INTERACTIONS BETWEEN SEABIRDS AND POLLUTION IN IRISH WATERS

Heidi Acampora

Submitted in fulfilment of the requirements of the degree of

Doctor of Philosophy

Supervised by Dr Ian O'Connor and Dr Philip White

Submitted to the Galway-Mayo Institute of Technology

January 2017

INTERACTIONS BETWEEN SEABIRDS AND POLLUTION IN IRISH WATERS

PhD Thesis

Heidi Acampora

M.Sc. Marine Biodiversity and Conservation

Submitted for fulfilment of Doctorate of Philosophy

Galway-Mayo Institute of Technology

Supervised by:

Dr Ian O'Connor & Dr Philip White [Galway-Mayo Institute of Technology]

January 2017

Author: Heidi Acampora

Title: Interactions between seabirds and pollution in Irish waters

ABSTRACT

Seabirds are abundant and ubiquitous globally. They suffer pressure from many contemporary threats such as fisheries, invasive species and pollution. This thesis focuses on two different types of pollution: plastic litter and persistent organic pollutants (POPs). Plastic litter affects seabirds in two main ways: ingestion and entanglement. At least 50% of the world's seabird species have been affected by plastic pollution in one way or another. Persistent organic pollutants are toxic compounds used in industry and sometimes produced naturally or as an unintentional by-product of anthropogenic activities. POPs are persistent in the environment, of toxic nature, have volatile properties and can bio-accumulate in biota. Legislation has been used to ban or restrict the use of most POPs and now concentrations of such substances are monitored to make sure they reach safe levels until complete elimination. Legislation has also called for monitoring of marine litter in the environment and in biota. As seabirds feed at a variety of trophic levels, they can provide information linked to all trophic levels. They have been extensively studied, are abundant and long-lived, making them ideal candidates for monitoring environmental changes, even when subtle. Data for both types of pollutants' interactions with seabirds are scarce in Ireland, even though the islands of Ireland and Britain have a total population of almost 8 million seabirds. The need to investigate the presence, levels and how such pollutants interact with seabird species was eminent, not only for a matter of scientific research, but also to assess the threat posed to seabirds in the context of legislative requirements to monitor the health of their populations. This research aimed to establish baseline levels of plastic and persistent organic pollutants in seabirds breeding in Ireland, along with the testing of different methodologies that may be appropriate for Ireland to implement monitoring such as the Oslo-Paris Convention (OSPAR) Ecological Quality Objectives (EcoQOs) should that become government policy. For that, Chapter 1 presents the background of what is known about these pollutants, how they can affect wildlife and seabirds, why it is important to monitor pollutants in seabirds and the knowledge gap in Ireland. Chapter 2 of this dissertation encompasses the suitability of beached bird surveys for marine

litter monitoring, baseline levels of plastic ingestion through stomach analysis, as well as an investigation of suitable species to comply with international monitoring programmes such as EcoQOs. Chapter 3 investigates alternative monitoring strategies for marine litter, this time via opportunistic sampling of live birds that are handled in colonies for banding or other research and through the collection of boluses as a passive diet sampling. This type of sampling allowed for chicks and parents to be investigated for plastic ingestion. Chapter 4 focuses on a single species, the European Storm Petrel (*Hydrobates pelagicus*), for persistent organic pollutant investigation. This chapter intended to establish baseline levels for different types of POPs in Storm Petrels in Ireland, but also to test different methodologies for live sampling for POPs. In this context, preen oil and feathers from the same birds were collected for investigation. Chapter 5 also focused on a single species, the Common Tern (*Sterna hirundo*) to investigate POP concentrations for Common Terns in Ireland, also testing different methodologies for live birds (preen oil and feathers), but additionally, sampling dead birds found in the same colony (which were investigated for plastic pollution as well), utilising two internal organs (liver and preen gland). This species is also used as a monitor for POPs in international monitoring programmes. Therefore, the investigation of such species in Ireland adds to the body of research needed to establish compliance with monitoring. Finally, chapter 6 addresses the conclusions incorporated by this research and how it fits to the current pollutant information globally, and informs policy in Ireland.

GMIT
INSTITIÚID TEICNEOLAÍOCHTA NA GAILLIMHE-MAIGH EO
GALWAY-MAYO INSTITUTE OF TECHNOLOGY

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of PhD is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed:  , candidate.

ID No. G00318243

Date: 31/01/2017

ACKNOWLEDGEMENTS

The biggest thank you to my supervisor Ian O'Connor, who has never been short of enthusiasm, patience, wisdom and ideas. Thank you for joining in the countless "Fulmar Emergencies" and still sing along all the way! You were truly a most honourable supervisor! Thanks to my co-supervisor Philip White for teaching me the ways of chemical analysis and having the patience to do so in such a short time. Thanks to Rick Officer and Roisin Nash for their early supervision. Thanks to Steve Newton and Simon Berrow for providing me with samples and for their enthusiasm for my research. Thanks to all volunteers who have walked the beach in nice and mostly not so nice weather and collected dead smelly birds throughout the past three years. The Republic of Ireland Beached Bird Survey only became a thing because of all of you! Special thanks to Rosemary Hill, Sean O'Gallaghan and Kieran Campbell. You guys deserve the best volunteer award for sure!

Thanks to all at Clean Coasts and BirdWatch Ireland for all the support. Special thanks to Annabel Fitzgerald, Niall Keogh, Brian Burke, Andrew Power, Jen Lynch and Helen Boland. Thanks to Olga Lyashevska for all the help with numbers! Thanks to Jan van Franeker for the teaching and training and friendship. Thanks to all the Applied Marine and Freshwater Biology students that helped with bird dissections. Special thanks to Danilo Hirota and Killian Coakley for their help in the lab. Thanks to Richard Cronin and Conall O'Connor at the Department of Housing, Planning, Community and Local Government (DHPCLG) for supporting my research. Thanks to Science without Borders (CAPES, BEX 1269/2013-05) for funding this research.

Thanks to Isabel Baker, Claire Moore, Michael Sheridan, Michael Griffin, Kevin French, Roxanne Duncan and Mar Marcos for their friendship and for keeping me sane. You guys were an endless source of fun and support! Thanks to Raissa Hogan and Barbara Oliveira for their continuous support and friendship. Thanks to all at the Marine & Freshwater Research Centre. I think we're all a great bunch, aren't we?

Thanks to my mother Rosane Acampora and my brothers James, Harrison and Ralph. You are the best family I could ever ask for and I don't think anyone else in the world gets happier for my accomplishments than the four of you. Thank you so much. Special thanks to my aunt Cristina and all my extended family. Thanks to Pringles. Thanks to

Darragh Ryan for making my life better every day, and even helping with bird necropsies!

For my grandmother Zelina Domingues Acampora and my father Jose Inaldo Bessa.

I can only hope you would have been proud.

 His grace abounds in deepest waters

Table of Contents

List of Figures

List of Tables

CHAPTER 1

GENERAL INTRODUCTION

"Those who contemplate the beauty of the earth find reserves of strength that will endure as long as life lasts. There is symbolic as well as actual beauty in the migration of the birds, the ebb and flow of the tides, the folded bud ready for the spring. There is something infinitely healing in the repeated refrains of nature – the assurance that dawn comes after night, and spring after the winter."

Rachel Carson

1.1. MARINE LITTER

As per the Oslo-Paris Convention (OSPAR), marine litter is defined as "any solid material which has been deliberately discarded, or unintentionally lost on beaches and on shores or at sea, including materials transported into the marine environment from land by rivers, draining or sewage systems or winds. It includes any persistent, manufactured or processed solid material" (OSPAR, 2010). The vast majority of marine litter is plastic and a recent study estimated that coastal populations input at least 8 million tons of plastics per year into the marine environment (Jambeck et al., 2015). Although the rate of decomposition of plastic is not yet fully understood, we do know however that plastics break down by wave action and weathering into smaller pieces. According to OSPAR, "This breakdown of larger items results in numerous tiny plastic fragments, which, when smaller than 5mm are called secondary microplastics. Other microplastics that can be found in the marine environment are categorised as primary microplastics since they are produced either for direct use, such as for industrial abrasives or cosmetics, or for indirect use, such as pre-production pellets or nurdles" (OSPAR, 2010).

Numerous studies have highlighted the negative economic, health and ecological impacts of marine litter (Derraik, 2002; Gall and Thompson, 2015). Economic impacts range from reduced tourism and amenity value due to polluted beaches and coastal areas, reducing and affecting the delivery of ecosystem services, including basic services such as water (Ballance et al., 2000; Newman et al., 2015), to the cost of intermittent beach clean ups (McIlgorm et al., 2011; Newman et al., 2015). Litter can also impact shipping and fishing activities by damaging vessels and fishing gear (Newman et al., 2015). Health and safety risks exist on polluted beaches, where sanitary and medical waste can be found, along with glass and sharps, additionally reducing beaches' aesthetic value with losses for tourism and expenditures related to potential hospitalisation (Newman et al., 2015).

Over 600 species are known to be affected by marine litter (either macro or microplastic) through ingestion or entanglement (Gall and Thompson, 2015) (Table 1). Ecological effects are mainly seen through the ingestion of synthetic material, such as

plastics (Avery-Gomm et al., 2013; Gall and Thompson, 2015; Kühn et al., 2015; Pierce et al., 2004), which can leach toxins to animals' internal organs (Tanaka et al., 2015), cause intestinal blockage, making them prone to malnutrition and death by starvation (Kühn et al., 2015; Pierce et al., 2004). In addition, many animals can become entangled in debris such as nets and ropes (Bond et al., 2012; Derraik, 2002; Kühn et al., 2015) and lose their ability to search for prey or be severely injured. The *in-situ* effects of microplastics are yet to be discovered, but laboratory experiments have shown a prompt ingestion of these tiny particles by a variety of marine species and the related reduced fitness of these animals after doing so (Besseling et al., 2013; Cole et al., 2013). Public concerns over ecological impacts and potential threats to seafood quality have induced many companies to introduce a voluntary phase out of microbeads in cosmetic products (e.g. Marine Conservation Society, Beat the Microbead).

TABLE 1 - NUMBER OF SPECIES THAT HAVE BEEN AFFECTED BY MARINE LITTER BY ENTANGLEMENT OR INGESTION. SOURCE: (GALL AND THOMPSON, 2015).

Species Group	**Number of known species**	**Number of species with entanglement records**	**Number of species with ingestion records**	**Total number of species with either entanglement or ingestion records**
Marine mammals	115	52 (45%)	30 (26%)	62 (54%)
Fish	16,754	66 (0.39%)	50 (0.30%)	114 (0.68%)
Seabirds	312	79 (25%)	122 (39%)	174 (56%)
Sea turtles	7	7 (100%)	6 (86%)	7 (100%)

1.2. PERSISTENT ORGANIC POLLUTANTS

Persistent organic pollutants (POPs) are generally man-made compounds or a result of anthropogenic activities. Such contaminants are of environmental concern due to their persistent, toxic nature and their ability to bio-accumulate (Jones and de Voogt, 1999), making top predators more vulnerable. The term POP is used to describe a range of different groups of chemicals with diverse properties used in industry and agriculture (Jones and de Voogt, 1999). This study focused on four different groups of POPs: Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and brominated flame retardants (BFRs). PCBs and BFRs are used as coolants and additives in industry products (Brinkman and De Kok, 1981), while OCPs are used in agriculture as insecticides (Espín et al., 2010). PAHs can be naturally occurring (through volcanism or forest fires) or formed as a result of anthropogenic activities such as the incomplete combustion of fossil fuels (Nizzetto et al., 2008).

Persistent organic pollutants have been found to cause nervous and endocrine disruption, which can lead to reproductive deformities and impairment, and to be carcinogenic to humans and wildlife (Furness, 1993; Jones and de Voogt, 1999; Stockholm Convention, 2001). Research has attributed significant population reductions in many bird species in the 1970s to the indiscriminate use of pesticides, such as Dichlorodiphenyltrichloroethane (DDT), known to cause egg-shell thinning (Jones and de Voogt, 1999; Stockholm Convention, 2001). Such realisation led to banning or restriction of most POPs, but due to their persistent nature and the way these substances interact with the environment, they are still ubiquitous in all environmental media (Jones and de Voogt, 1999; Pariatamby and Kee, 2016). POPs have volatile properties and can travel through the atmosphere to the most distant places, only to condense far from their original source (Van Den Brink, 1997). Thus, they are found globally, as far as the poles and in areas that would not generally be regarded as impacted (Mallory and Braune, 2012; Mwangi et al., 2016). Likewise, oceans provide a medium for environmental transportation of POPs along with migratory species and trophic transfer (Mwangi et al., 2016; Pariatamby and Kee, 2016; Roscales et al., 2011; Taniguchi et al., 2016; Walker, 1990).

The Stockholm Convention, adopted in 2001, but only in force since 2004, has banned or imposed restrictions on many POPs (Table 2). Of these substances, 16 are pesticides, 7 are industrial chemicals (2 are both) and 6 are unintentional products.

TABLE 2 - ANNEXES OF THE STOCKHOLM CONFERENCE (2001) LISTS BANNED AND RESTRICTED POPS. SOURCE: (STOCKHOLM CONVENTION, 2001).

Status	Substance
Banned (Annex A)	Aldrin, Chlordane, Chlordecone, Dieldrin, Endrin, Heptachlor, Hexabromobiphenyl, Hexabromocyclododecane (HBCD), Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether), Hexachlorobenzene (HCB), Hexachlorobutadiene, Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane, Lindane, Mirex, Pentachlorobenzene (PeCB), Pentachlorophenol and its salts and esters, Polychlorinated biphenyls (PCB), Polychlorinated naphthalenes, Technical endosulfan and its related isomers, Tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether) and Toxaphene
Restricted use (Annex B)	DDT and Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F)
Unnintentional production – must be reduced until elimination (Annex C)	Hexachlorobenzene (HCB), Pentachlorobenzene (PeCB), Polychlorinated biphenyls (PCB),

	Polychlorinated dibenzo-p-dioxins (PCDD), Polychlorinated dibenzofurans (PCDF) and Polychlorinated naphthalenes

1.3. SEABIRDS IN IRELAND

Ireland, along with Britain, has almost 8 million seabirds from 24 species, and > 40 seabird species have been recorded in Irish waters. Seabird populations of the British Isles represent a significant component of global seabird diversity, including 90% of the world's population of Manx Shearwaters (*Puffinus puffinus*), 68% of Northern Gannets (*Morus bassanus*) and 60% of Great Skuas (*Stercorarius skua*). This compares favourably with other seabird regions: Caribbean (1.3 million breeding seabirds from 22 species), Falkland Islands (> 4 million, 22 species), Barents Sea (13 million, 25 species), New Zealand (20 million, 55 species) and Alaska (20 million, 24 species) (Mitchell et al., 2004) (Table 3).

The North Atlantic population of Northern Fulmars (*Fulmarus glacialis*) is estimated at 10 million birds (Gaston et al., 2006). Per the most recent census in Britain and Ireland (1998-2002), there are over 32,000 breeding pairs of Northern Fulmars in Ireland. The county with the highest count of breeding Fulmars is County Mayo, with about 12,750 breeding pairs (Mitchell et al., 2004). The numbers of breeding pairs are similar to Manx Shearwaters (32,545), Northern Gannets (32,758) and Black-legged Kittiwakes (*Rissa tridactyla* – 36,100). However the most abundant species in Ireland are the Common Guillemots (*Uria aalge*), with around 138,108 breeding pairs, followed by the European Storm Petrel (*Hydrobates pelagicus*) with approximately 99,065 breeding pairs (Mitchell et al., 2004). A new census was carried out during the 2015 & 2016 breeding seasons, but it is yet to be published. Given the interval between the publication of the Seabird 2000 data and the timing of the current study, the author is not presenting these data as definitive population estimates for the purposes of this research.

TABLE 3 - SUMMARY OF BREEDING SEABIRD NUMBERS IN IRELAND 1998-2002 (MOST RECENT CENSUS – (MITCHELL ET AL., 2004)). NUMBERS ARE GIVEN IN BREEDING PAIRS.

Species	Scientific Name	Republic of Ireland	Northern Ireland	All-Ireland Total
Northern Fulmar	*Fulmarus glacialis*	32,918	5,992	38,910
Manx Shearwater	*Puffinus puffinus*	32,545	4,633	37,178
European Storm Petrel	*Hydrobates pelagicus*	99,065	0	99,065
Leach's Storm Petrel	*Oceanodroma leucorhoa*	310	0	310
Northern Gannet	*Morus bassanus*	32,758	0	32,758
Great Cormorant	*Phalacrocorax carbo*	4,548	663	5,211
European Shag	*Phalacrocorax aristotelis*	3,426	301	3,727
Great Skua	*Stercorarius skua*	1	0	1
Mediterranean Gull	*Larus melanocephalus*	3	2	5
Black-headed Gull	*Larus ridibundus*	3,876	10, 107	13,983
Common Gull	*Larus canus*	1,060	557	1,617

Lesser Black-backed Gull	*Larus fuscus*	2,876	1,973	4,849
Herring Gull	*Larus argentatus*	5,521	714	6,235
Great Black-backed Gull	*Larus marinus*	2,243	76	2,319
Black-legged Kittiwake	*Rissa tridactyla*	36,100	13,060	49,160
Sandwich Tern	*Sterna sandvicensis*	1,762	1,954	3,716
Roseate Tern	*Sterna dougallii*	734	4	738
Common Tern	*Sterna hirundo*	2,485	1,704	4,189
Arctic Tern	*Sterna paradisaea*	2,735	767	3,502
Little Tern	*Sterna albifrons*	206	0	206
Common Guillemot	*Uria aalge*	138,108	98,546	236,654
Razorbill	*Alca torda*	27,446	24,084	51,530
Black Guillemot	*Cepphus grylle*	3,367	1,174	4,541
Atlantic Puffin	*Fratercula arctica*	19,641	1,610	21,251

1.4. THREATS AND MONITORING

Mallory (2006) reviews some of the main threats to seabirds:

- Harvest
- Bycatch
- Oil spills
- Ecotourism
- Climate change
- Invasive species
- Particulate garbage
- Contaminants

Harvesting the eggs and meat of seabirds still remains a practice in some regions, especially in the circumpolar regions (Merkel and Barry, 2008). Although many decades ago birds were harvested for survival, nowadays it has become a matter of culture and sport (Zador et al., 2006). Such practices have declined in some regions, but are still significant in others such as Alaska, Canada, Greenland and Russia (Merkel and Barry, 2008; Zador et al., 2006). Harvesting numbers can vary enormously, with countries such as Norway taking up to 5,000 birds a year, while Iceland for instance could harvest 350,000 birds per year (Merkel and Barry, 2008).

Bycatch poses a significant threat to seabirds (Furness, 2003). As they forage in pelagic regions, fishing gear competes for the same habitat. Attracted by abundant and easy prey, the same way fish are, they can become trapped in nets or caught in hooks and drown (Lewison and Crowder, 2003). Pelagic longlines for instance, have been implicated in albatross population declines in the Southern ocean (Weimerskirch et al., 1997). Globally, longline fisheries are estimated to kill on average 160000 seabirds annually (Anderson et al., 2011). Published accounts of impacts of fisheries in Britain and Ireland tend to be by gillnets used to catch Bass (*Dicentrarchus labrax*) (Tasker et al., 2000). Such fisheries take hundreds to thousands of Razorbills (*Alca torda*) and Guillemots (*Uria aalge*) as bycatch (Tasker et al., 2000). Globally, monofilament

gillnets are regarded as the type of fixed fishing gear that kills the most seabirds and mammals as bycatch (Lien et al., 1989).

Oil spills can cause direct mortality of seabirds because the oiling of feathers affects their insulation properties, leaving birds vulnerable to hypothermia. The ingestion of toxic hydrocarbons can also lead to death (Peterson et al., 2003). Additionally, loss of habitat and food contamination are considered indirect effects (Peterson et al., 2003; Velando et al., 2005).

Seabird colonies are often an attractive market for ecotourism. However, appropriate management of such activities is needed as human disturbance can cause destruction of nests and desertion of offspring, consequently affecting reproductive success (Burger and Gochfeld, 1993; Yorio et al., 2001).

Climate change can have various impacts on seabird populations. Temperature changes and extreme weather events can affect marine productivity, shifting prey distribution and availability (Crick, 2004; Grémillet and Boulinier, 2009). Such changes can additionally cause direct habitat loss (Crick, 2004).

Invasive species such as rats contribute to the extinction and endangerment of seabird species through the predation of eggs, chicks and adults. Small burrow nesters are more vulnerable and it is estimated that at least 75 species of seabirds are affected by invasive rats along a chain of 61 islands reviewed (Jones et al., 2008).

The focus of this research was particulate garbage, also known as marine litter and, contaminants, such as persistent organic pollutants. Particulate garbage, or marine litter, has become one of the main visible threats to seabirds. Seabirds at sea mistake litter and especially plastic particles for food (Choy and Drazen, 2013; Lavers and Bond, 2015). Once ingested, particles can perforate the lining of digestive tract, leach toxic chemicals, block or accumulate in the stomach of birds, not providing any nutritional value, sometimes not leaving space for real food, leading to death by starvation (Kühn et al., 2015). Many times, parents regurgitate such particles to their offspring, hampering their development and preventing them from fledging (Carey, 2011). Litter such as ropes and twines can entangle birds at sea or in the nest when used for nest construction and enhancement (Derraik, 2002; Hartwig et al., 2007). Plastic is a growing threat to wildlife as plastic production and consumer/industrial demand is

ongoing (Thompson et al., 2004; Wilcox et al., 2015). A recent study has predicted that by 2050 all species of seabirds will have ingested plastic litter if effective waste management measures are not taken (Wilcox et al., 2015).

Contaminants such as persistent organic pollutants are, or have been, used in industry as stabilizers, flame retardants and additives for many decades (Jones and de Voogt, 1999). Additionally, they have been used as pesticides in agricultural practices (Earley, 1987). Their persistent nature and ability to bio-accumulate in biota are of special concern in the environment (Jaspers et al., 2006). Seabirds are often at the top of the food chain and are at special risk from these pollutants. As the marine environment can be regarded as a sink for such contaminants, fish eating birds could be more vulnerable to the bioccumulative effects of POPs (Walker, 1990). Effects of such substances in biota include endocrine disruption, affecting behavioural and reproductive systems (Gilbertson et al., 1976). Additionally, most POPs have been regarded as carcinogenic (Hays and Risebrough, 1972; Jones and de Voogt, 1999; Stockholm Convention, 2001).

All main threats presented here are derived from anthropogenic activities. Recent environmental legislation aims to mitigate effects and manage anthropogenic activities in such a way that ecosystem services and their sources are protected from depletion.

The Marine Strategy Framework Directive (MSFD) – 2008/56/EC – "aims to achieve Good Environmental Status (GES) of the EU's marine waters by 2020 and to protect the resource base upon which marine-related economic and social activities depend. The Directive enshrines in a legislative framework the ecosystem approach to the management of human activities having an impact on the marine environment, integrating the concepts of environmental protection and sustainable use" (Marine Strategy Framework Directive, 2008).

To achieve this goal, European waters have been divided into four marine regions: the Baltic Sea, the North-east Atlantic Ocean, the Mediterranean Sea and the Black Sea. The North-east Atlantic and the Mediterranean have been further sub-divided into sub-regions (e.g. the Celtic Seas, the Bay of Biscay, etc.). Thus, each member state is responsible for defining GES for their marine waters and for developing a strategy to maintain or achieve GES. These strategies include environmental targets and their associated monitoring programmes and indicators (Art. 8, 9, 10 & 11MSDF – 2008/56/EC) (Marine Strategy Framework Directive, 2008).

1.5. SEABIRDS AS MONITORS

As seabirds are species sensitive to changes in the environment (Burger and Gochfeld, 2004), they have been used as environmental indicators for many decades (Furness & Camphuysen, 1997). They feed at a variety of trophic levels, thus responding to changes in all levels (Mallory, 2006). Seabirds are abundantly distributed globally and are generally philopatric species, meaning that they return to the same place of birth to breed when mature, every season. Ringing of individuals can provide consistent information about individuals within populations every year. Such consistency and the fact that seabirds are long-lived species are important factors when considering long-term monitoring.

1.5.1. OF MARINE LITTER

Reports of seabirds ingesting plastic litter were as early as the 1960s (Harper and Fowler, 1987). But only in the 1970s when neuston samples revealed plastic particles in the Northwest Atlantic (Carpenter and Smith, 1972) that such abundance and the concern that they could become a source of plasticisers and toxic compounds such as PCBs into the food web became real (Ryan, 2015).

Early surveys of plastic abundance in Northern Fulmars (*Fulmarus glacialis*) in the North Atlantic showed differences in regional patterns of plastic ingestion, highlighting the suitability of this species as a monitor for abundance and distribution of plastic litter at sea (Bourne, 1976; Furness, 1985; Ryan, 2015; Van Franeker, 1985;. Van Franeker et al., 2011).

The Northern Fulmar has been used as the North Sea Indicator for marine litter presence in biota as a proxy for floating marine litter. The Fulmar Monitoring Programme began as a project in the Netherlands - Save the North Sea Fulmar, 1982 (Van Franeker et al., 2003) and it has been shaped as an official indicator for OSPAR regarding the amount of litter in the North Sea. OSPAR has set a target to translate the Ecological Quality Objectives (EcoQOs) in the North Sea and that is:

"There should be less than 10% of Northern Fulmars having 0.1 gram or more plastic in the stomach in samples of 50-100 beached Fulmars from each 5 different regions of the North Sea over a period of at least 5 years" (OSPAR Convention, 1992).

The Northern Fulmar is an oceanic species that feeds exclusively at sea and as most seabirds, only comes ashore to breed. Its diet has been reported to be mainly opportunistic, consisting of fish, fishery discards, squid and zooplankton. It never feeds on land and although Fulmars can dive shallow distances, they mainly feed at the surface (Hatch and Nettleship, 1998). The species has been reported to have the highest ingestion of plastics (Gall and Thompson, 2015), possibly because plastics make up to 90% of marine litter (Derraik, 2002), and it is generally positively buoyant (Choy and Drazen, 2013), overlapping with food these birds would be accustomed to eating. Fulmars belong to the Procellariiforme order of seabirds, which comprises Albatrosses, Shearwaters and Petrels. Birds from this order are known to have a narrow passage between the proventriculus and the gizzard, making it hard for them to fully regurgitate indigestible matter. Thus, these birds are known to ingest and accumulate litter in their stomach, being good candidates for monitoring marine litter at sea and a reflection of current environmental condition.

More recent European legislation, the Marine Strategy Framework Directive characterises the environmental status of the ocean using 11 qualitative descriptors (Annex I 2008/56/EC). Marine litter comes under the descriptor 10 and the overarching qualitative descriptor for determining good environmental status is that "*Properties and quantities of marine litter do not cause harm to the coastal and marine environment*" (EU, 2008). For such "target" to be reached a series of criteria have been adopted. These are, including micro particles: beach, water column, water surface, water floor and biota litter. The investigation and monitoring of trends for these criteria are supported by indicators, some of them common to other international agreements, such as OSPAR (beach and biota indicators) (Marine Strategy Framework Directive, 2008).

Ireland has to comply with obligations deriving from its commitment to OSPAR and the requirements of the MSDF. Little information is found on marine litter in the Irish Exclusive Economic Zone (EEZ). Plastic litter was reported in the stomachs of True's beaked whales stranded on Irish beaches (Lusher et al., 2015) and fisheries related litter was reported to be 51% of all litter reported in Irish waters during Bottom Trawl

Surveys between 2010 and 2014 (Moriarty et al., 2016). Until now, no previous research was found on plastic litter in biota, e.g. seabirds or Northern Fulmars.

1.5.2. OF PERSISTENT ORGANIC POLLUTANTS

DDT had an increase in popularity in 1945 as an effective tool in dealing with insect pests that harmed crops all around the world (El-Shahawi et al., 2010). However, years later, this compound and other POPs were associated with the decline of many raptor populations in the U.S. (Gilbertson et al., 1976; Tanabe et al., 1984).

Visible effects on wildlife called for the need to monitor concentrations of POPs in air, soil, water and maternal milk, with effective measures from Environmental Protection Agencies and the establishment of the Stockholm Convention, in 2001 (EPA, 1975; Stockholm Convention, 2001). As birds were visibly affected and are efficient environmental monitors, birds became a subject of research (Bustnes et al., 2008; Jaspers et al., 2011; Jaspers et al., 2006; Van den Steen et al., 2006; Walker, 1990).

More recently, persistent organic pollutants are also described in the Marine Strategy Framework Directive under descriptors 8 (Contaminants) and 9 (Contaminants in Seafood). The quality descriptor for descriptor 8 is that "*Contaminants are at a level not giving rise to pollution effects*". Similarly, for descriptor 9, for reaching good environmental status: "*Contaminants in fish and other seafood for human consumption do not exceed levels established by Community legislation or other relevant standards*" (Marine Strategy Framework Directive, 2008).

As seabirds feed at a variety of trophic levels and feed mainly on fish and other marine organisms, monitoring contaminant concentration in seabirds not only tells us about seabird populations, but also about organisms birds and humans are likely to ingest.

For specific species of seabirds, thresholds, where ill-effects from POPs are evident, have been established (Su et al., 2014). The goal of monitoring is to make sure contaminant concentration is at a level below that threshold, not affecting individual species and their populations. Contaminant information can inform about environmental changes regionally and globally. When sedentary/non-migratory bird species are used to

monitor concentrations, they can account for contamination locally. Migratory species however can give a transboundary account of pollutants.

The Stockholm Convention only entered in force in Ireland in 2010 and it requires a national implementation on POPs. The Irish Environmental Protection Agency (EPA) is the body responsible for implementing the Convention. So far a pre-screening of the National Implementation Plan on POPs has been carried out in order to determine if strategic environmental assessment (SEA) of the plan is required in accordance with relevant SEA legislation (EPA, 2010).

1.6. AIMS AND RATIONALE

The overall aim of this doctoral thesis was to investigate the interactions between seabirds and pollutants in Ireland, in compliance with environmental policies, such as MSFD and OSPAR. Little published information is available concerning plastics and persistent organic pollutants affecting seabirds in Ireland. The first goal was to bridge this gap by setting out baseline levels for pollutants such as plastic litter and POPs, to compare levels in Ireland with international data. Such an accomplishment would then lead us to our next goal, which was to enable Ireland to take part in national and regional pollutant monitoring programmes.

Ireland has sovereign rights over 900,000 km^2 of seabed, which is an area 10 times the size of its land (Hynes et al., 2014). This includes an EEZ (Exclusive Economic Zone) of 488,762 km^2 (MSDF – 2008/56/EC). As an island, Ireland derives obvious cultural, social, economic and environmental benefits from the marine environment. Data from 2010 calculated that the direct economic value of the Irish ocean economy was €1.2 billion, additionally providing employment for approximately 16,300 full time individuals (Hynes et al., 2014).

Ireland is perceived to be one of the most successful cases regarding preventing excessive pollution entering the ocean from land based pressures through the introduction of the plastic bag levy as early as 2002, generating a reduction in use of the order of 90%, and an associated gain in the form of reduced littering (Convery et al., 2007). However, plastic bags are not the only form of litter found on Irish beaches and in Irish waters. A recent study (Lusher et al., 2014) has estimated an average number of

2.46 plastic particles/ m^{-3} in the Northeast Atlantic. Most of this number (89%) has been classified as microplastics (<5mm).

As the Northern Fulmar is an abundant species in the North Atlantic, extending the monitoring of this species across the Irish MSFD region could allow for data comparison among regions, bringing coherence and consistency to the strategy at national and regional level. In parallel with assessing the applicability of Fulmar as a biotic indicator in an Irish context, other potential indicator species were investigated. This strategy is being employed by other parties to the convention who are also investigating the development of different biotic indicators appropriate to their areas of responsibility. If appropriate, the extension of the indicator could also then cover OSPAR regions II (Greater North Sea), III (Celtic Seas) and V (Wider Atlantic - partially). Additionally, it was intended to establish baseline levels of plastic pollution for seabirds breeding in Ireland.

Data for persistent organic pollutants in Ireland is scarce and dates to the 1960-70s (Borlakoglu et al., 1990; Earley, 1987; Knight and Walker, 1982; Koeman et al., 1967; Moore and Tatton, 1965). Such data are limited to certain species, types of contaminants and matrices. To establish baseline values for POPs in Irish birds, we set out to collect persistent organic pollutant data using different matrices in non-destructive and destructive (opportunistic) sampling. This would enable us to test the utility of different sampling techniques while establishing initial POP concentration values for seabird species breeding in Ireland.

As POPs are present in seawater, plastic litter drifting at sea is prone to be contaminated with such pollutants, due to their hydrophobic nature. Additionally, some of these contaminants are added to plastics during production. POPs might then serve as an additional threat to seabirds ingesting plastic litter. The way that monitoring of marine litter and persistent organic pollutants come together is by the collection of stranded birds, in which we were able to examine stomach contents for plastic litter and at the same time, tissues were collected to investigate POP concentrations.

This dissertation encompasses 6 chapters, which includes general introduction and conclusions. The four chapters in the body of the thesis comprise five peer-reviewed papers that have been either published or submitted for review.

Chapter 2: The use of beached bird surveys for marine plastic litter monitoring in Ireland.

To investigate the feasibility of monitoring marine litter through the use of seabirds in Ireland, the author created a project called The Republic of Ireland Beached Bird Survey (RIBBS). RIBBS is a citizen science initiative that relies on the help of volunteers to report and collect beached birds for plastic research. Primary aims:

- Establish baseline levels of plastic pollution affecting multispecies of seabirds breeding in Ireland;
- Investigate the feasibility of utilizing the Northern Fulmar or another species as a marine litter indicator for Ireland, in compliance with EU legislation.

This chapter has been published as a peer reviewed publication:

Acampora, H., Lyashevska, O., Van Franeker, J.A., O'Connor, I. (2016). The use of beached bird surveys for marine plastic litter monitoring in Ireland. Marine Environmental Research: 120 (122-129) dx.doi.org/10.1016/j.marenvres.2016.08.002.

Chapter 3: Passive diet sampling for plastic litter monitoring.

Plastic ingestion by seabirds is primarily measured using dead seabirds. Alternative methods through diet sampling could offer an insight into plastic ingestion in live birds, which offers the opportunity to sample birds for which we have none or low numbers from beached bird surveys. In addition, it may address questions concerning whether dead seabirds are representative of the population. This chapter is divided into two short papers that comprise two different methodologies. Primary aims:

- Establish baseline levels of plastic ingestion reported in live birds breeding in Ireland;
- Test alternative methodologies to plastic litter monitoring: live birds as opposed to dead ones;

- Test opportunistic sampling methodologies such as collection of spontaneous regurgitates and boluses.

Part A: Opportunistic sampling to quantify plastics in the diet of unfledged Black-Legged Kittiwakes (*Rissa tridactyla*), Northern Fulmars (*Fulmarus glacialis*) and Great Cormorants (*Phalacrocorax carbo*).

This chapter has been published as a peer reviewed publication:

Acampora, H., Newton, S., O'Connor, I. (2017). Opportunistic sampling to quantify plastics in the diet of unfledged Black-Legged Kittiwakes (*Rissa tridactyla*), Northern Fulmars (*Fulmarus glacialis*) and Great Cormorants (*Phalacrocorax carbo*). Marine Pollution Bulletin: 119 (171–174). https://doi.org/10.1016/j.marpolbul.2017.04.016

Part B: Presence of plastic litter in pellets from Great Cormorant (*Phalacrocorax carbo*) in Ireland.

This chapter has been published as a peer reviewed publication:

Acampora, H., Berrow, S., Newton, S., O'Connor, I. (2017). Presence of plastic litter in pellets from Great Cormorant (*Phalacrocorax carbo*) in Ireland. Marine Pollution Bulletin: 117.1 (512-514). https://doi.org/10.1016/j.marpolbul.2017.02.015

Chapter 4: Contrasting congener profiles for persistent organic pollutants and PAH monitoring in European Storm Petrels (*Hydrobates pelagicus*) breeding in Ireland: a preen oil vs feathers approach.

Investigation was conducted on a highly pelagic seabird, the European Storm Petrel (*Hydrobates pelagicus*), for which there is very little data on persistent organic pollutants and none in Ireland. Storm Petrels are abundant in Ireland, with over 99 thousand breeding pairs. Primary aims:

- Establish baseline levels for POPs in European Storm Petrels in Ireland, but also to add up to the very scarce data on pollutants for this species throughout;

- Compare two different types of non-destructive methodologies: preen oil and feathers.

This chapter is currently under review in Marine Environmental Research:

Acampora, H., White, P., Lyashevska, O., O'Connor, I. (2017). Contrasting congener profiles for persistent organic pollutants and PAH monitoring in European Storm Petrels (*Hydrobates pelagicus*) breeding in Ireland: a preen oil vs feathers approach. Marine Environmental Research: *In Review*.

Chapter 5: The presence of pollutants in a breeding Common Tern (*Sterna hirundo*) population in Ireland: POPs and Plastics.

This chapter looks at both aspects: plastics and persistent organic pollutants in Common Tern (*Sterna hirundo*) Stomach contents were investigated in dead birds as well as tissue (liver and preen gland) collected for POP analysis. Additionally, live birds (feathers and preen oil) were also sampled for POPs. Primary aims:

- Investigate ingestion of plastics by this species;
- Set baseline levels for POPs in Common Terns;
- Compare destructive versus non-destructive sampling.

This chapter has been published as a peer reviewed publication:

Acampora, H., White, P., Lyashevska, O., O'Connor, I. (2017). The presence of pollutants in breeding Common Tern (*Sterna hirundo*) populations in Ireland: POPs and Plastics. Environmental Science and Pollution Research: 24.14: (13025-13035). https://doi.org/10.1007/s11356-017-8931-7

Chapter 6: Conclusions.

In the concluding chapter, the main findings are summarized and put into context for the Irish environment and international research, with prospects for future research.

1.8. LITERATURE CITED

Anderson, O.R.J., Small, C.J., Croxall, J.P., Dunn, E.K., Sullivan, B.J., Yates, O., Black, A., 2011. Global seabird bycatch in longline fisheries. Endanger. Species Res. 14, 91–106.

Avery-Gomm, S., Provencher, J.F., Morgan, K.H., Bertram, D.F., 2013. Plastic ingestion in marine-associated bird species from the eastern North Pacific. Mar. Pollut. Bull. 72, 257–259. doi:10.1016/j.marpolbul.2013.04.021

Ballance, A., Ryan, P.G., Turpie, J.K., 2000. How much is a clean beach worth? The impact of litter on beach users in the Cape Peninsula, South Africa. S. Afr. J. Sci. 96, 210–213.

