Titanium as a contaminant of emerging concern in the aquatic environment and the current knowledge gap regarding seabird contamination

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ABSTRACT. Titanium (Ti) is considered a contaminant of emerging concern, since its use, mainly in the form of titanium dioxide (TiO_2) nanoparticles, has drastically increased in the last decades, due to its presence in several products, such as personal care products, cosmetics, sunscreens, photocatalysts and drug delivery systems, among others. Although its mechanisms of action are not yet fully understood, effective bioaccumulation, biomagnification and trophic transfer of these compounds in aquatic plants and fish have been reported in the literature. In addition, certain deleterious effects have been reported, including oxidative stress and adsorption and transfer of other metals and metalloids throughout the food chain, including apex predators and commercially important species. Thus, this contaminant may pose risks to both environmental and human health, leading to public health concerns. Seabirds are most likely exposed to Ti contamination through the trophic food web, as they are apex predators. However, investigations regarding Ti contamination in seabirds are almost nonexistent, and none delve further into possible deleterious Ti effects, indicating a significant knowledge scientific gap on the subject. In this context, Ti contamination in the aquatic environment is discussed herein. The few reports published in the literature on Ti contamination in seabirds are examined and wildlife and public health implications are evaluated. Ti concentrations ranged from 0.35 to 6.23 mg kg^{-1} in liver, 1.85 to 3.78 mg kg^{-1} in kidneys and from 0.1 to 17 mg kg^{-1} in feathers, presenting significant interspecies variations. The Mariana/Bento Rodrigues dam disaster and its potential deleterious effects on seabirds due to increased metal bioavailability are also discussed. This study, thus, demonstrates a huge knowledge gap concerning Ti in seabirds and indicates the urgent need to establish baseline data for this element in this group.
KEYWORDS: Environmental contamination; marine birds; public health; TiO_2; toxicity.

RESUMO. **Titânio como contaminante de preocupação emergente no ambiente aquático e a lacuna atual no conhecimento relativo à contaminação em aves marinhas**. O titânio é considerado um contaminante emergente e preocupante, uma vez que seu uso, principalmente na forma de nanopartículas de dióxido de titânio (TiO_2), aumentou drasticamente nas últimas décadas, devido à presença deste elemento em diversos produtos, como produtos de cuidados pessoais, cosméticos, protetores solares, fotocatalisadores e sistemas de entrega de drogas, entre outros. Embora seus mecanismos de ação ainda não sejam totalmente compreendidos, processos de bioacumulação, biomagnificação e transferência trófica destes compostos em plantas e peixes aquáticos têm sido relatados na literatura. Além disso, alguns efeitos deletérios têm sido relatados, incluindo estresse oxidativo e adsorção e transferência de outros metais e metalóides ao longo da cadeia alimentar, incluindo predadores de topo e espécies comercialmente importantes. Assim, este contaminante pode representar riscos para a saúde humana e ambiental, levando a preocupações de saúde pública. É provável que aves marinhas sejam expostas à contaminação por Ti através da cadeia trófica, uma vez que são predadores de topo de cadeia. No entanto, estudos acerca da contaminação por Ti em aves marinhas são quase inexistentes, e nenhuma investigação sobre possíveis efeitos prejudiciais do Ti foi encontrada, indicando uma lacuna de conhecimento científico significativa sobre o assunto. Neste contexto, a contaminação por Ti no ambiente aquático é discutida. Os poucos relatos publicados na literatura sobre a contaminação por Ti em aves marinhas são considerados e as implicações para a vida selvagem e para a saúde pública são avaliadas. As concentrações de Ti variaram de 0,35 a 6,23 mg kg^{-1} em fígado, 1,85 a 3,78 mg kg^{-1} em rins e 0,1 a 17 mg kg^{-1} em penas, apresentando significativas variações interespecíficas. O desastre da barragem de Mariana/Bento Rodrigues e seus potenciais efeitos deletérios sobre as aves marinhas devido ao aumento da biodisponibilidade de metais também são discutidos. Este estudo, portanto, demonstra uma enorme lacuna no conhecimento acerca de Ti em aves marinhas e indica a necessidade urgente de estabelecer dados de base para este elemento neste grupo.
PALAVRAS-CHAVE: Aves marinhas; Contaminação ambiental; Saúde Pública; TiO_2; toxicidade.

INTRODUCTION

Seabirds, or marine birds, are birds adapted to life in the marine environment. Most species nest in colonies, which can be small, comprising a few dozen birds, to huge, with millions of individuals. This group includes Sphenisciformes, Procellariiformes, Pelecaniformes and some Charadriiformes, among others, although no single definition for "seabird", exists in the literature. The most accepted is that this taxon must breed on land, and yet obtain food from the sea (Ballance 2007). This taxon comprises apex predators, which may suffer the effects of biomagnification and bioaccumulation processes regarding environmental contamination. Many studies have been carried out in this regard for different contaminants, including metals. Titanium, however, is becoming an increasing concern in the marine environment, and studies are almost non-existent with regard to contamination levels and the effects of this contaminant of emerging concern in seabirds.

Titanium, the ninth most abundant element in the Earth's crust (0.63% by mass) and the seventh most abundant among all elements, is a transition metal displaying a white-silvery-metallic color (Yang *et al*. 2017). This element has no known biological role, and displays low toxicity (Chen *et al*. 2011), inertness, and biocompatibility (Gui *et al*. 2011, Yin *et al*. 2012), due to its passive oxide coating. TiO_2 nanoparticles (NPs), on the other hand, are of especial concern regarding deleterious environmental and health effects.

