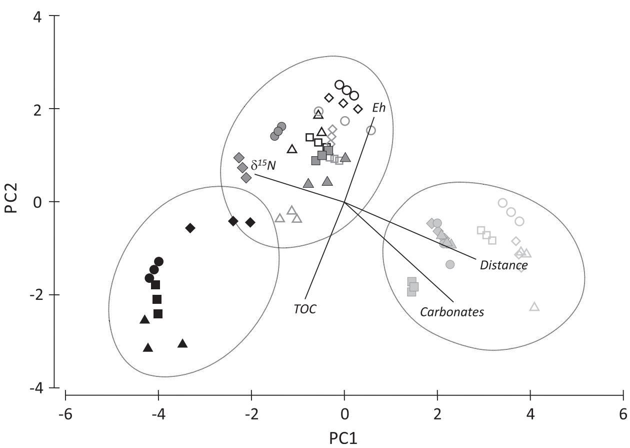

Fig. 3. Principal component analysis (PCA) on trace element data of Marinello pond sediment. Axes 1 and 2 explain 62.8% and 23.4% of the total variation respectively. Seasons are represented by different symbols: autumn (rhombus), winter (circle), spring (square), summer (triangle). Ponds are represented by different colours: VE (black), FP (dark grey), ME (light grey). Shore site is represented by open symbols, bottom site by filled symbols. Clusters (distance: 3.4) and vectors of the environmental variables correlated with trace elements (Pearson correlation coefficient $r > 0.5$) were superimposed on the PCA projection.

Table 3
Biogenic enrichment factor B calculated according to Brimble et al. (2009a). Values ⩾ 1 are indicated in bold.

	Autumn	Winter	Spring	Summer
As	**2.9**	**1.0**	0.9	**1.6**
Cd	**2.6**	0.3	**8.0**	**18.9**
Cr	**5.0**	**1.5**	**9.6**	**11.9**
Cu	**4.6**	**1.8**	**6.6**	**5.6**
Ni	**5.2**	**3.1**	**3.3**	**2.8**
Pb	**2.7**	0.4	**1.8**	**1.5**
THg	**9.3**	**9.3**	**6.9**	**6.7**
V	**1.9**	0.6	**4.6**	**3.5**
Zn	**13.1**	**4.8**	**14.7**	**12.5**

trace element concentration may reflect seasonal diet shifts and also variability in the trace element concentration of prey. Dietary changes over the reproductive and growth cycle of gulls due to varying gull nutritional requirements (Navarro et al., 2010) may also contribute to the variability observed, because diet selection is an important factor in gulls for successful breeding and recruitment (Moreno et al., 2010). The omnivorous and scavenger trophic habit of the yellow-legged gull, which relies on anthropogenic waste as its principal food source (Payne and Moore, 2006; Ramos et al., 2009; Moreno et al., 2010), combined with the abundance of refuse dumps close to the study area (*pers. obs.*), may explain the high trace element content of guano from the Marinello colony. Indeed, the high concentration of trace elements in faeces may reflect mechanisms for reducing body levels of contaminants. Highly positive correlations between Cd, Cr, Cu, Ni, V and Zn suggest a common intake-excretion metabolic pathway. For example, Cu, Zn and Cd are complexed into metallothionein (Otero, 1998; Liu et al., 2006).

4.2. Ornithogenic origin of sediment trace elements

In this study, both essential and non-essential trace elements were analysed in the surface sediment of three ponds with differing seabird influence. Trace elements showed decreasing values with increasing distance from the gull colony, showing that gulls play a substantial role in the spatial contamination trends. Similar trends were observed in Arctic and Antarctic regions (Brimble et al., 2009a; Nie et al., 2012) and in Chinese and Mediterranean island soils (Otero, 1998; Liu et al., 2006). The results are also comparable with previous studies in the same area (Ruta et al., 2009; Signa et al., 2013). However, to our knowledge, data from other seabird-impacted transitional areas in the Mediterranean are not available.