Besseling, E., Wegner, A., Foekema, E.M., van den Heuvel-Greve, M.J., Koelmans, A.A., 2013. Effects of Microplastic on Fitness and PCB Bioaccumulation by the Lugworm Arenicola marina (L.). Environ. Sci. Technol. 47, 593–600. doi:10.1021/es302763x

Bond, A.L., Montevecchi, W.A., Guse, N., Regular, P.M., Garthe, S., Rail, J.F., 2012. Prevalence and composition of fishing gear debris in the nests of northern gannets (Morus bassanus) are related to fishing effort. Mar. Pollut. Bull. 64, 907–911. doi:10.1016/j.marpolbul.2012.03.011

Borlakoglu, J., Wilkins, J., Walker, C., Dils, R., 1990. Polychlorinated Biphenyls (PCBs) In Fish-Eating Sea Birds: Molecular Features of PCB Isomers and Congeners in Adipose Tissue of Male and Female Razorbills (Alca torda) of British and Irish Coastal Waters. Comp. Biochem. Physiol. C-Pharmacology Toxicol. Endocrinol. 97, 151–160.

Bourne, W.R.P., 1976. Seabirds and pollution. Mar. Pollut. 6.

Brinkman, U.A.T., De Kok, A., 1981. Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins And Related Products, Production, Properties And Usage. Chem. Informationsd. 12.

Burger, J., Gochfeld, M., 2004. Marine Birds as Sentinels of Environmental Pollution. Ecohealth 1, 263–274. doi:10.1007/s10393-004-0096-4

Burger, J., Gochfeld, M., 1993. Tourism and short-term behavioural responses of nesting masked, red-footed, and blue-footed, boobies in the Galapagos. Environ. Conserv. 20, 255–259.

Bustnes, J.O., Fauchald, P., Tveraa, T., Helberg, M., Skaare, J.U., 2008. The potential impact of environmental variation on the concentrations and ecological effects of pollutants in a marine avian top predator. Environ. Int. 34, 193–201.

Carey, M.J., 2011. Intergenerational transfer of plastic debris by Short-tailed Shearwaters (Ardenna tenuirostris). Emu 111, 229–234. doi:10.1071/MU10085

Carpenter, E.J., Smith, K.L., 1972. Plastics on the Sargasso Sea surface. Science (80-.). 175, 1240–1241.

Choy, C.A., Drazen, J.C., 2013. Plastic for dinner? Observations of frequent debris ingestion by pelagic predatory fishes from the central North Pacific. Mar. Ecol. Prog. Ser. 485, 155–163. doi:10.3354/meps10342

Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., Galloway, T.S., 2013. Microplastic Ingestion by Zooplankton. Environ. Sci. Technol. 47, 6646–6655. doi:10.1021/es400663f

Convention, O., 1992. on the Assessment of the Quality of the Marine Environment. OSPAR Conv. 1.

Convery, F., McDonnell, S., Ferreira, S., 2007. The most popular tax in Europe? Lessons from the Irish plastic bags levy. Environ. Resour. Econ. 38, 1–11. doi:10.1007/s10640-006-9059-2

Crick, H.Q.P., 2004. The impact of climate change on birds. Ibis (Lond. 1859). 146, 48–56.

Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: A review. Mar. Pollut. Bull. 44, 842–852. doi:10.1016/S0025-326X(02)00220-5

Earley, J.J., 1987. Pesticides and PCBs in seabirds and coastal pollution. Biol. Indic. Pollut. 193, 200.

El-Shahawi, M.S., Hamza, A., Bashammakh, A.S., Al-Saggaf, W.T., 2010. An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants. Talanta 80, 1587–1597.

EPA, 2010. Irish Environmental Protection Agency [WWW Document]. URL http://www.epa.ie (accessed 1.13.17).

EPA, U., 1975. DDT Regulatory History: A Brief Survey (to 1975) 1–6.

Espín, S., Martínez-López, E., María-Mojica, P., García-Fernández, A.J., 2010. Development of an analytical method for extracting organochlorine pesticides from feathers., in: Anales de Veterinaria de Murcia. Facultad de Veterinaria, Universidad de Murcia, pp. 77–90.

Furness, RW; Camphuysen, C., 1997. Seabirds as monitors of the marine environment. ICES J. Mar. Sci. 54, 726–737.

Furness, R.W., 2003. Impacts of fisheries on seabird communities. Sci. Mar. 67, 33–45.

Furness, R.W., 1993. Birds as monitors of pollutants, in: Furness, R.W., Greenwood, J.J.D. (Eds.), Birds as Monitors of Environmental Change. Springer Netherlands, Dordrecht, pp. 86–143. doi:10.1007/978-94-015-1322-7_3

Furness, R.W., 1985. Plastic particle pollution: accumulation by Procellariiform seabirds at Scottish colonies. Mar. Pollut. Bull. 16, 103–106.

Gall, S.C., Thompson, R.C., 2015. The impact of debris on marine life. Mar. Pollut. Bull. doi:10.1016/j.marpolbul.2014.12.041

Gaston, A.J., Mallory, M.L., Gilchrist, H.G., O'Donovan, K., 2006. Status, trends and attendance patterns of the northern fulmar Fulmarus glacialis in Nunavut, Canada. Arctic 59, 165–178.

Gilbertson, M.M.R.D., Morris, R.D., Hunter, R.A., 1976. Abnormal chicks and PCB residue levels in eggs of colonial birds on the Lower Great Lakes (1971-73). Auk 93, 434–442.

Grémillet, D., Boulinier, T., 2009. Spatial ecology and conservation of seabirds facing global climate change: a review. Mar. Ecol. Prog. Ser. 391, 121–137.

Harper, P.C., Fowler, J.A., 1987. Plastic pellets in New Zealand storm-killed prions (Pachyptila spp.).

Hartwig, E., Clemens, T., Heckroth, M., 2007. Plastic debris as nesting material in a Kittiwake- (Rissa tridactyla) - colony at the Jammerbugt , Northwest Denmark 54, 595–597. doi:10.1016/j.marpolbul.2007.01.027

Hatch, S.A., Nettleship, D.N., 1998. Northern Fulmar(Fulmarus glacialis). Birds North Am. 32.

Hays, H., Risebrough, R.W., 1972. Pollutant concentrations in abnormal young terns from Long Island Sound. Auk 89, 19–35.

Hynes, S., Norton, D., Corless, R., 2014. Investigating societal attitudes towards the marine environment of Ireland. Mar. Policy 47, 57–65. doi:10.1016/j.marpol.2014.02.002

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science (80-.). 347.

Jaspers, V.L.B., Oorspoels, S., Covaci, A., Eens, M., 2006. Can predatory bird feathers be used as a non-destructive biomonitoring tool of organic pollutants? Biol. Lett. 2, 283–5. doi:10.1098/rsbl.2006.0450

Jaspers, V.L.B., Rodriguez, F.S., Boertmann, D., Sonne, C., Dietz, R., Rasmussen, L.M., Eens, M., Covaci, A., 2011. Body feathers as a potential new biomonitoring tool in raptors: a study on organohalogenated contaminants in different feather types and preen oil of West Greenland white-tailed eagles (Haliaeetus albicilla). Environ. Int. 37, 1349–1356.

Jones, H.P., Tershy, B.R., Zavaleta, E.S., Croll, D.A., Keitt, B.S., Finkelstein, M.E., Howald, G.R., 2008. Severity of the effects of invasive rats on seabirds: a global review. Conserv. Biol. 22, 16–26.

Jones, K., de Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. Environ. Pollut. 100, 209–221. doi:10.1016/S0269-7491(99)00098-6

Jones, K.C., de Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. Environ. Pollut. 100, 209–221. doi:http://dx.doi.org/10.1016/S0269-7491(99)00098-6

Knight, G.C., Walker, C.H., 1982. A study of the hepatic microsomal monooxygenase of sea birds and its relationship to organochlorine pollutants. Comp. Biochem. Physiol. Part C Comp. Pharmacol. 73, 211–221.

Koeman, J.H., Oskamp, A.A.G., Veen, J., Brouwer, E., Rooth, J., Zwart, P., vd Broek, E., Van Genderen, H., 1967. Insecticides as a factor in the mortality of the sandwich tern (Sterna sandvicensis). Meded. Rijksfac. Landbouwwet. Gent 32, 841.

Kühn, S., Bravo Rebolledo, E.L., Franeker, J.A., 2015. Marine Anthropogenic Litter, in: Bergmann, M., Gutow, L., Klages, M. (Eds.), . Springer International Publishing, Cham, pp. 75–116. doi:10.1007/978-3-319-16510-3_4

Lavers, J.L., Bond, A.L., 2015. Selectivity of flesh-footed shearwaters for plastic colour: Evidence for differential provisioning in adults and fledglings. Mar. Environ. Res. 113, 1–6. doi:10.1016/j.marenvres.2015.10.011

Lewison, R.L., Crowder, L.B., 2003. Estimating fishery bycatch and effects on a vulnerable seabird population. Ecol. Appl. 13, 743–753.

Lien, J., Stenson, G.B., Hsun Ni, I., 1989. A review of incidental entrapment of seabirds, seals and whales in inshore fishing gear in Newfoundland and Labrador: A problem for fishermen and fishing gear designers.

Lusher, A.L., Burke, A., O'Connor, I., Officer, R., 2014. Microplastic pollution in the Northeast Atlantic Ocean: Validated and opportunistic sampling. Mar. Pollut. Bull. 88, 325–333. doi:10.1016/j.marpolbul.2014.08.023

Lusher, A.L., Hernandez-Milian, G., O'Brien, J., Berrow, S., O'Connor, I., Officer, R., 2015. Microplastic and macroplastic ingestion by a deep diving, oceanic cetacean: The True's beaked whale Mesoplodon mirus. Environ. Pollut. 199, 185–191. doi:10.1016/j.envpol.2015.01.023

Mallory, M.L., 2006. The Northern Fulmar (Fulmarus glacialis) in Arctic Canada: ecology, threats, and what it tells us about marine environmental conditions. Environ. Rev. 14, 187–216. doi:10.1139/a06-003

Mallory, M.L., Braune, B.M., 2012. Tracking contaminants in seabirds of Arctic Canada: temporal and spatial insights. Mar. Pollut. Bull. 64, 1475–1484.

Marine Strategy Framework Directive, 2008. Marine Strategy Framework Directive (2008/56/EC). Regulation 164/19-164/40.

McIlgorm, A., Campbell, H.F., Rule, M.J., 2011. The economic cost and control of marine debris damage in the Asia-Pacific region. Ocean Coast. Manag. 54, 643–651. doi:10.1016/j.ocecoaman.2011.05.007

Merkel, F.R., Barry, T., 2008. Seabird harvest in the arctic. CAFF Tech. Rep. 1–77.

Mitchell, P.I., Newton, S.F., Ratcliffe, N., Eds, T.E.D., Dunn, T.E., Poyser, a D., May, L., 2004. Seabird populations of Britain and Ireland: Results of the Seabird 2000 census. JNCC, Poyser, London.

Moore, N.W., Tatton, J., 1965. Organochlorine insecticide residues in the eggs of sea birds.

Moriarty, M., Pedreschi, D., Stokes, D., Dransfeld, L., Reid, D.G., 2016. Spatial and temporal analysis of litter in the Celtic Sea from Groundfish Survey data: Lessons for monitoring. Mar. Pollut. Bull. doi:10.1016/j.marpolbul.2015.12.019

Mwangi, J.K., Lee, W.-J., Wang, L.-C., Sung, P.-J., Fang, L.-S., Lee, Y.-Y., Chang-Chien, G.-P., 2016. Persistent organic pollutants in the Antarctic coastal environment and their bioaccumulation in penguins. Environ. Pollut. 1–11. doi:10.1016/j.envpol.2016.07.001

Newman, S., Watkins, E., Farmer, A., Brink, P. ten, Schweitzer, J.-P., 2015. The Economics of Marine Litter, in: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Springer International Publishing, Cham, pp. 367–394. doi:10.1007/978-3-319-16510-3_14

Nizzetto, L., Lohmann, R., Gioia, R., Jahnke, A., Temme, C., Dachs, J., Herckes, P., Guardo, A. Di, Jones, K.C., 2008. PAHs in air and seawater along a North–South

Atlantic transect: trends, processes and possible sources. Environ. Sci. Technol. 42, 1580–1585.

OSPAR, 2010. The Ospar system of Ecological Quality Objectives for the North sea 16.

Pariatamby, A., Kee, Y.L., 2016. Persistent Organic Pollutants Management and Remediation. Procedia Environ. Sci. 31, 842–848. doi:10.1016/j.proenv.2016.02.093

Peterson, C.H., Rice, S.D., Short, J.W., Esler, D., Bodkin, J.L., Ballachey, B.E., Irons, D.B., 2003. Long-term ecosystem response to the Exxon Valdez oil spill. Science (80-.). 302, 2082–2086.

Pierce, K.E., Harris, R.J., Larned, L.S., Pokras, M.A., 2004. Obstruction and starvation associated with plastic ingestion in a Northern Gannet Morus bassanus and a Greater Shearwater Puffinus gravis. Mar. Ornithol. 32, 187–189.

Roscales, J.L., Gonzalez-Solis, J., Calabuig, P., Jimenez, B., 2011. Interspecies and spatial trends in polycyclic aromatic hydrocarbons (PAHs) in Atlantic and Mediterranean pelagic seabirds. Environ. Pollut. 159, 2899–2905. doi:10.1016/j.envpol.2011.04.034

Ryan, P.G., 2015. A brief history of marine litter research, in: Marine Anthropogenic Litter. Springer, pp. 1–25.

Stockholm Convention, 2001, 2001. Stockholm Convention on Persistent Organic Pollutants. p. http://chm.pops.int/.

Su, H., Wu, F., Zhang, R., Zhao, X., Mu, Y., Feng, C., Giesy, J.P., 2014. Toxicity reference values for protecting aquatic birds in China from the effects of polychlorinated biphenyls, in: Reviews of Environmental Contamination and Toxicology Volume. Springer, pp. 59–82.

Tanabe, S., Tanaka, H., Tatsukawa, R., 1984. Polychlorobiphenyls, $Σ$DDT, and hexachlorocyclohexane isomers in the western North Pacific ecosystem. Arch. Environ. Contam. Toxicol. 13, 731–738. doi:10.1007/BF01055937

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., Watanuki, Y., 2015. Facilitated leaching of additive-derived PBDEs from plastic by seabirds' stomach

oil and accumulation in tissues. Environ. Sci. Technol. 150901174241000. doi:10.1021/acs.est.5b01376

Taniguchi, S., Colabuono, F.I., Dias, P.S., Oliveira, R., Fisner, M., Turra, A., Izar, G.M., Abessa, D.M.S., Saha, M., Hosoda, J., Yamashita, R., Takada, H., Lourenço, R.A., Magalhães, C.A., Bícego, M.C., Montone, R.C., 2016. Spatial variability in persistent organic pollutants and polycyclic aromatic hydrocarbons found in beach-stranded pellets along the coast of the state of São Paulo, southeastern Brazil. Mar. Pollut. Bull. doi:10.1016/j.marpolbul.2016.03.024

Tasker, M.L., Camphuysen, C.J., Cooper, J., Garthe, S., Montevecchi, W.A., Blaber, S.J.M., 2000. The impacts of fishing on marine birds. ICES J. Mar. Sci. J. du Cons. 57, 531–547.

Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., Russell, A.E., 2004. Lost at sea: where is all the plastic? Science (80-.). 304, 838.

Van Den Brink, N.W., 1997. Directed transport of volatile organochlorine pollutants to polar regions: The effect of the contamination pattern of Antarctic seabirds. Sci. Total Environ. 198, 43–50. doi:10.1016/S0048-9697(97)05440-5

Van den Steen, E., Dauwe, T., Covaci, A., Jaspers, V.L.B., Pinxten, R., Eens, M., 2006. Within-and among-clutch variation of organohalogenated contaminants in eggs of great tits (Parus major). Environ. Pollut. 144, 355–359.

Van Franeker, J.A., 1985. Plastic ingestion in the North Atlantic fulmar. Mar. Pollut. Bull. 16, 367–369.

Van Franeker, J.A., Meijboom, A., de Jong, M.L., 2003. Marine litter monitoring by Northern Fulmars in the Netherlands 1982-2003. Wageningen, Alterra, Alterra-rapport 1093.

Van Franeker, J. a., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., Hansen, P.L., Heubeck, M., Jensen, J.K., Le Guillou, G., Olsen, B., Olsen, K.O., Pedersen, J., Stienen, E.W.M., Turner, D.M., 2011. Monitoring plastic ingestion by the northern fulmar Fulmarus glacialis in the North Sea. Environ. Pollut. 159, 2609–2615. doi:10.1016/j.envpol.2011.06.008

Velando, A., Munilla, I., Leyenda, P.M., 2005. Short-term indirect effects of the "Prestige"oil spill on European shags: changes in availability of prey. Mar. Ecol. Prog. Ser. 302, 263–274.

Walker, C.H., 1990. Persistent pollutants in fish-eating sea birds - bioaccumulation, metabolism and effects. Aquat. Toxicol. 17, 293–324. doi:10.1016/0166-445X(90)90014-G

Weimerskirch, H., Brothers, N., Jouventin, P., 1997. Population dynamics of wandering albatross Diomedea exulans and Amsterdam albatross D. amsterdamensis in the Indian Ocean and their relationships with long-line fisheries: conservation implications. Biol. Conserv. 79, 257–270.

Wilcox, C., Van Sebille, E., Hardesty, B.D., 2015. Threat of plastic pollution to seabirds is global, pervasive, and increasing. Proc. Natl. Acad. Sci. 201502108. doi:10.1073/pnas.1502108112

Yorio, P., Frere, E., Gandini, P., Schiavini, A., 2001. Tourism and recreation at seabird breeding sites in Patagonia, Argentina: current concerns and future prospects. Bird Conserv. Int. 11, 231–245.

Zador, S.G., Piatt, J.F., Punt, A.E., 2006. Balancing predation and egg harvest in a colonial seabird: A simulation model. Ecol. Modell. 195, 318–326.

CHAPTER 2:

THE USE OF BEACHED BIRD SURVEYS FOR MARINE PLASTIC MONITORING IN IRELAND

"We are accustomed to look for the gross and immediate effects and to ignore all else. Unless this appears promptly and in such obvious form that it cannot be ignored, we deny the existence of hazard. Even research men suffer from the handicap of inadequate methods of detecting the beginnings of injury. The lack of sufficiently delicate methods to detect injury before symptoms appear is one of the great unsolved problems in medicine."

Rachel Carson

This chapter is a verbatim reproduction from the following published paper, which can be found on Appendix 1:

Acampora, H., Lyashevska, O., Van Franeker, J.A., O'Connor, I. (2016). The use of beached bird surveys for marine plastic litter monitoring in Ireland. Marine Environmental Research: 120 (122-129). http://dx.doi.org/10.1016/j.marenvres.2016.08.002.

2.1. ABSTRACT

Marine plastic litter has become a major threat to wildlife. Marine animals are highly susceptible to entanglement and ingestion of debris at sea. Governments all around the world are being urged to monitor litter sources and inputs, and to mitigate the impacts of marine litter, which is primarily composed of plastics. European policies, such as Oslo-Paris Convention (OSPAR) and Marine Strategy Framework Directive (MSFD) have adopted the monitoring of a seabird species, the Northern Fulmar (*Fulmarus glacialis*), as an environmental quality indicator through the analysis of stomach contents of beached Fulmar specimens. The aims of this research were to: firstly set a baseline investigation of multispecies of seabirds in Ireland affected by the ingestion of litter and, secondly to investigate the feasibility of using Fulmar and/or other potential species of seabird as an indicator for marine debris in Ireland through beached bird surveys. Within 30 months, 121 birds comprising 16 different species were collected and examined for the presence of litter. Of these, 27.3% (n=33) comprising 12 different species were found to ingest litter, mainly plastics. The average mass of ingested litter was 0.141g. Among 14 sampled Northern Fulmars, 13 (93%) had ingested plastic litter, all of them over the 0.1g threshold used in OSPAR and MSFD policy target definitions. Results show that seabirds in Ireland are ingesting marine litter, as in many other countries in the world. Monitoring seabird litter ingestion has the potential to form part of a wider marine litter monitoring programme that can help to inform mitigation and management measures for marine litter.

2.2. INTRODUCTION

Marine litter has become a global concern. It has been estimated that at least 8 million tonnes of plastics enter the oceans every year (Jambeck et al., 2015) and plastics comprise >90% of marine litter (Galgani et al., 2015). Gall et al. (2015) list 693 marine species directly affected by marine litter through documented ingestion or entanglement.

The Northern Fulmar (*Fulmarus glacialis*), due to its abundance in the North Atlantic, extensive distribution, oceanic niche and its inclination to ingest marine litter, has been chosen as an indicator species for European policy compliance, such as the Oslo-Paris Convention (OSPAR) and the Marine Strategy and Framework Directive (MSFD). The use of this species to monitor marine litter originated in the Netherlands (Van Franeker & Meijboom, 2002) and, due to its efficacy, it has been incorporated into policy and expanded to other countries, where appropriate (Van Franeker & SNS Fulmar Study Group, 2013; Van Franeker et al., 2011). OSPAR has set a target for an acceptable amount of litter (EcoQO – Ecological Quality Objective) at 0.1g of plastic in no more than 10% of Fulmars found in samples from between 50 - 100 birds over a period of at least 5 years (OSPAR, 2010). The selection of a certain species as an indicator allows for analysis of trends and data comparison with other parts of the world if methodology is standardized. However, a multispecies approach may facilitate investigation of factors driving certain species to ingest plastic litter or account for variation in composition, amounts and trends among different species. Such an approach may also be useful in determining alternative species for use in a monitoring programme.

A recent study (Lusher et al., 2014) estimated an average number of 2.46 plastic particles m^{-3} in the Northeast Atlantic; however most of particles identified (89%) were classified as microplastics (<5mm) and 96% of items were thin, dust like fibers. Plastic litter was also reported in the stomachs of True's beaked whales stranded on Irish beaches (Lusher et al., 2015). Fisheries related litter was reported to be 51% of all litter reported in Irish waters during Bottom Trawl Surveys between 2010-2014 (Moriarty et al., 2016). While there is little information on abundance and distribution of marine litter in Ireland there is no published information concerning marine litter and seabirds in Irish waters.

Ireland, along with Great Britain, is home to almost 8 million breeding seabirds, comprising 25 different species, including 90% of the world's Manx Shearwaters (*Puffinus puffinus*), 68% of Northern Gannets (*Morus bassanus*), and 60% of Great Skuas (*Stercorarius skua*). About 34,000 pairs of Northern Fulmars breed in Ireland (Mitchell et al., 2004). Seabirds provide robust environmental monitoring information because they are long-lived, philopatric species and top predators that feed on a variety of levels of the food chain (Furness & Camphuysen, 1997). In order to investigate the feasibility of implementing a marine litter programme that could contribute to reporting for OSPAR and MSFD the work described here intended to: (1) provide a baseline assessment of the prevalence of marine litter affecting multi-species populations of seabirds in Ireland and to discuss the implications of said data; (2) investigate the implementation of the EcoQO for marine litter monitoring in Ireland.

2.3. MATERIALS AND METHODS

2.3.1. SAMPLING

The Republic of Ireland Beached Bird Survey (RIBBS) was a project created in January 2014 to collect dead seabirds along the shore and use them in an attempt to describe the ingestion of marine litter by seabird species in Ireland. Sampling for the current analysis continued to April 2016 and thus covers just over two years of effort. Two Fulmars collected during a preliminary survey in 2012 have been added to the results. Volunteers walked their selected beaches regularly and collected or reported the presence of dead seabirds of any species for subsequent return to the co-ordinator (Figure 1). Birds were kept frozen (-20□C) at the Marine & Freshwater Research Centre at the Galway-Mayo Institute of Technology, in Galway, until dissection.

FIGURE 1 - BEACHED NORTHERN FULMAR (*FULMARUS GLACIALIS*) AT CONNEMARA, CO. GALWAY, 2014 COLLECTED DURING A BEACHED BIRD SURVEY.

2.3.2. DISSECTIONS

Dissections were performed following the methodology of Van Franeker (2004) to allow for data comparability. Birds were scored for general condition index (0-9) according to the sum of subcutaneous fat, breast muscle and intestinal fat scores. Each organ was also scored for health condition. Age (juvenile, immature and adult) and sex were determined according to plumage and the maturity of sexual organs.

After dissection, stomach contents were washed and sieved through a 1mm mesh following methods in Van Franeker et al. (2011). All solids were retained and air-dried overnight (Figure 2). Contents were then examined under a Stereo microscope (MicrosAustria, 0.6x - 5x) and separated into categories according to Van Franeker et al. (2011). Litter items were divided into sub-categories (within plastic and non-plastic litter). As the focus of this study is plastic litter, plastic items only were weighed per sub-category to the nearest 0.0001g.

FIGURE 2 - STOMACH CONTENTS OF BEACHED NORTHERN FULMAR PORTRAYED IN FIGURE 1. FOAM AND HARD PLASTIC FRAGMENTS ARE THE MAIN COMPONENTS OF SAMPLE.

2.3.3. STATISTICAL ANALYSIS

Multi-species modelling was performed using R Core Team (2015) (package: lme4 version 1.1-12; (Bates and Mächler, 2016)); through a two-step approach (Duan et al., 1984; Min & Agresti, 2002), in which we assume that the data are generated by two underlying processes. The first process is modelled by a Bernoulli model which determines presence/absence ('prevalence') of litter in birds' stomachs. Conditionally on the positive outcome, the second process is modelled by a Gamma model and determines the amount of litter. This two-step approach is needed because the data are zero inflated (73% of the data is composed of zeroes). For both steps a Generalized Linear Mixed Model (GLMM) was used. GLMM is an extension of Generalized Linear Models (GLM), which includes both fixed and random effects (hence mixed models) in a linear predictor, via maximum likelihood.

On the first step, the data was analysed for presence/absence ('prevalence') of plastic litter in birds' stomachs. A linear predictor for 'Litter Presence' is the combination of the fixed and random effects. 'Family' was included as a random effect allowing for random intercept for each family. This is because birds within families are expected to correlate, whereas birds between families do not. All other variables were included as a fixed effect. This first step was modelled with a logit link function for having zero (no plastics) or positive values (plastics present), and included all variables assumed to influence the presence/absence of plastic litter. The fixed explanatory variables were: 'Sex', 'Age' and 'Feeding Source'. The model specification was: Litter. Presence ~ (1|Family) + Sex + Age + Feeding Source. This model included 104 observations as 17 were deleted due to missing values in one or more of the explanatory variables (usually sex or age, as it was not possible to determine these for every individual). Coefficients for 'Age' were very similar to each other as well as their standard errors. This suggests that age group was not of importance to litter presence. To test whether age was useful as a variable, it was then omitted from the model, refit and then compared to the original model according to the change in AIC. The same way, the model was tested by removing 'Family' as a random effect. The model fit was assessed using AIC values.

On the second step, conditionally on the positive outcome of the first step, the amount of plastic litter was modelled using log link function. This step modelled positive values (plastics present), by evaluating plastic litter mass as a function of the same variables as in the first step of the model. Again, 'Family' was taken as a random effect to account for statistical independence of such variable. The model specification was: Litter.Mass ~ (1|Family) + Sex + Age + Feeding Source. Due to aforementioned absence of explanatory data for 9 observations, this analysis was performed with 24 (positive) observations. Additionally, the second step of the model was applied on only the variable ("Family") found to be significant in the previous model to verify for any variation within the family itself and any additional influence by relevant variables. The model specification was: Litter.Mass ~ Species + Sex + Age. Significance level was set at <0.05.

Birds were aggregated into families due to the small sample size for some of the individual species. The variable "Feeding Source" was a factor with 3 levels and it included the species listed in Table 4 with the corresponding sources. The 'Marine' feeding source, included species known to feed mainly offshore; 'Mixed' included

species that have a mixed diet that consists of items found in coastal and terrestrial environments (including landfills); and lastly, 'Klepto' included species that are known for kleptoparasitism (Ashmole, 1971).

TABLE 4 - FEEDING SOURCE AGGREGATION AS WELL AS FAMILY GROUPING ARE DESCRIBED BY SPECIES' SCIENTIFIC AND COMMON NAMES. DUE TO THE SMALL SAMPLE SIZE FOR SOME SPECIES, THESE WERE GROUPED INTO FAMILIES TO MAKE STATISTICAL ANALYSIS POSSIBLE. DEFINITIONS ARE PROVIDED IN 'MATERIAL AND METHODS' SECTION.

Species (Common Name)	Scientific Name	Feeding Source	Family Grouping
Black Guillemot	*Cepphus grylle*		Alcidae
Black-legged Kittiwake	*Rissa tridactyla*		Laridae
Common Guillemot	*Uria aalge*		Alcidae
European Shag	*Phalacrocorax aristotelis*		Phalacrocoracidae
Manx Shearwater	*Puffinus puffinus*		Procellariidae
Northern Fulmar	*Fulmarus glacialis*	Marine	Procellariidae
Northern Gannet	*Morus bassanus*		Sulidae
Razorbill	*Alca torda*		Alcidae
Sabine's Gull	*Xema sabini*		Laridae
Atlantic Puffin	*Fratercula arctica*		Alcidae
Black-headed Gull	*Chroicocephalus ridibundus*		Laridae
Herring Gull	*Larus argentatus*	Mixed	Laridae
Iceland Gull	*Larus glaucoides*		Laridae
Arctic Skua	*Stercorarius parasiticus*		Stercorariidae
Great Black-backed Gull	*Larus marinus*	Klepto	Laridae
Lesser Black-backed Gull	*Larus fuscus*		Laridae

As birds with no litter (zeroes) represent actual outcomes of the data, they have to be incorporated in the averaged results. Thus averages for number and mass of plastics in

stomachs are given as 'population averages', in which all zero values are included with data variability given as standard error (±se) (Van Franeker et al., 2011).

2.4. RESULTS

For the present study, 121 seabirds were analysed, comprising 16 different species described in Table 5. Specimens were collected in the following years: 2012 (2 – archived samples), 2014 (36), 2015 (62) and 2016 (21) in 12 different counties and four coastal islands (Figure 3), in Ireland. Of the 121 birds collected, 33 individuals (27.3%) had ingested plastic litter. This represented 12 (75%) of the 16 species collected. The species specific prevalence and abundance by number and mass of ingested plastic litter is listed per species in Table 6.

TABLE 5 - SAMPLE DESCRIPTION (SEX AND AGE NOT ALWAYS KNOWN); ORDERED BY SAMPLE SIZE.

Species' Common Name	**Sample Size (n)**	**Sex Male/Female**	**Age Juvenile/Immature/Adult**
Common Guillemot	25	13/12	5/10/9
Northern Gannet	15	4/6	2/0/9
Razorbill	15	7/7	1/8/5
Northern Fulmar	14	3/7	3/2/5
Herring Gull	13	5/6	6/4/2
European Shag	10	6/4	1/7/2
Black-headed Gull	9	3/5	1/4/3
Great Black-Backed Gull	4	2/1	0/2/1
Black-legged Kittiwake	4	0/4	2/1/1
Manx Shearwater	3	2/1	0/1/2
Atlantic Puffin	3	3/0	1/2/0
Lesser Black-backed Gull	2	1/0	0/1/1

Arctic Skua	1	1/0	1/0/0
Black Guillemot	1	1/0	1/0/0
Iceland Gull	1	0/1	0/1/0
Sabine's Gull	1	0/1	1/0/0

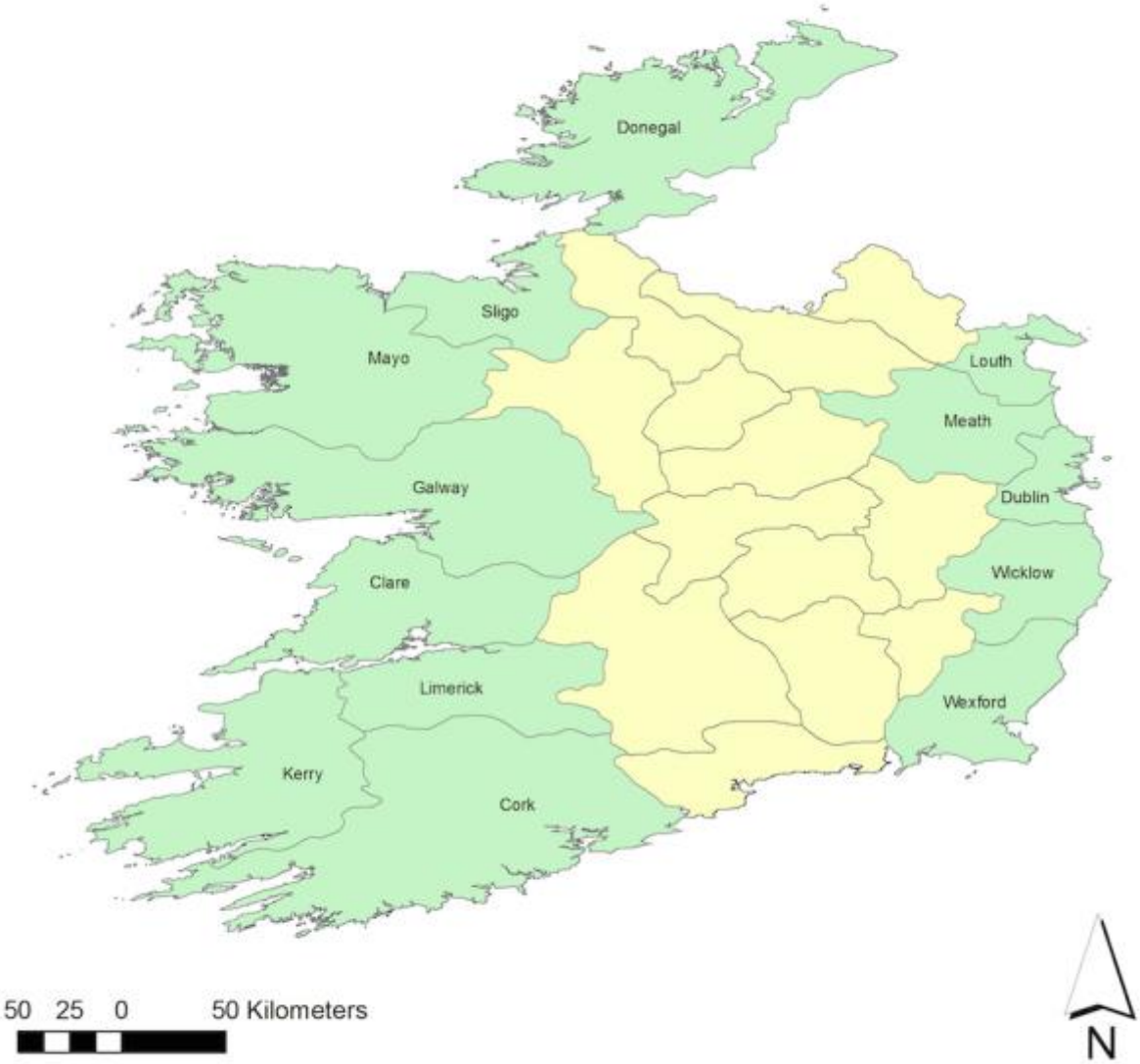


FIGURE 3 - COUNTIES IN GREEN COLOUR DENOTE SAMPLED SITES, ALONG WITH COASTAL ISLANDS OFF COUNTIES DONEGAL, DUBLIN AND KERRY. SITES ON THE WEST ARE ON THE ATLANTIC COAST, WHILST SITES ON THE EAST COAST ARE SURROUNDED BY THE IRISH SEA.

TABLE 6 - PLASTIC LITTER ABUNDANCE PER SPECIES (ORDERED BY SAMPLE SIZE; POPULATION AVERAGES ARE PROVIDED AND INCLUDED ZERO VALUES).

Species	**Sample (n)**	**Prevalence (%)**	**Average Number of Particles n ± se**	**Average Mass g ± se**
Common Guillemot	25	12 %	0.12 ± 0.06	0.0001 ± 0.0001
Northern Gannet	15	27 %	0.46 ± 0.23	0.0225 ± 0.0175
Razorbill	15	0 %	0	0
Northern Fulmar	14	93 %	65.35 ± 32.67	1.1147 ± 0.5681
Herring Gull	13	32 %	1.3 ± 1.22	0.0011 ± 1.1147
European Shag	10	10 %	0.2 ± 0.2	0.0001 ± 0.0001
Black-headed Gull	9	22 %	1.33 ± 0.94	0.0063 ± 0.0054
Black-legged Kittiwake	4	50 %	2 ± 1.41	0.0069 ± 0.0066
Great Black-backed Gull	4	25 %	9 ± 9	0.0200 ± 0.02
Manx Shearwater	3	33 %	0.33 ± 0.33	0.0004 ± 0.0004
Atlantic Puffin	3	33 %	1.33 ± 1.33	0.0077 ± 0.0077
Lesser Black-backed Gull	2	100 %	1 ± 0	0.4324 ± 0.2786
Parasitic Jaeger	1	100 %	30	0.0460
Sabines Gull	1	0 %	0	0
Black Guillemot	1	0 %	0	0
Iceland Gull	1	0 %	0	0

Plastic ingestion was most prevalent in Northern Fulmars. Among the 14 Fulmar stomachs sampled, there was a 93% prevalence with an average number of 65±33 plastic particles and average mass of 1.1±0.6 gram of plastic per individual bird. The 13 Fulmars that contained plastic in their stomachs exceeded the threshold of 0.1 g of plastic as used by OSPAR and EU for defining policy targets of ecological or environmental quality (Figure 4). The averaged data was strongly affected by a single bird having more than 8 grams of plastic in the stomach (Figure 5). The geometric mean

mass of plastics in Fulmars was 0.3367 g. By category of plastic, the average Fulmar had 1.14 industrial particles (0.032 g) and 64 user plastic particles (1.0739 g). Within user plastics sub-category, foam (Av. number = 33, Av. mass = 0.2407 g) and fragments (Av. number = 26, Av. mass = 0.8024 g) were the most frequent items.