Nanoparticles (NPs), generally defined as ranging between 1 and 100 nm in size (Skocaj *et al*. 2011), can be classified as either natural (such as those originating from volcanic or lunar dust or mineral composites), incidental (resulting from anthropogenic activities, such as exhaust resulting from combustion processes or welding fumes) or engineered (Masarikova *et al*. 2012). Titanium dioxide (TiO_2) NPs are one of the most highly manufactured and widely used NPs worldwide (Jomini *et al*. 2015), and are generally present in the highest concentrations in all environmental compartments, reflecting high worldwide production volumes of NPs (Nam *et al*. 2014). They are present mainly in foodstuffs (as additives), personal care products, such as toothpastes, sunscreens, shampoos, deodorants, shaving creams and drugs (Weir, *et al*. 2012).

TiO_2 NPs are discharged into the aquatic environment through many routes, such as in feces and urine, washed off from surfaces where these NP have been applied, or disposed as sewage that enters wastewater treatment plants (WWTPs). Although WWTPs are capable of removing larger-sized TiO_2 from influent sewage, TiO_2 NPs have still been found in treated effluents in several studies (Kiser *et al*. 2009, Weir *et al*. 2012, Westerhoff *et al*. 2011). These NPs are subsequently released to surface waters, where they can interact with living organisms (Weir *et al*. 2012).

Many lower trophic-level organisms show the potential to become a source of NPs for higher organisms (Asztemborska *et al*. 2018, Hosseini *et al*. 2015). This indicates that seabirds are most likely exposed to Ti contamination through the trophic food web. However, investigations regarding Ti contamination in seabirds are almost nonexistent, and none delve further into the possible deleterious effects of this emerging contaminant, indicating a significant knowledge gap on the subject.

METHODS

A scientometric approach was carried out in August 2018 on the Pubmed and Web of Science databases using the search terms "seabird*" or "bird*" and "titanium" or "TiO_2" or "TiO_2 nanoparticles" or "titanium nanoparticles". Only one result was obtained, indicating that index terms in this regard are not oriented towards an ecotoxicological or public health discussion. The extremely few published reports found were only obtained after an exhaustive search on the Google Scholar database by reading all returned results to evaluate adequacy towards the topic in discussion. A search carried out using seabird groups at both databases was also carried out, and no hits were obtained. In addition, seabird is a relative denomination, and some studies do not use this index term. Probably more studies would be found searching per specific species.

RESULTS

The areas where the only five studies published in this regard using the term "seabird" were carried out are indicated in Figure 1, and described below.

In one study, 29 wild seabirds collected from Tsushima Island, in Japan, were evaluated regarding several metals in liver and kidneys, including Ti (Mochizuki *et al*. 2012). However, the study does not clearly state how many species were assessed, stating only the analysis of two species (*Gavia pacifica* and *Gavia arctica*), one group (Gaviidae), individuals unidentifiable to the species level owing to oil contamination and one unknown species. The island is important as a staging post for various migratory wild birds, including seabirds. Sixteen of the birds were killed by an oil spill around Tsushima Island in February 2006, and 13 were rescued oiled seabirds that died after rescue. Metals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The authors reported that Ti concentrations in kidneys (μg g^{-1} dry weight, dw) were significantly higher in birds found dead compared to rescued birds (comprising Pacific Loon *Gavia pacifica* (Lawrence 1858), Black Throated Loon *Gavia arctica* (Linnaeus 1758)) and several Gaviidae, and that the lower concentrations in rescued birds can be blamed, in part, by decreased food intake.

In another study, Ti concentrations in kidney samples from several seabirds (Greater scaup *Aythya marila* (Linnaeus 1761), tufted duck *Aythya fuligula* (Linnaeus 1758), Eurasian pochard *Aythya ferina* (Linnaeus 1758), common scoter *Melanitta nigra* (Linnaeus 1758), and great crested grebe *Podiceps cristatus* (Linnaeus 1758), sampled from various areas in Japan were analyzed by ICP-AES (Mochizuki *et al*. 2011). Unfortunately, Ti concentrations were given for all birds combined, and not per species, determined as 0.80 ± 0.34 ug

