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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.

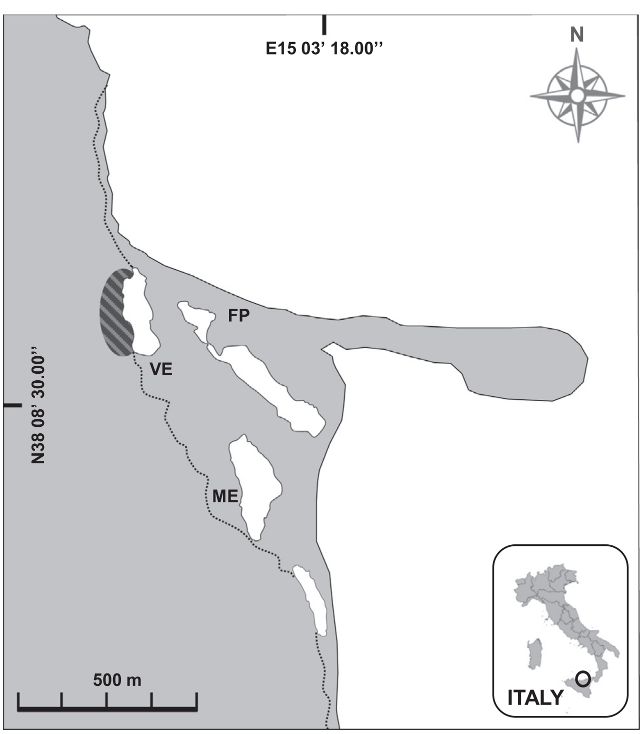

Fig. 1. Map of the study area with sampling ponds: Verde (VE), Fondo Porto (FP) Mergolo (ME). Dotted lines indicate the edge of the promontory of Tindari. The grey striped oval indicates the gull colony site on the Tindari cliff.

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.