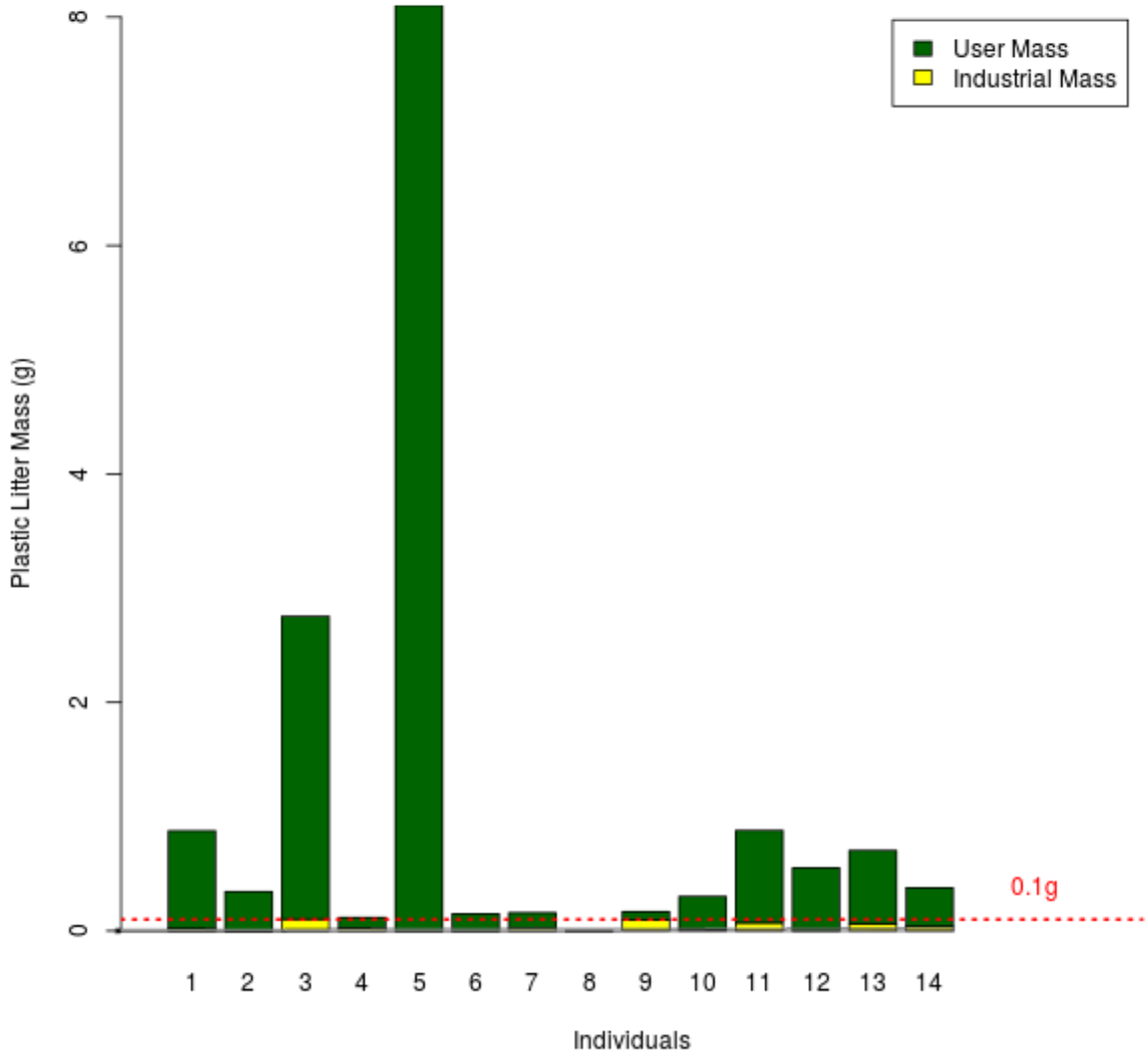


FIGURE 4 - INDIVIDUAL FULMARS PLOTTED AGAINST PLASTIC LITTER MASS. ALL BIRDS WITH PLASTICS SURPASS THE ECOQO THRESHOLD OF 0.1G. USER MASS IS THE MAIN TYPE OF PLASTIC LITTER FOUND, ALTHOUGH INDUSTRIAL PLASTIC LITTER (NURDLES) IS OCCASIONALLY PRESENT IN SAMPLES. INDIVIDUAL NUMBER 5 IS AN EXTREME EXAMPLE, WITH OVER 8 G OF PLASTIC LITTER MASS. INDIVIDUAL NUMBER 8 WAS THE ONLY ONE THAT CONTAINED NO PLASTICS.

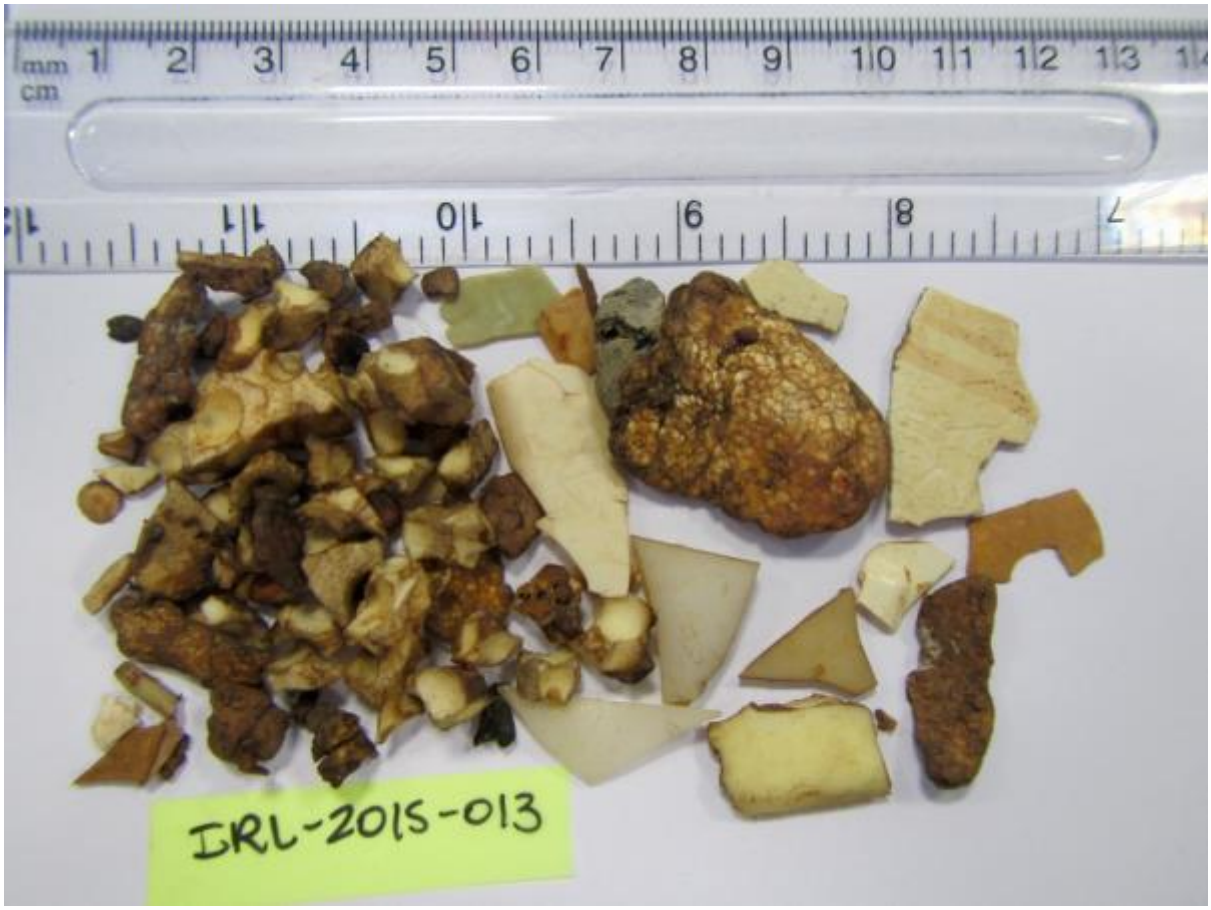


FIGURE 5 - STOMACH CONTENTS OF A BEACHED NORTHERN FULMAR, WHICH AMOUNTED TO 8 G OF PLASTIC LITTER. FOAM AND HARD FRAGMENTS ARE PREVALENT.

Further data for species with sample size exceeding 10 individuals showed contrast between Common Guillemot (12% prevalence) and Razorbill (0%) and plastic ingestion in 27% of Northern Gannets and 32% of Herring Gulls. For species with sample size of 10 or less, see Table 6 for details.

Multispecies samples consisted of 45.4% females (n=55), 42.1% males (n=51) and 12.3% of unknown sex (n=15); 20.7% juveniles (n=25), 35.5% immature (n=43), 33.0% adults (n=40) and 10.7% of unknown age (n=13). Out of the 33 birds that had ingested plastics, 45.4% (n=15) were females, 27.3% (n=9) were males and 27.3% (n=9) were of unknown sex.

Results from the first step of the multispecies model (GLMM Bernoulli distribution with logit link function) analysis, found the reduced version (excluding 'Age') to be more adequate by comparing AIC values (108.6 x 105.5). Feeding source 'Mixed' is

significant in both models, with a stronger significance (p=0.0451) in the reduced model. This suggests that feeding source has an effect on litter presence. Since the responses modelled directly were using a logit link, an inverse of the link function exp(x)/(1+exp(x)) was needed to extract and back transform the fixed effect terms and interpret the model. Such approach has shown that the significant value for 'Mixed' feeding source needs to be taken with caution as the predicted probability of litter presence in a bird with a mixed feeding type is 18.46%. When looking at 'Family' as a random effect, the estimated variability in the intercept of the random effect is 1.51, which is distinguishable from zero, meaning therefore that the random effect 'Family' is of importance to the model. The among 'Family' standard deviation is 1.23 and the variance is $1.23^2 = 1.51$. To assess model fit, 'Family' was also removed as a random effect and by comparing AIC values (105.5 x 115.04), it was confirmed that the GLMM was more adequate than a regular GLM. When interpreting the random effect analysis, the family 'Procellariidae' appears to have a much higher effect on positive litter presence than other families from this study (intercept= 0.8692). For a complete list of statistical outputs, see Tables 7 and 8.

For the second step of the model, which analysed the positive values for litter presence and investigated the influence of additional explanatory variables such as "Litter Mass", the best fitting model was Gamma with a log link: Litter Mass ~ (1|Family) + Sex + Age + Feeding Source. This model also identified significant effects of the feeding source 'Mixed' (p=0.0243) and 'Marine' (p=0.0060), suggesting that feeding source could have an influence on the amount of plastic litter ingested. Also in accordance with the first step of the model, this part identified significant effects for the family 'Procellariidae'. It was necessary to back-transform random effect using exp(x), which resulted in an intercept= 94.1868, meaning that birds in the family 'Procellariidae' were found to have ingested more plastic litter than the birds from other families analysed. Additional analysis, in which the second part of the model was run using only the Family Procellariidae, which contained only two species (Northern Fulmar and Manx Shearwater), showed a significant difference between these two species regarding the amount of ingested litter ($p<0.0001$). The variables 'Age' and 'Sex' however did not show significant influence. Caution should be taken when interpreting results from this study due to limited sample size. Outputs are listed in Tables 9 and 10.

TABLE 7 - OUTPUT FROM FIXED EFFECTS ON PART 1 MODEL. VALUES ARE GIVEN ON A LOGIT SCALE.

	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	0.9540	1.3250	0.720	0.4715
SexM	-0.7298	0.5837	-1.250	0.2112
FeedingMarine	-1.8235	1.2491	-1.460	0.1443
FeedingMixed	-2.4389	1.2174	-2.003	0.0451 *

TABLE 8 - OUTPUT FROM RANDOM EFFECTS ON PART 1 MODEL. VALUES HAVE BEEN BACK-TRANSFORMED USING EXP(X)/(1+EXP(X)).

	(Intercept)
Alcidae	0.2892417
Laridae	0.5028966
Phalacrocoracidae	0.3604330
Procellariidae	0.8692135
Stercorarius	0.6217054
Sulidae	0.3393089

TABLE 9 - OUTPUT FROM FIXED EFFECTS ON PART 2 MODEL. VALUES ARE GIVEN ON LOG SCALE.

	Estimate	Std. Error	t value	Pr(>|z|)
(Intercept)	-0.6871	1.7774	-0.387	0.69906
SexM	-0.5229	0.9628	-0.543	0.58707
Age.L	0.0252	0.5711	0.044	0.96480
Age.Q	-0.3774	0.7880	-0.479	0.63205
FeedingMarine	-3.4094	1.5145	-2.251	0.02437 *
FeedingMixed	-3.9973	1.4560	-2.745	0.00604 **

TABLE 10 - OUTPUT FROM RANDOM EFFECTS ON PART 2 MODEL. VALUES HAVE BEEN BACK-TRANSFORMED USING EXP(X).

	(Intercept)
Alcidae	0.4881587
Laridae	0.8400705
Phalacrocoracidae	0.1294125
Procellariidae	94.1868416
Stercorarius	0.2555198
Sulidae	0.5313960

2.5. DISCUSSION

This study intended to provide baseline data for marine litter in seabirds in Ireland. Our results have shown that at least 12 out of the 16 analysed species have ingested plastic litter. In agreement with other studies globally, Alcids (Guillemots, Razorbills and Puffins) are shown to ingest low levels of plastic litter (9.3%) (Laist, 1997; Provencher et al., 2010; Robards et al., 1995). Procellariiformes, such as e.g. Fulmars and Shearwaters, in accordance with other studies, have high levels of plastic ingestion (82.3%) (Gall & Thompson, 2015; Provencher et al., 2009; Provencher et al., 2014 A; Trevail et al., 2015; Van Franeker et al., 2011; Kühn et al., 2015). Based on the current results (n=14 Fulmars) in Ireland there is a 93% prevalence of plastic litter. Since all individual Fulmars with ingested plastic exceeded the threshold of 0.1g of plastic (Figure 4), the current EcoQO performance for Ireland is 93%. This, at the moment, exceeds the OSPAR target of below 10%. This value is similar to that seen in the English-French Channel (99%), which is the highest in the North Sea range (62%) (Van Franeker & SNS Fulmar Study Group, 2013; Van Franeker et al., 2011; Van Franeker & Law, 2015). Currently, in the Netherlands, 57% of the Fulmars (n=171) exceed the EcoQO between 2010-2014 (Van Franeker, 2015). Procellariiformes were statistically significantly (Table 4) more prone to ingesting litter than other families included in this study. Reasons behind the amounts of litter found in Procellariiformes could relate to their surface feeding habits (Mallory, 2006; Van Franeker et al., 2011), which would

overlap with positively buoyant plastic debris. Additionally, the narrow connector between the proventriculus and the gizzard, which prevents efficient regurgitation, could perhaps facilitate longer retention times (Ryan, 2015; Van Franeker & Law, 2015). However, when comparing Procellariiformes in this study, there was also a significant difference in the amount of plastic litter ingested by Fulmars and Manx Shearwaters ($p<0.0001$), though the small sample size of Manx Shearwaters may have contributed to the result. Literature indicates that there are high prevalence and amounts of plastic litter ingested by both species as they share similar gastrointestinal tract morphology (Acampora et al., 2014; Bond et al., 2014; Kühn et al., 2015; Lavers et al., 2014); however Fulmars are reported to be the species with the highest number of individuals ingesting debris (Gall and Thompson, 2015).

For the Suliformes (Gannets and Shags), most studies have reported nest incorporation of debris rather than ingestion (Bond et al., 2012; Montevecchi, 1991), as ingestion seems to be low for this order (Codina-García et al., 2013; Laist, 1997). However a study has reported death by starvation of a Northern Gannet by the occlusion of the digestive tract by debris (Pierce et al., 2004). The reported prevalence in Suliformes from the current study (26.7%) is similar to the 23.9% reported for Pelecaniformes by Kühn et al. (2015), but higher than the 13% reported for Northern Gannets alone in the Mediterranean (Codina-García et al., 2013).

Birds from the family Laridae ingested less litter (26.5%) than expected as some of these species have mixed diets, and are known to feed from terrestrial areas such as landfills (Belant et al., 1998; Duhem et al., 2003; Lindborg et al., 2012), for instance. However, birds that regurgitate their stomach contents, such as most gulls, likely eject indigestible matter at least once a day (Barrett et al., 2007). Thus, stomach contents from necropsies might be a reflection of this emptying. The family Laridae are not suitable candidates for oceanic marine litter monitoring, but could be the subject of other types of studies, such as occurrence, type of debris, retention times and, more appropriately, the monitoring of coastal areas.

Ingested litter in the stomach of beached birds reflects temporal trends and/or spatial difference of plastic litter abundance at sea (Van Franeker et al., 2011; Van Franeker & Law, 2015), but there is no way of inferring what the amount of ingested litter represents in terms of the quantitative abundance of plastic litter at sea. An individual

bird could have been carrying a larger amount of litter and may have passed some of it either through regurgitation, faeces, or through feeding of chicks. For species that regurgitate indigestible matter, perhaps a better way to collect information about these would be through the collection of boluses at breeding colonies (Avery-Gomm et al., 2013; Hammer et al., 2016; Ryan & Fraser, 1988). For birds that cannot regurgitate, it is necessary to assess how much these birds can carry as extra weight without affecting their regular activities. For instance, research that involves satellite or other tracking devices has come to the conclusion that birds can carry approximately an additional 3-5% of their body mass (Adams et al., 2009) without having their regular niche activities negatively affected. However, recent studies have shown that even when the 3-5% rule is applied, some tagged birds have taken longer in regular activities, and took more extensive foraging trips or reduced chick provisioning (Adams et al., 2009; Heggøy et al., 2015). The amounts of marine litter ingested by seabirds reported in this study suggest that except for possible incidental cases (e.g. Fulmar with more than 8 g), they did not die directly from plastic ingestion. If seabirds are however, unable to regurgitate or excrete ingested plastic there may be indirect lethal effects. Several authors have suggested indirect impacts such as reduced foraging efficiency, or a reduced feeding rate due to feeling satiated as the stomach is full (Azzarello & Van Vleet, 1987; Ryan, 1988; Ryan, 1990).

In addition to gathering baseline data, it was possible with the help of volunteers to collect an amount of birds to investigate presence/absence of litter in birds and to run a pilot marine litter monitoring project. Engaging citizens in environmental work has benefits for society by raising awareness (Smith et al., 2014), for the environment by the large collection of data more effectively (Silvertown, 2009) and allows for local research with international impact. It has become common to involve citizens in beach cleaning efforts (Ribic et al., 1997) and species surveys (Camphuysen, 1998; Parrish et al., 2007, Sullivan et al., 2009); these could be extended to becoming a beached bird survey without greater effort.

The second aim of the current study was to investigate the implementation of the EcoQO for marine litter monitoring in Ireland. Results from the current study suggest that implementation of a programme utilising OSPAR's and MSFD's Common Indicator (Vinet and Zhedanov, 2010) for marine litter can be achieved in Ireland. Although numbers of beached Fulmars can be unpredictable, they can provide

information and comparability with data collected by other countries in the North East Atlantic. To date, 12 specimens between 2014 and early 2016 (January-April), along with 2 more provided from 2012 before the start of the project, were analysed. This could be considered a small sample. However, according to Van Franeker & Meijboom (2002), a sample of 40 birds is enough to provide one with a reliable figure for plastic ingestion, and in the Irish case such a sample size seems realistically possible for the 5-year time frame used in EcoQO monitoring. Fulmars collected in Ireland had high levels of plastic ingestion, with one Fulmar alone containing over 8g of plastics.

In order for a species to be considered a good monitor for marine litter, there are some aspects to be considered: 1) monitoring location: offshore or coastal as that will define what species can be considered; 2) local species abundance, through either breeding pairs or migration routes; 3) stranding occurrence; and 4) likely accumulation of ingested marine litter. In addition, certain areas could be difficult to access, thus restricting surveying effort, or the presence of scavengers could reduce carcass availability.

Based on the criteria above and the data gathered in this study, we would not recommend another candidate monitoring species other than Northern Fulmar. An exception could be other Procellariiform species, such as Shearwaters, which have similar internal anatomy permitting the accumulation of debris in the digestive tract. However, some species of Shearwaters appear to feed more at the sub-surface than Fulmars, which are surface feeders (Mallory, 2006). Perhaps this results in Shearwaters encountering litter/plastic less frequently than Fulmars, as most plastics are positively buoyant, at least before they are colonized by organisms (Wright et al., 2013). The higher rate of plastic ingestion by Fulmars compared to Manx Shearwaters seen in this study could also be attributed to regional or species-specific differences, as some species of Shearwaters, such as Great, Sooty and Short-tailed Shearwaters have among the highest rates of ingestion of marine litter (Provencher et al., 2014 B).

2.6. CONCLUSION

The prevalence of plastic ingestion by seabirds in Ireland is at similar levels to other parts of the world. Additionally, current data indicates the marine litter monitoring

through Fulmars in Ireland to be possible. The preliminary data suggest high levels of prevalence of plastic litter ingestion, as well as high litter mass. Although it is important to comply with policy to focus on the Fulmar as a priority monitoring species, this study has shown that different species with different habitats and biology are prone to being affected by marine litter. It is relevant that all occurrences, even at low levels are reported so a better understanding of marine litter is gained globally, which allows for optimal management and mitigation of plastic pollution.

2.7. ACKNOWLEDGEMENTS

This work was supported by Science Without Borders (CAPES, Brazil) and the Department of Housing, Planning, Community and Local Government (DHPCLG, Ireland). We thank all volunteers who have embraced the Republic of Ireland Beached Bird Survey. Without you this project would not be possible. Many thanks to all at BirdWatch Ireland and Clean Coasts. Special thanks to Rosemary Hill, Kieran Campbell, Sean O'Gallaghan, Steve Newton, Niall Keogh, Richard Cronin, Annabel Fitzgerald, Rick Officer and Roisin Nash.

2.8. LITERATURE CITED

Acampora, H., Schuyler, Q. A., Townsend, K. A., & Hardesty, B. D. (2014). Comparing plastic ingestion in juvenile and adult stranded short-tailed shearwaters (Puffinus tenuirostris) in eastern Australia. *Marine Pollution Bulletin*, *78*(1-2), 63–68.

Adams, J., Scott, D., McKechnie, S., Blackwell, G., Shaffer, S. a, & Moller, H. (2009). Effects of geolocation archival tags on reproduction and adult body mass of sooty shearwaters (Puffinus griseus). *New Zealand Journal of Zoology*, *36*(3), 355–366. doi:10.1080/03014220909510160

Ashmole, N. P. (1971). Seabird ecology and the marine environment. *Avian Biology*, *1*, 223–286.

Avery-Gomm, S., Provencher, J. F., Morgan, K. H., & Bertram, D. F. (2013). Plastic

ingestion in marine-associated bird species from the eastern North Pacific. *Marine Pollution Bulletin*, *72*(1), 257–259. doi:10.1016/j.marpolbul.2013.04.021

Azzarello, M., & Van Vleet, E. (1987). Marine birds and plastic pollution . *Marine Ecology Progress Series*, *37*, 295–303. doi:10.3354/meps037295

Barrett, R. T., Camphuysen, K., Anker-Nilssen, T., Chardine, J. W., Furness, R. W., Garthe, S., … Veit, R. R. (2007). Diet studies of seabirds: A review and recommendations. *ICES Journal of Marine Science*, *64*(9), 1675–1691. doi:10.1093/icesjms/fsm152

Bates, D., & Mächler, M. (2016). Package "lme4." Retrieved from https://cran.r-project.org/web/packages/lme4/lme4.pdf (accessed 14 March 2016).

Belant, J. L., Ickes, S. K., & Seamans, T. W. (1998). Importance of landfills to urban-nesting herring and ring-billed gulls. *Landscape and Urban Planning*, *43*(1-3), 11–19. doi:10.1016/S0169-2046(98)00100-5

Bond, A. L., Montevecchi, W. A., Guse, N., Regular, P. M., Garthe, S., & Rail, J. F. (2012). Prevalence and composition of fishing gear debris in the nests of northern gannets (Morus bassanus) are related to fishing effort. *Marine Pollution Bulletin*, *64*(5), 907–911. doi:10.1016/j.marpolbul.2012.03.011

Bond, A. L., Provencher, J. F., Daoust, P. Y., & Lucas, Z. N. (2014). Plastic ingestion by fulmars and shearwaters at Sable Island, Nova Scotia, Canada. *Marine Pollution Bulletin*, *87*(1), 68–75. doi:10.1016/j.marpolbul.2014.08.010

Camphuysen, K. (1998). Beached bird surveys indicate decline in chronic oil pollution in the North Sea. *Marine Pollution Bulletin*, *36*(7), 519–526. doi:10.1016/S0025-326X(98)80018-0

Codina-García, M., Militão, T., Moreno, J., & González-Solís, J. (2013). Plastic debris in Mediterranean seabirds. *Marine Pollution Bulletin*, *77*(1-2), 220–226. doi:10.1016/j.marpolbul.2013.10.002

Duan, N., Manning, W. G., Morris, C. N., & Newhouse, J. P. (1984). Choosing Between the Sample-Selection Model and the Multi-Part Model. *Journal of Business & Economic Statistics*, *2*(3), 283–289.

doi:10.1080/07350015.1984.10509396

Duhem, C., Vidal, E., Legrand, J., & Tatoni, T. (2003). Opportunistic feeding responses of the Yellow-legged gull Larus michahellis to accessibility of refuse dumps: the gulls adjust their diet composition and diversity according to refuse dump accessibility. *Bird Study*, *50*(April), 61–67. doi:10.1080/00063650309461291

Furness, RW; Camphuysen, C. (1997). Seabirds as monitors of the marine environment. *ICES Journal of Marine Science, 54*, 726–737.

Galgani, F., Hanke, G., & Maes, T. (2015). Marine Anthropogenic Litter. In M. Bergmann, L. Gutow, & M. Klages (Eds.), (pp. 29–56). Cham: Springer International Publishing. doi:10.1007/978-3-319-16510-3_2

Gall, S. C., & Thompson, R. C. (2015). The impact of debris on marine life. *Marine Pollution Bulletin*. doi:10.1016/j.marpolbul.2014.12.041

Hammer, S., Nager, R. G., Johnson, P. C. D., Furness, R. W., & Provencher, J. F. (2016). Plastic debris in great skua (Stercorarius skua) pellets corresponds to seabird prey species. *Marine Pollution Bulletin*. doi:10.1016/j.marpolbul.2015.12.018

Heggøy, O., Christensen-Dalsgaard, S., Ranke, P. S., Chastel, O., & Bech, C. (2015). GPS-loggers influence behaviour and physiology in the black-legged kittiwake Rissa tridactyla. *Marine Ecology Progress Series*, *521*, 237–248. doi:10.3354/meps11140

Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., … Law, K. L. (2015). Plastic waste inputs from land into the ocean. *Science*, *347*(6223).

Kühn, S., Bravo Rebolledo, E. L., & Franeker, J. A. (2015). Marine Anthropogenic Litter. In M. Bergmann, L. Gutow, & M. Klages (Eds.), (pp. 75–116). Cham: Springer International Publishing. doi:10.1007/978-3-319-16510-3_4

Laist, D. (1997). *Marine Debris*. (J. M. Coe & D. B. Rogers, Eds.)*Society*. New York, NY: Springer New York. doi:10.1007/978-1-4613-8486-1

Lavers, J. L., Bond, A. L., & Hutton, I. (2014). Plastic ingestion by flesh-footed

shearwaters (Puffinus carneipes): Implications for fledgling body condition and the accumulation of plastic-derived chemicals. *Environmental Pollution*, *187*, 124–129. doi:10.1016/j.envpol.2013.12.020

Lindborg, V. a., Ledbetter, J. F., Walat, J. M., & Moffett, C. (2012). Plastic consumption and diet of Glaucous-winged Gulls (Larus glaucescens). *Marine Pollution Bulletin*, *64*(11), 2351–2356. doi:10.1016/j.marpolbul.2012.08.020

Lusher, A. L., Burke, A., O'Connor, I., & Officer, R. (2014). Microplastic pollution in the Northeast Atlantic Ocean: Validated and opportunistic sampling. *Marine Pollution Bulletin*, *88*(1-2), 325–333. doi:10.1016/j.marpolbul.2014.08.023

Lusher, A. L., Hernandez-Milian, G., O'Brien, J., Berrow, S., O'Connor, I., & Officer, R. (2015). Microplastic and macroplastic ingestion by a deep diving, oceanic cetacean: The True's beaked whale Mesoplodon mirus. *Environmental Pollution*, *199*, 185–191. doi:10.1016/j.envpol.2015.01.023

Mallory, M. L. (2006). The Northern Fulmar (Fulmarus glacialis) in Arctic Canada: ecology, threats, and what it tells us about marine environmental conditions. *Environmental Reviews*, *14*(3), 187–216. doi:10.1139/a06-003

Mitchell, P. I., Newton, S. F., Ratcliffe, N., Eds, T. E. D., Dunn, T. E., Poyser, a D., & May, L. (2004). Seabird populations of Britain and Ireland: Results of the Seabird 2000 census. *JNCC, Poyser, London.*, (August).

Montevecchi, W. a. (1991). Incidence and types of plastic in gannets' nests in the northwest Atlantic. *Canadian Journal of Zoology*, *69*, 295–297. doi:10.1139/z91-047

Moriarty, M., Pedreschi, D., Stokes, D., Dransfeld, L., & Reid, D. G. (2016). Spatial and temporal analysis of litter in the Celtic Sea from Groundfish Survey data: Lessons for monitoring. *Marine Pollution Bulletin*. doi:10.1016/j.marpolbul.2015.12.019

OSPAR. (2010). The Ospar system of Ecological Quality Objectives for the North sea, 16.

Parrish, J. K., Bond, N., Nevins, H., Mantua, N., Loeffel, R., Peterson, W. T., & Harvey, J. T. (2007). Beached birds and physical forcing in the California Current System. *Marine Ecology Progress Series*, *352*, 275–288. doi:10.3354/meps07077

Pierce, K. E., Harris, R. J., Larned, L. S., & Pokras, M. A. (2004). Obstruction and starvation associated with plastic ingestion in a Northern Gannet Morus bassanus and a Greater Shearwater Puffinus gravis. *Marine Ornithology*, *32*(2), 187–189.

Provencher, J. F., Bond, A. L., Hedd, A., Montevecchi, W. A., Muzaffar, S. Bin, Courchesne, S. J., … Mallory, M. L. (2014). Prevalence of marine debris in marine birds from the North Atlantic. *Marine Pollution Bulletin*, *84*(1-2), 411–417. doi:10.1016/j.marpolbul.2014.04.044

Provencher, J. F., Bond, A. L., & Mallory, M. L. (2014). Marine birds and plastic debris in Canada: a national synthesis, and a way forward. *Environmental Reviews*, *In press*(July 2014), 1–13. doi:10.1139/er-2014-0039

Provencher, J. F., Gaston, A. J., & Mallory, M. L. (2009). Evidence for increased ingestion of plastics by northern fulmars (Fulmarus glacialis) in the Canadian Arctic. *Marine Pollution Bulletin*, *58*(7), 1092–1095. doi:10.1016/j.marpolbul.2009.04.002

Provencher, J. F., Gaston, A. J., Mallory, M. L., O'hara, P. D., & Gilchrist, H. G. (2010). Ingested plastic in a diving seabird, the thick-billed murre (Uria lomvia), in the eastern Canadian Arctic. *Marine Pollution Bulletin*, *60*(9), 1406–1411. doi:10.1016/j.marpolbul.2010.05.017

Ribic, C. A., Johnson, S. W., & Cole, C. A. (1997). Marine Debris: Sources, Impacts, and Solutions. In J. M. Coe & D. B. Rogers (Eds.), (pp. 35–47). New York, NY: Springer New York. doi:10.1007/978-1-4613-8486-1_5

Robards, M. D., Piatt, J. F., & Wohl, K. D. (1995). Increasing Frequency of Plastic Ingested by Seabirds in the Subarctic North Pacific. *Marine Pollution Bulletin*, *30*(2), 151–157. doi:0025-326X(94)00121-9

Ryan, P. G. (1988). Effects of ingested plastic on seabird feeding: evidence from chickens. *Marine Pollution Bulletin*, *19*(3), 125–128.

Ryan, P. G. (1990). The effects of ingested plastic and other marine debris on seabirds. *Second International Conference on Marine Debris*, 2–7.

Ryan, P. G. (2015). How quickly do albatrosses and petrels digest plastic particles? *Environmental Pollution*, *207*, 438–440. doi:10.1016/j.envpol.2015.08.005

Ryan, P. G., & Fraser, M. W. (1988). The use of great skua pellets as indicators of plastic pollution in seabirds. *Emu*, *88*(July), 16–19.

Silvertown, J. (2009). A new dawn for citizen science. *Trends in Ecology & Evolution (Personal Edition)*, *24*(9), 467–71. doi:10.1016/j.tree.2009.03.017

Smith, S. D. A., Gillies, C. L., & Shortland-Jones, H. (2014). Patterns of marine debris distribution on the beaches of Rottnest Island, Western Australia. *Marine Pollution Bulletin*, *88*(1-2), 188–193. doi:10.1016/j.marpolbul.2014.09.007

Sullivan, B. L., Wood, C. L., Iliff, M. J., Bonney, R. E., Fink, D., & Kelling, S. (2009). eBird: A citizen-based bird observation network in the biological sciences. *Biological Conservation*, *142*(10), 2282–2292. doi:10.1016/j.biocon.2009.05.006

Trevail, A. M., Gabrielsen, G. W., Kühn, S., & Van Franeker, J. a. (2015). Elevated levels of ingested plastic in a high Arctic seabird, the northern fulmar (Fulmarus glacialis). *Polar Biology*. doi:10.1007/s00300-015-1657-4

Van Franeker, J. a. (2004). Save the North Sea fulmar-Litter-EcoQO Manual Part 1: Collection and dissection procedures., 38. Retrieved from http://edepot.wur.nl/40451

Van Franeker, J. a, & Meijboom, a. (2002). Marine litter monitoring by Northern fulmars: a pilot study, 72.

Van Franeker, J. a, Meijboom, a, & de Jong, M. L. (2003). Marine litter monitoring by Northern Fulmars in the Netherlands 1982-2003. *Van Franeker, J.A., A. Meijboom & M.L. de Jong, 2004. Marine Litter Monitoring by Northern Fulmars in the Netherlands 1982-2003. Wageningen, Alterra, Alterra-Rapport 1093.*

Van Franeker, J. a, & SNS Fulmar Study Group. (2013). Fulmar Litter EcoQO monitoring along Dutch and North Sea coasts - Update 2010 and 2011, (May), 61.

Van Franeker, J. A. (2014). *Fulmar Litter EcoQO Monitoring in the Netherlands*. IMARES, Wageningen UR.

Van Franeker, J. a., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., … Turner, D. M. (2011). Monitoring plastic ingestion by the northern fulmar Fulmarus glacialis in the North Sea. *Environmental Pollution*, *159*(10), 2609–2615. doi:10.1016/j.envpol.2011.06.008

Van Franeker, J. A., & Law, K. L. (2015). Seabirds, gyres and global trends in plastic pollution. *Environmental Pollution*, *203*, 89–96. doi:10.1016/j.envpol.2015.02.034

Van Franeker, J. a., & Law, K. L. (2015). Seabirds, gyres and global trends in plastic pollution. *Environmental Pollution*, *203*, 89–96. doi:10.1016/j.envpol.2015.02.034

Vinet, L., & Zhedanov, A. (2010). A “missing” family of classical orthogonal polynomials, (1), 1–5. doi:10.1088/1751-8113/44/8/085201

Wright, S. L., Thompson, R. C., & Galloway, T. S. (2013). The physical impacts of microplastics on marine organisms: a review. *Environmental Pollution (Barking, Essex : 1987)*, *178*, 483–92. doi:10.1016/j.envpol.2013.02.031

CHAPTER 3:

PASSIVE DIET SAMPLING FOR PLASTIC LITTER MONITORING

PART A: OPPORTUNISTIC SAMPLING TO QUANTIFY PLASTICS IN THE DIET OF UNFLEDGED BLACK-LEGGED KITTIWAKES (*RISSA TRIDACTYLA*), NORTHERN FULMARS (*FULMARUS GLACIALIS*) AND GREAT CORMORANTS (*PHALACROCORAX CARBO*).

PART B: PRESENCE OF PLASTIC LITTER IN PELLETS FROM GREAT CORMORANT (*PHALACROCORAX CARBO*) IN IRELAND.

To the bird watcher, the suburbanite who derives joy from birds in his garden, the hunter, the fisherman or the explorer of wild regions, anything that destroys the wildlife of an area for even a single year has deprived him of pleasure to which he has a legitimate right."

Rachel Carson

This chapter (3A) is reproduced from the following published paper, which can be found on Appendix 1:

Acampora, H., Newton, S., O'Connor, I. (2017). Opportunistic sampling to quantify plastics in the diet of unfledged Black-Legged Kittiwakes (*Rissa tridactyla*), Northern Fulmars (*Fulmarus glacialis*) and Great Cormorants (*Phalacrocorax carbo*). Marine Pollution Bulletin: 119 (171–174). https://doi.org/10.1016/j.marpolbul.2017.04.016

PART A

3.1 ABSTRACT

Seabirds can interact with marine litter, mainly by entanglement or ingestion. The ingestion of plastics can lead to starvation or physical damage to the digestive tract. For chicks, it could additionally lead to reduced growth, affecting survival and fledging. This study quantified the ingestion of plastics by seabird chicks via an opportunistic sampling strategy. When ringing is carried out at colonies, birds may spontaneously regurgitate their stomach contents due to the stress or as a defence mechanism. Regurgitates were collected from nestlings of three different species: Black-legged Kittiwake (Rissa tridactyla, n = 38), Northern Fulmar (Fulmarus glacialis, n = 14) and Great Cormorant (Phalacrocorax carbo, n = 28). Plastic was present in all species, with the highest frequency of occurrence (FO) in Northern Fulmar chicks (28.6%), followed by Black-legged Kittiwakes (7.9%) and Great Cormorants (7.1%). The observed load of plastics on chicks, which have not yet left the nest, highlights the pervasive nature of plastic pollution.

Marine litter has been recognised as a threat to wildlife and the marine environment (Bergmann et al., 2015; Derraik, 2002; Gall & Thompson, 2015). Kühn et al. (2015) report that 557 species, including 50% of all seabird species, are affected by marine litter. Seabirds are affected by marine litter through two main ways: ingestion and entanglement. Ingestion can block an animal's digestive tract, cause ulcers or perforations, produce a false satiation feeling, causing the bird not to feed, leading to impairment or starvation (Derraik, 2002; Ryan, 1988). There are also possible effects originating from compounds either added to plastics during production processes or adsorbed by them when drifting at sea (Koelmans, 2015; Tanaka et al., 2015). Entanglement can cause injuries or trap animals, impairing their ability to search for food (Laist, 1997), or if used in nest construction, ensnare young and prevent them from fledging (Bond et al., 2012; Lavers et al., 2013).

Ingestion of plastic debris has been widely reported globally for adult seabirds (Avery-Gomm et al., 2013; Gall & Thompson, 2015; Kühn et al., 2015; Provencher et al., 2016; Provencher et al., 2014; Roman et al., 2016; Van Franeker & Law, 2015), but there has been fewer reports in the peer-reviewed literature for chicks (Bond et al., 2010; Carey, 2011; Cousin et al., 2015; Rodríguez et al., 2012; Ryan, 1988), except for albatross chicks, which have high levels of plastic litter in their digestive tract and have been extensively studied (Sievert & Sileo, 1993; Sileo et al., 1990; Young et al., 2009). Chicks are not able to feed by themselves, so they receive their food from their parents, in many species via regurgitation. Chick survival can be dependent on a range of factors including: predation, thermal stress and, food availability. The fact that seabirds are long lived species, with delayed sexual maturity, that lay small clutch sizes compounds the potential impact that an additional threat, such as plastic litter could have on seabird populations.

Dietary studies through the collection of expelled boluses and spontaneous regurgitation are minimally invasive, and yet can provide an insight into the presence/absence of plastic litter in 'healthy' seabirds, as opposed to beached birds and carcasses found in breeding colonies (Hammer et al., 2016; Lindborg et al., 2012). During the course of demographic research activities such as ringing, many birds spontaneously regurgitate stomach contents as a response to the stress of being handled or as a defence

mechanism. Regurgitation does not always expel the entire stomach contents, sometimes permitting that only the upper stomach contents to be expelled (Barrett et al., 2007; Bond and Lavers, 2013). However, regurgitates provide an opportunity to sample the diet of seabirds *in situ* and alive, as opposed to laboratory experiments and the examination of carcasses. Understanding trends in ingestion of plastic litter by different species has the potential to inform policy and generate mitigation measures.