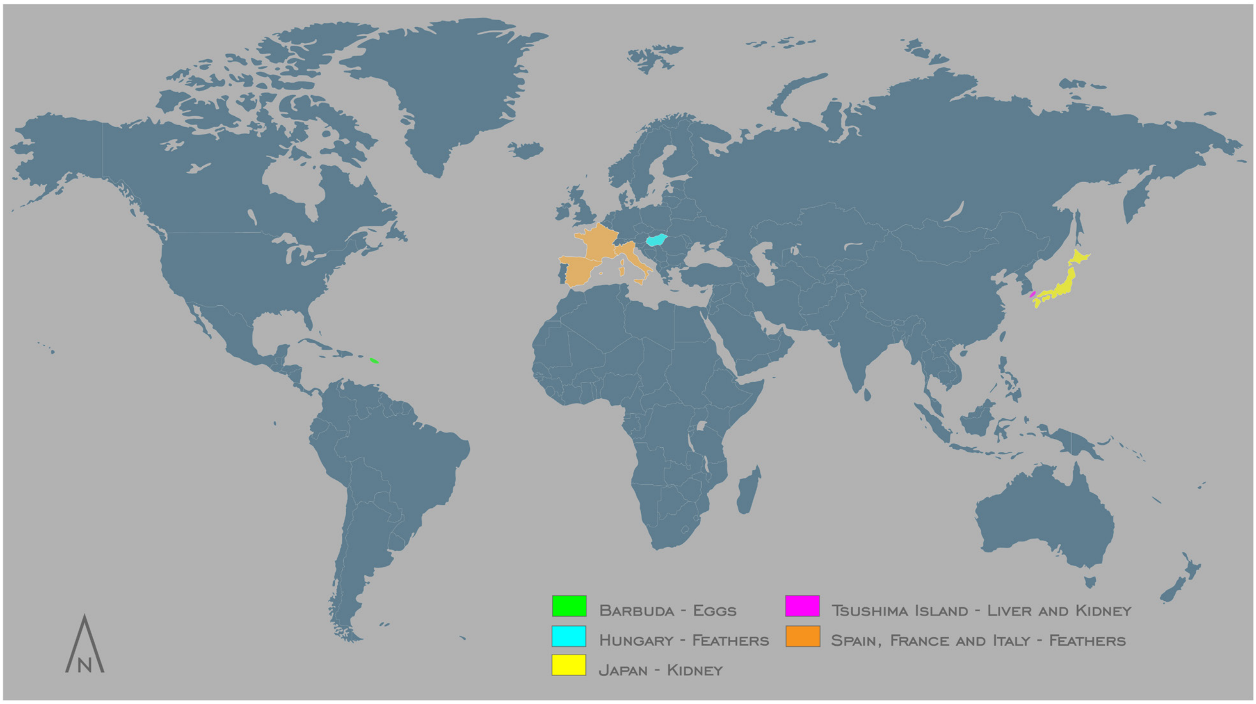

Figure 1. Location of the five areas where studies concerning Ti contamination in seabirds were carried out.

g^{-1} dw). In addition, Anatidae (n=65), Cormorants (n=30) and Ardeidae (n=10) were also analyzed, which also make use of the marine environment. Concentrations for each were determined as 2.07 ± 0.56 ug g^{-1} dw, 1.32 ± 0.34 ug g^{-1} dw and 2.94 ± 0.88 ug g^{-1} dw, respectively.

Another report determined Ti in the feathers of wild Eurasian Greater Flamingo *Phoenicopterus roseus* (Pallas 1811) fledglings, from 4 colonies in Western Europe (Spain, France, Sardinia, and North-eastern Italy) and from one group of adults from a zoo (Borghesi *et al*. 2016), by inductively coupled plasma atomic emission spectroscopy (ICP-AES) or inductively coupled plasma quadrupole-based mass spectrometry (ICP-QMS). The authors indicated that captive bird means (about 0.8 mg kg^{-1} – actual data not known as they were displayed as a graph) were significantly lower than the mean values of wild birds (about 4 mg kg^{-1} – actual data not known as they were displayed as a graph) for Ti, indicating that Ti was of external origin. The authors note, as reported previously in other studies, that external feather contamination may be due to direct atmospheric deposition, contact with contaminated soil, dust or water, or from contaminant deposition during preening, and specifically state that waterfowls and seabirds may also secrete metals through their salt gland and deposit them on their feathers when embrocating them (Dauwe *et al*. 2003, Dmowski 1999). The authors also indicate that external Ti is capable of masking bioaccumulation signals, and that further studies are required in this regard.

In a similar research carried out with feathers, Sand martin *Riparia riparia* (Linnaeus 1758) Ti levels in tail feathers from individuals captured in Hungary during the breeding season were determined from 1996–2000 by inductively coupled plasma optical emission spectrometer (ICP-OES). Ti levels ranged from about 6 to 12 mg kg^{-1} in the Rakamaz colony, from about 0.1 to 6 mg kg^{-1} in the Tiar colony, and a wider dispersion range from about 0.1 to 17 mg kg^{-1} at the Tiszatelek colony). Again, actual data not known as they were displayed as a graph in that paper. Ti concentrations were higher in tail feathers grown in winter, and older birds were found to excrete smaller amounts of trace elements than juveniles, suggesting an age effect on excretion for physiological or behavioral reasons (Szép *et al*. 2003).

Ti levels have also been determined in frigate bird eggs sampled at a breeding colony of approximately 2,000 pairs in coastal mangrove lagoon in Barbuda, in the West Indies (Trefry *et al*. 2013). Ti concentrations were determined by Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES). In this case, Ti was below the limits of detection (LOD) in the 5 sampled eggs (a limit which was, in fact, not stated in the study).

Data concerning studies on Ti in seabirds found in the present review are displayed in Table I.

Table I. Data concerning studies on Ti in seabirds found in the present review. Data are displayed as mg kg^{-1}.

Reference	Species/group	Matrix	Ti (min-max)	Analytical technique
Mochizuki *et al*. (2012)	*Gavia pacifica*	Liver	2.64-3.66	ICP-AES
		Kidneys	1.85-3.75	
	Gavia arctica	Liver	2.04-6.23	
		Kidneys	2.17-2.73	
	Gaviidae	Liver	2.48	
		Kidneys	2.46	
	Unknown	Liver	0.35	
		Kidneys	3.78	
Mochizuki *et al*. (2011)	*Aythya marila* *Aythya fuligula* *Melanitta nigra* *Podiceps cristatus*	Kidneys	0.8 – 2.7	ICP-AES
	Anatidae	Kidneys	2.07 ± 0.56	
	Cormorants		1.32 ± 0.34	
	Ardeidae		2.94 ± 0.88	
Borghesi *et al*. (2016)	*Phoenicopterus roseus*	Feathers	~ 0.8 – 4 (actual data not stated, only graphs are presented)	ICP-AES and ICP-QMS
Szép *et al*. (2003)	*Riparia riparia*	Feathers	0.1 - 17	ICP- OES
Trefry *et al*. (2013)	*Fregata magnificens*	Eggs	<LOD (unknown)	ICP- OES

DISCUSSION

After entering the body through several routes, including inhalation, ingestion and skin uptake, TiO_2 NPs are efficiently distributed to different organs through the circulatory system (Migdal *et al*. 2010). They have also have been shown to display several deleterious effects, predominantly via induction of oxidative stress (Skocaj *et al*. 2011). This, in turn, leads to cell damage and consequent genotoxic and carcinogenic effects, observed in several biological systems, such as mussels, fish, and mammalian cells (Migdal *et al*. 2010, Sund *et al*. 2014). However, there is still a lack of an overall evaluation of their toxicological effects in terms of harmful interactions with the biological and chemical systems and the environment (Shah *et al*. 2017).