The opposite direction of $\delta^{15}N$ and distance vectors in the PCA multivariate ordination clearly indicates the lower influence of guano on the sedimentary compartment with increasing distance from the colony, $\delta^{15}N$ being a well-recognised proxy for ornithogenic influence (Wainright et al., 1998; Blais et al., 2005; Keatley et al., 2009; Michelutti et al., 2009; Signa et al., 2012). A number of environmental variables, especially pH, Eh, water temperature and organic matter, are important in controlling metal speciation, mobility, solubility and bioavailability of elements in marine sediments (Hatje et al., 2003; Du Laing et al., 2009). Among these factors, Eh and TOC appear dominant in influencing trace element distribution in the Marinello ponds.

Due to the high affinity of trace elements with fine-grained sediment and organic matter because of their adsorptive nature (e.g. Eggleton and Thomas, 2004; Du Laing et al., 2009), their accumulation was higher in VE, where a high seabird-induced organic matter load was previously demonstrated (Signa et al., 2012). In turn, surplus sedimentary organic matter is one of the main causes of oxygen depletion in near-bottom waters and sediments, because of the high oxygen consumption rate of organic matter microbial oxidation (Kristensen, 2000). Besides, interstitial fluids trapped in organic carbon-rich sediments can commonly form a strongly reducing (anoxic) environment that favour the complexation of trace elements, such as Cd, Pb and Zn, by insoluble organic matter or their binding to sulphide minerals (John and Leventhal, 1995).

The influence of the adjacent sea on pond contamination spatial variability can be excluded, as the recent common origin of the whole coastal area through the formation of sand barriers with terrigenous sediments carried by both the Timeto and Elicona watercourses (Crisafi et al., 1981; Saccà et al., 2011) ensures that the elemental background of the entire area is the same. Further, recent studies showed low trace element concentration in adjacent marine sediments (Saccà et al., 2011; Signa et al., 2013). Biological factors, including microbial activity, aquatic organism uptake and bioaccumulation, may also strongly influence trace element distribution and may be responsible for the THg spatial pattern, which is clearly different from those of the other trace elements, despite the THg high concentrations detected in guano. Biomagnification of THg occurs in Marinello ponds, while other trace elements (i.e. As, Cd, Pb) showed a significant biodilution through the food chains (as discussed in Signa et al. (2013)). Intense methylation of the Hg pool by sulphate-reducing bacteria, the activity of which is enhanced by reducing conditions and high organic load (Sunderland et al., 2006), may result in higher metal availability to the biota and a reduction in the sedimentary THg pool of ornithogenic origin.

Small-scale variability between shore and bottom sites of the ponds also emerged from this study. Trace element concentrations were higher overall at the bottom than along the shores in VE and ME, while FP appeared more homogeneous. At a multivariate level, PCA confirmed this pattern, FP sites overlapping each other, ME sites being quite distinct and VE sites even more distinct.

Many factors affect the sedimentary conditions in transitional environments: morphology and hydrodynamics are among the most important (Hilton, 1985). The deepest part of the ponds, especially those with a conical shape and low hydrodynamic energy, such as VE and ME, acts as a sink where sediment deposition and accumulation are enhanced. The continuous input of guano, affecting water column and sediments of VE (Signa et al., 2012), plays an important role in amplifying the differences between shore and bottom sites. In contrast, a lower and homogenous depth, an elongated shape and higher hydrodynamic energy (Mazzola et al., 2010) contribute to the uniformity of FP. Further, although trace elements respond in different ways to changes in Eh, positive Eh values, such as those recorded in shore sites, may play a role, increasing metal mobility and availability and enhancing the transition from sedimentary to dissolved phase (Du Laing et al., 2009).

Unlike spatial variations, trace element seasonal variations differed between metal species and sites. Thus, identifying which variables best explain the observed trends was not straightforward. Temperature and salinity, the variables most affected by seasonal variation, are acknowledged to exert an important effect on metal speciation, sorption/desorption processes and influx/efflux rates between sediment and water column (e.g. Elder, 1989). Accordingly, soluble Cd, Cr and Cu concentrations usually rise with increasing salinity, while Ni and Pb mobility is not significantly affected by salinity (Du Laing et al., 2009). Nevertheless, the behaviour of trace elements may vary because most factors are interrelated (John and Leventhal, 1995). Likewise, the interrelatedness of the metals themselves and with other sedimentary chemicals (e.g. Ca^{++}, Fe/Mn oxides, sulphides; (Eggleton and Thomas, 2004) may have a role in determining trace element variations, creating further complexity for data interpretation. In any case, spatial variability in the Marinello ponds seems to affect trace metal distribution and variation much more than temporal variability.