This study aimed to provide baseline data for the ingestion of plastics by seabird chicks in Ireland. Spontaneous regurgitates were collected at four different breeding colonies during ringing and demographic colony work, from three different species: Black-Legged Kittiwake (*Rissa tridactyla*), Northern Fulmar (*Fulmarus glacialis*) and Great Cormorant (*Phalacrocorax carbo*). Through the examination of chick regurgitates, it is possible to obtain insight into the diet of seabird chicks and how they interact with plastic pollution and, consequently into the same interactions in breeding adults when considering seabird populations in Ireland as a whole.

Regurgitate samples were collected from 80 individuals at four different colonies in the years 2011, 2012, 2013 & 2015 (Table 11) via opportunistic sampling while chicks were ringed in the nest during colony work. Samples were collected in plastic bags and frozen until further analysis. After thawing overnight, each sample was washed through a 1mm mesh sieve and every solid item retained in petri dishes. Solid contents were air dried overnight and examined under a Stereo microscope (MicrosAustria, 0.6x - 5x). They were separated into food and non-food categories according to Van Franeker et al. (2003). Litter items were weighed to the nearest 0.0001g and food items were identified to Family level and counted.

TABLE 11 - REGURGITATE SAMPLE DESCRIPTION PER SPECIES ORDERED BY YEAR OF COLLECTION AND LOCATION.

Species	**Year**	**Regurgitates (n)**	**Location**
Great Cormorant (*Phalacrocorax carbo*)	**2011**	25	St. Patrick's, Co. Donegal & Great Saltee, Co. Wexford

	2012	3	Ireland's Eye, Co. Dublin
Great Cormorant Total		28	
Black-legged Kittiwake (*Rissa tridactyla*)	**2013**	17	Rockabill, Co. Dublin
	2015	21	Rockabill, Co. Dublin
Black-legged Kittiwake Total		38	
Northern Fulmar (*Fulmarus glacialis*)	**2015**	14	Great Saltee, Co. Wexford
Northern Fulmar Total		14	
Sample Total		80	

Statistical analysis were carried out using R studio version 0.98.1102 (2009-2014, R Studio, Inc.). Data were non-normal, skewed and zero-inflated. For that reason, non-parametric tests such as Mann-Whitney and Kruskal-Wallis were used. The variables 'Litter Presence' and 'Litter Mass' were tested against relevant variables such as 'Food Presence' and the main food categories using a Mann-Whitney-Wilcoxon Test. A Kruskal-Wallis test was used to investigate if the variables 'Litter Presence' and 'Litter Mass' were influenced by the variable 'Species'.

The present study analysed 80 individual regurgitates from chicks of 3 different species. Samples were collected from 2011 – 2015 at 4 different breeding colonies along the coast of Ireland, described in Table 1. Due to the opportunistic nature of this sampling, sample sizes were limited and spatial and temporal differences were not taken into account in this particular work. Instead, all colonies and years were considered together in order to improve the power of statistical analysis. From all regurgitates analysed (n = 80), 11.3% (n = 9) contained plastic litter (Figure 6). Regurgitates from all 3 studied species contained plastic litter, from 3 different colonies: Black-legged Kittiwakes (n = 3), Great Cormorants (n = 2) and Northern Fulmars (n = 4). Plastic categories were

fragments (44.4%), sheet (33.3%) and foam (22.2%). Two individuals (1 Black-legged Kittiwake and 1 Great Cormorant) contained also non-plastic litter (fragments of paraffin wax).

FIGURE 6 - SAMPLE CONTAINING PLASTIC LITTER (TYPE: SHEET) FOUND IN REGURGITATE FROM A BLACK-LEGGED KITTIWAKE CHICK. ROCKABILL, CO. DUBLIN, 2013.

Plastic litter ingestion was higher in Northern Fulmar chicks, with a 28.6% frequency of occurrence (FO), an average mass of 0.0129 g (Range: 0 – 0.1043 g. SD ± 0.0317) and an average number of particles of 0.50 (Range: 0 – 3. SD ± 0.90); followed by Black-legged Kittiwakes with 7.9% FO, 0.0001 g average plastic mass (Range: 0 – 0.0045 g. SD ± 0.0007) and 0.08 average number of particles (Range: 0 – 1. SD ± 0.26); and lastly, Great Cormorants with 7.1% FO, an average mass of 0.0123 g (Range: 0 – 0.3450 g. SD ± 0.0640), average number of particles of 0.21 (Range: 0 – 5. SD ± 0.93) (Table 12).

When testing if species had any effect on the mass of plastic litter, we found no significant differences among all three study species ($p = 0.075$). No significant difference was found when testing if food presence, or any of selected food items had an influence on the presence of plastic litter.

This study aimed to investigate ingestion of plastics by chicks of three species of seabird in Ireland and set baseline data by using an opportunistic sampling method (spontaneous regurgitation). Our results have shown that chicks are ingesting litter, mainly plastics. These birds have not left the nest and yet, have been contaminated by the ingestion of anthropogenic debris fed to them via parents.

Our results show that the frequency of plastic occurrence in chick regurgitates of Northern Fulmars was higher (28.6%) than Black-legged Kittiwakes (7.9%) and Great Cormorants (7.1%). Ingestion of plastics has been connected to foraging strategy by various studies (Azzarello & Van Vleet, 1987; Ryan, 1988; Shephard et al., 2015). Surface seizing birds would be more likely to come across positively buoyant plastics (Moser & Lee, 1992). Birds with a generalist diet are more prone to mistaking plastics for food items (Moser & Lee, 1992). Northern Fulmars are both surface feeders and generalist feeders (Burg et al., 2003; Mallory, 2006), with our results thus reinforcing such connection between plastic ingestion and feeding strategy and diet. Previous authors have reported that young birds have more plastics in their stomachs than adults (Acampora, 2014; Carey, 2011). This could be explained by parental delivery when feeding chicks, or perhaps because young birds could be more naïve when feeding by themselves. In the case of the birds in this study, the former would apply as samples were collected from chicks, which were still completely dependent on parents for their food requirements. When comparing prevalence of plastic litter in adult birds from the same region, Acampora et al. (2016) found a higher prevalence (93%) in corpses of Northern Fulmars, with an equal sample size (n=14) to the chick regurgitates from this study. The same was true for stomach contents of Black-legged Kittiwakes, with a 50% prevalence, but in a smaller sample size (n=4). No previous assessment of litter in Great Cormorant's diet has been done before in Ireland.

When using this type of dietary analysis, comparison between species should be done with caution, taking species' biology regarding accumulation and regurgitation into consideration (Lindborg et al., 2012). For instance, Procellariiform birds have a

restricted regurgitation ability due to the constriction between their proventriculus and their gizzard (Azzarello & Van Vleet, 1987), so even when they regurgitate their stomach contents as a defence mechanism (stomach oil), they would only be able to regurgitate the upper part of the stomach (proventriculus), but not the part that accumulates the hard, indigestible matter (gizzard) (Karnovsky et al., 2012). Therefore, sampling regurgitates from such species only provides a snapshot of what their stomach contents are. This has to be taken into account in both stages: when the parent delivers the food to the chick and when the chick regurgitates as a response to disturbance. Yet in this study, Northern Fulmars had the highest prevalence of plastic ingestion.

Although Black-legged Kittiwakes chicks had a lower rate of plastic litter ingestion in this study, the FO (7.9%) is similar to that reported by Robards et al. (1995) of 7.8% and by Poon et al. (2017) of 9% for adult birds. However, plastic litter has been reportedly used as nesting material for Black-legged Kittiwakes in 57% of nests in Danish colonies (Hartwig et al., 2007), perhaps providing chicks with opportunities for accidental ingestion or entanglement.

For birds that regurgitate indigestible matter daily (Cormorants) or after each meal (Gulls and Skuas) (Barrett et al., 2007), there may be a lower probability of detecting plastics in their stomachs via necropsies of dead birds, as particles could have been previously expelled via a bolus. However, in our study adults have delivered plastics to chicks and, whilst at low levels, in the case of Great Cormorants (7.1%), chicks' regurgitates also represent a reflection of the parents' diet, even if the plastics quantified in this study only reflect the last ingested meal or meals throughout the day in which the samples were collected (Johnstone et al., 1990). Additionally, it is necessary to take into account that colony sampling means adults could be feeding chicks differently than they would feed themselves outside of the chick rearing period (Bearhop et al., 2001). Nevertheless, chicks are being exposed to plastic litter via regurgitation through their parents, which could affect growth and fledgling survival.

The majority of the Irish populations of Northern Fulmar and Black-legged Kittiwake (30 largest colonies in the country, comprising about 90 - 95% of the population in year 2000) were resurveyed in the summer of 2015 (Newton et al. 2015, unpublished report to National Parks & Wildlife Service). These showed that Northern Fulmars had declined by 12% and Black-legged Kittiwakes by 33% over a 15 year period. The most

likely explanations for this are declining prey fish stocks, perhaps related to climate change or overfishing or diminishing discarding. This study, along with the growing body of literature on plastic pollution, has demonstrated that populations of seabirds are vulnerable to interactions with plastics throughout their life cycle, thus more research into the prevalence and impacts of plastics is needed to investigate as to whether ingested plastics could yet be another factor involved in such demographic decline. A plastic diet could prevent seabird chicks from getting adequate body condition prior to fledging, which is essential for fledgling survival (Arizaga et al., 2015; Lavers et al., 2014)

The presence of plastics in chick's diet confirms that plastics are present in many seabird species throughout their life cycle. The use of chick regurgitates has proved to be a valid approach, when consideration is taken related to anatomic differences in species. Our previous work (Acampora et al., 2016) has utilised beached birds as a tool for multispecies monitoring of marine litter. Different approaches of monitoring, rather than a single one, offer more reliable information and, with such compilation of data, it is expected in the future to be able to infer a health status for seabird populations in Ireland.

TABLE 12 - PLASTIC LITTER ABUNDANCE PER SPECIES (ORDERED BY SAMPLE SIZE; POPULATION AVERAGES ARE PROVIDED AND INCLUDED ZERO VALUES).

Species	**Sample (n)**	**Prevalence (%)**	**Average number of particles (n) ± SD**	**Average mass (g) ± SD**
Black-legged Kittiwake	38	7.9	0.08 ± 0.26	0.0002 ± 0.0007
Great Cormorant	28	7.1	0.21 ± 0.93	0.0123 ± 0.0640
Northern Fulmar	14	28.6	0.50 ± 0.90	0.0129 ± 0.0317

3.3. ACKNOWLEDGMENTS

This work was supported by Science Without Borders (CAPES, Brazil) scheme. We thank all at BirdWatch Ireland. Special thanks to John Lusby, Niall Tierney, Helen Boland, Niall Keogh, Brian Burke and Andrew Power for collection and help in the field. We also thank the input of anonymous reviewers, which helped to improve the manuscript.

3.4. LITERATURE CITED

Acampora, H., Lyashevska, O., Van Franeker, J.A., O'Connor, I., 2016. The use of beached bird surveys for marine plastic litter monitoring in Ireland. Mar. Environ. Res. 120, e87–e91. doi:10.1016/j.marenvres.2016.08.002

Acampora, H., Schuyler, Q.A., Townsend, K.A., Hardesty, B.D., 2014. Comparing plastic ingestion in juvenile and adult stranded short-tailed shearwaters (Puffinus tenuirostris) in eastern Australia. Mar. Pollut. Bull. 78, 63–68.

Arizaga, J., Herrero, A., Aldalur, A., Cuadrado, J.F., Oro, D., 2015. Effect of pre-fledging body condition on juvenile survival in Yellow-legged Gull Larus michahellis. Acta Ornithol. 50, 1–9. doi:10.3161/00016454AO2015.50.2.002

Avery-Gomm, S., Provencher, J.F., Morgan, K.H., Bertram, D.F., 2013. Plastic ingestion in marine-associated bird species from the eastern North Pacific. Mar. Pollut. Bull. 72, 257–259. doi:10.1016/j.marpolbul.2013.04.021

Azzarello, M., Van Vleet, E., 1987. Marine birds and plastic pollution . Mar. Ecol. Prog. Ser. 37, 295–303. doi:10.3354/meps037295

Barrett, R.T., Camphuysen, K., Anker-Nilssen, T., Chardine, J.W., Furness, R.W., Garthe, S., Hüppop, O., Leopold, M.F., Montevecchi, W. a., Veit, R.R., 2007. Diet studies of seabirds: A review and recommendations. ICES J. Mar. Sci. 64, 1675–1691. doi:10.1093/icesjms/fsm152

Bearhop, S., Thompson, D.R., Phillips, R.A., Waldron, S., Hamer, K.C., Gray, C.M.,

Votier, S.C., Ross, B.P., Furness, R.W., 2001. Annual variation in great skua diets: the importance of commercial fisheries and predation on seabirds revealed by combining dietary analyses. Condor 103, 802–809. doi:10.1650/0010-5422(2001)103[0802:avigsd]2.0.co;2

Bergmann, M., Gutow, L., Klages, M., 2015. Marine anthropogenic litter, Marine Anthropogenic Litter. doi:10.1007/978-3-319-16510-3

Bond, A.L., Jones, I.L., Williams, J.C., Byrd, G.V., 2010. Auklet (Charadriiformes: Alcidae, Aethia spp.) chick meals from the Aleutian Islands, Alaska, have a very low incidence of plastic marine debris. Mar. Pollut. Bull. 60, 1346–1349. doi:10.1016/j.marpolbul.2010.05.001

Bond, A.L., Lavers, J.L., 2013. Effectiveness of emetics to study plastic ingestion by Leach's Storm-petrels (Oceanodroma leucorhoa). Mar. Pollut. Bull. 70. doi:10.1016/j.marpolbul.2013.02.030

Bond, A.L., Montevecchi, W.A., Guse, N., Regular, P.M., Garthe, S., Rail, J.F., 2012. Prevalence and composition of fishing gear debris in the nests of northern gannets (Morus bassanus) are related to fishing effort. Mar. Pollut. Bull. 64, 907–911. doi:10.1016/j.marpolbul.2012.03.011

Burg, T.M., Lomax, J., Almond, R., Brooke, M.D.L., Amos, W., 2003. Unravelling dispersal patterns in an expanding population of a highly mobile seabird, the northern fulmar (Fulmarus glacialis). Proc. Biol. Sci. 270, 979–984. doi:10.1098/rspb.2002.2322

Carey, M.J., 2011. Intergenerational transfer of plastic debris by Short-tailed Shearwaters (Ardenna tenuirostris). Emu 111, 229–234. doi:10.1071/MU10085

Cousin, H.R., Auman, H.J., Alderman, R., Virtue, P., 2015. The frequency of ingested plastic debris and its effects on body condition of Short-tailed Shearwater (Puf fi nus tenuirostris) pre- fl edging chicks in Tasmania , Australia. Emu 115, 6–11.

Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: A review. Mar. Pollut. Bull. 44, 842–852. doi:10.1016/S0025-326X(02)00220-5

Gall, S.C., Thompson, R.C., 2015. The impact of debris on marine life. Mar. Pollut.

Bull. doi:10.1016/j.marpolbul.2014.12.041

Hammer, S., Nager, R.G., Johnson, P.C.D., Furness, R.W., Provencher, J.F., 2016. Plastic debris in great skua (Stercorarius skua) pellets corresponds to seabird prey species. Mar. Pollut. Bull. doi:10.1016/j.marpolbul.2015.12.018

Hartwig, E., Clemens, T., Heckroth, M., 2007. Plastic debris as nesting material in a Kittiwake- (Rissa tridactyla) - colony at the Jammerbugt , Northwest Denmark 54, 595–597. doi:10.1016/j.marpolbul.2007.01.027

Johnstone, I.G., Harris, M.P., Wanless, S., Graves, J. a., 1990. The usefulness of pellets for assessing the diet of adult shags Phalacrocorax aristotelis. Bird Study 37, 37–41. doi:10.1080/00063659009477030

Karnovsky, N.J., Hobson, K.A., Iverson, S.J., 2012. From lavage to lipids: Estimating diets of seabirds. Mar. Ecol. Prog. Ser. 451, 263–284. doi:10.3354/meps09713

Koelmans, A.A., 2015. Marine Anthropogenic Litter, in: Bergmann, M., Gutow, L., Klages, M. (Eds.), . Springer International Publishing, Cham, pp. 309–324. doi:10.1007/978-3-319-16510-3_11

Kühn, S., Bravo Rebolledo, E.L., Franeker, J.A., 2015. Marine Anthropogenic Litter, in: Bergmann, M., Gutow, L., Klages, M. (Eds.), . Springer International Publishing, Cham, pp. 75–116. doi:10.1007/978-3-319-16510-3_4

Laist, D., 1997. Marine Debris, Society, Springer Series on Environmental Management. Springer New York, New York, NY. doi:10.1007/978-1-4613-8486-1

Lavers, J.L., Bond, A.L., Hutton, I., 2014. Plastic ingestion by flesh-footed shearwaters (Puffinus carneipes): Implications for fledgling body condition and the accumulation of plastic-derived chemicals. Environ. Pollut. 187, 124–129. doi:10.1016/j.envpol.2013.12.020

Lavers, J.L., Hodgson, J.C., Clarke, R.H., 2013. Prevalence and composition of marine debris in Brown Booby (Sula leucogaster) nests at Ashmore Reef. Mar. Pollut. Bull. 77, 320–324. doi:10.1016/j.marpolbul.2013.09.026

Lindborg, V. a., Ledbetter, J.F., Walat, J.M., Moffett, C., 2012. Plastic consumption and

diet of Glaucous-winged Gulls (Larus glaucescens). Mar. Pollut. Bull. 64, 2351–2356. doi:10.1016/j.marpolbul.2012.08.020

Mallory, M.L., 2006. The Northern Fulmar (Fulmarus glacialis) in Arctic Canada: ecology, threats, and what it tells us about marine environmental conditions. Environ. Rev. 14, 187–216. doi:10.1139/a06-003

Moser, M., Lee, D., 1992. a 14-Year Survey of Plastic Ingestion By Western North-Atlantic Seabirds. Colon. Waterbirds 15, 83–94. doi:10.2307/1521357

Poon, F.E., Provencher, J.F., Mallory, M.L., Braune, B.M., Smith, P.A., 2017. Levels of ingested debris vary across species in Canadian Arctic seabirds. Mar. Pollut. Bull.

Provencher, J., Bond, A., Aver-Gomm, S., Borrelle, S., Bravo Rebolledo, E., Hammer, S. eth]ur, Kuhn, S., Lavers, J., Mallory, M., Trevail, A., van Franeker, J., 2016. Quantifying ingested debris in marine megafauna: a review and recommendations for standardization. Anal. Methods. doi:10.1039/C6AY02419J

Provencher, J.F., Bond, A.L., Mallory, M.L., 2014. Marine birds and plastic debris in Canada: a national synthesis, and a way forward. Environ. Rev. In press, 1–13. doi:10.1139/er-2014-0039

Robards, M.D., Piatt, J.F., Wohl, K.D., 1995. Increasing Frequency of Plastic Ingested by Seabirds in the Subarctic North Pacific. Mar. Pollut. Bull. 30, 151–157. doi:0025-326X(94)00121-9

Rodríguez, A., Rodríguez, B., Nazaret Carrasco, M., 2012. High prevalence of parental delivery of plastic debris in Cory's shearwaters (Calonectris diomedea). Mar. Pollut. Bull. 64. doi:10.1016/j.marpolbul.2012.06.011

Roman, L., Schuyler, Q.A., Hardesty, B.D., Townsend, K.A., 2016. Anthropogenic Debris Ingestion by Avifauna in Eastern Australia 1–14. doi:10.5061/dryad.p48f7

Ryan, P.G., 1988. Effects of ingested plastic on seabird feeding: evidence from chickens. Mar. Pollut. Bull. 19, 125–128.

Ryan, P.G., 1988. Intraspecific Variation in Plastic Ingestion by Seabirds and the Flux of Plastic Through Seabird Populations. Condor 90, 446–452.

Shephard, S., van Hal, R., de Boois, I., Birchenough, S.N.R., Foden, J., O'Connor, J., Geelhoed, S.C.V., Van Hoey, G., Marco-Rius, F., Reid, D.G., Schaber, M., 2015. Making progress towards integration of existing sampling activities to establish Joint Monitoring Programmes in support of the MSFD. Mar. Policy 59, 105–111. doi:10.1016/j.marpol.2015.06.004

Sievert, P.R., Sileo, L., 1993. The effects of ingested plastic on growth and survival of albatross chicks. status, Ecol. Conserv. Mar. birds North Pacific. 212–217.

Sileo, L., Sievert, P.R., Samuel, M.D., 1990. Causes of mortality of albatross chicks at Midway Atoll. J. Wildl. Dis. 26, 329–38. doi:10.7589/0090-3558-26.3.329

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., Watanuki, Y., 2015. Facilitated leaching of additive-derived PBDEs from plastic by seabirds' stomach oil and accumulation in tissues. Environ. Sci. Technol. 150901174241000. doi:10.1021/acs.est.5b01376

Van Franeker, J.A., Law, K.L., 2015. Seabirds, gyres and global trends in plastic pollution. Environ. Pollut. 203, 89–96. doi:10.1016/j.envpol.2015.02.034

Van Franeker, J.A., Meijboom, A., de Jong, M.L., 2003. Marine litter monitoring by Northern Fulmars in the Netherlands 1982-2003. Wageningen, Alterra, Alterra-rapport 1093.

Young, L.C., Vanderlip, C., Duffy, D.C., Afanasyev, V., Shaffer, S. a., 2009. Bringing home the trash: Do colony-based differences in foraging distribution lead to increased plastic ingestion in Laysan albatrosses? PLoS One 4, 11–13. doi:10.1371/journal.pone.0007623

This chapter (3B) is reproduced from the following published paper, which can be found on Appendix 1:

Acampora, H., Berrow, S., Newton, S., O'Connor, I. (2017). Presence of plastic litter in pellets from Great Cormorant (*Phalacrocorax carbo*) in Ireland. Marine Pollution Bulletin: 117.1 (512-514). https://doi.org/10.1016/j.marpolbul.2017.02.015

PART B

3.5. ABSTRACT

Plastic pollution has been the subject of much research in the last decade. Seabirds can mistake plastic fragments for prey, which can perforate or block the digestive tract and cause ulcers. Most commonly, seabirds accumulate this indigestible matter in their stomachs, obtaining no nutrition and may die from starvation. Certain species of seabirds however, have the ability of regurgitating indigestible matter in the form of pellets. This study aimed to investigate the ingestion of plastics by live seabirds through the examination of regurgitated pellets (n = 92) from a Great Cormorant (*Phalacrocorax carbo*) breeding colony and a winter roost in Ireland. Plastic prevalence was consistently 3.2% at both sites. The presence of plastic litter highlights the fact that all species of seabird are susceptible to interact with marine litter regardless of feeding habits, although at different rates. More research is needed to understand the driving factors involved in plastic ingestion among different species.

3.6. BASELINE

The presence of litter in the diet of marine top predators has been the subject of global research. At least 50% species of seabird species are known to interact with marine plastic litter (Kühn et al., 2015). This interaction can occur in two main ways: ingestion and entanglement. The effects of entanglement are more readily understood (Kühn et al., 2015). For ingestion however, besides physical effects such as perforation or

occlusion of the digestive tract, there may be secondary effects. If seabirds ingest sufficient quantities of litter to fill their stomachs, they may have a feeling of satiation, but without nutritive benefits. This can lead to a loss of body condition and perhaps, mortality through starvation. Wilcox et al. (2015) has predicted that by 2050, all seabird species will have ingested some plastic debris.

The use of seabirds as environmental monitors has been widely documented (Burger & Gochfeld, 2004; Furness & Camphuysen, 1997; Mallory et al., 2010; Monteiro & Furness, 1995). The Northern Fulmar (*Fulmarus glacialis*) has been the main focus for monitoring ingestion of plastic litter, which has been incorporated into European environmental policies such as the Oslo-Paris Convention (OSPAR) and the Marine Strategy Framework Directive (MSFD) (Van Franeker et al., 2011). Fulmars are in the order Procellariiformes, which have a very limited ability to regurgitate indigestible matter, thus ingested litter is accumulated. Many species of seabird however, regurgitate pellets or boluses, which comprise items they cannot digest, including fish bones, otoliths, squid beaks and stones (Barrett et al., 2007). Regurgitated pellets are frequently used in dietary studies as they can be collected with minimal disturbance at colonies and can provide valuable information on seabird diet (Barrett et al., 2007). Using regurgitated pellets may underestimate the presence of soft prey (Bearhop et al., 2001), hence it is important to be cautious when interpreting results and not limit dietary studies to evidence from pellets only.

Monitoring plastic litter through seabird diet has been primarily achieved through the analysis of the stomach contents of dead birds (Acampora et al., 2014; Avery-Gomm et al., 2013; Van Franeker et al., 2011), but monitoring of live birds could also provide complementary information from species that do not always accumulate plastics in their digestive tract. Such species could be considered as being less prone to ingesting plastic litter due to the possible masking effects of pellet regurgitation. Thus, other methods, such as the use of regurgitates and pellets could provide supporting or additional information on the incidence of marine plastic litter in their diet.

The family Phalacrocoracidae comprises Cormorants and Shags which occur in both freshwater and marine environments. This study focuses on the Great Cormorant (*Phalacrocorax carbo*) (hereafter Cormorant). Whilst Shags are predominantly a marine species, Cormorants can be also found foraging and breeding in lakes and rivers.

Cormorants are relatively abundant in Irish waters, with 4,548 breeding pairs recorded between 1998 and 2002 during the last published national census (Mitchell et al., 2004). Cormorants feed primarily on fish, and are mainly benthic divers (Gremillet et al., 1998).

Both macro and micro plastics are widespread in Irish waters. Lusher et al. (2014) reported an average of 2.46 microplastic particles/m^3 of seawater during sub-surface transects in the Northeast Atlantic, while the presence of litter was reported in 57% of trawl stations sampled in the Celtic Sea, with 84% of this litter found to be plastic (Moriarty et al., 2016). There is little information on the presence of marine litter in seabirds in Ireland. Recently, Acampora et al. (2016) investigated the presence of plastics through stomach content analysis of dead birds, and reported the ingestion of plastics by 27% of specimens examined (n=121), however due to the opportunistic nature of such sampling methodology, no data for Cormorants were available.

This study sets a baseline for the presence of plastic litter in pellets regurgitated by breeding and non-breeding Cormorants in Ireland. This technique is believed to be complementary to data collected from dead seabirds.

In total, 92 pellets were collected between the years 2011-2015 (Table 13) from two sites: Money Point, County Clare, on the western seaboard and from Great Saltee Island, County Wexford, off the southeast coast. Cormorant pellets were collected during winter at a roost site (Money Point), and in summer during ringing operations on Great Saltee Island. Pellets were placed in plastic bags and frozen until subsequent analysis. Pellets were soaked in water in individual containers for 24 hours before being washed through a 1mm mesh sieve and every solid item retained in petri-dishes. Solid contents were air dried overnight and examined under a stereo microscope (MicrosAustria, 0.6x - 5x). They were then separated into categories according to Van Franeker et al. (2003). Only litter items were weighed, to the nearest 0.0001g. Food items were identified to groups and counted.

TABLE 13 - LIST OF SAMPLES BY YEAR, SEASON, AND LOCATION.

Species	Year	Season	Bolus (n)	Location
Cormorant	2011	Summer	29	Great Saltee, Co. Wexford
	2014	Winter	3	Money Point, Co. Clare
	2015	Winter	60	Money Point, Co. Clare

Three of 92 analysed pellets (3.2%) contained plastic litter (Figure 7). The proportion of pellets containing plastics was consistent between sampling sites (c. 3%). The average plastic mass was 0.0002 g (Range: 0 – 0.01. SE ± 0.0001), with a 0.043 average number of particles (Range: 0 – 2. SE ± 0.0263). Types of plastic litter included sheet, foam and fragment. Table 14 describes abundance of different food types in pellets.

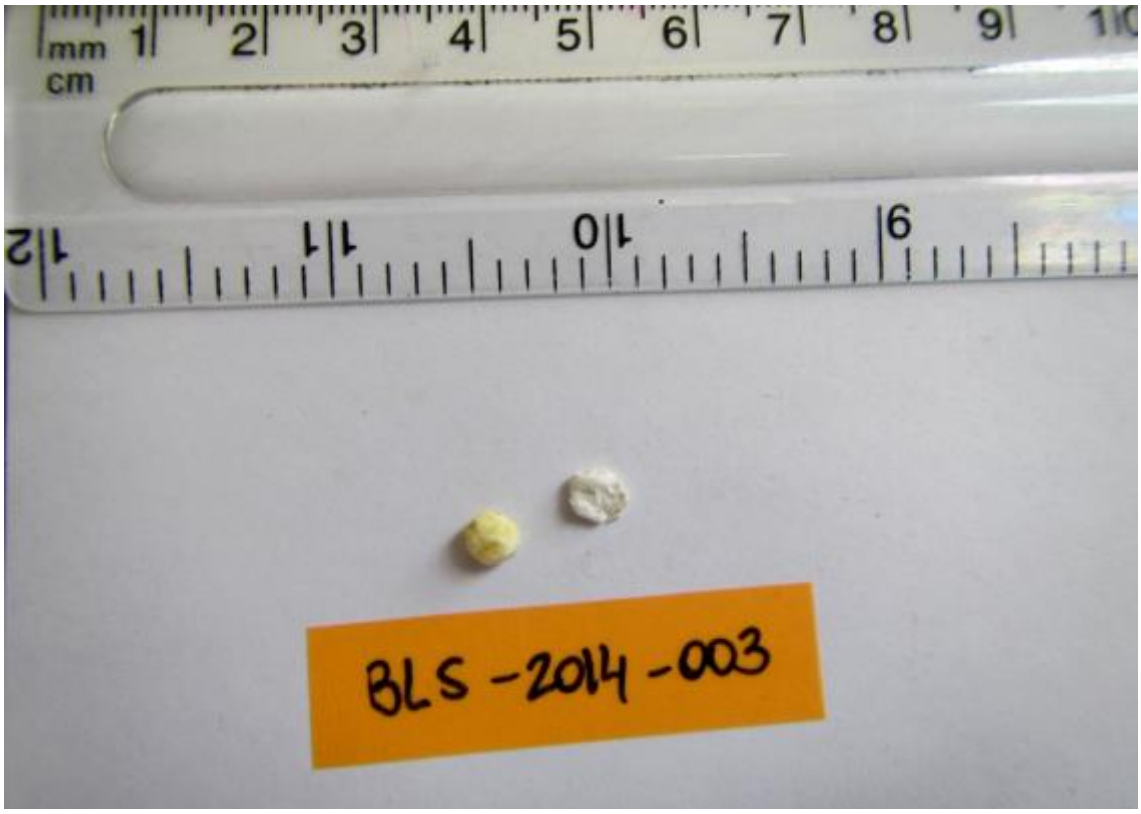


FIGURE 7 - PLASTIC FRAGMENTS (FOAM) FOUND IN A CORMORANT PELLET, DURING THE NON-BREEDING SEASON, IN MONEY POINT, COUNTY CLARE, 2014.

TABLE 14 - MAIN ITEMS FOUND IN PELLETS. NUMBERS ARE PROPORTION OF ITEMS IN RELATION TO TOTAL ITEMS AND PROPORTION OF PELLETS CONTAINING SAID ITEM.

	Otoliths	Lens	Bones	Crustacean	Plant	Seaweed	Stones	Parasitic Worms
Proportion of items %	26.7	4.0	50.2	8.7	3.8	0.8	4.7	0.9
Proportion of pellets %	79.3	43.4	59.7	36.9	40.2	15.2	32.6	15.2

According to Johnstone et al. (1990), plastics quantified in pellets only reflect the last ingested meal or meals consumed throughout the previous day. Cormorants are known to regurgitate pellets daily, whilst Gulls and Skuas, regurgitate after each meal (Barrett et al., 2007). Thus sampling regurgitated pellets reflects short time-scales, implying pellets are produced within hours of a meal. Additionally, collecting samples at nest sites might reflect the diet fed to chicks as adult birds could provision their chicks with different prey compared to what they would feed themselves outside of the chick rearing period (Bearhop et al., 2001). Thus, a comparison between breeding and non-breeding season is appropriate.

There are no data for the presence of plastic litter in Cormorants in Ireland, but Shags (*Phalacrocorax aristotelis*), a related species, found beached in Ireland (n=10) had a prevalence of plastic litter of 10% (n= 10) (Acampora et al., 2016), which is higher than 3.1% found in pellets in this study. Such differences could be explained by species-specific feeding habits, small sample size, or additionally, biased towards starving birds which is the case for most beached birds. Robards et al. (1995) found a 20% prevalence in stomachs of a related species: the Pelagic Cormorant (*Phalacrocorax pelagicus*) between 1988-1990. Burthe et al. (2014) classified plastics as a 'low' threat to Great Cormorants.

Multiple studies have connected plastic ingestion to foraging strategy (Azzarello & Van Vleet, 1987; Ryan, 1988; Shephard et al., 2015). Diving seabirds should not be as prone to ingesting plastic litter as those feeding at the surface due to the buoyant nature of most plastic types. Such birds could, on the other hand, be prone to secondary

ingestion, which means they might have obtained plastic litter from their prey. When considering such factors, birds that are able to regurgitate indigestible matter, such as plastic litter, have an effective mechanism to counter the potential accumulation or effects of plastic litter.

It is important to set a baseline for the presence of marine litter in seabirds using a variety of sampling methods, in order to obtain a more reliable and extensive record. Sampling live birds compared to dead birds, within the breeding season alongside non-breeding birds, and from a range of species, has the potential to provide a multi-dimensional record of plastic pollution in the marine environment not only in Ireland, but globally.

3.7. ACKNOWLEDGEMENTS

This work was supported by Science Without Borders (CAPES, Brazil) scheme through a doctoral scholarship awarded to Heidi Acampora. We thank all at BirdWatch Ireland. Special thanks to John Lusby, Niall Tierney and Niall Keogh for sample collection and storage in the field.

3.8. LITERATURE CITED

Acampora, H., Lyashevska, O., Van Franeker, J. A., & O'Connor, I. (2016). The use of beached bird surveys for marine plastic litter monitoring in Ireland. *Marine Environmental Research*, *120*, e87–e91. http://doi.org/10.1016/j.marenvres.2016.08.002

Acampora, H., Schuyler, Q. A., Townsend, K. A., & Hardesty, B. D. (2014). Comparing plastic ingestion in juvenile and adult stranded short-tailed shearwaters (Puffinus tenuirostris) in eastern Australia. *Marine Pollution Bulletin*, *78*(1–2), 63–68.

Avery-Gomm, S., Provencher, J. F., Morgan, K. H., & Bertram, D. F. (2013). Plastic ingestion in marine-associated bird species from the eastern North Pacific. *Marine Pollution Bulletin*, *72*(1), 257–259. http://doi.org/10.1016/j.marpolbul.2013.04.021

Azzarello, M., & Van Vleet, E. (1987). Marine birds and plastic pollution . *Marine Ecology Progress Series*, *37*, 295–303. http://doi.org/10.3354/meps037295

Barrett, R. T., Camphuysen, K., Anker-Nilssen, T., Chardine, J. W., Furness, R. W., Garthe, S., … Veit, R. R. (2007). Diet studies of seabirds: A review and recommendations. *ICES Journal of Marine Science*, *64*(9), 1675–1691. http://doi.org/10.1093/icesjms/fsm152

Bearhop, S., Thompson, D. R., Phillips, R. A., Waldron, S., Hamer, K. C., Gray, C. M., … Furness, R. W. (2001). Annual variation in great skua diets: the importance of commercial fisheries and predation on seabirds revealed by combining dietary analyses. *The Condor*, *103*(4), 802–809. http://doi.org/10.1650/0010-5422(2001)103[0802:avigsd]2.0.co;2

Burger, J., & Gochfeld, M. (2004). Marine Birds as Sentinels of Environmental Pollution. *EcoHealth*, *1*(3), 263–274. http://doi.org/10.1007/s10393-004-0096-4

Burthe, S. J., Wanless, S., Newell, M. A., Butler, A., & Daunt, F. (2014). Assessing the vulnerability of the marine bird community in the western North Sea to climate change and other anthropogenic impacts. *Marine Ecology Progress Series*, *507*, 277–295.

Furness, RW; Camphuysen, C. (1997). Seabirds as monitors of the marine environment. *ICES Journal of Marine Science, 54*, 726–737.

Gremillet, D., Argentin, G., Schulte, B., & Culik, B. (1998). Flexible foraging techniques in breeding Cormorants Phalacrocorax carbo and Shags Phalacrocorax aristotelis: benthic or pelagic feeding? *IBIS*, *140*(May 1994), 113–119.

Johnstone, I. G., Harris, M. P., Wanless, S., & Graves, J. a. (1990). The usefulness of pellets for assessing the diet of adult shags Phalacrocorax aristotelis. *Bird Study*, *37*(1), 37–41. http://doi.org/10.1080/00063659009477030

Kühn, S., Bravo Rebolledo, E. L., & Franeker, J. A. (2015). Marine Anthropogenic Litter. In M. Bergmann, L. Gutow, & M. Klages (Eds.), (pp. 75–116). Cham: Springer International Publishing. http://doi.org/10.1007/978-3-319-16510-3_4

Lavers, J. L., Bond, A. L., & Hutton, I. (2014). Plastic ingestion by flesh-footed

shearwaters (Puffinus carneipes): Implications for fledgling body condition and the accumulation of plastic-derived chemicals. *Environmental Pollution*, *187*, 124–129. http://doi.org/10.1016/j.envpol.2013.12.020

Lusher, A. L., Burke, A., O'Connor, I., & Officer, R. (2014). Microplastic pollution in the Northeast Atlantic Ocean: Validated and opportunistic sampling. *Marine Pollution Bulletin*, *88*(1–2), 325–333. http://doi.org/10.1016/j.marpolbul.2014.08.023

Lusher, A. L., Hernandez-Milian, G., O'Brien, J., Berrow, S., O'Connor, I., & Officer, R. (2015). Microplastic and macroplastic ingestion by a deep diving, oceanic cetacean: The True's beaked whale Mesoplodon mirus. *Environmental Pollution*, *199*, 185–191. http://doi.org/10.1016/j.envpol.2015.01.023

Mallory, M. L., Robinson, S. a., Hebert, C. E., & Forbes, M. R. (2010). Seabirds as indicators of aquatic ecosystem conditions: A case for gathering multiple proxies of seabird health. *Marine Pollution Bulletin*, *60*(1), 7–12. http://doi.org/10.1016/j.marpolbul.2009.08.024

Mitchell, P. I., Newton, S. F., Ratcliffe, N., Eds, T. E. D., Dunn, T. E., Poyser, a D., & May, L. (2004). Seabird populations of Britain and Ireland: Results of the Seabird 2000 census. *JNCC, Poyser, London.*, (August).