In addition to the toxicity of the TiO_2 NPs themselves, these particles are also of concern regarding their ability to adsorb and, consequently, transfer, other compounds, such as other metals throughout the aquatic trophic web (Engates & Shipley 2011). This is due to the fact that TiO_2 NPs possess certain unique properties such as increased specific surface area, an increased number of surface activation sites, and therefore, high sorption capacity (Chen *et al*. 2011). This adsorption capacity may not only increase the toxicity of this particle but also influence the mobility and bioavailability of toxic metals (Chen *et al*. 2011). For example, it has been demonstrated that TiO_2 NPs act as Cd carriers in sub-lethal concentrations in the protozoan *Tetrahymena thermophila* (Yang *et al*. 2014), as well as in the small planktonic crustacean known as the water flea, *Daphnia magna*, which inhabits the water-column, and the California blackworm *Lumbriculus variegatus* (Müller 1774), a sediment-dwelling organism, demonstrating that TiO_2 NPs can interact with this contaminant in both environmental compartments, altering absorption rates (Hartmann *et al*. 2012). Enhanced bioaccumulation of other elements has also been demonstrated, such as both Cd and arsenate in the presence of TiO_2 NPs in carp *Cyprinus carpio* (Linnaeus 1758) (Sun *et al*. 2007, Zhang *et al*. 2007). The former study observed increased Cd concentrations adsorbed onto TiO_2 NPs in 146%, with a positive correlation between Cd and TiO_2 concentrations, and considerable Cd and TiO_2 accumulation in fish viscera and gills after 25 d of exposure. The latter study exposed carp to arsenic-contaminated water in the presence of TiO_2 nanoparticles, and reported significant As accumulation by 132% after 25 days exposure. The authors report considerable As and TiO_2 accumulated in fish intestines, stomachs and gills, with lower accumulation in muscle.

Trophic transfer of contaminants adsorbed onto TiO_2 NPs has also been demonstrated. One study evaluated the ability of TiO_2 NPs to transfer Cr, Cu, Pb and Se through a three trophic level aquatic food chain comprising *Ceratium tripos* ((Müller) Nitzsch, 1817) as the phytoplankton, *Daphnia* *hyalina* (Leydig 1860) as the zooplankton and *Liza abu* (Heckel 1843), a commercially important fish species in several areas around the world, as the predator (Hosseini *et al*. 2015). The dinoflagellate was exposed to 0, 0.2 and 0.5 µg L^{-1} of TiO_2 and, subsequently, each species was fed to the zooplankton *Daphnia hyalina*, which was then used as food for the Abu mullet *Liza abu*. The authors observed significant differences between Cr, Pb and Se among the trophic groups, and that Cr and Se were biomagnified through the food chain, whereas, Cu, an essential element, was regulated through homeostasis processes by the exposed organisms. Pb was the only element not biomagnified through the chain. Thus, it is clear that TiO_2 NPs are able to adsorb and transfer other toxic compounds throughout the trophic web, leading to contamination of higher-level organisms not only by TiO_2, but also by other metals of toxicological importance.

Studies on TiO_2 NPs contamination in several aquatic organisms are plentiful, demonstrating effective bioaccumulation, biomagnification and trophic transfer of TiO_2 NPs or ions originating from NPs in aquatic plants and fish (Asztemborska *et al*. 2018). For example, bioaccumulation was demonstrated in one study carried out on the sub-lethal effects of exposure of low and high concentrations of TiO_2 NPs on goldfish *Carassius auratus* (Linnaeus 1758) (Ates *et al*. 2013). Accumulation of TiO_2 NPs increased significantly in intestines and gills with increasing exposure doses from 10 to 100 mg L^{-1} TiO_2 NPs, while no significant accumulation in muscle or brain was detected.

Trophic transfer studies have also demonstrated that TiO_2 NPs are easily transferred to higher trophic levels. One study evaluated the benthic trophic transfer of TiO_2 NPs at 10, 50 and 100 mg L^{-1} from clamworms *Perinereis aibuhitensis* (Grube 1878) to juvenile turbots *Scophthalmus maximus* (Linnaeus 1758) (Wang *et al*. 2016), where increasing TiO_2 NPs accumulation was observed in juvenile turbots with increasing Ti contents in clamworms during dietary exposure, with several deleterious effects on the turbots, such as lower protein and higher lipid content, as well as reduced growth and abnormal liver and spleen symptoms, while waterborne exposure led to higher Ti accumulation in turbots compared to the dietary exposure.

In another study, the trophic transfer of TiO_2 NPs from marine microalga *Nitzschia closterium* ((Ehrenberg) Smith 1853) to Farrer's scallop *Chlamys farreri* (Müller 1776) was demonstrated (Wang *et al*. 2016). Tissue TiO_2 NPs burden in the top organism, in this case, scallops, were higher through aqueous exposure compared to dietary exposure. Deleterious scallop effects were also observed, including increased lysosomal membrane permeability, DNA damage, and histopathological effects, again, mainly observed after aqueous exposure rather than dietary exposure. Thus, it is clear that trophic transfer of TiO_2 NPs is possible, and even, likely, in the environment.