Biogenic enrichment factor B (Brimble et al., 2009a) further confirms the hypothesis that Marinello pond sediments are enriched in trace elements because of guano subsidies. All trace elements reported B values higher than 1, indicating that all are likely to undergo biogenic enrichment. The seasonal trend in B mirrors the trace element seasonal fluctuations of guano, confirming its influence in the system.

While the role of seabirds as biovectors of As, Cd, Cu, Pb, THg and Zn in coastal sediments and soils has been recognised (Headley, 1996; Otero, 1998; García et al., 2002; Blais et al., 2005; Liu et al., 2006; Brimble et al., 2009b; Michelutti et al., 2009; Nie et al., 2012), this paper reveals the occurrence of gull-derived sediment enrichment of further elements (e.g. Cr, Ni and V).

4.3. Evaluation of environmental quality

Sedimentary trace element concentrations from Marinello ponds were compared to the US NOAA's sediment quality guidelines (SQGs, ERL/ERM: effect range-low/medium, Long et al., 1995; TEL/PEL: threshold/possible effects level, Macdonald et al., 1996) to investigate contextually the seabird-induced environmental contamination levels in the area and their biological/ecotoxicological significance. Vanadium is the only element in this study that was not taken into account by the SQGs, thus it will not be discussed further. Among the other trace elements, both essential (i.e. Cr, Cu, Zn) and non-essential ones (i.e. As, Cd, Hg, Ni, Pb) can be toxic when above their respective critical levels. Marinello ponds, VE and FP in particular, presented As and Cu concentrations that fell between the ERL/ERM and TEL/PEL thresholds (As: 8.2/70.0 and 7.2/41.6 mg kg^{-1}; Cu: 34.0/270.0 and 18.7/108.0 mg kg^{-1}), indicating moderate contamination and occasional biological effects. Nickel concentrations in VE and FP were even higher than ERM and PEL (51.6 and 42.8 mg kg^{-1}), indicating a high contamination level frequently associated with negative biological effects. Indeed, nickel toxicity effects have frequently been observed in aquatic organisms, both invertebrates and vertebrates, in terms of reduced survival, reproduction, and growth (e.g. Hunt et al., 2002; Pane et al., 2004). The highest As and Cu concentrations detected in this study were higher than in areas affected by conspicuous bird colonies (Otero, 1998; Liu et al., 2006; Brimble et al., 2009b), whereas Ni was between 10 and 20 times higher than in peat profiles from the Arctic (Headley, 1996). Among the others, Pb and THg exceeded ERL and TEL concentrations sporadically (Pb: 46.7 and 30.2 mg kg^{-1}; THg: 0.15 and 0.13 mg kg^{-1}), while Cd, Cr and Zn were lower than ERL/TEL, indicating rare adverse biological effects. Nevertheless, considering the continuous input of guano, we cannot rule out possible detrimental effects on benthic communities due to long-term exposure to even low concentrations of metals, as observed in other studies (e.g. Amiard et al., 2006; Golovanova, 2008). This clearly demands further investigation.

5. Conclusions

Gulls represent important biovectors of As, Cd, Cr, Cu, Ni, Pb, THg, V, Zn in the small Nature Reserve of Marinello ponds (South Tyrrhenian Sea, Mediterranean). Despite the limited size of the gull colony and the almost pristine character of the Marinello area, highly marked spatial differences in trace element contamination were detected among the ponds.

The strong spatial gradient of trace element contamination, similar to the $\delta^{15}N$ gradient, which is a useful proxy of seabird influence, indicates that trace elements in the study area are essentially a consequence of guano subsidies to the pond closest to the gull colony. This study thus showed that gulls concentrate a number of trace elements in guano, confirming the important influence of anthropogenic food resources on contaminant accumulation. As a consequence of the constant input of guano, trace element release into receptor sites may also be crucial in triggering environmental contamination. Indeed, when compared with the US NOAA's SQGs, As, Cu and especially Ni showed high contamination levels, frequently associated with moderate and negative biological effects. Given the environmental and human concern caused by trace elements in coastal systems and the abundance of seabird colonies in coastal areas, our research confirms the need to broaden the interpretation of ecological processes in transitional areas, including seabirds as key factors.

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