Monteiro, L. R., & Furness, R. W. (1995). Seabirds as indicators of mercury in the marine environment. *Water Air and Soil Pollution*, *80*, 851–870.

Moriarty, M., Pedreschi, D., Stokes, D., Dransfeld, L., & Reid, D. G. (2016). Spatial and temporal analysis of litter in the Celtic Sea from Groundfish Survey data: Lessons for monitoring. *Marine Pollution Bulletin*. http://doi.org/10.1016/j.marpolbul.2015.12.019

Robards, M. D., Piatt, J. F., & Wohl, K. D. (1995). Increasing Frequency of Plastic Ingested by Seabirds in the Subarctic North Pacific. *Marine Pollution Bulletin*, *30*(2), 151–157. http://doi.org/0025-326X(94)00121-9

Ryan, P. G. (1988). Intraspecific Variation in Plastic Ingestion by Seabirds and the Flux of Plastic Through Seabird Populations. *The Condor*, *90*(2), 446–452. Retrieved from http://links.jstor.org/sici?sici=0010-

5422(198805)90:2%3C446:IVIPIB%3E2.0.CO;2-R

Shephard, S., van Hal, R., de Boois, I., Birchenough, S. N. R., Foden, J., O'Connor, J., … Schaber, M. (2015). Making progress towards integration of existing sampling activities to establish Joint Monitoring Programmes in support of the MSFD. *Marine Policy*, *59*(2015), 105–111. http://doi.org/10.1016/j.marpol.2015.06.004

Van Franeker, J. A., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., … Turner, D. M. (2011). Monitoring plastic ingestion by the northern fulmar Fulmarus glacialis in the North Sea. *Environmental Pollution*, *159*(10), 2609–2615. http://doi.org/10.1016/j.envpol.2011.06.008

Van Franeker, J. A., Meijboom, A., & de Jong, M. L. (2003). Marine litter monitoring by Northern Fulmars in the Netherlands 1982-2003. *Wageningen, Alterra, Alterra-Rapport 1093*.

Watanuki, Y., Daunt, F., Takahashi, A., Newell, M., Wanless, S., Sato, K., & Miyazaki, N. (2008). Microhabitat use and prey capture of a bottom-feeding top predator, the European shag, shown by camera loggers. *Marine Ecology Progress Series*, *356*, 283–293. http://doi.org/10.3354/meps07266

Wilcox, C., Van Sebille, E., & Hardesty, B. D. (2015). Threat of plastic pollution to seabirds is global, pervasive, and increasing. *Proceedings of the National Academy of Sciences*, 201502108. http://doi.org/10.1073/pnas.1502108112

CHAPTER 4:

CONTRASTING CONGENER PROFILES FOR PERSISTENT ORGANIC POLLUTANTS AND PAH MONITORING IN EUROPEAN STORM PETRELS (*HYDROBATES PELAGICUS*) BREEDING IN IRELAND: A PREEN OIL VERSUS FEATHERS APPROACH

"The question is whether any civilization can wage relentless war on life without destroying itself, and without losing the right to be called civilized."

Rachel Carson

This chapter is reproduced from the following paper, which is under review and may be accepted subject to changes:

Acampora, H., White, P., Lyashevska, O., O'Connor, I. (2017). Contrasting congener profiles for persistent organic pollutants and PAH monitoring in European Storm Petrels (*Hydrobates pelagicus*) breeding in Ireland: a preen oil vs feathers approach. Marine Environmental Research: *In Review*.

4.1. ABSTRACT

Persistent organic pollutants (POPs) are anthropogenic contaminants present in all environmental matrices, and are ubiquitous in the marine environment. Polycyclic Aromatic Hydrocarbons (PAHs) however might also arise from natural sources, such as the incomplete combustion of fossil fuels. Polychlorinated biphenyls (PCBs), Organochlorine pesticides (OCPs), Brominated Flame Retardants (BFRs) and Polycyclic Aromatic Hydrocarbons (PAHs) are chemicals of environmental concern due to their persistence in the environment and capacity to accumulate in biota. Many of these contaminants have been found to have ill-effects over wildlife and humans. Birds are known to be particularly affected through endocrine disruption and egg-shell thinning. POPs have been banned or restricted through the Stockholm Convention (2001), making monitoring essential for tracking effects of regulation. Seabirds have been used as monitoring tools for being top predators and consuming a diverse array of prey in different trophic levels. Non-destructive sampling has become widely popular using feathers and preen oil, as opposed to carcasses and internal organs. This study aimed to set baseline levels of POP concentration in a highly pelagic and abundant seabird in Ireland and the Atlantic, the European Storm Petrel, *Hydrobates pelagicus*; and to investigate the profiles of contaminant congeners in preen oil and feathers, comparatively. Mean concentrations in preen oil followed: PCB (10.1 ng/g ww) > PAH (7.1 ng/g ww) > OCP (5.4 ng/g ww) > BFR (3.9 ng/g ww), whilst mean concentrations in feathers followed the order: PAH (38.9 ng/g ww) > PCB (27.2 ng/g ww) > OCP (17.9 ng/g ww) > BFR (4.5 ng/g ww). Congener profiles highly differed between preen oil and feathers and little correlation was found between the matrices. These results demonstrate that the sampling of a single matrix alone (preen oil or feathers) might

produce confounding results on contamination in seabirds and that more than one matrix is recommended to obtain a full picture of contamination by persistent organic pollutants.

4.2. INTRODUCTION

Persistent Organic Pollutants (POPs) are chemical compounds used for various industrial purposes. Most of them are of anthropogenic origin. Polycyclic Aromatic Hydrocarbons (PAHs) however might also arise from natural sources, such as the incomplete combustion of fossil fuels. POPs include Polychlorinated biphenyls (PCBs), Organochlorine pesticides (OCs) and Brominated Flame Retardants (BFRs). Along with PAHs, these are lipophilic compounds that accumulate in the environment, in biological tissues and magnify through food webs (Jaspers et al., 2006) .

Polychlorinated biphenyls (PCBs) are used in a range of industrial products due to their stabilizing nature and low flammability (Brinkman and De Kok, 1981; Stockholm Convention, 2001). PCBs have been shown to cause endocrine disruption and consequently have been connected to population decline in birds (Jones and de Voogt, 1999; Stockholm Convention, 2001).

Organochlorine pesticides (OCPs) have been found to negatively impact nervous, immune and endocrine systems, consequently affecting reproduction (Furness, 1993). Some OCP compounds have been correlated with failed reproduction in fish eating bird populations (Bosveld and van den Berg, 2002; Giesy et al., 1994; Kubiak et al., 1989).

Various PBDE congeners have been reported to cause endocrine disruption and developmental abnormalities (Darnerud, 2008; Eng et al., 2012; Winter et al., 2013) in birds. Although they are highly hydrophobic and supposedly difficult to leach out from plastics, studies have shown that stomach oil, present in Procellariiform birds, such as Storm Petrels, may facilitate and accelerate leaching due to their high lipid content (Tanaka et al., 2015).

PAHs have been shown to bioaccumulate in invertebrate species (Meador et al., 1995) and are known to be highly toxic, carcinogenic and mutagenic (Laffon et al., 2006; Stockholm Convention, 2001). In the aquatic environment, they tend to accumulate in sediments (MacRae and Hall, 1998), affecting benthic organisms at the bottom of the

food web (Roscales et al., 2011). However, recent studies have revealed that bioaccumulation via food webs is negligible for PAHs (Nfon et al., 2008; Perugini et al., 2007; Wan et al., 2007).

The Stockholm Convention established a list of POPs that were to be banned or restricted; this treaty signed by various countries in 2001, came into effect in 2004 (Stockholm Convention, 2001). Levels of PCBs and DDT have decreased recently due to restrictions imposed by legislation (Jones and de Voogt, 1999). It is part of the treaty that countries monitor the amounts of the listed pollutants and the convention has also been amended with emerging POPs. POPs magnify through the food webs via contamination of lipid rich food (Fromant et al., 2016; Matthies et al., 2016; Safe and Hutzinger, 1984) and are globally distributed through long-range atmospheric and oceanic transport mechanisms (Jones and de Voogt, 1999). Since seabirds are top predators, contaminants might have been bioaccumulated in prey before ingested by them, making seabirds ideal candidates for persistent organic pollutant monitoring (Borlakoglu et al., 1990).

The different distribution of congeners in organisms and trophic levels is ruled by differences in bioaccumulation and metabolism that can vary in different matrices (Wang et al., 2015). For a long time, POPs have been monitored through tissue such as liver, muscle or brain (Falkowska et al., 2016; Mallory and Braune, 2012; Sagerup et al., 2009), but subsequent research has called for non-destructive ways of monitoring. The use of eggs has become widespread (Elliott et al., 2005; Jörundsdóttir et al., 2010). A single egg can provide baseline levels for a whole clutch (Van den Steen et al., 2006), but various species of seabirds produce a single egg per season, making this type of monitoring more sensitive to restrictions. Blood sampling is also considered a non-destructive and efficient approach, but it requires more cautious training and restrictive storage of samples in the field (Van Den Brink and Bosveld, 2001). The use of feathers (Jaspers et al., 2006) and subsequently, preen oil has proved successful. Preen oil has been shown to provide levels comparable to internal organs (Jaspers et al., 2008).

Many studies have focused on non-migratory species to reflect local contamination (Chen et al., 2013; Jaspers et al., 2006), but few studies have taken migratory pelagic species, from which migratory routes are known and could account for local and/or transboundary contamination. This study focused on a highly pelagic species, the

European Storm-Petrel (*Hydrobates pelagicus*), which is very abundant in the North Atlantic (over 99,000 breeding pairs in Ireland). The aim of this research was to 1) set baseline levels for four different classes of pollutants in a European Storm Petrel population breeding in Ireland; and, 2) to investigate the relative contribution of pollutants and their profiles in feathers and in preen oil.

4.3. MATERIAL AND METHODS

4.3.1. PREEN OIL AND FEATHER SAMPLING

Storm Petrels (*Hydrobates pelagicus*) were caught (n=32) using mist nets at Portacloy, County Mayo, Ireland, under license numbers C124/2015 & C125/2015 from Ireland's National Parks and Wildlife Service (NPWS) in August 2015. Each bird was weighed, had its wing span measured and was ringed. Preen oil was collected using sterile cotton swabs and metal forceps once the preen gland was exposed and gently pressed to express the oil. Swabs were placed in individual sterile glass jars with foil covered lids. Additionally, 4 breast feathers were collected from each bird and placed into individual paper envelops. Upon completion of sampling and ringing birds were released. Preen oil swabs were kept frozen at -80^{o} C, whilst feathers were kept at room temperature. Extraction methods were performed according to Espin et al., 2012; Jaspers et al., 2008; Van Den Brink, 1997.

4.3.2. PREEN OIL EXTRACTION

All utensils were washed with methanol (Merck SupraSolv). Cotton swabs were removed from glass containers using forceps and transferred into glass beakers and were spiked with internal standards. Sample jars were also rinsed with methanol, which was added to the sample. In total, 150 ml of methanol was poured into each beaker (in three aliquots) and the contents agitated for 1 minute. The combined aliquots were transferred to another beaker and heated gently on a hot plate (60^{o} C max) to remove excess solvent. The remaining 1 ml were transferred into labelled GC vials. Samples were kept frozen at -20^{o} C until subsequent analysis using Gas-Chromatography Mass-Spectrometry (GC-MS).

4.3.3. FEATHER EXTRACTION

All utensils were washed with methanol (Merck SuprSolv). Four feathers from each bird were placed in individual beakers. Feathers were washed with distilled water, using forceps to separate the barbs, and stirred. Feathers were left soaking for 20 minutes and then left to dry in folded tissue paper for 2 hours or until fully dried. After drying, each sample was weighed. Each feather sample (4) was placed inside a beaker and had internal standards added along with 15 ml of 37% HCl (Merck EMSURE) and 20 ml of 2:1 v:v n-hexane (VWR Analar Normapur): acetone (Merck SupraSolv). Beakers were covered with tin foil and placed in an oven at 37^{o} C for approximately 15 hours. 40 ml of a 3:1 v:v n-hexane:acetone solvent mixture was added to the sample before they were placed in a clean separatory funnel and shaken vigorously. The aqueous layer was removed to a beaker. The remaining organic layer was decanted into previously labelled glass vials before the aqueous layer was re-extracted with 20 ml of fresh 2:1 n-hexane:acetone solvent mixture. The organic layers were combined and transferred into a TurboVap LP (Biotage) and evaporated under Nitrogen (40^{o} C, 7.35 psi max) to 1 ml. This was subsequently transferred to pre-labelled GC vials using disposable glass pipettes. Samples were kept frozen at -20^{o} C until subsequent analysis using GC/MS.

4.3.4. GAS-CHROMATOGRAPHY MASS-SPECTROMETRY (GC-MS)

Preen oil and feather solvent extracts were then analysed for PCBs, PAHs, OCPs and BFRs. An Agilent GC-MS (5977E) with 'Masshunter' software run in EI mode with a J&W DB-1 30 m. A 0.25 mm x 0.25 um column was used. The inlet was operated in splitless mode with the temperature at 260^{o} C, the ion source at 230^{o} C and the quadrupole at 150^{o} C. The auxiliary transfer line was set at 280^{o} C. Varying column oven temperature programs were used for different compound suites. Helium was the carrier gas. The individual analytes were initially identified by MS scan (50 – 550 *m/z*) using individuals and the NIST 'structural elucidation' software. Once the compounds were identified the machine was then operated in SIM (Single Ion Monitoring) and quantification was achieved spiking samples with 100 mg of internal standards (BFR: ^{13}C PBDE – 47,153. PAH: acenaphthere$_{-d10}$, phenanthrene$_{-d10}$, chrysene$_{-d12}$ and perylene$_{-d12}$. PCB: ^{13}C-PCB 52 and 153, OCP: Pesticide Mix 20). Quality was satisfied using procedural blanks and the analysis of Certified Reference Materials (CRMs). Cod Liver

Oil (Commission of the European Communities, Community Bureau of Reference – BCR. Reference Material nº 349. Chlorobiphenyls in cod liver oil nº 0831) and NIST 1947 (Lake Michigan Fish Tissue. U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899) were used.

4.3.5. STATISTICAL ANALYSIS

A Principal Component Analysis (PCA) was conducted in R (R Core Team, 2015), version 3.2.3 using 'prcomp' package. The directions of maximum variance in high-dimensional data were identified and projected onto a smaller dimensional subspace while retaining most of the information. The calculation was done by a singular value decomposition of the centred and scaled data matrix. Original variables were transformed into a set of values of orthogonal variables called principal components (PCs). PCs are normalized linear combinations of the original predictors in a data set. PC1 captures the maximum variance and determines the direction of highest variability in the data. The following principle components (e.g. PC2, PC3) capture the remaining variance. This analysis was used to identify the main contributors to the burden of each contaminant in each matrix (preen oil and feather) and, to investigate any differences between the two matrices. Congeners that had over 50% of values below the level of detection (LOD) were excluded from statistical analysis (Behrooz et al., 2009; Jaspers et al., 2007b; Jaspers et al., 2006). Pearson's correlation was calculated for each contaminant group to see if there was any correlation between the two matrices sampled (preen oil and feathers) at the individual level and through aggregated data.

Enrichment factors (EF) were calculated for three main PCB commercial mixtures (Aroclor 1248, 1254 and 1260) using the same method used by Borlakoglu et al. (1990), in which PCB abundance concentration is compared to that of popular industrial mixtures. An enrichment factor > 1 suggests the accumulation of the pollutant, rather than the excretion. Whilst an enrichment factor < 1 suggests the metabolising of the pollutant and its removal from adipose tissue by the body (Borlakoglu et al., 1990) (Table 1).

Additionally, potential sources of PAHs were calculated using the ratio Phenanthrene/ Anthracene (P/A) and Fluoranthene/ Pyrene (Fl/ Py) (Webster et al., 2000). A P/A ratio < 10 indicates a pyrogenic source, whilst a > 10 ratio indicates a petrogenic source. A Fl/Py ratio > 1 suggests a pyrogenic source of contamination, and a < 1 ratio indicates a petrogenic source.

4.4. RESULTS

In total, 16 PCB congeners were detected in preen oil and feathers. The average total PCB in preen oil was 10.01 ng/g ww preen oil (Range: 2.75 – 18.71 ng/g ww). The average sum of 7 PCBs indicator (PCB 28, -52, -101, -118, -153, -138, -180) was 7.28 ng/g ww preen oil (Range: 2.37 – 14.62 ng/g ww). In feathers, the average total PCB was 27.2 ng/g ww feather (Range: 4.23 – 136.7 ng/g ww). The average sum of 7 PCBs was 20.2 ng/g ww feather (Range: 3.24 – 99.3 ng/g ww) (Table 15; Figure 8). Results from the PCA analysis for preen oil showed that over 81% of the variance was explained by the first three components (Cumulative proportion for principal components (PC): PC1= 0.56, PC2 = 0.71, PC3= 0.81). The congeners that had a higher relative contribution to PCB burden in preen oil were PCB- 156, - 153 and 18, respectively. For feathers, similarly, the first three components explained 82% of the variance (PC1 = 0.58, PC2= 0.73, PC3= 0.82). The highest contributing congeners were PCB 105 (closely with PCB 28), -170 and -209, respectively.

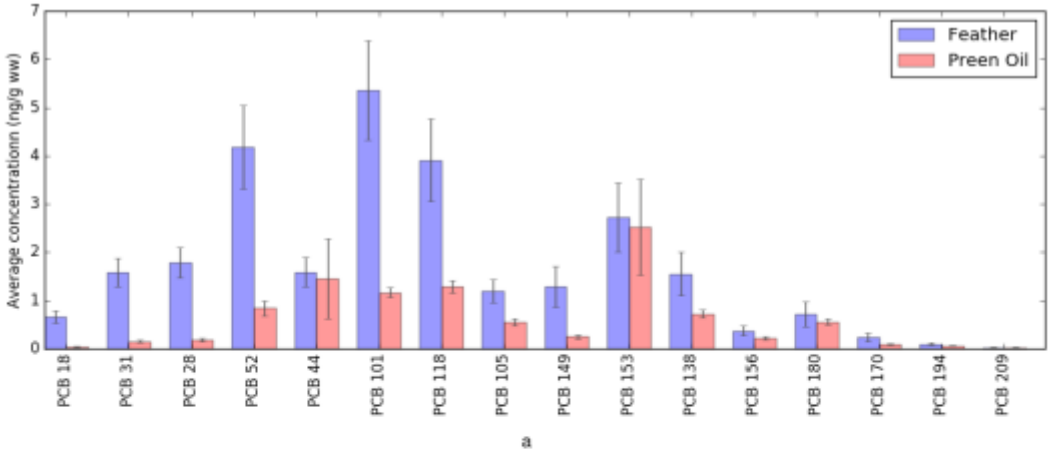
Fifteen PAH congeners were detected, however, five of these were only detected in feather samples, but not in preen oil. The average total PAH in preen oil was 7.1 ng/g ww preen oil (Range: 1.81 – 14.1 ng/g ww). In feathers, the average total PAH was 38.9 ng/g ww feather (Range: 9.59 – 218.9 ng/g ww) (Table 16; Figure 8). The P/ A ratio for PAHs in preen oil indicated a pyrogenic source (P/ A= 54.5), whilst the Fl/ Py ratio suggested a petrogenic source (Fl/Py = 0.42). These ratios for feathers however, for both P/A (19.3) and Fl/Py (0.3) suggested petrogenic sources. Results from the PCA analysis for preen oil showed that the first 5 components retained 75% of the variation (PC1= 0.26, PC2= 0.42, PC3= 0.55, PC4= 0.66, PC5= 0.75). Congeners that most contributed to the PAH burden in preen oil were Pyrene, Fluorene, Fluoranthene and Benzo(a)pyrene together, and Benzo(ghi)perylene, respectively. In feathers, the four first components explained 78% of the variation (PC1= 0.38, PC2= 0.54, PC3= 0.68,

PC4= 0.78). The most contributing congeners for PAH burden in feathers were Fluoranthene, Dibenzo (a, h) anthracene, Benzo (a) pyrene and Indeno (1, 2, 3, CD) pyrene, respectively.

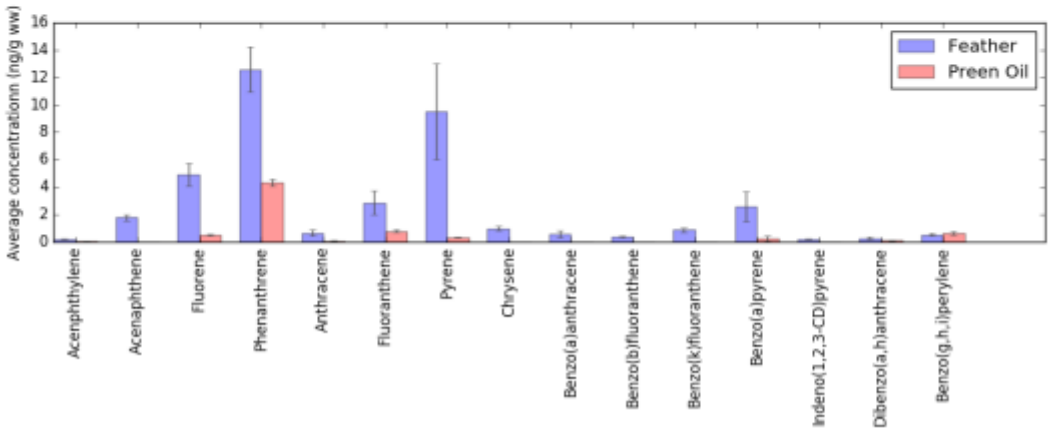
Fifteen OCP congeners were detected in preen oil and feathers. The average total OCP in preen oil was 5.4 ng/g ww preen oil (Range: 3.19 – 12.9 ng/g ww). The average total OCP in feathers was 17.9 ng/g ww feather (Range: 3.48 – 46.2 ng/g ww) (Table 17; Figure 8). PCA results for preen oil showed that 64% of the total variance was explained by the first five components (PC1= 0.19, PC2= 0.34, PC3= 0.47, PC4= 0.56, PC5= 0.64). Congeners that contributed most to OCP burden in preen oil were pp-DDD, Isodrin, Heptachlor epoxide and op-DDT, respectively. In feathers, the five first components explained 71% of the variation (PC1= 0.26, PC2= 0.41, PC3= 0.54, PC4= 0.63, PC5= 0.71). Congeners that most contributed to the OCP burden in feathers were Dieldrin together with HCB, Endosulphan B, Isobenzan and Aldrin, respectively.

Seven BFR congeners in total were detected in preen oil and feathers. One of these, however, was only detected in feathers (BFR 183). The average total BFR in preen oil was 3.91 ng/g ww preen oil (Range: 1.74 – 34.4 ng/g ww). For the feathers, average total BFR was 4.59 ng/g ww feather (Range: 1.96 – 15.9 ng/g ww) (Table 18; Figure 8). Table 19 lists the average concentration of BFR congeners in comparison to three main commercial mixtures (penta, octa and deca). Concentrations in preen oil and feathers are higher in all congeners compared to commercial mixtures, except in BFR 47 and –99 or when not available (not measured). PCA results for preen oil have shown that the three first components explained 86% of the variation (PC1= 0.48, PC2= 0.73, PC3= 0.86). The congeners that most contributed to BFR burden in preen oil were BFR 100, -183 and -153, respectively. In feathers, the four first components explained 79% of the variation (PC1= 0.25, PC2= 0.49, PC3= 0.65, PC4= 0.79). Congeners that contributed most to the BFR burden in feathers were BFR 28, -100, -153 and -183, respectively.

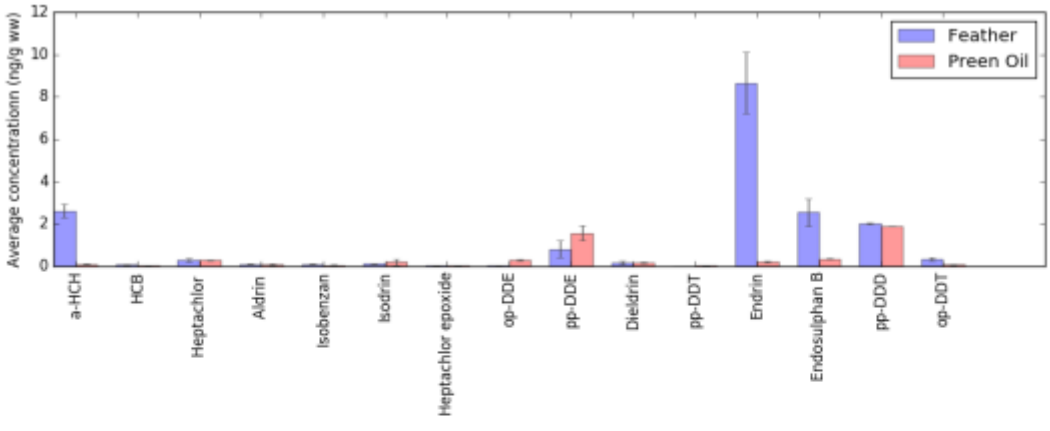
Results from the Pearson's correlation matrices showed no correlation or a weak correlation between preen oil and feathers for all contaminants investigated at the individual level (Figure 9). A positive correlation was only found for pp-DDE and BFR 47 and -154. On aggregated data however, PCB showed a moderate correlation (0.61), while PAH showed a strong correlation (0.78) between feathers and preen oil.


Feather
Preen Oil
Average concentrationn (ng/g ww)
PCB 18
PCB 31
PCB 28
PCB 52
PCB 44
PCB 101
PCB 118
PCB 105
PCB 149
PCB 153
PCB 138
PCB 156
PCB 180
PCB 170
PCB 194
PCB 209

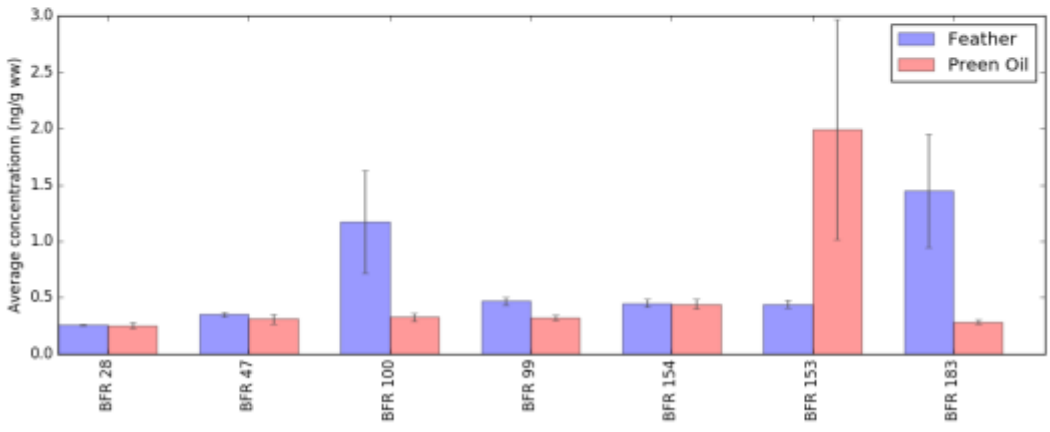
a


Feather
Preen Oil
Average concentrationn (ng/g ww)
Acenphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Chrysene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-CD)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene

b


Feather
Preen Oil
Average concentrationn (ng/g ww)
a-HCH
HCB
Heptachlor
Aldrin
Isobenzan
Isodrin
Heptachlor epoxide
op-DDE
pp-DDE
Dieldrin
pp-DDT
Endrin
Endosulphan B
pp-DDD
op-DDT

c


Feather
Preen Oil
Average concentrationn (ng/g ww)
BFR 28
BFR 47
BFR 100
BFR 99
BFR 154
BFR 153
BFR 183

d

FIGURE 8 - AVERAGE CONCENTRATION (NG/G WW) OF PCBS (A), PAHS (B), OCPS (C) AND BFRS (C) COMPARATIVELY FOR FEATHERS AND PREEN OIL PER CONGENER.

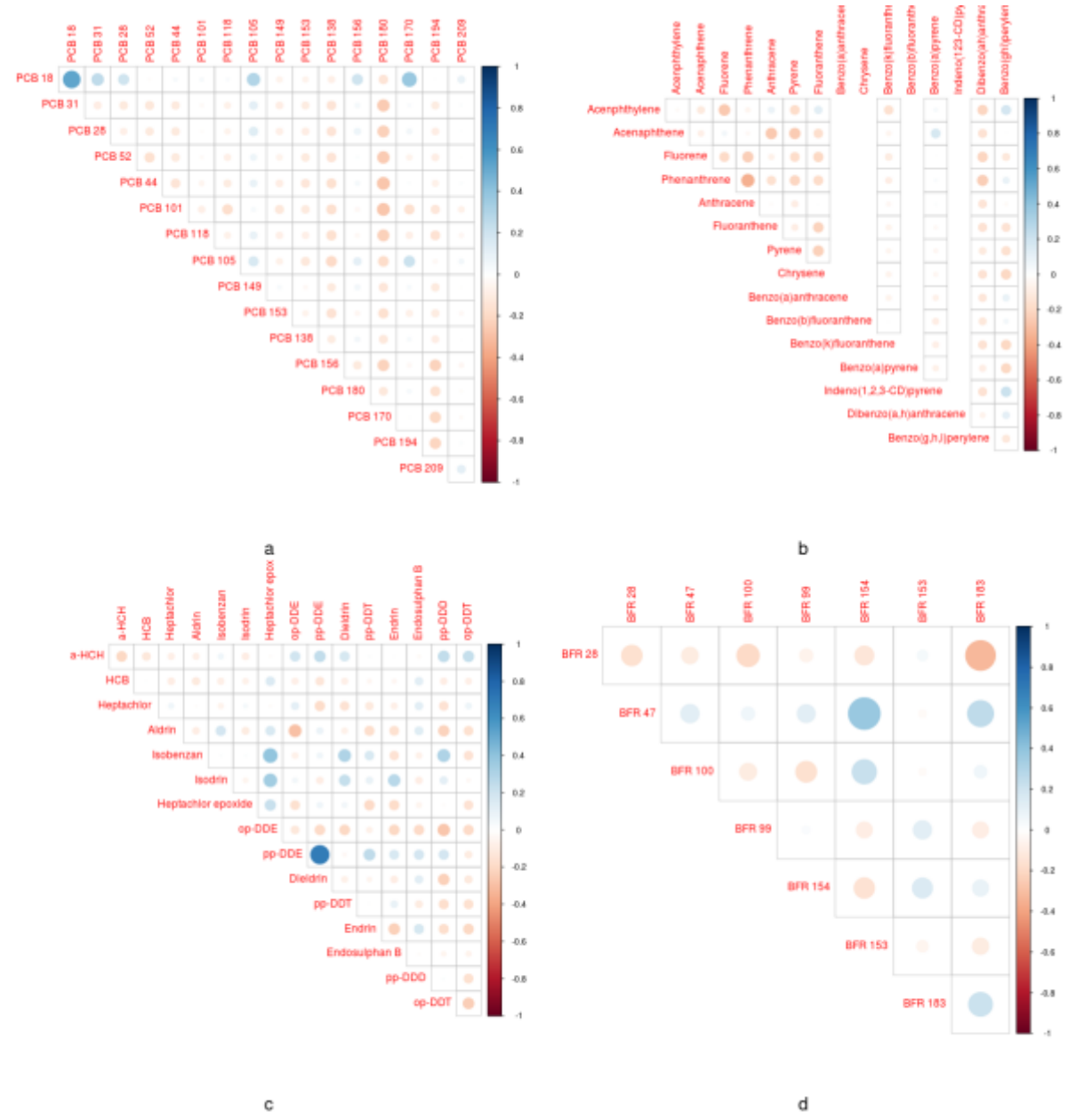


FIGURE 9 - A PEARSON'S CORRELATION MATRIX FOR PCB (A), PAH (B), OCP (C) AND BFR (D). BLUE DENOTES POSITIVE CORRELATION, RED DENOTES NEGATIVE CORRELATION. THE STRONGER CORRELATION THE DARKER THE COLOUR AND LARGER THE DOT. A STRONG POSITIVE CORRELATION IS FOUND FOR PP-DDE AND BFR 47 AND -154.

TABLE 15 - PCB CONGENERS DETECTED IN PREEN OIL AND FEATHERS ARE LISTED, INCLUDING THEIR MEAN CONCENTRATION ± STANDARD DEVIATION (SD) AND ENRICHMENT FACTORS IN COMPARISON TO THREE OF THE MOST POPULAR COMMERCIAL MIXTURES (AROCLOR 1248, 1254 AND 1260). NM = NOT MEASURED, PO= PREEN OIL, FE= FEATHERS.

PCB	Preen Oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD	Enrichment Factor (Aroclor 1248)		Enrichment Factor (Aroclor 1254)		Enrichment Factor (Aroclor 1260)	
			PO	FE	PO	FE	PO	FE
PCB 18	0.04 ± 0.08	0.66 ± 0.75	0.13	0.74	1.70	9.75	8.50	48.74
PCB 31	0.15 ± 0.19	1.58 ± 1.71	0.34	1.06	6.61	20.72	46.27	145.03
PCB 28	0.19 ± 0.21	1.79 ± 1.78	0.41	1.18	12.12	34.50	76.74	218.48
PCB 52	0.84 ± 0.89	4.18 ± 4.88	1.83	2.75	1.90	2.85	42.57	63.86
PCB 44	1.45 ± 4.7	1.59 ± 1.68	1.46	1.15	3.22	2.53	248.05	194.56
PCB 101	1.16 ± 0.58	5.36 ± 5.81	7.46	10.41	1.76	2.45	4.50	6.28
PCB 118	1.29 ± 0.7	3.90 ± 4.87	6.65	6.09	2.13	1.95	32.56	29.83
PCB 105	0.55 ± 0.45	1.19 ± 1.34	4.59	3.00	2.22	1.45	30.24	19.77
PCB 149	0.25 ± 0.23	1.29 ± 2.43	9.13	14.31	0.83	1.29	0.34	0.54
PCB 153	2.53 ± 5.6	2.73 ± 4.05	42.17	23.28	4.81	2.66	1.93	1.07
PCB 138	0.72 ± 0.48	1.55 ± 2.52	21.45	13.89	1.52	0.98	1.34	0.87
PCB	0.22 ±	0.37 ± 0.57	65.71	33.99	3.21	1.66	5.05	2.61

156	0.23							
PCB 180	0.55 ± 0.36	0.72 ± 1.49	31.91	12.49	10.00	3.91	0.59	0.23
PCB 170	0.09 ± 0.11	0.23 ± 0.50	13.94	10.73	2.14	1.65	0.27	0.21
PCB 194	0.06 ± 0.06	0.10 ± 0.11	NM	NM	73.58	35.65	0.36	0.17
PCB 209	0.02 ± 0.03	0.02 ± 0.01	NM	NM	NM	NM	NM	NM
∑ all PCBs	10.10 ± 0.66	27.26 ± 1.56						
∑ 7 PCBs	7.28 ± 1.78	20.23 ± 1.56						

TABLE 16 - PAH CONGENERS AND THEIR MEAN CONCENTRATION ± STANDARD DEVIATION (SD) IN PREEN OIL AND FEATHER SAMPLES. ND = NOT DETECTED.

PAH	Preen Oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD
Acenphthylene	0.04 ± 0.11	0.19 ± 0.20
Acenaphthene	0.01 ± 0.05	1.78 ± 1.33
Fluorene	0.50 ± 0.46	4.91 ± 4.65
Phenanthrene	4.36 ± 1.47	12.59 ± 9.27
Anthracene	0.08 ± 0.15	0.65 ± 1.34
Pyrene	0.80 ± 0.45	9.55 ± 4.93
Fluoranthene	0.34 ± 0.23	2.87 ± 19.8
Benzo(a)anthracene	ND	0.60 ± 0.95
Chrysene	ND	0.98 ± 1.46
Benzo(k)fluoranthene	ND	0.88 ± 0.46
Benzo(b)fluoranthene	ND	0.38 ± 0.88
Benzo(a)pyrene	0.24 ± 1.17	2.59 ± 6.20
Indeno(1,2,3-CD)pyrene	ND	0.20 ± 0.11

Dibenzo(a,h)anthracene	0.09 ± 0.25	0.28 ± 0.57
Benzo(g,h,i)perylene	0.65 ± 0.72	0.52 ± 0.54
∑ PAH	7.10 ± 1.06	38.96 ± 3.59

TABLE 17 - OCP MEAN CONCENTRATION ± STANDARD DEVIATION (SD) PER CONGENER MEASURED IN PREEN OIL AND FEATHER SAMPLES.

OCP	Preen Oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD
a-HCH	0.11 ± 0.05	2.63 ± 1.79
HCB	0.02 ± 0.03	0.07 ± 0.18
Heptachlor	0.28 ± 0.12	0.30 ± 0.37
Aldrin	0.10 ± 0.21	0.10 ± 0.18
Isobenzan	0.07 ± 0.05	0.10 ± 0.11
Isodrin	0.19 ± 0.73	0.11 ± 0.07
Heptachlor epoxide	0.04 ± 0.03	0.05 ± 0.04
op-DDE	0.30 ± 0.22	0.03 ± 0.02
pp-DDE	1.57 ± 1.97	0.82 ± 2.23
Dieldrin	0.16 ± 0.19	0.17 ± 0.39
pp-DDT	0.05 ± 0.06	0.02 ± 0.02
Endrin	0.20 ± 0.23	8.66 ± 8.20
Endosulphan B	0.35 ± 0.16	12.54 ± 3.57
pp-DDD	1.89 ± 0.03	2.02 ± 0.19
op-DDT	0.08 ± 0.09	0.33 ± 0.44
∑ OCP	5.40 ± 0.54	17.94 ± 2.19

TABLE 18 - BFR MEAN CONCENTRATION ± STANDARD DEVIATION (SD) PER CONGENER GIVEN IN PREEN OIL AND FEATHERS. ND = NOT DETECTED.

BFR	Preen Oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD
BFR 28	0.25 ± 0.15	0.25 ± 0.03
BFR 47	0.31 ± 0.24	0.35 ± 0.11
BFR 100	0.32 ± 0.19	1.17 ± 2.5
BFR 99	0.32 ± 0.13	0.46 ± 0.21
BFR 154	0.44 ± 0.24	0.45 ± 0.19
BFR 153	1.99 ± 5.54	0.44 ± 0.21
BFR 183	0.28 ± 0.11	1.44 ± 2.86
∑ BFR	3.91 ± 0.58	4.59 ± 0.42

TABLE 19 - PROPORTION (%) OF BFR CONGENERS FOUND IN PREEN OIL AND FEATHERS IN COMPARISON TO MAIN BFR COMMERCIAL MIXTURES (PENTA, OCTA AND DECA). PO = PREEN OIL, FE = FEATHERS, ND = NOT DETECTED, EF= ENRICHMENT FACTOR.