TiO_2 NPs are recognized and taken up by immune cells, such as macrophages, monocytes, platelets, leukocytes and dendritic cells, and can trigger inflammatory responses (Skocaj *et al*. 2011), and have been reported as leading to immune system disorders in several organisms, such as mussels and mammals (Barmo *et al*. 2013, Bettini *et al*. 2017). It stands to reason that this may also be true for birds. In this context, a lowered immune system may lead to increasing outbreaks of infectious diseases among these animals, which have been linked to anthropogenic impacts to the oceans, including chemical pollution (Ward & Lafferty 2004). Consequences of these outbreaks include increased mortality, leading to a trophic cascade effect, altering community structures (Ward & Lafferty 2004). Many of the infectious diseases reported in birds can affect other animals, as well as humans, through exposure to seabird excrements, prey remains and seabird carcasses. In fact, several micro-organisms of significant animal and human health importance have already been identified in free-living seabirds, such as arboviruses, Influenza A, Newcastle, Herpes, and several microorganisms, including *Chlamydophila psittaci* (Lillie 1930), *Anaplasma phagocytophilum* (Foggie 1949), *Borrelia burgdorferi* (Johnson *et al*. 1984), *Campylobacter jejuni* (Jones *et al*. 1931), *Salmonella enterica* (Kauffmann and Edwards 1952), *Pasteurella multocida*, *Mycobacterium avium* (Runyon 1965) and *Candida* spp. (HUBÁLEK 2004). Autochthonous bacteria from aquatic environments such as *Vibrio* sp. and *Aeromonas* sp., that cause animal, human and zoonotic diseases, as well as several enterobacteria, have also been identified in seabirds worldwide (Atterby *et al*. 2016, Cardoso *et al*. 2018, Cardoso *et al*. 2014, Dolejska *et al*. 2016, Grond *et al*. 2014, Kinzelman *et al*. 2008, Masarikova *et al*. 2012, Rodríguez *et al*. 2010, Pereira *et al*. 2007, Saviolli *et al*. 2016, Vigo *et al*. 2011). Significantly, migratory birds can disseminate these microorganisms over long distances, and even residents can fly for up to 100 km, transferring these pathogens to other birds and other vertebrates, including humans (Hubálek 2004). In addition, birds from different species use the same stopping points during migration, which favors disease transmission among species, especially when other stressors, such as chemical contamination, lower their already low immunity, due to migration stress, even more (Hubálek 2004, Ward & Lafferty 2004). Therefore, in a public health context, birds are an important link in the epidemiological chain of transmissible diseases (Saviolli *et al*. 2016), and TiO_2 contamination may play a significant role in this scenario.

Furthermore, seabirds, often present high contaminant loads, due to biomagnification and bioaccumulation processes (Fisk 2003), as they ingest a wide variety of food items in their diets, feed at varying trophic levels, and have been demonstrated as the dominant vectors for the transport of marine-derived contaminants to other areas, including land, through their guano (Michelutti *et al*. 2010). For example, one study observed that sediments of coastal ponds affected by seabirds displayed 60-fold more DDT, 25-fold more Hg, and 10-fold more hexachlorobenzene concentrations than nearby control sites (Blais *et al*. 2005), while another study demonstrated that phosphorus, Cd, K, Zn, and As were identified as seabird-derived elements, in a series of 10 ponds located along a gradient of seabird influence the high Arctic, present in high concentrations in guano and in low concentrations in background pond sediments (Brimble *et al*. 2009). As seabirds usually form large breeding colonies, these animals can, thus, also create contamination hotspots, by discharging marine-derived contaminants through their excrement (Blais *et al*. 2007), which may lead to extremely high contaminant concentrations, which may, in turn, exceed environmental guidelines for wildlife protection (Brimble *et al*. 2009), and possibly be transported to other areas through contact with migratory animals. Thus, entire food chains may be affected, leading to public health concerns. Therefore, TiO_2 contamination may be even more significant in an environmental and public health context than previously thought, and our significant gap in knowledge demonstrated herein indicate the need for further studies regarding Ti contamination in seabirds in order to establish a database baseline for future comparisons and allow for further study on the effects of this emerging contaminant.

Concerning Ti contamination in Brazil, a recent environmental catastrophe, the Mariana/Bento Rodrigues dam disaster, may lead to possible long-term effects on seabirds. This incident is considered the worst environmental disaster in Brazil's history (do Carmo *et al*. 2017). The accident occurred when an iron ore tailings dam in Mariana, in the state of Minas Gerais, Brazil, suffered a catastrophic failure in 2015, resulting in an immense flooding that destroyed a neighboring village, killing at least 17 people and releasing around 60 million cubic meters of iron waste in the environment (BBC 2015). The toxic waste, which contains high concentrations of several metals, including titanium (GREENPEACE 2017), flowed into the Doce River, affecting over 230 municipalities, causing toxic mudflows to pollute the river and beaches near the mouth, and also travelled 620 km downstream, reaching the Atlantic Ocean 17 days later (Figure 2).

Figure 2. Route of the toxic mud from the Bento Rodrigues dam disaster, travelling throughout the Doce River and reaching the Atlantic Ocean. The arrow indicates current flow, leading the toxic mud towards Abrolhos. Map.

Since then, the toxic mud has spread across the entire Espírito Santo coast, which is a very important breeding area for certain seabirds, such as the Sandwich tern *Sterna sandvicensis eurygnatha* (Latham 1787) (EFE *et al*. 2000), and visiting territory for several poorly-known migrating species, such as the Laughing Gull *Leucophaeus atricilla* (Linnaeus 1758) and breeding Black Noddy *Anous minutus* (Boie 1844) individuals at Trindade and Martin Vaz Islands, respectively (Dias *et al*. 2010). In addition, the mud has also reached the southern Bahia littoral zone, near the Abrolhos Marine National Park wildlife, considered of vital importance to the Brazilian ecosystem, since it hosts the major marine biodiversity in the whole southern Atlantic ocean (ABC 2016), including several seabirds, such as the Brown Booby *Sula leucogaster* (Boddaert 1783), terns and frigates, among many others (ICMBIO 2018). Some studies are now being carried out in the mud-affected areas, indicating probable increase of trace metal bioavailability and contamination risks (Queiroz *et al*. 2018), although no results regarding seabirds have yet been published. Thus, the potential long-term effects of this environmental disaster towards this group have not yet been unraveled, and should be monitored in the long term.

In sum, although the importance of assessing Ti concentrations in the environment and evaluating possible deleterious effects have been stated in several studies, most research has been conducted as laboratory assays with lower aquatic organisms, thus demonstrating a major gap in knowledge regarding levels and toxicological effects of this compound of emerging concern with regard to higher trophic levels, such as seabirds. The scarce studies discussed herein do nothing more than report Ti concentrations (and even so, some methodological flaws such as not reporting method limits of detection in some cases, are observed) and do not link these concentrations to environmental Ti concentrations (e.g., food, soil), much less discuss toxicological implications of this contaminant and possible deleterious effects in these animals. In this regard, it is extremely important to begin establishing baseline data for this element, in order to increase future understanding on its possible roles in toxicological and health assessments of wildlife populations, which, in turn, may lead to public health concerns.

REFERENCES

ABC 2016. **Samarco mine tragedy: Toxic mud from Brazil mine spill reaches Atlantic Ocean**. Available at: <http://www.abc.net.au/news/2015-11-22/brazil-mine-spill-mud-to-hit-atlantic-ocean/6962040>. Access on: [11/08/2018].

Asztemborska, M., Jakubiak, M., Stęborowski, R., Chajduk, E. & Bystrzejewska-Piotrowska, G. 2018. Titanium dioxide nanoparticle circulation in an aquatic ecosystem. **Water, Air, and Soil Pollution 229** :208-217.

Ates, M., Demir, V., Adiguzel, R. & Arslan, Z. 2013. Bioaccumulation, sub-acute toxicity, and tissue distribution of engineered titanium dioxide (TiO2) nanoparticles in goldfish (*Carassius auratus*). **Journal of Nanomaterials** 2013:460518.

Atterby, C., Ramey, A. M., Hall, G. G., Järhult, J., Börjesson, S. & Bonnedahl, J. 2016. Increased prevalence of antibiotic-resistant *E. coli* in gulls sampled in Southcentral Alaska is associated with urban environments. **Infection, Ecology & Epidemiology 6**:107.

Ballance, L. T. 2007. Understanding seabirds at sea: why and how? **Marine Ornithology 35** (2):127–135.

Barmo, C., Ciacci, C., Canonico, B., Fabbri, R., Cortese, K., Balbi, T., Marcomini, A., Pojana, G., Gallo, G. & Canesi, L. 2013. *In vivo* effects of n-TiO2 on digestive gland and immune function of the marine bivalve *Mytilus galloprovincialis*. **Aquatic Toxicology 15** (132-133):9-18.

BBC 2015. **Brazil dam collapse death toll rises to 17, BHP says**. Available at: <http://www.bb.com/news/business-35158646>. Access on: [11/08/2018].

Bettini, S., Boutet-Robinet, E., Cartier, C., Coméra, C., Gaultier, E., Dupuy, J., Naud, N., Taché, S., Grysan, P., Reguer, S., Thieriet, N., Réfrégiers, M., Thiaudière, D., Cravedi, J.-P., Carrière, M., Audinot, J.-N., Pierre, F. H., Guzylack-Piriou, L. & Houdeau, E. 2017. Food-grade TiO2 impairs intestinal and systemic immune homeostasis, initiates preneoplastic lesions and promotes aberrant crypt development in the rat colon. **Scientific Reports 7**: 40373.

Blais, J. M., Kimpe, L. E., Mcmahon, D., Jkeatley, B. E., Mallory, M. L., Douglas, M. S. & Smol, J. P. 2005. Arctic seabirds transport marine-derived contaminants. **Science 309** (5733):445.

Blais, J. M., Macdonald, R. W., Mackay, D., Webster, E., Harvey, C. & Smol, J. P. 2007. Biologically mediated transport of contaminants to aquatic systems. **Environmental Science and Technology 41** (4):1075-1084.

Borghesi, F., Migani, F., Andreotti, A., Baccetti, N., Bianchi, N., Birke, M. & Dinelli, E. 2016. Metals and trace elements in feathers: A geochemical approach to avoid misinterpretation of analytical responses. **Science of the Total Environment 544**: 476-494.

Brimble, S. K., Foster, K. L., Mallory, M. L., Macdonald, R. W., Smol, J. P. & Blais, J. M. 2009. High Arctic ponds receiving biotransported nutrients from a nearby seabird colony are also subject to potentially toxic loadings of arsenic, cadmium, and zinc. **Environmental Toxicology and Chemistry 28** (11): 2426-2433.

Cardoso, M. D., Lemos, L. S., Roges, E. M., Moura, J. F., Tavares, D. C., Matias, C. A. R., Rodrigues, D. P. & Sicilano, S. 2018. A comprehensive survey of *Aeromonas* sp. and *Vibrio* sp. in seabirds from southeastern Brazil: Outcomes for public health. **Journal of Applied Microbiology 124** (5):1283-1293.

Cardoso, M. D., Moura, J. F., Tavares, D. C., Gonçalves, R. A., Colabuono, F. I., Roges, E. M., Souza, R. L., Rodrigues, D. P., Montone, R. C. & Siciliano, S. 2014. The Manx shearwater (*Puffinus puffinus*) as a candidate sentinel of Atlantic Ocean health. **Aquatic Biosystems 10**:1-6.

Chen, J., Dong, X., Xin, Y. & Zhao, M. 2011. Effects of titanium dioxide nano-particles on growth and some histological parameters of zebrafish (*Danio rerio*) after a long-term exposure. **Aquatic Toxicology 101** (3-4): 493-499.

Dauwe, T., Bervoets, L., Pinxten, R., Blust, R. & Eens, M. 2003. Variation of heavy metals within and among feathers of birds of prey: Effects of molt and external contamination. **Environmental Pollution 124** (3): 429-436.