BFR	% PO	% FE	Penta Bromkal 70-5DE			Octa DE-79 %	Deca Bromkal 82-ODE %
			%	PO EF	FE EF		
BFR 28	7.95	5.88	0.1	79.5	58.8	ND	ND
BFR 47	8.36	8.05	42.8	0.19	0.18	ND	ND
BFR 100	8.25	26.80	7.82	1.05	3.42	ND	ND
BFR 99	11.25	10.70	44.8	0.25	0.23	ND	ND
BFR 154	50.58	10.30	2.68	18.8	3.84	1.07	ND
BFR 153	7.19	10.11	5.32	1.35	1.90	8.66	ND
BFR 183	6.99	28.17	0.33	21.1	85.3	42	ND

4.5. DISCUSSION

Data for persistent organic pollutant levels in seabirds in Ireland is limited and dates back between the 1960s-80s (Earley, 1987; Knight and Walker, 1982; Koeman et al., 1967; Moore and Tatton, 1965). PCBs and some OCPs have been measured in egg, brain and adipose tissue of guillemots, puffins, razorbills (Borlakoglu et al., 1990), tern species (Koeman et al., 1967), shags and cormorants (Borlakoglu et al., 1990; Earley, 1987; Knight and Walker, 1982; Moore and Tatton, 1965). This data is of low comparability to this work due to the difference in matrices (destructive vs non-destructive sampling) and species, but it provides an idea of the presence and levels of POPs in Irish seabird populations in the latter half of the 20th century. To our knowledge, no data is available for POPs in European Storm Petrels in Ireland.

The first aim of this work was to set baseline concentration values for the main persistent organic pollutants and PAHs found in European Storm Petrels breeding in Ireland. The mean concentration of PCBs in preen oil was 10.1 ng/g ww preen oil (∑ 7 PCBs= 7.28 ng/g ww), while for feathers was 27.2 ng/g ww feather (∑ 7 PCBs= 20.2 ng/g ww). The level in feathers differ from the ones found in Leach's Storm Petrels, a similar species in the UK, which are higher (∑ 7 PCBs= 36.2 ng/g) and in Canada, which are lower (∑ 7 PCBs= 10.6 ng/g) (Megson et al., 2014). Leach's in Alaska also had lower concentration levels in comparison to our samples from European Storm Petrels in ∑ PCB in liver composites (0.24 ng/g). Differences can be explained by the difference in matrices and the levels of industrialisation (Roscales et al., 2011).

Enrichment factor calculations suggest that the great majority of PCBs are being accumulated rather than excreted by European Storm Petrels. For the three main commercial mixtures, 78, 93 and 73% of the congeners in preen oil are being accumulated in comparison to Aroclor 1248, 1254 and 1260, respectively. In feathers, 92, 93 and 66% are accumulated rather than excreted. When compared to Aroclor 1248, the metabolisation is of low chlorinated congeners as opposed to Aroclor 1260, in which low enrichment factors are present in high chlorinated congeners. In theory, low molecular weight compounds are easier to metabolise and can be excreted over time (Borlakoglu et al., 1990; Ludwig et al., 1996). In reality, fish eating seabirds have low capacity to metabolise PCBs efficiently, regards of their molecular weight (Walker, 1990).

∑ PAH concentrations in feathers (38.9 ng/g ww) were 5-fold higher than the ones found for preen oil (7.1 ng/g ww). This value is similar, yet higher for the White-faced Storm Petrel, a related species reported by (Roscales et al., 2011) to have a mean concentration of 29.8 ng/g ww in liver. Sources of PAHs for preen oil suggested high pyrogenic and low petrogenic origins. Whilst for feathers, both ratios indicated petrogenic sources. Petrogenic sources indicate that PAHs detected originated from petroleum and crude oils (Stogiannidis and Laane, 2015), which is fitting for a bird that spends most of its time at sea. While a pyrogenic source indicates that PAHs are derived from the combustion of fuels (Stogiannidis and Laane, 2015). Since preen oil is renewed and metabolised constantly, it makes sense that it could contain PAH from different sources, whilst feathers could be retaining them from time spent at sea. PAHs have been demonstrated not to have high degrees of bioaccumulation (Nfon et al., 2008; Perugini et al., 2007; Wan et al., 2007), thus it is more likely that they have been acquired from the environment rather than from prey items.

OCP concentrations were approximately 2-fold higher in feathers (17.94 ng/g ww) than in preen oil (5.40 ng/g ww). ∑ DDT was higher in preen oil (0.13 ng/g ww) and feathers (0.35 ng/g ww) in European Storm Petrels from our study than from liver composites of the related Leach's Storm Petrel in Alaska (0.007 ng/g) (Ricca et al., 2008). The same is true for pp-DDE, which was 0.067 ng/g for Leach's Storm Petrels, in comparison to our species' concentration in preen oil (1.57 ng/g ww) and feathers (0.82 ng/g ww). Additionally, concentrations were lower for ∑ DRIN in Leach's (0.007 ng/g) in comparison to 0.65 ng/g ww in preen oil and 9.04 ng/g ww for feathers in European Storm Petrels. Concentrations were similar for ∑ CHLOR in Leach's (0.027 ng/g) in comparison with 0.032 ng/g ww in preen oil and 0.35 ng/g ww for feathers in birds from our study (Ricca et al., 2008)

BFR concentrations in eggs of Leach's Storm Petrels were similar (3.38 ng/g) (Elliott et al., 2005) to that found in our studies with preen oil and feathers (3.91 and 4.59 ng/g ww), respectively. Brominated flame retardants have become of greater concern recently due to plastic pollution at sea (Jaspers et al., 2006; Karlsson et al., 2006; Miller et al., 2014; Tanaka et al., 2013). Many of these components are used as plastic additives and have been found to leach from plastic products, not only at sea, but also when plastics are ingested by seabirds (Tanaka et al., 2015). Procellariiform birds (such as the European Storm Petrel) are a family of birds from which many species have

a tendency not only to ingest plastic, but also to accumulate it in their digestive tract due to a narrow connector between the gizzard and the proventriculus, which prevents regurgitation and can consequently affect excretion (Van Franeker et al., 2011). These birds are also known for containing a specific lipid rich stomach oil, which they use as a defence mechanism by squirting it at predators when they feel threatened (Ackman, 1989; Connan et al., 2007). Research has shown that BFRs are more prone to leaching from plastics when immersed in stomach oil rather than in sea water (Tanaka et al., 2015), indicating that this family of birds could be more affected by potential BFR leaching and contamination than other organisms or birds. Plastic ingestion has been reported for other species of petrels (Bond and Lavers, 2013; Colabuono et al., 2009; Ryan, 2015; van Franeker and Bell, 1988), but not for the European Storm Petrel. Enrichment factors were calculated in comparison to the penta-DE mixture. In preen oil, 43% of the congeners are being accumulated rather than excreted, whilst in feathers, the number increases to 71%.

There are many factors that can influence the burden of persistent organic pollutants. Feathers receive pollutants through the blood supply while growing. Once they're fully grown, the blood supply stops and levels receive no internal input from contamination (Jaspers et al., 2004). However, feathers can have their burdens increased by external contamination and the preening of feathers (Jaspers et al., 2008, 2007a; Van Den Brink, 1997). Time of moult is therefore an important factor when quantifying levels in feathers. In our study, storm petrels were sampled during the breeding season. The European Storm Petrel is known to moult during breeding (Ginn and Melville, 1983), meaning that feathers were receiving blood supply along with its contaminants. This might explain why levels in feathers were much higher than levels in preen oil in the same individuals. Feathers would have the additional burden of blood, preening and external contamination, although the latter has been considered negligible (Jaspers et al., 2007a). Migration is another important factor contributing to variation in contaminant levels (Perkins and Barclay, 1997). European Storm Petrels winter in southern Africa and spend their breeding season in Europe (Robert et al., 1998). Long migrations such as these take a toll into a bird's energy reserves. If at the beginning of a long-haul migration a bird's fat reserves are high, at the end, they are very low and the mobilization of lipid reserves to attend a bird's demands can increase contaminant concentration, the same way starvation can (Perkins and Barclay, 1997). Starving birds

are expected to have higher contaminant concentration due to mobilisation of their fat reserves (Barron et al., 1995). Birds from this study were sampled in late August, meaning they were at the end of their breeding season, which was also confirmed by repairing brooding patches. By then, it is expected that body mass has been regained to cope with energetic breeding demands. This assumption was supported by data on the mass of the birds sampled, which ranged between 22.1 – 27.4 g (Sanz-Aguilar et al., 2009). Breeding also means that females can transfer contaminants to eggs and alleviate their own burden (Bustnes et al., 2008). In this study, sexing of live birds was not possible, therefore it is not possible to address sex-specific individual levels of persistent organic pollutants, but it is important to consider that during the breeding season eggs are a pathway for excretion of such contaminants for female birds. Another factor that could influence the way pollutants are perceived during the breeding season is that some birds might change their diet during this period (Hammer et al., 2016), in order to provide more nutritious and energetic food to their young, perhaps making more use of higher trophic organisms. Persistent organic pollutants are known to bio-accumulate throughout the food web, making predators more vulnerable to such contaminants (Jones and de Voogt, 1999; Walker, 1990). The diet of the European Storm Petrels in the UK consists mainly of zooplankton (52%) and a further 37% on benthic organisms (Albores-Barajas et al., 2011; D'elbeei and Hemer, 1998). This diet favours low trophic level organisms; thus, it is consistent with the relatively low level of contaminants found in this study. In addition, pelagic birds are less exposed to industrialisation and contamination than birds of coastal habitats (Elliott et al., 2005).

Our study has demonstrated that the sampling of live birds can be efficient in quantifying contaminant burden is seabird species. This study has quantified and set baseline levels for persistent organic pollutant burden in the European Storm Petrel. Our statistical analyses have shown none or weak correlation between preen oil and feathers at the individual level. Between groups of contaminants, a moderate and a strong correlation was seen for PCBs and PAHs. However, congener profiles have shown to differ completely. Thus, choosing a specific matrix can show confounding levels of contaminants. Feathers had higher concentrations of pollutants in comparison to preen oil. While this alone could lead to misleading results when one samples preen oil only, differences in congener profiles have shown that a single matrix might not be sufficient, but sampling different matrices in the same birds might be a more realistic and suitable

way to monitor organic pollutants in birds. As mentioned before, feather levels are expected to be higher due to the input of preen oil itself on the feathers in the act of preening, along with blood supply and potential external contamination. In this study, levels in feathers were 2-5-fold higher than in preen oil, except in BFRs, in which similar levels were obtained in both matrices. However, the fact that congener signatures are different between matrices suggests that utilising feathers or preen oil alone is not enough to obtain an accurate picture of contamination in birds. European Storm Petrels expressed little preen oil when being sampled, in comparison to other species, nevertheless in most contaminants, congeners were present consistently between feathers and preen oil equally.

4.6. ACKNOWLEDGEMENTS

This work was supported by Science Without Borders (CAPES, Brazil, BEX: 1269-13-5). Many thanks to BirdWatch Ireland. Thanks to Niall Keogh and Declan Manley for assistance in the field. Thanks to Danilo Hirota, Killian Coakley and Bill Delee for assistance in the lab.

4.7. LITERATURE CITED

Ackman, R.G., 1989. Marine biogenic lipids, fats and oils. CRC Press.

Albores-Barajas, Y.V., Riccato, F., Fiorin, R., Massa, B., Torricelli, P., Soldatini, C., 2011. Diet and diving behaviour of European Storm Petrels Hydrobates pelagicus in the Mediterranean (ssp. melitensis). Bird Study 58, 208–212. doi:10.1080/00063657.2011.560244

Barron, M.G., Galbraith, H., Beltman, D., 1995. Comparative reproductive and developmental toxicology of PCBs in birds. Comp. Biochem. Physiol. Part C Pharmacol. Toxicol. Endocrinol. 112, 1–14.

Behrooz, R.D., Esmaili-Sari, A., Ghasempouri, S.M., Bahramifar, N., Covaci, A., 2009. Organochlorine pesticide and polychlorinated biphenyl residues in feathers of birds from different trophic levels of South-West Iran. Environ. Int. 35, 285–290.

doi:10.1016/j.envint.2008.07.001

Bond, A.L., Lavers, J.L., 2013. Effectiveness of emetics to study plastic ingestion by Leach's Storm-petrels (Oceanodroma leucorhoa). Mar. Pollut. Bull. 70. doi:10.1016/j.marpolbul.2013.02.030

Borlakoglu, J., Wilkins, J., Walker, C., Dils, R., 1990. Polychlorinated Biphenyls (PCBs) In Fish-Eating Sea Birds: Molecular Features of PCB Isomers and Congeners in Adipose Tissue of Male and Female Razorbills (Alca torda) of British and Irish Coastal Waters. Comp. Biochem. Physiol. C-Pharmacology Toxicol. Endocrinol. 97, 151–160.

Borlakoglu, J.T., Wilkins, J.P.G., Walker, C.H., Dils, R.R., 1990. Polychlorinated-Biphenyls (Pcbs) in Fish-Eating Sea Birds .1. Molecular-Features of Pcb Isomers and Congeners in Adipose-Tissue of Male and Female Razorbills (Alca-Tarda) of British and Irish Coastal Waters. Comp. Biochem. Physiol. C-Pharmacology Toxicol. Endocrinol. 97, 151–160.

Bosveld, A.T.C., van den Berg, M., 2002. Reproductive failure and endocrine disruption by organohalogens in fish-eating birds. Toxicology 181–182, 155–159. doi:http://dx.doi.org/10.1016/S0300-483X(02)00273-1

Brinkman, U.A.T., De Kok, A., 1981. Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins And Related Products, Production, Properties And Usage. Chem. Informationsd. 12.

Bustnes, J.O., Fauchald, P., Tveraa, T., Helberg, M., Skaare, J.U., 2008. The potential impact of environmental variation on the concentrations and ecological effects of pollutants in a marine avian top predator. Environ. Int. 34, 193–201.

Chen, D., Martin, P., Burgess, N.M., Champoux, L., Elliott, J.E., Forsyth, D.J., Idrissi, A., Letcher, R.J., 2013. European starlings (Sturnus vulgaris) suggest that landfills are an important source of bioaccumulative flame retardants to Canadian terrestrial ecosystems. Environ. Sci. Technol. 47, 12238–12247.

Colabuono, F.I., Barquete, V., Domingues, B.S., Montone, R.C., 2009. Plastic ingestion by Procellariiformes in Southern Brazil. Mar. Pollut. Bull. 58, 93–96. doi:10.1016/j.marpolbul.2008.08.020

Connan, M., Cherel, Y., Mayzaud, P., 2007. Lipids from stomach oil of procellariiform seabirds document the importance of myctophid fish in the Southern Ocean. Limnol. Oceanogr. 52, 2445–2455.

D'elbeei, J., Hemer, G., 1998. Diet and Foraging Behaviour of the British Storm Petrel Hydrobates pelagicus in the Bay of Biscay During Summer. Ardea 86, 1–10.

Darnerud, P.O., 2008. Brominated flame retardants as possible endocrine disrupters. Int. J. Androl. 31, 152–160.

Earley, J.J., 1987. Pesticides and PCBs in seabirds and coastal pollution. Biol. Indic. Pollut. 193, 200.

Elliott, J., Wilson, L.K., Wakeford, B., 2005. Polybrominated Diphenyl Ether Trends in Eggs of Marine and Freshwater Birds from British Columbia , Canada , 1979 - 2002. Environ. Sci. Technol. 39, 5584–5591.

Eng, M.L., Elliott, J.E., MacDougall-Shackleton, S.A., Letcher, R.J., Williams, T.D., 2012. Early Exposure to 2,2′,4,4′,5-Pentabromodiphenyl Ether (BDE-99) Affects Mating Behavior of Zebra Finches. Toxicol. Sci. 127, 269–276. doi:10.1093/toxsci/kfs076

Espin, S., Martinez-Lopez, E., Maria-Mojica, P., Garcia-Fernandez, A.J., 2012. Razorbill (Alca torda) feathers as an alternative tool for evaluating exposure to organochlorine pesticides. Ecotoxicology 21, 183–190. doi:10.1007/s10646-011-0777-z

Falkowska, L., Reindl, A.R., Grajewska, A., Lewandowska, A.U., 2016. Organochlorine contaminants in the muscle, liver and brain of seabirds (Larus) from the coastal area of the Southern Baltic. Ecotoxicol. Environ. Saf. 133, 63–72. doi:10.1016/j.ecoenv.2016.06.042

Fromant, A., Carravieri, A., Bustamante, P., Labadie, P., Budzinski, H., Peluhet, L., Churlaud, C., Chastel, O., Cherel, Y., 2016. Wide range of metallic and organic contaminants in various tissues of the Antarctic prion, a planktonophagous seabird from the Southern Ocean. Sci. Total Environ. 544, 754–764. doi:10.1016/j.scitotenv.2015.11.114

Furness, R.W., 1993. Birds as monitors of pollutants, in: Furness, R.W., Greenwood, J.J.D. (Eds.), Birds as Monitors of Environmental Change. Springer Netherlands, Dordrecht, pp. 86–143. doi:10.1007/978-94-015-1322-7_3

Giesy, J.P., Ludwig, J.P., Tillitt, D.E., 1994. Dioxins, Dibenzofurans, PCBs and Colonial, Fish-Eating Water Birds, in: Schecter, A. (Ed.), Dioxins and Health. Springer US, Boston, MA, pp. 249–307. doi:10.1007/978-1-4899-1462-0_9

Ginn, H.B., Melville, D.S., 1983. Moult in birds: BTO guide. British Trust for Ornithology.

Hammer, S., Nager, R.G., Alonso, S., McGill, R.A.R., Furness, R.W., Dam, M., 2016. Legacy Pollutants are Declining in Great Skuas (Stercorarius skua) but Remain Higher in Faroe Islands than in Scotland. Bull. Environ. Contam. Toxicol. doi:10.1007/s00128-016-1856-x

Jaspers, V., Dauwe, T., Pinxten, R., Bervoets, L., Blust, R., Eens, M., 2004. The importance of exogenous contamination on heavy metal levels in bird feathers. A field experiment with free-living great tits, Parus major. J. Environ. Monit. 6, 356–360.

Jaspers, V.L.B., Covaci, A., Deleu, P., Neels, H., Eens, M., 2008. Preen oil as the main source of external contamination with organic pollutants onto feathers of the common magpie (Pica pica). Environ. Int. 34, 741–748. doi:10.1016/j.envint.2007.12.002

Jaspers, V.L.B., Covaci, A., Van den Steen, E., Eens, M., 2007a. Is external contamination with organic pollutants important for concentrations measured in bird feathers? Environ. Int. 33, 766–772. doi:10.1016/j.envint.2007.02.013

Jaspers, V.L.B., Covaci, A., Voorspoels, S., Dauwe, T., Eens, M., Schepens, P., 2006. Brominated flame retardants and organochlorine pollutants in aquatic and terrestrial predatory birds of Belgium: levels, patterns, tissue distribution and condition factors. Environ. Pollut. 139, 340–352.

Jaspers, V.L.B., Oorspoels, S., Covaci, A., Eens, M., 2006. Can predatory bird feathers be used as a non-destructive biomonitoring tool of organic pollutants? Biol. Lett. 2, 283–5. doi:10.1098/rsbl.2006.0450

Jaspers, V.L.B., Voorspoels, S., Covaci, a., Lepoint, G., Eens, M., 2007b. Evaluation of the usefulness of bird feathers as a non-destructive biomonitoring tool for organic pollutants: A comparative and meta-analytical approach. Environ. Int. 33, 328–337. doi:10.1016/j.envint.2006.11.011

Jones, K., de Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. Environ. Pollut. 100, 209–221. doi:10.1016/S0269-7491(99)00098-6

Jones, K.C., de Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. Environ. Pollut. 100, 209–221. doi:http://dx.doi.org/10.1016/S0269-7491(99)00098-6

Jörundsdóttir, H., Löfstrand, K., Svavarsson, J., Bignert, A., Bergman, Å., 2010. Organochlorine compounds and their metabolites in seven icelandic seabird species - A comparative study. Environ. Sci. Technol. 44, 3252–3259. doi:10.1021/es902812x

Karlsson, M., Ericson, I., van Bavel, B., Jensen, J.-K., Dam, M., 2006. Levels of brominated flame retardants in Northern Fulmar (Fulmarus glacialis) eggs from the Faroe Islands. Sci. Total Environ. 367, 840–846.

Knight, G.C., Walker, C.H., 1982. A study of the hepatic microsomal monooxygenase of sea birds and its relationship to organochlorine pollutants. Comp. Biochem. Physiol. Part C Comp. Pharmacol. 73, 211–221.

Koeman, J.H., Oskamp, A.A.G., Veen, J., Brouwer, E., Rooth, J., Zwart, P., vd Broek, E., Van Genderen, H., 1967. Insecticides as a factor in the mortality of the sandwich tern (Sterna sandvicensis). Meded. Rijksfac. Landbouwwet. Gent 32, 841.

Kubiak, T.J., Harris, H.J., Smith, L.M., Schwartz, T.R., Stalling, D.L., Trick, J.A., Sileo, L., Docherty, D.E., Erdman, T.C., 1989. Microcontaminants and reproductive impairment of the Forster's tern on Green Bay, Lake Michigan-1983. Arch. Environ. Contam. Toxicol. 18, 706–727. doi:10.1007/BF01225009

Laffon, B., Fraga-Iriso, R., Pérez-Cadahía, B., Méndez, J., 2006. Genotoxicity associated to exposure to Prestige oil during autopsies and cleaning of oil-contaminated birds. Food Chem. Toxicol. 44, 1714–1723.

Ludwig, J.P., Colborn, T.L., Giesvi, J.P., 1996. Persistent synthetic chlorinated hydrocarbons in albatross tissue samples from Midway Atoll. Environ. Toxicol. Chem. 15, 1793–1800.

MacRae, J.D., Hall, K.J., 1998. Biodegradation of polycyclic aromatic hydrocarbons (PAH) in marine sediment under denitrifying conditions. Water Sci. Technol. 38, 177–185.

Mallory, M.L., Braune, B.M., 2012. Tracking contaminants in seabirds of Arctic Canada: temporal and spatial insights. Mar. Pollut. Bull. 64, 1475–1484.

Matthies, M., Solomon, K., Vighi, M., Gilman, A., Tarazona, J. V, 2016. The origin and evolution of assessment criteria for persistent, bioaccumulative and toxic (PBT) chemicals and persistent organic pollutants (POPs). Environ. Sci. Process. Impacts 18, 1114–1128.

Meador, J.P., Stein, J.E., Reichert, W.L., Varanasi, U., 1995. Bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms, in: Reviews of Environmental Contamination and Toxicology. Springer, pp. 79–165.

Megson, D., Brown, T.A., Johnson, G.W., O'Sullivan, G., Bicknell, A.W.J., Votier, S.C., Lohan, M.C., Comber, S., Kalin, R., Worsfold, P.J., 2014. Identifying the provenance of Leach's storm petrels in the North Atlantic using polychlorinated biphenyl signatures derived from comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. Chemosphere 114, 195–202. doi:10.1016/j.chemosphere.2014.04.061

Miller, A., Elliott, J.E., Elliott, K.H., Guigueno, M.F., Wilson, L.K., Lee, S., Idrissi, A., 2014. Spatial and temporal trends in brominated flame retardants in seabirds from the Pacific coast of Canada. Environ. Pollut. 195, 48–55. doi:10.1016/j.envpol.2014.08.009

Moore, N.W., Tatton, J., 1965. Organochlorine insecticide residues in the eggs of sea birds.

Nfon, E., Cousins, I.T., Broman, D., 2008. Biomagnification of organic pollutants in benthic and pelagic marine food chains from the Baltic Sea. Sci. Total Environ. 397, 190–204.

Perkins, C.R., Barclay, J.S., 1997. Accumulation and mobilization of organochlorine contaminants in wintering greater scaup. J. Wildl. Manage. 444–449.

Perugini, M., Visciano, P., Giammarino, A., Manera, M., Di Nardo, W., Amorena, M., 2007. Polycyclic aromatic hydrocarbons in marine organisms from the Adriatic Sea, Italy. Chemosphere 66, 1904–1910.

R Core Team, 2015. A language and environment for statistical computing.

Ricca, M.A., Miles, A.K., Anthony, R.G., 2008. Sources of organochlorine contaminants and mercury in seabirds from the Aleutian archipelago of Alaska: inferences from spatial and trophic variation. Sci. Total Environ. 406, 308–323.

Robert, J., Medeiros, R.J., Pollard, A.L., 1998. Evidence for foraging by nocturnal inter-tidal European Storm-petrels Hydrobates pelagicus during migration researchers 87–96.

Roscales, J.L., Gonzalez-Solis, J., Calabuig, P., Jimenez, B., 2011. Interspecies and spatial trends in polycyclic aromatic hydrocarbons (PAHs) in Atlantic and Mediterranean pelagic seabirds. Environ. Pollut. 159, 2899–2905. doi:10.1016/j.envpol.2011.04.034

Roscales, J.L., González-Solís, J., Muñoz-Arnanz, J., Jiménez, B., 2011. Geographic and trophic patterns of OCs in pelagic seabirds from the NE Atlantic and the Mediterranean: a multi-species/multi-locality approach. Chemosphere 85, 432–440.

Ryan, P.G., 2015. How quickly do albatrosses and petrels digest plastic particles? Environ. Pollut. 207, 438–440. doi:10.1016/j.envpol.2015.08.005

Safe, S., Hutzinger, O., 1984. Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs): biochemistry, toxicology, and mechanism of action. CRC Crit. Rev. Toxicol. 13, 319–395.

Sagerup, K., Helgason, L.B., Polder, A., Strøm, H., Josefsen, T.D., Skåre, J.U., Gabrielsen, G.W., 2009. Persistent organic pollutants and mercury in dead and dying glaucous gulls (Larus hyperboreus) at Bjørnøya (Svalbard). Sci. Total Environ. 407, 6009–6016.

Sanz-Aguilar, A., Massa, B., Lo Valvo, F., Oro, D., Minguez, E., Tavecchia, G., 2009. Contrasting age-specific recruitment and survival at different spatial scales: a case study with the European storm petrel. Ecography (Cop.). 32, 637–646.

Stockholm Convention, 2001, 2001. Stockholm Convention on Persistent Organic Pollutants. p. http://chm.pops.int/.

Stogiannidis, E., Laane, R., 2015. Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: an overview of possibilities, in: Reviews of Environmental Contamination and Toxicology. Springer, pp. 49–133.

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., Watanuki, Y., 2015. Facilitated leaching of additive-derived PBDEs from plastic by seabirds' stomach oil and accumulation in tissues. Environ. Sci. Technol. 150901174241000. doi:10.1021/acs.est.5b01376

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., Watanuki, Y., 2013. Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics. Mar. Pollut. Bull. 69, 219–222.

Van Den Brink, N.W., 1997. Directed transport of volatile organochlorine pollutants to polar regions: The effect of the contamination pattern of Antarctic seabirds. Sci. Total Environ. 198, 43–50. doi:10.1016/S0048-9697(97)05440-5

Van Den Brink, N.W., Bosveld, A.T.C., 2001. PCB concentrations and metabolism patterns in common terns (Sterna hirundo) from different breeding colonies in The Netherlands. Mar. Pollut. Bull. 42, 280–285. doi:10.1016/S0025-326X(00)00151-X

Van den Steen, E., Dauwe, T., Covaci, A., Jaspers, V.L.B., Pinxten, R., Eens, M., 2006. Within-and among-clutch variation of organohalogenated contaminants in eggs of great tits (Parus major). Environ. Pollut. 144, 355–359.

van Franeker, J.A., Bell, P.J., 1988. Plastic ingestion by petrels breeding in Antarctica. Mar. Pollut. Bull. 19, 672–674. doi:10.1016/0025-326X(88)90388-8

Van Franeker, J. a., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., Hansen, P.L., Heubeck, M., Jensen, J.K., Le Guillou, G., Olsen, B., Olsen, K.O.,

Pedersen, J., Stienen, E.W.M., Turner, D.M., 2011. Monitoring plastic ingestion by the northern fulmar Fulmarus glacialis in the North Sea. Environ. Pollut. 159, 2609–2615. doi:10.1016/j.envpol.2011.06.008

Walker, C.H., 1990. Persistent pollutants in fish-eating sea birds - bioaccumulation, metabolism and effects. Aquat. Toxicol. 17, 293–324. doi:10.1016/0166-445X(90)90014-G

Wan, Y., Jin, X., Hu, J., Jin, F., 2007. Trophic dilution of polycyclic aromatic hydrocarbons (PAHs) in a marine food web from Bohai Bay, North China. Environ. Sci. Technol. 41, 3109–3114.

Wang, J., Caccamise, S. a. L., Woodward, L.A., Li, Q.X., 2015. Polychlorinated Biphenyls in the Plasma and Preen Oil of Black-Footed Albatross (Diomedea nigripes) Chicks and Adults on Midway Atoll, North Pacific Ocean. PLoS One 10, e0123041. doi:10.1371/journal.pone.0123041

Webster, L., McIntosh, A.D., Moffat, C.F., Dalgarno, E.J., Brown, N.A., Fryer, R.J., 2000. Analysis of sediments from Shetland Island voes for polycyclic aromatic hydrocarbons, steranes and triterpanes. J. Environ. Monit. 2, 29–38.

Winter, V., Williams, T.D., Elliott, J.E., 2013. A three-generational study of In ovo exposure to PBDE-99 in the zebra finch. Environ. Toxicol. Chem. 32, 562–568.

CHAPTER 5:

THE PRESENCE OF POLLUTANTS IN A BREEDING COMMON TERN (*STERNA HIRUNDO*) POPULATION IN IRELAND: POPS AND PLASTICS

"But man is a part of nature, and his war against nature is inevitably a war against himself."

Rachel Carson

This chapter is reproduced from the following published paper, which can be found on Appendix 1:

Acampora, H., White, P., Lyashevska, O., O'Connor, I. (2017). The presence of pollutants in breeding Common Tern (*Sterna hirundo*) populations in Ireland: POPs and Plastics. Environmental Science and Pollution Research: 24.14: (13025-13035). https://doi.org/10.1007/s11356-017-8931-7

5.1. ABSTRACT

Persistent organic pollutants (POPs) are chemical compounds of environmental concern due to their toxic, persistent nature and their ability to bio-accumulate in biological tissue. Seabirds, for often being at the top of the food web, have been used as monitors of environmental pollutants. Adverse effects caused by POPs have been reported in Common Terns (*Sterna hirundo*) since the 1970s. Egg shell thinning, embryo and hatchling deformities have been reported for this species. Environmental legislation, such as the Oslo-Paris Convention (OSPAR) has agreed on the monitoring of concentration of POPs in Common Terns. This study set out to investigate contemporary concentrations of PCBs, polycyclic aromatic hydrocarbons (PAHs), OCPs and Brominated Flame Retardants (BFRs) in Common Terns breeding in Ireland, along with congener profiles. Investigation was conducted in live (n=15) and dead birds (n=20) to test for the efficiency of different methodologies using preen oil and feathers versus liver and preen gland. Mean concentrations of POPs followed the order: PCB (36.48 ng/g ww feather) > PAH (30.01 ng/g ww feather) > OCP (13.36 ng/g ww feather) > BFR (1.98 ng/g ww feather) in live birds; and PAH (46.65 ng/g ww preen gland) > PCB (44.11 ng/g ww preen gland) > OCP (15.15 ng/g ww liver) > BFR (5.07 ng/g ww liver) in dead birds. Comparison of contaminant results with toxicity pre-established levels concluded that this population of Common Terns in Ireland is not at risk of anomalies caused by POPs. However, some levels are higher in comparison to the ones established by OSPAR's EcoQO and must be monitored periodically.

5.2. INTRODUCTION

Persistent organic pollutants (POPs) are chemical compounds of environmental concern due to their environmentally resilient and toxic nature. Such compounds are generally man-made or the result of anthropogenic activities and have become ubiquitous in the environment (Jones & de Voogt, 1999; Pariatamby & Kee, 2016). POPs have been used for many purposes in industrial, commercial and agricultural activities (Stockholm Convention, 2001; Van Den Brink, 1997), but in past decades have been found to cause ill-effects on humans and, mainly wildlife (Jones & de Voogt, 1999; Stockholm Convention, 2001).

Persistent organic pollutants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and brominated flame retardants (BFRs) have been found to cause endocrine disruption and to have carcinogenic effects (Barron et al., 1995; UNEP, 2001). These compounds can be biomagnified along the food web reaching levels of toxicological importance in top predators (Jaspers et al., 2006). In birds, for instance, PCBs were found responsible for egg shell thinning in many raptor species in the 1970s causing concerning population decline (Tanabe et al., 1984). POPs have been correlated to low reproductive success in fish-eating birds (Giesy et al., 1994), embryonic abnormalities (Gilbertson & Fox, 1977), reduced growth (Gilbertson & Fox, 1977) and physiological and biochemical alterations (Elliott et al., 1989). When such severe ill-effects were brought to light by research, legislation throughout the world imposed ban or restriction to most well-known POPs (Stockholm Convention, 2001). The Stockholm Convention came into force in 2004 and with it, the need to monitor concentrations and levels in all environmental matrices, including biota (Stockholm Convention, 2001).

Measuring the concentration of pollutants in birds is often done through destructive sampling, where a certain number of birds were sacrificed, although sometimes found dead, and serve as proxy for a given population. Such sampling would involve the collection of internal organs such as liver, muscle or brain (Falkowska et al., 2016; Roscales et al., 2011). Eggs are an alternative to destructive sampling (Elliott et al., 2005; Moore & Tatton, 1965; Mora et al., 2016; Peck et al., 2016), but when certain

species of birds lay a single egg per season care should be taken to make sure such species would relay. Non-destructive sampling techniques became necessary and feathers started being used as a proxy for contamination levels in internal organs (Jaspers et al., 2007; Jaspers et al., 2011; Van den Steen et al., 2007). Additionally, preen oil has also been regarded as a non-destructive technique (Wang et al., 2015; Yamashita et al., 2007).

Persistent organic pollutant concentrations in Common Terns (*Sterna hirundo*) have been measured in many parts of the world since the 1960s (Bosveld et al., 1995; Gilbertson et al., 1976; Scharenberg, 1991; Van Den Brink & Bosveld, 2001; Custer et al., 2016). POPs were found to cause death, feminization of male embryos and other embryonic developmental abnormalities in this species (Becker et al., 1993; Fox, 1976; Hays & Risebrough, 1972; Hoffman et al., 1998; Hoffman et al., 1993; Scharenberg, 1991). Since then, toxicity levels over which embryonic development would be affected have been established (Hays & Risebrough, 1972; Hoffman et al., 1998; Scharenberg, 1991).

Monitoring of POPs in eggs of Common Terns is one of the Oslo-Paris Convention's (OSPAR) Ecological Quality Objectives (EcoQO) (OSPAR, 2010). EcoQOs establish threshold contaminant levels for certain species and parties must monitor levels to meet the treaty's requirements (Dittmann et al., 2012).

Common Terns are a highly migratory seabird , globally distributed, with tropical wintering areas in the south and northern breeding areas (Austin, 1953). Their diet consists mainly of fish (Massias & Becker, 1990). In Ireland, there are over two and a half thousand pairs of breeding Common Terns (Mitchell et al., 2004). Main threats to Common Tern populations are habitat loss and pollution (Mitchell et al., 2004). To our knowledge, there are no persistent organic pollutant data for Common Terns breeding in Ireland. Most recent published data for closely related species such as Roseate (*Sterna dougallii*) and Sandwich (*Sterna sandvicensis*) Terns date from 1965 (Koeman et al., 1967). Given the absence of data in Ireland for a species of conservation importance, the research presented here intended to (1) gather contemporary data on concentrations of PCBs, PAHs, OCPs and BFRs in Common Terns breeding in Ireland; (2) to investigate congener profiles, along with destructive and non-destructive sampling methods, using preen oil and feathers in live birds; and liver and preen gland in corpses

found in breeding colonies; (3) to investigate contaminant levels of toxicological importance.

5.3. MATERIAL AND METHODS

5.3.1. SAMPLING LOCATION

Rockabill is a 0.9 ha island located 7 km off the north coast of county Dublin, Ireland (Grid Ref. O320627). Rockabill is home to approximately 2000 pairs of Common Terns, along with 1550 pairs (47% of the entire European population) of Roseate Terns (*Sterna dougallii*) and smaller numbers of breeding Arctic Terns (*Sterna paradisaea*), Black-legged Kittiwakes (*Rissa tridactyla*) and Black Guillemots (*Cepphus grylle*) (Burke et al., 2016). The major disturbance to Tern nests on the island is predation by Great Black-backed Gulls (*Larus marinus*) (Burke et al., 2016). Common Tern diet composition consists mostly of Clupeids, Sandeels and Gadoids (Burke et al., 2016).

5.3.2. DEAD BIRDS SAMPLING

NECROPSIES

In total, 38 Common Tern corpses were collected at Rockabill colony, during the breeding seasons of 2015-16. Birds were necropsied following Van Franeker et al. (2004) methodology. When possible, sex, age class and cause of death were inferred. Preen gland and liver were collected from 20 birds for Persistent Organic Pollutants (POP) analysis. All thirty-eight stomachs were additionally analysed for plastic litter according to Van Franeker et al. (2004) by sieving contents through a 1 mm mesh sieve. All retained solids were collected in petri-dishes and air-dried overnight. Only a single piece of plastic (fragment) was found in all stomachs analysed. Mass of the item was 0.1538 g and it was perforating the stomach lining, causing an ulcer.

5.3.3. LIVER AND PREEN GLAND EXTRACTIONS

In total, 20 livers and preen glands were analysed from necropsied birds. All utensils were previously washed using n-hexane (VWR Analar Normapur). Tissue samples (liver and preen gland) were cut into small pieces. Preen gland samples also had remaining feathers removed. Samples were weighed in beakers to the nearest 0.0001 g. A solvent mixture of 3 parts of hexane and 1 part of acetone (Merck SupraSolv) was added to samples (approximately 30 ml). Samples were spiked with internal standards (PAH 24D, 13C PCB and BFR, OCP Pesticide Mix 20). Samples were homogenised using an UltraTurrax (IKA T10 Basic) for 1 min, then 20 ml of pure water was added to the sample, and the mixture was homogenised again for another min. Samples were transferred to centrifuge tubes and placed on the centrifuge (Hehich Zentrifugen Mikro 220R) for 5 min at 4000 rpm. Using disposable pipette tips, the top layer (solvent) was transferred to glass vials. The cleaning process was achieved by placing 2 g of pre-treated (300°C for 3 h, with 5% weight by water) Silica Gel (Molekula) in a glass column for each sample. The solvent layer in the glass vials was then poured into the glass column followed by a solvent mixture of 60 ml of hexane and 10 ml of acetone. Clean samples were collected in a conical flask by opening the tap of the glass column. Samples were then evaporated in the TurboVap LP (Biotage) to approximately 1 ml and transferred into GC vials.