Dias, R. A., Agne, C. E., Gianuca, D., Gianuca, A., Barcellos-Silveira, A. & Bugoni, L. 2010. New records, distribution and status of six seabird species in Brazil. **Iheringia - Série Zoologia 100** (4): 379-390.

Dmowski, K. 1999. Birds as bioindicators of heavy metal pollution: review and examples concerning European species. **Acta Ornithologica 34** (1): 1-25.

Do Carmo, F. F., Kamino, L. H. Y., Junior, R. T., De Campos, I. C., Do Carmo, F. F., Silvino, G., De Castro, K. J. S. X., Mauro, M. L., Rodrigues, N. U. A., Miranda, M. P. S. & Pinto, C. E. F. 2017. Fundão tailings dam failures: the environment tragedy of the largest technological disaster of Brazilian mining in global context. **Perspectives in Ecology and Conservation 15** (3): 145-151.

Dolejska, M., Masarikova, M., Dobiasova, H., Jamborova, I., Karpiskova, R., Havlicek, M., Carlile, N., Priddel, D., Cizek, A. & Literak, I. 2016. High prevalence of Salmonella and IMP-4-producing Enterobacteriaceae in the silver gull on Five Islands, Australia. **Journal of Antimicrobial Chemotherapy 71** (1): 63-70.

Efe, M. A., Do Nascimento, J. L. X., Do Nascimento, I. L. S. & Musso, C. 2000. Distribuição e ecologia reprodutiva de *Sterna sandvicensis eurygnatha* no Brasil. **Melopsittacus 3** (3): 110-121.

Engates, K. E. & Shipley, H. J. 2011. Adsorption of Pb, Cd, Cu, Zn and Ni to titanium dioxide nanoparticles: Effect of particle size, solid concentration, and exhaustion. **Environmental Science and Pollution Research 18** (3) :386-395.

Fisk, A. T. 2003. Contaminant levels, trends and effects in the biological environment – Canadian arctic contaminants assessment report II (Indian and northern affairs Canada, Ottawa). 11–61.

Greenpeace 2017. **Girinos como bioindicadores da qualidade da água do Rio Doce**.

Grond, K., Ryu, H., Baker, A. J., Santo-Domigo, J. W. & Buehler, D. M. 2014. Gastro-intestinal microbiota of two migratory shorebird species during spring migration staging in Delaware Bay, USA. **Journal of Ornithology 155** (4): 969-977.

Gui, S., Zhang, Z., Zheng, L., Cui, Y., Liu, X., Li, N., Sang, X., Sun, Q., Gao, G., Cheng, Z., Cheng, J., Wang, L., Tang, M. & Hong, F. 2011. Molecular mechanism of kidney injury of mice caused by exposure to titanium dioxide nanoparticles. **Journal of Hazardous Materials 195**: 365–370.

Hartmann, N. B., Legros, S., Von Der Kammer, F., Hofmann, T. & Baun, A. 2012. The potential of TiO2 nanoparticles as carriers for cadmium uptake in *Lumbriculus variegatus* and *Daphnia magna*. **Aquatic Toxicology 118-119**:1-8.

Hosseini, M., Rahmanpour, S. H. & Moradi, M. 2015. Heavy metal ions on titanium dioxide nano-particle: Biomagnification in an experimental aquatic food chain. **International Journal of Marine Science and Engineering 5** (1): 23-29.

Hubálek, Z. 2004. An annotated checklist of pathogenic microorganisms associated with migratory birds. **Journal of Wildlife Diseases 40** (4): 639-659.

Icmbio 2018. Access on:

Jomini, S., Clivot, H., Bauda, P. & Pagnout, C. 2015. Impact of manufactured TiO2 nanoparticles on planktonic and sessile bacterial communities. **Environmental Pollution 202**:196-204.

Kinzelman, J., Mclellan, S. L., Amick, A., Preedit, J., Scopel, C. O., Olapade, O., Gradus, S., Singh, A. & Sedmak, G. 2008. Identification of human enteric pathogens in gull feces at Southwestern Lake Michigan bathing beaches. **Canadian Journal of Microbiology 54** (12):1006-1015.

Kiser, M. A., Westerhoff, P., Benn, T., Wang, Y., Pérez-Rivera, J. & Hristovski, K. 2009. Titanium nanomaterial removal and release from wastewater treatment plants. **Environmental Science and Technology 43** (17): 6757-6763.

Masarikova, M., Manga, I., Cizek, A., Dolejska, M., Oravcova, V., Myskova, P., Karpiskova, R. & Literak, I. 2012. *Salmonella enterica* resistant to antimicrobials in wastewater effluents and black-headed gulls in the Czech Republic. **Science of the Total Environment 542** (Pt A): 102-107.

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. **PNAS 107** (23): 10543-10548.

Migdal, C., Rahal, R., Rubod, A., Callejon, S., Colomb, E., Atrux-Tallau, N., Haftek, M., Vincent, C., Serres, M. & Daniele, S. 2010. Internalisation of hybrid titanium dioxide/para-amino benzoic acid nanoparticles in human dendritic cells did not induce toxicity and changes in their functions. **Toxicology Letters 199** (1): 34-42.

Mochizuki, M., C., K., Mori, M., Hondo, R. & Ueda, F. 2011. An innovative approach to biological monitoring using wildlife. In: Environmental Monitoring, IntechOpen,157-168. Available at: https://www.intechopen.com/books/environmental-monitoring/an-innovative-approach-to-biological-monitoring-using-wildlife. Access on: [11/08/2018].

Mochizuki, M., Yamamoto, H., Yamamura, R., Suzuki, T., Ochiai, Y., Kobayashi, J., Kawasumi, L., Arai, T., Kajig, H. & Ueda, F. 2012. Contents of various elements in the organs of seabirds killed by an oil spill around Tsushima Island, Japan. **Journal of Veterinary Medical Science 75** (5): 667-670.

Nam, D.-H., Lee, B.-C., Eom, I.-C., Kim, P. & Yeo, M.-K. 2014. Uptake and bioaccumulation of titanium- and silver-nanoparticles in aquatic ecosystems. **Molecular and Cellular Toxicology 10** (1): 9-17.

Pereira, C. S., Amorim, S.D., Santos, A. F. M., Siciliano, S., Moreno, I. B., Ott, P. H., & Rodrigues, D. P. 2007. *Vibrio* spp. isolated from marine mammals captured in coastal regions from southwestern to southern Brazil. **Pesquisa Veterinária Brasileira 27** (2): 81-83.

Queiroz, H. M., Nóbrega, G. N., Ferreira, T. O., Almeida, L. S., Romero, T. B., Santaella, S. T., Bernardino, F. & Otero, X. L. 2018. The Samarco mine tailing disaster: A possible time-bomb for heavy metals contamination? **Science of The Total Environment 637-638**: 498-506.

Rodríguez, J., López, P., Muñoz, J. & Rodríguez, N. 2010. Detección de *Vibrio cholerae* no toxigenico en aves migratorias y residentes (Charadriiformes) en una laguna costera del nororiente de Venezuela. **Saber 22** (2): 122-126.

Saviolli, J. Y., Cunha, M. P. V., Guerra, M. F. L., Irino, K., Catão-Dias, J. L. & Carvalho, V. M. 2016. Free-ranging frigates (*Fregata magnificens*) of the southeast coast of

Brazil harbor extraintestinal pathogenic *Escherichia coli* resistant to antimicrobials. **PLoS ONE 11** (2): e0148624.

Shah, S. N. A., Shah, Z., Hussain, M. & Khan, M. 2017. Hazardous effects of titanium dioxide nanoparticles in ecosystem. **Bioinorganic Chemistry and Applications 2017**: 1-12.

Skocaj, M., Filipic, M., Petkovic, J. & Novak, S. 2011. Titanium dioxide in our everyday life; Is it safe? **Radiology and Oncology 45** (4): 227-247.

Sun, H., Zhang, X., Niu, Q., Chen, Y. & Crittenden, J. C. 2007. Enhanced accumulation of arsenate in carp in the presence of titanium dioxide nanoparticles. **Water, Air, and Soil Pollution 178** (1-4): 245-254.

Sund, J., Palomäki, J., Ahonen, N., Savolainen, K., Alenius, H. & Puustinen, A. 2014. Phagocytosis of nano-sized titanium dioxide triggers changes in protein acetylation. **Journal of Proteomics 108**: 469-483.

Szép, T., Møller, A. P., Vallner, J., Kovács, B. & Norman, D. 2003. Use of trace elements in feathers of sand martin *Riparia riparia* for identifying moulting areas. **Journal of Avian Biology 34** (3): 307-320.

Trefry, S. A., Diamond, A. W., Spencer, N. C. & Mallory, M. L. 2013. Contaminants in magnificent frigatebird eggs from Barbuda, West Indies. **Marine Pollution Bulletin 75** (1-2):317-321.

Vigo, G. B., Leotta, G. A., Caffer, M. I., Salve, A., Binsztein, N. & Pichel, M. 2011. Isolation and characterization of *Salmonella enterica* from Antarctic wildlife. **Polar Biology 34** (5): 675–681.

Wang, Z., Cia, B., Chen, B., Sun, X., Zhu, L., Zhao, J., Du, P. & Xing, B. 2016. Trophic transfer of TiO2 nanoparticles from marine microalga (*Nitzschia closterium*) to scallop (*Chlamys farreri*) and related toxicity. **Environmental Science: Nano 4**:415-424.

Wang, Z., Yin, L., Zhano, J. & Xing, B. 2016. Trophic transfer and accumulation of TiO2 nanoparticles from clamworm (*Perinereis aibuhitensis*) to juvenile turbot (*Scophthalmus maximus*) along a marine benthic food chain. **Water Research 95** (2): 250-259.

Ward, J. R. & Lafferty, K. D. 2004. The elusive baseline of marine disease: Are diseases in ocean ecosystems increasing? **Plos Biology 2**: 542-547.

Weir, A., Westerhoff, P., Fabricius, L. & Von Goetz, N. 2012. Titanium dioxide nanoparticles in food and personal care products. **Environmental Science and Technology 46**: 2242-2250.

Westerhoff, P., Song, G., Hristovski, K. & Kiser, M. A. 2011. Occurrence and removal of titanium at full scale wastewater treatment plants: Implications for TiO2 nanomaterials. **Journal of Environmental Monitoring 13** (5): 1195-1203.

Yang, L., Hsu, K., Baughman, B., Godfrey, D., Medina, F., Menon, M. & Wiener, S. 2017. Electron Beam Technology. In: **Additive Manufacturing of Metals: The Technology, Materials, Design and Production**. 63-67.

Yang, W. W., Wang, Y., Huang, B., Wang, N. X., Wei, Z. B., Luo, J., Miao, A. J. & Yang, L. 2014. TiO2 nanoparticles act as a carrier of Cd bioaccumulation in the ciliate Tetrahymena thermophila. **Environmental Science and Technology 48** (13): 7568-7575.

Yin, J. J., Liu, J., Ehrenshaft, M., Roberts, J. E., Fu, P. P., Mason, R. P. & Zhao, B. 2012. Phototoxicity of nano titanium dioxides in HaCaT keratinocytes - Generation of reactive oxygen species and cell damage. **Toxicology and Applied Pharmacology 263** (1): 81-88.

Zhang, C., Sun, H., Zhan, Z., Niu, Q., Chen, Y. & Crittenden, J. C. 2007. Enhanced bioaccumulation of cadmium in carp in the presence of titanium dioxide nanoparticles. **Chemosphere 67** (1): 160-166.