5.3.4. LIVE BIRDS SAMPLING

In total, 15 Common Terns were hand caught at Rockabill colony, county Dublin during the breeding season, under licence No. C124/2015 and C125/2015 from National Parks and Wildlife Service (NPWS), in July 2015. Birds were weighed, had their wingspan measured and were ringed if they had not been previously ringed. Preen oil cotton swabs were collected by exposing the preen gland and gently pressing it to express the oil. Swabs were placed in sterile glass jars with foil covered lids. Furthermore, six breast feathers were collected from each individual and kept in paper envelopes. Preen oil samples were kept frozen at -80ºC, whilst feather samples were kept at room temperature until analysis.

5.3.5. PREEN OIL EXTRACTION

All utensils were previously washed using methanol (Merck SupraSolv). Cotton swabs were transferred into glass beakers by using metal forceps. Sample jars were then rinsed with SupraSolv methanol to remove any remaining preen oil in the glass jar. This methanol was also poured into the beaker containing the corresponding cotton swab. In total, 150 ml of methanol was poured into each beaker (in three aliquots). Contents were stirred for 1 min each time. Samples were spiked with internal standards (PAH 24D, 13C PCB and BFR, OCP Pesticide Mix 20). Only the liquid sample was then transferred to another beaker and covered with aluminium foil. Samples were placed in a TurboVap LP (Biotage) to evaporate the volume to approximately 1 ml. Using disposable glass pipettes, the remaining sample was transferred into previously labelled GC vials. Samples were kept frozen at -80^{o}C until subsequent analysis using Gas-Chromatography/Mass-Spectrometry GC/MS.

5.3.6. FEATHER EXTRACTION

All utensils were previously washed with methanol. Samples of four feathers per bird were placed in individual beakers. Feathers were washed with distilled water, using forceps to separate the barbs, and stirred. They were left soaking for 20 min and then left to dry in folded tissue paper for 2 h or until fully dried. After drying each sample was weighed to the nearest 0.0001 g and placed inside a beaker with 15 ml of 37% HCl (Merck EMSURE) and 20 ml of a solvent mixture of 2 parts of hexane and 1 part of acetone. Samples were spiked with internal standards (PAH 24D, 13C PCB and BFR, OCP Pesticide Mix 20). Beakers were covered with aluminium foil and put in the oven at 37^{o}C overnight (in total for approximately 15 h). Consequently, 40 ml of a solvent mixture of 3 parts of hexane and 1 part of acetone was added to each sample. Samples were then placed within a separation funnel and shaken vigorously. The subsequent aqueous layer was removed by opening the tap on the separation funnel and pouring the liquid into a beaker. The remaining lipid layer was decanted into previously labelled glass vials. This separation procedure was repeated by placing the aqueous layer back into the separation funnel and adding 20 ml of fresh hexane/acetone solvent mixture. Samples were transferred into a TurboVap LP (Biotage) and evaporated under a nitrogen stream until approximately 1 ml remained. Samples were subsequently

transferred to pre-labelled GC vials using disposable glass pipettes. Samples were kept frozen at -80^{o}C until subsequent analysis using (GC/MS).

5.3.7. GAS-CHROMATOGRAPHY MASS-SPECTROMETRY

Liver, preen gland, preen oil and feather solvent extractions were then analysed for Polychlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), Organochlorine Pesticides (OCPs) and Brominated Flame Retardants (BFRs) using gas-chromatography mass spectrometry (Agilent GC-MS (5977E)) equipped with an auto-sampler. GCMS was run in EI mode, with a J&W 30m BD1 MS column, with helium being the carrier gas. Quality control was guaranteed by the use of blanks per batch of samples and Certified Reference Materials (CRMs). For preen gland, preen oil and liver analysis, Cod Liver Oil (Commission of the European Communities, Community Bureau of Reference – BCR. Reference Material n^{o} 349. Chlorobiphenyls in cod liver oil n^{o} 0831) was used as a CRM and for feather analysis, Fish Tissue (NIST 1947 Lake Michigan Fish Tissue. U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899).

5.3.8. STATISTICAL ANALYSIS

Statistical analysis were carried out using R (R Core Team, 2015), version 3.2.3 and 'prcomp' package. To investigate potential relationships between matrices: preen oil and feathers; liver and preen gland, Pearson's correlation was computed for each group of contaminants. This was done in two ways: through a correlation matrix at the individual level and through aggregated data. A correlation matrix was combined with hierarchical clustering using complete hierarchical clustering method. The input to a hierarchical clustering algorithm consists of the measurement of the similarity (or dissimilarity) between each pair of objects. The goal of the clustering algorithm is then to partition the objects into homogeneous groups, such that the within-group similarities are large compared to the between-group similarities. Aggregated data on the other hand uses means and standard deviations of each congener to compute correlation by homogenising individual samples.

A Principal Component Analysis (PCA) was used to investigate which congeners contributed most to the variance in each group of contaminants. The principal components were extracted to represent the patterns encoding the highest variance in the data set. However, in many high-dimensional data sets, the most dominant patterns, i.e. those captured by the first principal components, are those separating different subgroups of the samples from each other. The first principal component (PC1) captures the maximum variance and will determine the direction of highest variability in the data. The following components (e.g. PC2, PC3, etc.) capture the remaining variance. The same analysis was then used to investigate if live sampling (e.g. preen oil and feathers) can potentially serve as a proxy for organs (e.g. liver and preen gland). Congeners with over 50% of values below the level of detection (LOD) were excluded from statistical analysis (Jaspers et al., 2008).

5.4. RESULTS

5.4.1. LIVE BIRDS – PREEN OIL AND FEATHERS

In total, 16 PCBs were detected in preen oil and feathers. The mean concentration of ∑PCBs was 4.23 ng/g ww preen oil (Range: 1.78 - 9.11 ng/g ww) and 36.48 ng/g ww feathers (Range: 14.96 - 113.48 ng/g ww). The mean concentration of ∑7 PCBs was 3.45 ng/g ww preen oil and 27.25 ng/g ww feathers (Table 21). Results from the PCA showed that in preen oil, the three first components (PC1, PC2 and PC3) explained 72% of the variance, whilst in feathers, it explained 91%. In preen oil, the congeners that contributed more to PCB burden were PCBs 118, - 153 and - 138, whilst in feathers, highest contributions came from PCBs 101, - 149 and - 138.

Twelve PAH congeners were detected in preen oil and feathers. The mean concentration of PAHs was 10.52 ng/g ww preen oil (Range: 6.42 - 18.74 ng/g ww) and 30.01 ng/g ww feathers (Range: 18.53 - 53.46 ng/g ww) (Table 22). PCA results showed that in preen oil, the three first components explained 69% of the variance; and in feathers, 63%. Congeners that mostly contributed to PAH burden in preen oil were Chrysene, Benzo(b)fluoranthene and Benzo(a)anthracene, whilst for feathers were Pyrene, Fluoranthene and Benzo(b)fluoranthene.

Fifteen OCPs were detected in feather and preen oil. The mean concentration of OCPS was 3.69 ng/g ww preen oil (Range: 2.86 - 5.02 ng/g ww) and 13.36 ng/g ww feathers (Range: 6.23 - 25.01 ng/g ww) (Table 23). PCA results showed that the first three components retained 59% of the variance for preen oil and 94% for feathers. Congeners that had the highest contribution to PAH burden were Heptachlor, Dieldrin and pp−DDE in preen oil, and Endrin, a−HCH and Heptachlor in feathers.

In total, 6 BFRs were detected in feathers and preen oil. The mean concentration of BFRs was 1.86 ng/g ww preen oil (Range: 1.54 - 2.20 ng/g ww) and 1.98 ng/g ww feathers (Range: 1.87 - 2.90 ng/g ww) (Table 24). The first three components in the Principal Component Analysis explained 84% of the variance in preen oil, and 75% in feathers. Congeners that contributed most to BFR burden in preen oil were BFRs 47, - 99 and - 100, and BFRs 100, - 154 and - 183 in feathers.

Congener profiles differed between feathers and preen oil. That was confirmed by the correlation matrices combined with hierarchical clustering. Correlations were either negative or very low between congeners. Aggregated data on the other hand, showed a strong correlation between feathers and preen oil for BFR (0.97), PCB (0.73) and PAH (0.72); and a moderate correlation for OCP (0.51).

5.4.2. DEAD BIRDS – LIVER AND PREEN GLAND

In total, 16 PCBs were detected in liver and preen gland. The mean concentration of PCBs was 41.43 ng/g ww liver (Range: 11.01 - 103.93 ng/g ww) and 44.11 ng/g ww preen gland (Range: 4.74 - 115.6 ng/g ww). The mean concentration for □7 PCBs was 35.34 ng/g ww liver and 34.85 ng/g ww preen gland (Table 21). The three first principal components explained 82% of the variance in liver and 85% in preen gland. In liver, the congeners that contributed most to PCB burden were PCBs 153, - 138 and - 180, whilst in preen gland, highest contributions came from PCBs 138, - 153 and - 118.

Fifteen PAH congeners were detected in preen gland and only 13 in liver. The mean concentration of PAHs was 27.64 ng/g ww liver (Range: 4.49 - 78.76 ng/g ww) and 46.65 ng/g ww preen gland (Range: 12.34 - 124.37 ng/g ww) (Table 22). The first three components of the PCA explained 61% of the variance in preen oil and preen gland

equally. Congeners that mostly contributed to PAH burden in liver were Phenanthrene, Fluoranthene and Pyrene, whilst for preen gland were Phenanthrene, Acenaphthene and Fluoranthene.

Seventeen OCPs were detected in liver and preen gland. The mean concentration of OCPS was 15.15 ng/g ww liver (Range 4.84 - 38.08 ng/g ww) and 13.48 ng/g ww preen gland (Range: 4.80 - 28.85 ng/g ww) (Table 23). The three first components explained 52% of the variance in preen oil and the same in feathers. Congeners that had the highest contribution to OCP burden were Dieldrin, HCB and pp−DDE in liver, and op−DDT, Dieldrin and op−DDE in preen gland.

In total, 7 BFRs were detected in liver and preen gland. The mean concentration of BFRs was 5.07 ng/g ww liver (Range: 2.04 - 18.81 ng/g ww) and 4.37 ng/g ww preen gland (2.06 - 8.53 ng/g ww) (Table 24). Principal components 1, 2 and 3 explained 83% of the variance in liver and 78% in preen gland. Congeners that contributed most to BFR burden in liver were BFRs 99, - 153 and - 100, and BFRs 47, - 28 and - 99 in preen gland.

Results from the correlation matrices between congeners of liver and preen gland showed weak or negative correlations. Aggregated data correlation however, showed a strong correlation between liver and preen gland for PCB (0.96) and BFR (0.94), but a weak correlation for PAH (0.6) and OCP (0.55).

5.4.3. LIVE VERSUS DEAD

Results from the PCA comparing feathers as a proxy for liver (Figure 12) and preen oil as a proxy for preen gland (Figure 13) showed a clear separation between the two types of sample (live and dead), with much clustering in live bird samples, whilst dead bird samples show larger variance between individuals.

TABLE 20 - PCB MEAN CONCENTRATIONS (NG/G WW) ± STANDARD DEVIATION (SD) SEPARATED PER CONGENER, DETECTED IN PREEN OIL, FEATHERS, LIVER AND PREEN GLAND. 7 PCBS ARE: - 28, - 52, - 101, - 118, - 153, - 138 AND - 180.

PCB	Live Common Terns	Dead Common Terns

	Preen oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD	Liver (ng/g ww) ± SD	Preen Gland (ng/g ww) ± SD
PCB 18	0.03 ± 0.03	0.71 ± 0.74	0.07 ± 0.04	1.25 ± 4.59
PCB 28	0.07 ± 0.06	2.42 ± 1.83	0.76 ± 0.63	0.97 ± 1.14
PCB 31	0.06 ± 0.05	2.27 ± 1.94	0.65 ± 0.62	0.83 ± 0.84
PCB 52	0.20 ± 0.18	6.75 ± 3.86	1.94 ± 1.69	2.89 ± 4.48
PCB 44	0.15 ± 0.18	2.51 ± 1.40	0.98 ± 0.80	1.83 ± 4.45
PCB 101	1.13 ± 0.54	9.16 ± 7.41	5.64 ± 3.37	5.36 ± 5.51
PCB 118	0.69 ± 0.43	3.88 ± 3.67	5.51 ± 3.48	5.80 ± 5.74
PCB 105	0.08 ± 0.06	0.74 ± 0.93	0.68 ± 0.53	2.00 ± 3.17
PCB 149	0.30 ± 0.13	2.65 ± 2.59	3.10 ± 3.64	1.71 ± 2.08
PCB 153	0.68 ± 0.35	2.45 ± 2.41	11.71 ± 6.69	9.69 ± 9.43
PCB 138	0.44 ± 0.23	2.26 ± 2.13	8.25 ± 5.28	6.92 ± 6.41
PCB 156	0.09 ± 0.05	0.19 ± 0.22	0.28 ± 0.26	0.78 ± 0.71
PCB 180	0.24 ± 0.14	0.33 ± 0.24	1.53 ± 1.35	3.22 ± 3.18
PCB 170	0.04 ± 0.04	0.08 ± 0.08	0.24 ± 0.28	0.42 ± 0.53
PCB 194	0.02 ± 0.01	0.07 ± 0.06	0.07 ± 0.07	0.29 ± 0.74
PCB 209	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.02	0.15 ± 0.41
∑ all PCBs	4.23 ± 0.30	36.48 ± 2.47	41.43 ± 3.33	44.11 ± 2.68
∑ 7 PCBs	3.45 ± 0.34	27.25 ± 2.81	35.34 ± 3.69	34.85 ± 2.68

TABLE 21 - PAH MEAN CONCENTRATIONS (NG/G WW) ± STANDARD DEVIATION (SD) SEPARATED PER CONGENER, DETECTED IN PREEN OIL, FEATHERS, LIVER AND PREEN GLAND. ND = NOT DETECTED.

PAH	**Live Common Terns**		**Dead Common Terns**	
	Preen oil (ng/g ww) ± SD	**Feathers (ng/g ww) ± SD**	**Liver (ng/g ww) ± SD**	**Preen Gland (ng/g ww) ± SD**
Acenphthylene	1.0 ± 0.01	0.23 ± 0.12	0.19 ± 0.10	0.72 ± 0.28
Acenaphthene	ND	ND	ND	2.78 ± 1.62
Fluorene	ND	ND	ND	5.07 ± 2.20
Phenanthrene	3.89 ± 2.45	9.99 ± 3.34	7.03 ± 8.92	7.59 ± 3.36
Anthracene	0.50 ± 0.56	0.67 ± 0.26	0.88 ± 1.29	0.43 ± 0.43
Fluoranthene	0.63 ± 0.38	3.21 ± 1.53	2.17 ± 2.34	0.83 ± 0.45
Pyrene	ND	ND	3.72 ± 5.27	2.69 ± 1.23
Benzo(a)anthracene	0.43 ± 0.54	0.54 ± 0.66	0.99 ± 1.54	3.29 ± 4.33
Chrysene	0.76 ± 0.64	0.49 ± 0.60	0.39 ± 0.62	1.51 ± 1.12
Benzo(b)fluoranthene	0.45 ± 0.55	0.48 ± 0.15	2.91 ± 7.12	5.99 ± 8.27
Benzo(k)fluoranthene	0.43 ± 0.36	0.23 ± 0.08	0.85 ± 1.97	5.46 ± 15.48
Benzo(a)pyrene	0.62 ± 0.71	0.70 ± 1.27	4.06 ± 6.16	4.43 ± 4.03
Indeno(1,2,3-CD)pyrene	1.21 ± 1.09	12.67 ± 8.60	3.25 ± 4.56	0.89 ± 1.31
Dibenzo(a,h)anthracene	0.38 ± 0.41	0.62 ± 0.05	0.84 ± 0.72	1.42 ± 2.24
Benzo(g,h,i)perylene	0.22 ± 0.18	0.18 ± 0.20	0.36 ± 0.36	3.55 ± 4.11
∑ PAH	10.52 ± 0.94	30.01 ± 4.06	27.64 ± 1.92	46.65 ± 2.13

TABLE 22 - OCP MEAN CONCENTRATIONS (NG/G WW) ± STANDARD DEVIATION (SD) SEPARATED PER CONGENER, DETECTED IN PREEN OIL, FEATHERS, LIVER AND PREEN GLAND. ND = NOT DETECTED.

OCP	**Live Common Terns**		**Dead Common Terns**	
	Preen oil (ng/g ww) ± SD	**Feathers (ng/g ww) ± SD**	**Liver (ng/g ww) ± SD**	**Preen Gland (ng/g ww) ± SD**
a-HCH	0.17 ± 0.15	2.78 ± 1.55	0.88 ± 1.04	0.33 ± 0.22
HCB	0.08 ± 0.05	0.09 ± 0.06	1.46 ± 2.04	0.07 ± 0.06
g-HCH	ND	ND	1.23 ± 3.67	2.43± 2.96
b-HCH	ND	ND	0.43 ± 1.94	0.35 ± 1.56
Heptachlor	0.17 ± 0.13	1.77 ± 2.67	0.25 ± 0.39	0.39 ± 0.20
Aldrin	0.01 ± 0.02	0.13 ± 0.19	0.12 ± 0.15	0.35 ± 0.25
Isobenzan	0.02 ± 0.02	0.11 ± 0.24	0.09 ± 0.07	0.37 ± 0.60
Isodrin	0.02 ± 0.02	0.26 ± 0.40	0.45 ± 1.06	0.20 ± 0.12
Heptachlor epoxide	0.01 ± 0.02	0.15 ± 0.29	0.34 ± 0.38	0.32 ± 0.17
op-DDE	0.20 ± 0.24	0.17 ± 0.21	0.63 ± 0.63	0.42 ± 1.36
pp-DDE	0.49 ± 0.49	0.21 ± 0.24	1.77 ± 4.34	0.14 ± 0.23
Dieldrin	0.03 ± 0.02	0.29 ± 0.33	0.91 ± 1.25	0.43 ± 1.00
pp-DDT	0.01 ± 0.02	0.39 ± 0.41	0.41 ± 0.43	0.15 ± 0.20
Endrin	0.18 ± 0.23	2.83 ± 4.97	1.28 ± 1.28	3.70 ± 6.03
Endosulphan B	0.40 ± 0.42	0.50 ± 0.81	1.16 ± 1.12	0.42 ± 0.41
pp-DDD	1.87 ± 0.01	2.84 ± 1.51	2.93 ± 1.09	2.90 ± 2.19

op-DDT	0.03 ± 0.03	0.84 ± 0.94	0.81 ± 0.92	0.51 ± 0.52
∑ OCP	3.69 ± 0.45	13.36 ± 1.04	15.15 ± 0.69	13.48 ± 1.05

TABLE 23 - BFR MEAN CONCENTRATIONS (NG/G WW) ± STANDARD DEVIATION (SD) SEPARATED PER CONGENER, DETECTED IN PREEN OIL, FEATHERS, LIVER AND PREEN GLAND. ND = NOT DETECTED.

BFR	**Live Common Terns**		**Dead Common Terns**	
	Preen oil (ng/g ww) ± SD	**Feathers (ng/g ww) ± SD**	**Liver (ng/g ww) ± SD**	**Preen Gland (ng/g ww) ± SD**
BFR 28	0.31 ± 0.02	0.30 ± 0.02	0.37 ± 0.12	0.45 ± 0.14
BFR 47	0.48 ± 0.11	0.58 ± 0.24	0.93 ± 0.66	0.84 ± 0.68
BFR 100	0.34 ± 0.04	0.33 ± 0.04	0.77 ± 0.61	0.69 ± 0.45
BFR 99	0.32 ± 0.05	0.37 ± 0.07	0.78 ± 0.97	0.61 ± 0.43
BFR 154	0.38 ± 0.10	0.37 ± 0.05	0.45 ± 0.23	0.41 ± 0.14
BFR 153	ND	ND	0.70 ± 1.65	0.52 ± 0.34
BFR 183	0.03 ± 0.02	0.03 ± 0.04	1.07 ± 0.72	0.85 ± 0.69
∑ BFR	1.86 ± 0.55	1.98 ± 0.16	5.07 ± 0.22	4.37 ± 0.16

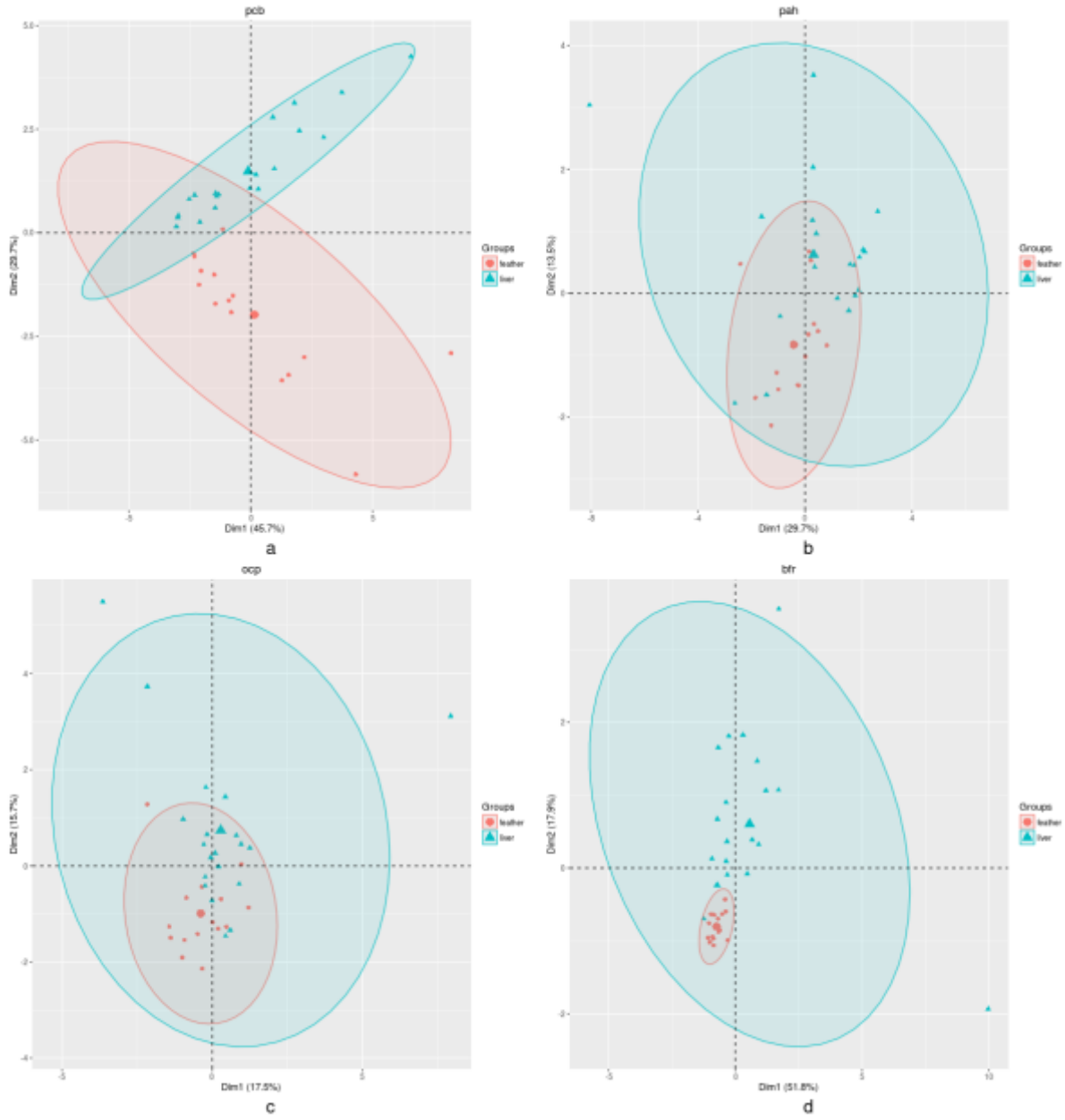


FIGURE 10 - PRINCIPAL COMPONENT ANALYSIS (PCA) COMPARING FEATHERS (RED DOTS) AS A PROXY FOR LIVER (BLUE TRIANGLES) FOR PCB (A), PAH (B), OCP (C) AND BFR (D). THERE IS A CLEAR SEPARATION BETWEEN THE TWO GROUPS, WITH FEATHERS BEING MUCH MORE CLUSTERED TOGETHER, WHILST LIVER SAMPLES APPEAR TO BE MORE SPREAD. ELLIPSES DRAWN AROUND INDIVIDUAL SAMPLES SHOW A 95% CONCENTRATION OF POINTS.

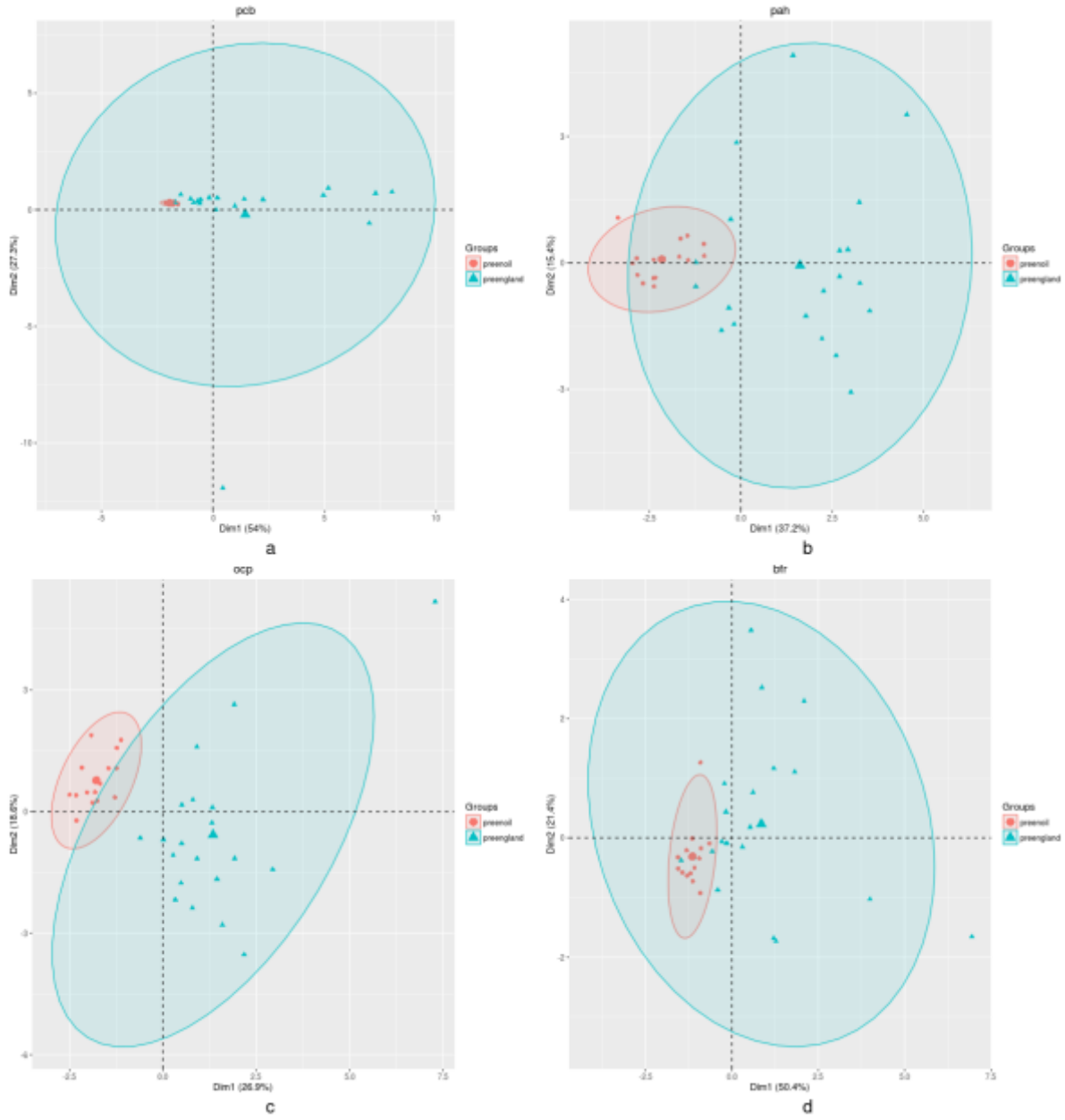


FIGURE 11 - PRINCIPAL COMPONENT ANALYSIS (PCA) COMPARING PREEN OIL (RED DOTS) AS A PROXY FOR PREEN GLAND (BLUE TRIANGLES) FOR PCB (A), PAH (B), OCP (C) AND BFR (D). THERE IS A CLEAR SEPARATION BETWEEN THE TWO GROUPS, WITH PREEN OIL SAMPLES BEING MUCH MORE CLUSTERED TOGETHER, WHILST PREEN GLAND SAMPLES APPEAR TO BE MORE SPREAD. ELLIPSES DRAWN AROUND INDIVIDUAL SAMPLES SHOW A 95% CONCENTRATION OF POINTS.

6. DISCUSSION

To our knowledge, this is the first study to provide data on persistent organic pollutants in Common Terns in Ireland. Whilst there are data on POPs from Sandwich and Roseate Terns in Ireland, this originates from the 1960s and it is comprised of only two OCP congeners (Koeman et al., 1967).

Total PCB concentrations were 9-fold higher in feathers (36.48 ng/g) than in preen oil (4.23 ng/g) in live birds and similar between liver (41.43 ng/g) and preen gland (44.11 ng/g) in dead birds, though a strong correlation was seen between both sets of sampling techniques: preen oil vs feathers (0.73) and liver vs preen gland (0.96). All samples were dominated by high-molecular weight components, suggesting an accumulation of such congeners and potential metabolising of low-molecular weight congeners. Concentrations in all matrices, apart from preen oil exceed the EcoQO for ∑ PCB, which is 20 ng/g in eggs (Dittmann et al., 2012). Research on Foster's Terns (*Sterna forsteri*) suggests that 3 PCB congeners (- 126, - 77 and - 105) might contribute to 90% of toxicity in eggs (Kubiak et al., 1989). Laboratory experiments that involved the injection of PCB 126 in Common Tern eggs showed that all three different dosage levels given from 44 to 434 ng/g caused significant mortality (27 - 53%) after a week of treatment. The median lethal dose (LD50) for PCB 126 in Common Tern eggs, based on hatching success of said study is approximately 104 ng/g (Hoffman et al., 1998). Deformities in bills (crosses and shortened) increased with higher doses (Hoffman et al., 1998). PCBs 126 and – 77 were not detected in Common Terns from Rockabill colony. PCB 105 however was detected in all matrices, but at low levels (0.08 – 2.00 ng/g ww). The lowest observed adverse effects level (LOAEL) in Common Terns affected reproduction and is reported to be 8 mg/kg (= 8000 ng/g) (Bosveld & Berg, 1994; Su et al., 2014).

Total PAH concentrations were 3-fold higher in feathers when compared to preen oil, while mean concentrations in liver were approximately twice as high than in preen gland. The contribution profile of congeners differs highly between preen oil and feathers, but it shows two of the same congeners for liver and preen gland. In general, PAH levels were low and comparable to values found in livers of Cory's Shearwaters (*Calonectris diomedia*) in the Atlantic Ocean (Range: 3.32 – 17.1 ng/g) (Roscales & Gonzalez-Solis, et al., 2011). It has been reported that PAH levels in the tissues of birds

far from industrialised areas and non-contaminated sites tend to be low (Hall & Coon, 1988). Additional studies have also found higher levels of PAH in tissues of birds that feed on lower trophic prey, such as invertebrates, rather than higher trophic prey, such as pelagic fish (Broman et al., 1990; Custer et al., 2001), which is the main Common Tern prey (Cabot & Nisbet, 2013). This is possibly due to the fact that PAH tend to accumulate mostly in sediments and have been shown to have low bio-magnification properties (MacRae & Hall, 1998; Nfon et al., 2008; Perugini et al., 2007; Wan et al., 2007).

Total OCP mean concentrations were 4-fold higher in feathers than in preen oil. Mean concentrations in liver and preen gland were similar. Heptachlor highly contributed to the burden in preen oil and feathers, whilst for liver and preen gland Dieldrin and DDE isomers were the common contributors. HCB was present in all matrices. Mean concentrations did not exceed the EcoQO of 2 ng/g for eggs, with mean values between 0.07 ng/g preen gland and 1.46 ng/g liver. ∑ DDT was below the EcoQO (10 ng/g) for eggs in all matrices, with the highest mean in liver (6.55 ng/g). ∑ HCH was above the EcoQO (2 ng/g) for eggs in all matrices, but preen oil, with the lowest mean at 2.54 ng/g in liver and the highest at 3.11 ng/g in preen gland. PCBs, DDT and DDE were associated with abnormalities in chicks. Hays & Risebrough (1972) recorded various deformities in bill, eye and foot in Common and Roseate Terns unhatched and chicks up to a few days old. Premature feather losses (PFL) were also recorded in young chicks, sometimes preventing them from fledging. These abnormalities were similar to the chick edema disease in poultry, associated with the toxic compound chlorinated dibenzo-p-dioxin, a substance that has been reported to contaminate commercial PCB mixtures (Barron et al., 1995). Sub-lethal effects in adult birds include reduced parental attentiveness and abnormal reproductive behaviour (Barron et al., 1995).

Total BFR mean concentrations were similar between matrices for both preen oil and feathers; and liver and preen gland. Feathers and liver appear to have a higher contribution from high molecular weight congeners, whilst preen oil and preen gland appear to have lower molecular weight congeners. Common Tern carcasses in the north Atlantic have reported a much higher ∑ BFR concentration (121 ± 25 ng/g lipid weight) (Jenssen et al., 2007) compared to values from this study in liver and preen gland. The same is true for the Arctic Tern (95.4 ± 36 and 40.9 ± 8.4 ng/g lipid weight) (Jenssen et

al., 2007). BFRs from our study were just above the Level of Quantification (LOQ). BFRs are applied in industry to combustible materials to meet safety regulations (Jenssen et al., 2007). Such additives can leach out of products in certain conditions and have become of environmental importance due to their persistent and toxic nature. In experimental conditions, BFRs have been shown to leach out of plastic products 20 – 50 times more in stomach and fish oil than in seawater (Tanaka et al., 2015). Due to the ubiquity of plastic pollution at sea, BFR dispersal and bioaccumulation has become of greater concern (Derraik, 2002).

In general, feathers have demonstrated more similar concentrations to internal organs than did preen oil. That could be explained by the fact that feathers tend to carry a higher burden due to the various sources of contaminant input: the blood stream when feathers are grown, external contamination (although that has been claimed to be irrelevant by Jaspers et al., 2008) and additionally, preen oil, due to the constant act of preening of the feathers. In the case of Common Terns, they undergo a post-breeding moult (Ginn & Melville, 1983), which means that in the case of these samples, collected during the breeding season, birds would still be carrying contaminants acquired during winter and southern migration. Preen oil on the other hand is constantly produced and is more likely to reflect local contamination (Jacob & Ziswiler, 1982), like eggs in the case of income breeders (Arnold et al., 2004; Janke et al., 2015).

Pollutant concentrations in seabirds depend on a variety of factors. Moulting influences the uptake of contaminants onto feathers by the blood stream (Jaspers et al., 2006; Van den Steen et al., 2007). Migration can alter contaminant burden in two ways: by exposing the birds to more or less contaminated areas and by the mobilization of lipids to cope with energy expenditure. Such mobilisation affects contaminant load in starving birds in the same way (Barron et al., 1995; Jaspers et al., 2008). Breeding affects the burden of female birds, which are known to pass from 4 - 45% (45% in Arctic Terns - *Sterna paradisaea*) of their burden to their eggs (Lemmetyinen et al., 1982; Tanabe et al., 1984), contaminating unborn chicks. Variation in contaminant load and different congener profiles can be attributed to species specific metabolism and elimination and congener specific toxicokinetics (Barron et al., 1995; Brunström et al., 1990; Hoffman et al., 1998; Hoffman et al., 1996; Smith et al., 1990).

Results from the PCA analysis between dead and live Common Terns revealed that the utility of organs (e.g. dead birds) for POP monitoring might bring biased results due to great variation among individuals. If death is accidental, birds might have recently experienced starvation, migration, moulting, or even intoxication. These unknown factors result in great individual variation.

POPs in Common Terns in Ireland are not at toxicological levels to cause embryonic deformities, or reproductive failure. However, some levels are higher than recommended by European policy, such as OSPAR's EcoQO in eggs (OSPAR, 2010). In reality, effects of certain compounds are difficult to properly quantify as biota and environmental media is pre-contaminated with various pollutants, thus it is recommended to keep periodic monitoring of concentrations and potential effects.

7. ACKNOWLEDGMENTS

This work was supported by Science Without Borders (CAPES, Brazil, BEX: 1269-13-5). Many thanks to all at BirdWatch Ireland. Thanks to Steve Newton. Special thanks to Rockabill wardens Brian Burke and Andrew Power. Thanks to Niall Keogh for assistance in the field. Thanks to Danilo Hirota, Killian Coakley and Bill Delee for assistance in the lab.

8. LITERATURE CITED

Arnold, J. M., Hatch, J. J., & Nisbet, I. C. T. (2004). Seasonal declines in reproductive success of the common tern Sterna hirundo: timing or parental quality? *Journal of Avian Biology*, *35*(1), 33–45.

Austin, O. L. (1953). The migration of the Common Tern (Sterna hirundo) in the Western Hemisphere. *Bird-Banding*, 39–55.

Barron, M. G., Galbraith, H., & Beltman, D. (1995). Comparative reproductive and developmental toxicology of PCBs in birds. *Comparative Biochemistry and Physiology Part C: Pharmacology, Toxicology and Endocrinology*, *112*(1), 1–14.

Becker, P. H., Schuhmann, S., & Koepff, C. (1993). Hatching failure in Common Terns (Sterna hirundo) in relation to environmental chemicals, *79*, 207–213.

Bosveld, A. T. C., & Berg, M. Van den. (1994). Effects of polychlorinated biphenyls, dibenzo-p-dioxins, and dibenzofurans on fish-eating birds. *Environmental Reviews*, *2*(2), 147–166.

Bosveld, A. T. C., Gradener, J., Murk, A. J., Brouwer, A., Van Kampen, M., Evers, E. H. G., & Van den Berg, M. (1995). Effects of PCBs, PCDDs and PCDFs in common tern (Sterna hirundo) breeding in estuarine and coastal colonies in the Netherlands and Belgium. *Environmental Toxicology and Chemistry*, *14*(1), 99–115.

Broman, D., Näuf, C., Lundbergh, I., & Zebühr, Y. (1990). An in situ study on the distribution, biotransformation and flux of polycyclic aromatic hydrocarbons (pahs) in an aquatic food chain (seston-Mytilus edulis L.-Somateria mollissima L.) from the baltic: An ecotoxicological perspective. *Environmental Toxicology and Chemistry*, *9*(4), 429–442.

Brunström, B., Andersson, L., Nikolaidis, E., & Dencker, L. (1990). Non-ortho-and mono-ortho-chlorine-substituted polychlorinated biphenyls—embryotoxicity and inhibition of lymphoid development. *Chemosphere*, *20*(7–9), 1125–1128.

Burke, B., Kinchin-Smith, D., Somers, S., & Newton, S. (2016). *Rockabill Tern Report 2016*. *BirdWatch Ireland Seabird Conservation Report*. BirdWatch Ireland Seabird Conservation Report.

Cabot, D., & Nisbet, I. (2013). *Terns*. (S. A. Corbet, R. West, D. Streeter, & J. Silvertown, Eds.)*Journal of Field Ornithology* (Vol. 85). London: HarperCollins Publishers.

Custer, T. W., Custer, C. M., Dickerson, K., Allen, K., Melancon, M. J., & Schmidt, L. J. (2001). Polycyclic aromatic hydrocarbons, aliphatic hydrocarbons, trace elements, and monooxygenase activity in birds nesting on the North Platte River, Casper, Wyoming, USA. *Environmental Toxicology and Chemistry*, *20*(3), 624–631.

Custer, T. W., Erwin, R. M., & Stafford, C. (1980). Organochlorine Residues in

Common Tern Eggs from Nine Atlantic Coast Colonies. *Waterbird Society*, *6*(1983), 197–204.

Derraik, J. G. B. (2002). The pollution of the marine environment by plastic debris: A review. *Marine Pollution Bulletin*, *44*(9), 842–852. http://doi.org/10.1016/S0025-326X(02)00220-5

Dittmann, T., Becker, P. H., Bakker, J., Bignert, A., Nyberg, E., Pereira, M. G., … Toft, G. O. (2012). Large-scale spatial pollution patterns around the North Sea indicated by coastal bird eggs within an EcoQO programme. *Environmental Science and Pollution Research*, *19*(9), 4060–4072.

Elliott, J. E., Butler, R. W., Norstrom, R. J., & Whitehead, P. E. (1989). Environmental contaminants and reproductive success of great blue herons Ardea herodias in British Columbia, 1986–1987. *Environmental Pollution*, *59*(2), 91–114.

Elliott, J., Wilson, L. K., & Wakeford, B. (2005). Polybrominated Diphenyl Ether Trends in Eggs of Marine and Freshwater Birds from British Columbia , Canada , 1979 - 2002. *Environmental Science & Technology*, *39*(15), 5584–5591.

Falkowska, L., Reindl, A. R., Grajewska, A., & Lewandowska, A. U. (2016). Organochlorine contaminants in the muscle, liver and brain of seabirds (Larus) from the coastal area of the Southern Baltic. *Ecotoxicology and Environmental Safety*, *133*, 63–72. http://doi.org/10.1016/j.ecoenv.2016.06.042

Fox, G. A. (1976). Eggshell quality: its ecological and physiological significance in a DDE-contaminated Common Tern population. *The Wilson Bulletin*, *88*(3), 459–477.

Giesy, J. P., Ludwig, J. P., & Tillitt, D. E. (1994). Dioxins, Dibenzofurans, PCBs and Colonial, Fish-Eating Water Birds. In A. Schecter (Ed.), *Dioxins and Health* (pp. 249–307). Boston, MA: Springer US. http://doi.org/10.1007/978-1-4899-1462-0_9

Gilbertson, M., & Fox, G. A. (1977). Pollutant-associated embryonic mortality of Great Lakes herring gulls. *Environmental Pollution (1970)*, *12*(3), 211–216.

Gilbertson, M. M. R. D., Morris, R. D., & Hunter, R. A. (1976). Abnormal chicks and PCB residue levels in eggs of colonial birds on the Lower Great Lakes (1971-73).

The Auk, *93*(3), 434–442.

Ginn, H. B., & Melville, D. S. (1983). *Moult in birds: BTO guide*. British Trust for Ornithology.

Hall, R. J., & Coon, N. C. (1988). *Interpreting residues of petroleum hydrocarbons in wildlife tissues*. US Fish and Wildlife Service.

Hays, H., & Risebrough, R. W. (1972). Pollutant concentrations in abnormal young terns from Long Island Sound. *The Auk*, *89*(1), 19–35.

Hoffman, D. J., Melancon, M. J., Klein, P. N., Eisemann, J. D., & Spann, J. W. (1998). Comparative developmental toxicity of planar polychlorinated biphenyl congeners in chickens, american krestels, and common terns. *Environmental Toxicology and Chemistry*, *17*(4), 747–757.

Hoffman, D. J., Rice, C. P., & Kubiak, T. J. (1996). PCBs and dioxins in birds. *Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations*, 165–207.

Hoffman, D. J., Smith, G. J., & Rattner, B. A. (1993). Biomarkers of contaminant exposure in common terns and black-crowned night herons in the Great Lakes. *Environmental Toxicology and Chemistry*, *12*(6), 1095–1103. http://doi.org/10.1002/etc.5620120615

Jacob, J., & Ziswiler, V. (1982). The uropygial gland. *Avian Biology*, *6*, 199–324.

Janke, A. K., Anteau, M. J., Markl, N., & Stafford, J. D. (2015). Is income breeding an appropriate construct for waterfowl? *Journal of Ornithology*, *156*(3), 755–762. http://doi.org/10.1007/s10336-015-1200-y

Jaspers, V. L. B., Covaci, A., Deleu, P., Neels, H., & Eens, M. (2008). Preen oil as the main source of external contamination with organic pollutants onto feathers of the common magpie (Pica pica). *Environment International*, *34*(6), 741–748. http://doi.org/10.1016/j.envint.2007.12.002

Jaspers, V. L. B., Oorspoels, S., Covaci, A., & Eens, M. (2006). Can predatory bird feathers be used as a non-destructive biomonitoring tool of organic pollutants? *Biology Letters*, *2*(2), 283–5. http://doi.org/10.1098/rsbl.2006.0450

Jaspers, V. L. B., Rodriguez, F. S., Boertmann, D., Sonne, C., Dietz, R., Rasmussen, L. M., … Covaci, A. (2011). Body feathers as a potential new biomonitoring tool in raptors: a study on organohalogenated contaminants in different feather types and preen oil of West Greenland white-tailed eagles (Haliaeetus albicilla). *Environment International*, *37*(8), 1349–1356.

Jaspers, V. L. B., Voorspoels, S., Covaci, a., Lepoint, G., & Eens, M. (2007). Evaluation of the usefulness of bird feathers as a non-destructive biomonitoring tool for organic pollutants: A comparative and meta-analytical approach. *Environment International*, *33*(3), 328–337. http://doi.org/10.1016/j.envint.2006.11.011

Jenssen, B. M., Sørmo, E. G., Bæk, K., Bytingsvik, J., Gaustad, H., Ruus, A., & Skaare, J. U. (2007). Brominated flame retardants in North-East Atlantic marine ecosystems. *Environmental Health Perspectives*, *115*(SUPPL1), 35–41. http://doi.org/10.1289/ehp.9355

Jones, K. C., & de Voogt, P. (1999). Persistent organic pollutants (POPs): state of the science. *Environmental Pollution*, *100*(1–3), 209–221. http://doi.org/http://dx.doi.org/10.1016/S0269-7491(99)00098-6

Koeman, J. H., Oskamp, A. A. G., Veen, J., Brouwer, E., Rooth, J., Zwart, P., … Van Genderen, H. (1967). Insecticides as a factor in the mortality of the sandwich tern (Sterna sandvicensis). *Meded. Rijksfac. Landbouwwetenschappen Gent*, *32*, 841.

Kubiak, T. J., Harris, H. J., Smith, L. M., Schwartz, T. R., Stalling, D. L., Trick, J. A., … Erdman, T. C. (1989). Microcontaminants and reproductive impairment of the Forster's tern on Green Bay, Lake Michigan-1983. *Archives of Environmental Contamination and Toxicology*, *18*(5), 706–727. http://doi.org/10.1007/BF01225009

Lemmetyinen, R., Rantamäki, P., & Karlin, A. (1982). Levels of DDT and PCB's in different stages of life cycle of the Arctic tern Sterna paradisaea and the herring gull Larus argentatus. *Chemosphere*, *11*(10), 1059–1068.

MacRae, J. D., & Hall, K. J. (1998). Biodegradation of polycyclic aromatic hydrocarbons (PAH) in marine sediment under denitrifying conditions. *Water*

Science and Technology, *38*(11), 177–185.

Massias, A., & Becker, P. H. (1990). Nutritive value of food and growth in Common Tern Sterna hirundo chicks. *Ornis Scandinavica*, 187–194.

Mitchell, P. I., Newton, S. F., Ratcliffe, N., Eds, T. E. D., Dunn, T. E., Poyser, a D., & May, L. (2004). Seabird populations of Britain and Ireland: Results of the Seabird 2000 census. *JNCC, Poyser, London.*, (August).

Moore, N. W., & Tatton, J. (1965). Organochlorine insecticide residues in the eggs of sea birds.

Mora, M. A., Durgin, B., Hudson, L. B., & Jones, E. (2016). Temporal and latitudinal trends of p,p'-DDE in eggs and carcass of North American birds from 1980-2005. *Environmental Toxicology and Chemistry*, n/a-n/a. http://doi.org/10.1002/etc.3360

Nfon, E., Cousins, I. T., & Broman, D. (2008). Biomagnification of organic pollutants in benthic and pelagic marine food chains from the Baltic Sea. *Science of the Total Environment*, *397*(1), 190–204.

OSPAR. (2010). The Ospar system of Ecological Quality Objectives for the North sea, 16.

Pariatamby, A., & Kee, Y. L. (2016). Persistent Organic Pollutants Management and Remediation. *Procedia Environmental Sciences*, *31*, 842–848. http://doi.org/10.1016/j.proenv.2016.02.093

Peck, L. E., Gilchrist, H. G., Mallory, C. D., Braune, B. M., & Mallory, M. L. (2016). Persistent organic pollutant and mercury concentrations in eggs of ground-nesting marine birds in the Canadian high Arctic. *Science of The Total Environment*, *556*(March), 80–88. http://doi.org/10.1016/j.scitotenv.2016.02.205

Perugini, M., Visciano, P., Giammarino, A., Manera, M., Di Nardo, W., & Amorena, M. (2007). Polycyclic aromatic hydrocarbons in marine organisms from the Adriatic Sea, Italy. *Chemosphere*, *66*(10), 1904–1910.

R Core Team. (2015). A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing. Retrieved from https://www.r-project.org

Roscales, J. L., Gonzalez-Solis, J., Calabuig, P., & Jimenez, B. (2011). Interspecies and spatial trends in polycyclic aromatic hydrocarbons (PAHs) in Atlantic and Mediterranean pelagic seabirds. *Environmental Pollution*, *159*(10), 2899–2905. http://doi.org/10.1016/j.envpol.2011.04.034

Scharenberg, W. (1991). Prefledging terns (Sterna paradisaea, Sterna hirundo) as bioindicators for organochlorine residues in the German Wadden Sea. *Archives of Environmental Contamination and Toxicology*, *21*(1), 102–105.

Smith, L. M., Schwartz, T. R., Feltz, K., & Kubiak, T. J. (1990). Determination and occurrence of AHH-active polychlorinated biphenyls, 2, 3, 7, 8-tetrachloro-p-dioxin and 2, 3, 7, 8-tetrachlorodibenzofuran in Lake Michigan sediment and biota. The question of their relative toxicological significance. *Chemosphere*, *21*(9), 1063–1085.

Stockholm Convention, 2001. (2001). Stockholm Convention on Persistent Organic Pollutants (p. http://chm.pops.int/).

Su, H., Wu, F., Zhang, R., Zhao, X., Mu, Y., Feng, C., & Giesy, J. P. (2014). Toxicity reference values for protecting aquatic birds in China from the effects of polychlorinated biphenyls. In *Reviews of Environmental Contamination and Toxicology volume* (pp. 59–82). Springer.

Tanabe, S., Tanaka, H., & Tatsukawa, R. (1984). Polychlorobiphenyls, $Σ$DDT, and hexachlorocyclohexane isomers in the western North Pacific ecosystem. *Archives of Environmental Contamination and Toxicology*, *13*(6), 731–738. http://doi.org/10.1007/BF01055937

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., & Watanuki, Y. (2015). Facilitated leaching of additive-derived PBDEs from plastic by seabirds' stomach oil and accumulation in tissues. *Environmental Science & Technology*, 150901174241000. http://doi.org/10.1021/acs.est.5b01376

Van Den Brink, N. W. (1997). Directed transport of volatile organochlorine pollutants to polar regions: The effect of the contamination pattern of Antarctic seabirds. *Science of the Total Environment*, *198*(1), 43–50. http://doi.org/10.1016/S0048-9697(97)05440-5

Van Den Brink, N. W., & Bosveld, A. T. C. (2001). PCB concentrations and metabolism patterns in common terns (Sterna hirundo) from different breeding colonies in The Netherlands. *Marine Pollution Bulletin*, *42*(4), 280–285. http://doi.org/10.1016/S0025-326X(00)00151-X

Van den Steen, E., Covaci, A., Jaspers, V. L. B., Dauwe, T., Voorspoels, S., Eens, M., & Pinxten, R. (2007). Experimental evaluation of the usefulness of feathers as a non-destructive biomonitor for polychlorinated biphenyls (PCBs) using silastic implants as a novel method of exposure. *Environment International*, *33*(2), 257–264.

Van Franeker, J. a. (2004). Save the North Sea fulmar-Litter-EcoQO Manual Part 1: Collection and dissection procedures., 38. Retrieved from http://edepot.wur.nl/40451

Wan, Y., Jin, X., Hu, J., & Jin, F. (2007). Trophic dilution of polycyclic aromatic hydrocarbons (PAHs) in a marine food web from Bohai Bay, North China. *Environmental Science & Technology*, *41*(9), 3109–3114.

Wang, J., Caccamise, S. a. L., Woodward, L. A., & Li, Q. X. (2015). Polychlorinated Biphenyls in the Plasma and Preen Oil of Black-Footed Albatross (Diomedea nigripes) Chicks and Adults on Midway Atoll, North Pacific Ocean. *Plos One*, *10*(4), e0123041. http://doi.org/10.1371/journal.pone.0123041

Yamashita, R., Takada, H., Murakami, M., Fukuwaka, M. A., & Watanuki, Y. (2007). Evaluation of noninvasive approach for monitoring PCB pollution of seabirds using preen gland oil. *Environmental Science and Technology*, *41*(14), 4901–4906. http://doi.org/10.1021/es0701863

CHAPTER 6:

CONCLUSIONS

"In nature, nothing exists alone."

Rachel Carson

6. CONCLUSIONS

6.1. MARINE LITTER MONITORING THROUGH SEABIRDS

6.1.1. THE REPUBLIC OF IRELAND BEACHED BIRD SURVEY

The Republic of Ireland Beached Bird Survey (RIBBS) was created to assess the utility of seabird strandings to investigate presence and marine litter ingestion by seabirds in Ireland. It is co-ordinated by the author, as a part of their doctoral research and it is additionally supported by the Department of Housing, Planning, Community and Local Government (DECLG).

Bird necropsies were conducted by the author, following OSPAR protocols (Van Franeker, 2004), following training in the Netherlands, at IMares by Jan Andries van Franeker, coordinator of the Fulmar Litter EcoQO Monitoring Project along Dutch and North Sea Coasts.

When seabirds die at sea their remains may be brought ashore by tide, wind and currents. Seabird wrecks are relatively common occurrences, but contrary to cetacean strandings, seabird strandings are often ignored by society. There are many possible and interacting reasons for seabird wrecks including shifts in food availability, starvation and severe storm events (Acampora et al., 2014; Parrish et al., 2007).

This project relied on volunteer work through the public and institutions that commit to walk beaches on a regular basis and report/collect dead seabirds for research. This has optimised sampling by encompassing multiple locations and species, and by engaging citizens in environmental awareness and science related activities. Taking advantage of seabird strandings is a non-destructive way to monitor for marine litter presence and ingestion. Another approach to monitoring marine litter in seabirds, rather than collecting them at beaches was to collect them at breeding colonies during the summer. It is natural to have casualties at breeding colonies for multiple reasons and if access is granted, collecting those carcasses can be an alternative sample supply during the summer, when fewer weather related casualties are beached.

Although both strategies have taken advantage of a multi-species approach to establish baseline values for plastic pollution interacting with seabirds in Ireland, it was of particular interest evaluating the feasibility of the Northern Fulmar as an indicator species nationally, following the example of the North Sea (OSPAR, 2010). Our research has concluded that the Northern Fulmar is the most appropriate species for monitoring in Ireland as it is in the North Sea. This is due to its tendency of ingesting and accumulating plastic litter (Van Franeker et al., 2003), in especially high rates of prevalence (93%), number of particles (65.35 ± 32.67 SE) and mass (1.11 g ± 0.56 SE) in Ireland, in comparison with the Netherlands, for instance, where in 2014 (n=11), there was a 100% prevalence, an average of 22.6 ± 4.0 number of particles and 0.38 g ± 015 mass of plastics (Van Franeker, 2014). Beached numbers can be variable, like in any other species, since strandings are a chance event. According to Van Franeker et al. (2011), a sample of 40 Fulmars in the space of five years is sufficient to verify trends in plastic litter. Additionally, this study has demonstrated that all species (n= 16) of marine birds investigated (n= 121) are susceptible to ingesting litter (Acampora et al., 2016), thus it is considered to be important to monitor other species as well, as for instance, the likelihood of ingestion can change and it is crucial to monitor those changes and inform policy.

6.1.2. ALTERNATIVE METHODOLOGIES: NON-DESTRUCTIVE SAMPLING

As strandings are a chance event, it was decided to investigate alternatives. Plastic litter is not always the primary cause of death in birds (Kühn et al., 2015; Rochman et al., 2016), thus it is suitable to investigate ways to monitor for marine litter in live birds using non-destructive sampling. The techniques used in this approach were purely opportunistic, but can be done via a planned sampling strategy if necessary. As demographic work and ringing are carried out on breeding colonies every summer, there is an opportunity to collect additional samples, such as boluses expelled by certain seabird species. Many species expel boluses made of indigestible items, such as fish bones, otoliths and potentially, litter (Barrett et al., 2007). Additionally, due to the stress of being handled or as a defence mechanism, many birds regurgitate upper stomach contents (Barrett et al., 2007). If one is prepared, contents can be easily collected for subsequent analysis in the lab.

Boluses from Great Cormorants (*Phalacrocorax carbo*) were collected during summer and winter (breeding colony and winter roost site) and analysed for plastic litter presence and abundance. Plastic prevalence was consistent between both seasons and was present at a low rate (3.2%, n= 92). There are very little published data on prevalence of plastic litter in Great Cormorants globally and none in Ireland. It is important to report such findings to promote data comparability. Ingestion in many species is not reported because little or no plastic was found. This prevents the identification of patterns of ingestion among different species.

Additionally, spontaneous regurgitates from three different species of seabird chicks were collected: Northern Fulmar (*Fulmarus glacialis*), Black-legged Kittiwake (*Rissa tridactyla*) and Great Cormorant (*Phalacrocorax carbo*). Unfledged chicks were only fed by their parents via regurgitation, so regurgitates would show plastic in the diet of chicks, which is a knowledge gap for many species, especially in Ireland, but such regurgitates are also a proxy for the parents' diet. Plastic was found in all three species, with the largest prevalence in Fulmar chicks (28.6%) and the smallest in Great Cormorants (7.1%). Chicks get all nutrition from their parents and need a larger amount of food in the first two weeks of their lives to cope with growth and development before fledging (Arizaga et al., 2015; Carey, 2011). Plastics in their diet could be hampering development and prevent fledging. The presence of plastic in a birds' diet is particularly more harmful then at such age when affecting fledging could lead to population effects.

Additionally, when combined with data from adult boluses and stomach analyses, regurgitate data confirm that plastic litter is present throughout the life cycle of many seabird species. In combination, these alternative techniques provided an insight into the incidence of plastic in the diet of live chicks and adult seabirds. Through their use in conjunction with ringing, it may be possible to investigate effects on individuals if previously known birds are encountered in subsequent breeding seasons.

6.2. PERSISTENT ORGANIC POLLUTANT MONITORING IN SEABIRDS

6.2.1. NON-DESTRUCTIVE SAMPLING METHODOLOGIES

Non-destructive sampling allows for a larger number of individuals to be sampled, and for multiple species. However, the goal is that non-destructive sampling be a proxy for what one would find in destructive sampling, e.g. in internal organs (Jaspers et al., 2011; Wang et al., 2015; Yamashita et al., 2007). Preen oil and feather samples collected from Storm Petrels (*Hydrobates pelagicus*) revealed similar concentrations to similar species in same and different matrices around the world. For instance, PCB concentrations in feathers (∑ 7 PCBs= 20.2 ng/g) of European Storm Petrels were lower than the ones found in Leach's Storm Petrels from the UK, but yet comparable (∑ 7 PCBs= 36.2 ng/g) (Megson et al., 2014). Additionally, BFR concentrations in eggs of Leach's Storm Petrels (*Oceanodroma leucorhoa*) were very similar (3.38 ng/g) to the ones found in feathers (4.38 ng/g) and preen oil (3.69 ng/g) (Elliott et al., 2005).

POP concentrations from Common Terns (*Sterna hirundo*) were also comparable to others found globally. For instance, PAH levels in preen oil, feathers, liver and preen gland were similar to the values in liver of Cory's Shearwaters (*Calonectris diomedia*) (Range: 3.32 – 17.1 ng/g) (Roscales et al., 2011). When comparing destructive and non-destructive sampling from our study, concentrations in internal organs were slightly higher than feathers and preen oil, but more similar to feathers. For instance, ∑ PCB in preen oil was 4.21 ng/g, compared to 36.47 ng/g in feathers, 41.44 ng/g in liver and 44.1 ng/g in preen gland. However, it is important to consider individual differences as these were different birds, even if from the same colony. Larger values are expected as internal organs are the ones accumulating, metabolising or distributing contaminants. Plus, persistent organic pollutants are highly lipophilic and hydrophobic, being more concentrated in lipid rich tissue (Jones and de Voogt, 1999). Additionally, body condition of live birds was very different than most corpses, which normally were in bad condition and might have starved.

When comparing the two alternatives, feathers had, for the most part, in Storm Petrels and Common Terns, higher concentrations than preen oil. This may have been due to

the fact that as feathers have the additional input of the preen oil itself and external contamination, as well as blood flow when feathers are growing (Jaspers et al., 2008).

The fact that a large number of congeners was found in preen oil and feathers for all four investigated contaminants, in comparable concentrations to what is found in literature led to the conclusion that both preen oil and feathers are suitable alternatives for POP monitoring of multi-species of seabirds and they can allow for larger data sets to be collected, thus establishing baseline values for many species of seabirds in Ireland. However, congener profiles differed highly between both sampling matrices. Feathers, instead of preen oil might give a more absolute concentration of contaminants as they encompass the burden from the blood and the input of the preen oil, but due to the specificity of congeners, it could also leave out important congener toxicity information. Differences in congeners can be attributed to species-specific metabolism and elimination, thus making it possible to overlook the absence of a certain congener (Barron et al., 1995). Overall, it is recommended, when possible, that more than a single matrix to be used to establish POP concentrations.

6.2.2. DESTRUCTIVE SAMPLING

Destructive sampling was used on Common Terns that were found dead, thus no birds were sacrificed specifically for this sampling. The internal organs of colony corpses (that were additionally used for plastic research) were sampled and analysed for persistent organic pollutants. This was done in order to investigate whether or not the presence of plastic litter in dead birds had an effect on the concentration of pollutants, since some of these are used as additives in the manufacturing of plastic products and because many POPs adhere to the surface of waterborne plastic particles due to their hydrophobic properties (Colabuono et al., 2010). However, based on the data from this study, the majority of Common Terns sampled did not contain any plastic. Only one single piece was found in one specimen (n=40). Nevertheless, organs such as liver and preen gland receive the processing or the result of the metabolising of POPs, thus if these compounds are present, they are expected to be present at higher levels in such organs (Falkowska et al., 2016).

It is advisable that when birds are found dead, to take the opportunity to look at the concentration of POPs in such specimens to compare such values with the ones acquired in non-destructive sampling, as it was seen on this research that concentrations and congener profiles can differ very much from one another. However, death by starvation can affect the way the lipid reserves are mobilised and concentrations of pollutants are expected to be higher in such cases (Jaspers et al., 2008). Starvation was the inferred cause of death in most beached or colony birds sampled during the present study therefore that must be taken into consideration. For that, it is reinforced that multiple approaches are more suitable to monitor contamination, thus investigating live birds, through non-destructive sampling in a joint effort along with the investigation of corpses has the power to provide more reliable information about the actual status of persistent organic pollution contamination in seabirds breeding in Ireland. Internal organs from dead seabirds alone resulted in much individual variation as birds were found dead in different circumstances and conditions, thus such sampling could bias results if used alone.

Concentrations found in Common Terns' liver and preen gland in Ireland were compared with values where known toxicological effects of POPs have been reported. Concentrations of POPs in Common Terns in Ireland (4.21 – 44.1 ng/g for PCBs and 3.68 – 15.14 for OCPs) are much less than reported toxicological levels (The lowest observed adverse effects level (LOAEL) in Common Terns is 8 mg/kg (= 8000 ng/g) (Bosveld and Berg, 1994) and this population is not believed to be at risk of embryonic, reproductive and endocrine disruption. However, some of the levels found in birds from this study exceeded monitoring levels established for POPs in eggs of Common Terns, such as the Ecological Quality Objectives (EcoQO) by the Olso-Paris Convention (OSPAR) (OSPAR, 2010). This fact enhances the importance of a periodical and continuous monitoring of POP concentrations in Common Terns.

6.3. PROSPECTS FOR FUTURE RESEARCH

Marine litter research and its interaction with seabirds in Ireland is only beginning to establish itself and there is still a long way to go in data collection to provide a full

status of the subject regionally and how it is affecting the Irish environment and wildlife. This research has concluded that the methods tested were efficient in obtaining baseline values for how several species of seabirds are interacting with plastic pollution. Future research should focus on more data collection, through multiple approaches rather than one, in all seabird species breeding in Ireland to verify interaction of marine litter, especially plastics with additional species. Additionally, biometric data can be collected in colonies along with regurgitates and when birds are recaptured, potential impacts can be identified if attributed to plastic interactions. Boluses can be collected systematically and regurgitation can be induced if it is regarded an essential sampling procedure. Additionally, observations in colonies of ingestion and entanglement can be another type of data to broaden the view of plastic pollution nationally. Satellite tagging can provide spatial coverage for the areas at sea where birds are feeding and where potentially plastic could have been ingested, if they were to reflect the pollution of the environment where they inhabit.

For persistent organic pollutants, additional species should be sampled to establish baseline data. Alternative methodologies such as eggs must additionally be tested to comply with policy. When destructive methodologies are used, plastics found in the digestive tract of birds can additionally be tested for persistent organic pollutants to perhaps enable a linkage between both types of pollutants. As persistent organic pollutants are hydrophobic compounds and known to adhere to plastic particles at sea (Rios et al., 2010), research into how plastic pollution is affecting POP concentrations is welcome. It was not possible to be addressed during this research as no European Storm Petrels corpses were found and only a single piece of plastics was found in the stomach of Common Terns. However, the importance of this work was to establish data for POPs in these species, where there was none before. Additionally, the testing of methodologies was also beneficial for research. Standardisation of methods is important for the global picture, but it is important to initially test main alternatives to verify which one is more suitable due to regional differences.

I conclude this research hoping that this body of work has contributed to the establishment of crucial baseline for non-existent data on plastics and persistent organic pollutants in seabirds in Ireland, an update on the status of seabird populations in Ireland in relation to pollution, an impact on citizens regarding environmental pollution awareness and a positive influence on environmental policy.

6.4. LITERATURE CITED

Acampora, H., Lyashevska, O., Van Franeker, J.A., O'Connor, I., 2016. The use of beached bird surveys for marine plastic litter monitoring in Ireland. Mar. Environ. Res. 120, e87–e91. doi:10.1016/j.marenvres.2016.08.002

Acampora, H., Schuyler, Q.A., Townsend, K.A., Hardesty, B.D., 2014. Comparing plastic ingestion in juvenile and adult stranded short-tailed shearwaters (Puffinus tenuirostris) in eastern Australia. Mar. Pollut. Bull. 78, 63–68.

Arizaga, J., Herrero, A., Aldalur, A., Cuadrado, J.F., Oro, D., 2015. Effect of pre-fledging body condition on juvenile survival in Yellow-legged Gull Larus michahellis. Acta Ornithol. 50, 1–9. doi:10.3161/00016454AO2015.50.2.002

Barrett, R.T., Camphuysen, K., Anker-Nilssen, T., Chardine, J.W., Furness, R.W., Garthe, S., Hüppop, O., Leopold, M.F., Montevecchi, W. a., Veit, R.R., 2007. Diet studies of seabirds: A review and recommendations. ICES J. Mar. Sci. 64, 1675–1691. doi:10.1093/icesjms/fsm152

Barron, M.G., Galbraith, H., Beltman, D., 1995. Comparative reproductive and developmental toxicology of PCBs in birds. Comp. Biochem. Physiol. Part C Pharmacol. Toxicol. Endocrinol. 112, 1–14.

Bosveld, A.T.C., Berg, M. Van den, 1994. Effects of polychlorinated biphenyls, dibenzo-p-dioxins, and dibenzofurans on fish-eating birds. Environ. Rev. 2, 147–166.

Carey, M.J., 2011. Intergenerational transfer of plastic debris by Short-tailed Shearwaters (Ardenna tenuirostris). Emu 111, 229–234. doi:10.1071/MU10085

Colabuono, F.I., Taniguchi, S., Montone, R.C., 2010. Polychlorinated biphenyls and organochlorine pesticides in plastics ingested by seabirds. Mar. Pollut. Bull. 60, 630–634. doi:10.1016/j.marpolbul.2010.01.018

Elliott, J., Wilson, L.K., Wakeford, B., 2005. Polybrominated Diphenyl Ether Trends in Eggs of Marine and Freshwater Birds from British Columbia , Canada , 1979 - 2002. Environ. Sci. Technol. 39, 5584–5591.

Falkowska, L., Reindl, A.R., Grajewska, A., Lewandowska, A.U., 2016.

Organochlorine contaminants in the muscle, liver and brain of seabirds (Larus) from the coastal area of the Southern Baltic. Ecotoxicol. Environ. Saf. 133, 63–72. doi:10.1016/j.ecoenv.2016.06.042

Jaspers, V.L.B., Covaci, A., Deleu, P., Neels, H., Eens, M., 2008. Preen oil as the main source of external contamination with organic pollutants onto feathers of the common magpie (Pica pica). Environ. Int. 34, 741–748. doi:10.1016/j.envint.2007.12.002

Jaspers, V.L.B., Rodriguez, F.S., Boertmann, D., Sonne, C., Dietz, R., Rasmussen, L.M., Eens, M., Covaci, A., 2011. Body feathers as a potential new biomonitoring tool in raptors: a study on organohalogenated contaminants in different feather types and preen oil of West Greenland white-tailed eagles (Haliaeetus albicilla). Environ. Int. 37, 1349–1356.

Jones, K.C., de Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. Environ. Pollut. 100, 209–221. doi:http://dx.doi.org/10.1016/S0269-7491(99)00098-6

Kühn, S., Bravo Rebolledo, E.L., Franeker, J.A., 2015. Marine Anthropogenic Litter, in: Bergmann, M., Gutow, L., Klages, M. (Eds.), . Springer International Publishing, Cham, pp. 75–116. doi:10.1007/978-3-319-16510-3_4

Megson, D., Brown, T.A., Johnson, G.W., O'Sullivan, G., Bicknell, A.W.J., Votier, S.C., Lohan, M.C., Comber, S., Kalin, R., Worsfold, P.J., 2014. Identifying the provenance of Leach's storm petrels in the North Atlantic using polychlorinated biphenyl signatures derived from comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. Chemosphere 114, 195–202. doi:10.1016/j.chemosphere.2014.04.061

OSPAR, 2010. The Ospar system of Ecological Quality Objectives for the North sea 16.

Parrish, J.K., Bond, N., Nevins, H., Mantua, N., Loeffel, R., Peterson, W.T., Harvey, J.T., 2007. Beached birds and physical forcing in the California Current System. Mar. Ecol. Prog. Ser. 352, 275–288. doi:10.3354/meps07077

Rios, L.M., Jones, P.R., Moore, C., Narayan, U. V, 2010. Quantitation of persistent organic pollutants adsorbed on plastic debris from the Northern Pacific Gyre's "eastern garbage patch". J. Environ. Monit. 12, 2226–2236. doi:10.1039/c0em00239a

Rochman, C.M., Browne, M.A., Underwood, A.J., van Franeker, J.A., Thompson, R.C., Amaral-Zettler, L.A., 2016. The ecological impacts of marine debris: unraveling the demonstrated evidence from what is perceived. Ecology 97, 302–312. doi:10.1890/14-2070.1

Roscales, J.L., Gonzalez-Solis, J., Calabuig, P., Jimenez, B., 2011. Interspecies and spatial trends in polycyclic aromatic hydrocarbons (PAHs) in Atlantic and Mediterranean pelagic seabirds. Environ. Pollut. 159, 2899–2905. doi:10.1016/j.envpol.2011.04.034

van Franeker, J.A., 2014. Fulmar Litter EcoQO Monitoring in the Netherlands. IMARES, Wageningen UR.

Van Franeker, J.A., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., Hansen, P.L., Heubeck, M., Jensen, J.K., Le Guillou, G., Olsen, B., Olsen, K.O., Pedersen, J., Stienen, E.W.M., Turner, D.M., 2011. Monitoring plastic ingestion by the northern fulmar Fulmarus glacialis in the North Sea. Environ. Pollut. 159, 2609–2615. doi:10.1016/j.envpol.2011.06.008

Van Franeker, J.A., Meijboom, A., de Jong, M.L., 2003. Marine litter monitoring by Northern Fulmars in the Netherlands 1982-2003. Wageningen, Alterra, Alterra-rapport 1093.

Van Franeker, J. a, 2004. Save the North Sea fulmar-Litter-EcoQO Manual Part 1: Collection and dissection procedures. 38.

Wang, J., Caccamise, S. a. L., Woodward, L.A., Li, Q.X., 2015. Polychlorinated Biphenyls in the Plasma and Preen Oil of Black-Footed Albatross (Diomedea nigripes) Chicks and Adults on Midway Atoll, North Pacific Ocean. PLoS One 10, e0123041. doi:10.1371/journal.pone.0123041

Yamashita, R., Takada, H., Murakami, M., Fukuwaka, M.A., Watanuki, Y., 2007. Evaluation of noninvasive approach for monitoring PCB pollution of seabirds

using preen gland oil. Environ. Sci. Technol. 41, 4901–4906. doi:10.1021/es0701863

APPENDIX 1

Marine Environmental Research 120 (2016) 122–129

Contents lists available at ScienceDirect

Marine Environmental Research

journal homepage: www.elsevier.com/locate/marenvrev

The use of beached bird surveys for marine plastic litter monitoring in Ireland

Heidi Acampora [a, *], Olga Lyashevska [a], Jan Andries Van Franeker [b], Ian O'Connor [a]

[a] Galway-Mayo Institute of Technology, Marine & Freshwater Research Centre, Dublin Rd, Galway, Ireland
[b] IMARES, Ankerpark 27, 1781, AG Den Helder, The Netherlands

ARTICLE INFO

Article history:
Received 7 June 2016
Received in revised form
28 July 2016
Accepted 1 August 2016
Available online 2 August 2016

Keywords:
Ingestion
Plastic litter
Fulmar
Multispecies
Beached bird survey

ABSTRACT

Marine plastic litter has become a major threat to wildlife. Marine animals are highly susceptible to entanglement and ingestion of debris at sea. Governments all around the world are being urged to monitor litter sources and inputs, and to mitigate the impacts of marine litter, which is primarily composed of plastics. European policies, such as Oslo-Paris Convention (OSPAR) and Marine Strategy Framework Directive (MSFD) have adopted the monitoring of a seabird species, the Northern Fulmar (*Fulmarus glacialis*), as an environmental quality indicator through the analysis of stomach contents of beached Fulmar specimens. The aims of this research were to: firstly set a baseline investigation of multispecies of seabirds in Ireland affected by the ingestion of litter and, secondly to investigate the feasibility of using Fulmar and/or other potential species of seabird as an indicator for marine debris in Ireland through beached bird surveys. Within 30 months, 121 birds comprising 16 different species were collected and examined for the presence of litter. Of these, 27.3% (n = 33) comprising 12 different species were found to ingest litter, mainly plastics. The average mass of ingested litter was 0.141 g. Among 14 sampled Northern Fulmars, 13 (93%) had ingested plastic litter, all of them over the 0.1 g threshold used in OSPAR and MSFD policy target definitions. Results show that seabirds in Ireland are ingesting marine litter, as in many other countries in the world. Monitoring seabird litter ingestion has the potential to form part of a wider marine litter monitoring programme that can help to inform mitigation and management measures for marine litter.

1. Introduction

Marine litter has become a global concern. It has been estimated that at least 8 million tonnes of plastics enter the oceans every year (Jambeck et al., 2015) and plastics comprise >90% of marine litter (Galgani et al., 2015). Gall and Thompson (2015) list 693 marine species directly affected by marine litter through documented ingestion or entanglement.

The Northern Fulmar (*Fulmarus glacialis*), due to its abundance in the North Atlantic, extensive distribution, oceanic niche and its inclination to ingest marine litter, has been chosen as an indicator species for European policy compliance, such as the Oslo-Paris Convention (OSPAR) and the Marine Strategy and Framework Directive (MSFD). The use of this species to monitor marine litter originated in the Netherlands (Van Franeker and Meijboom, 2002) and, due to its efficacy, it has been incorporated into policy and expanded to other countries, where appropriate (Van Franeker and SNS Fulmar Study Group, 2013; Van Franeker et al., 2011). OSPAR has set a target for an acceptable amount of litter (EcoQO – Ecological Quality Objective) at 0.1 g of plastic in no more than 10% of Fulmars found in samples from between 50 and 100 birds over a period of at least 5 years (OSPAR, 2010). The selection of a certain species as an indicator allows for analysis of trends and data comparison with other parts of the world if methodology is standardized. However, a multispecies approach may facilitate investigation of factors driving certain species to ingest plastic litter or account for variation in composition, amounts and trends among different species. Such an approach may also be useful in determining alternative species for use in a monitoring programme.

A recent study (Lusher et al., 2014) estimated an average number of 2.46 plastic particles m^{-3} in the Northeast Atlantic; however most of particles identified (89%) were classified as microplastics (<5 mm) and 96% of items were thin, dust like fibers. Plastic litter was also reported in the stomachs of True's beaked whales stranded

* Corresponding author.
E-mail address: heidiacampora@gmail.com (H. Acampora).

http://dx.doi.org/10.1016/j.marenvres.2016.08.002
0141-1136/

on Irish beaches (Lusher et al., 2015). Fisheries related litter was reported to be 51% of all litter reported in Irish waters during Bottom Trawl Surveys between 2010 and 2014 (Moriarty et al., 2016). While there is little information on abundance and distribution of marine litter in Ireland there is no published information concerning marine litter and seabirds in Irish waters.

Ireland, along with Great Britain, is home to almost 8 million breeding seabirds, comprising 25 different species, including 90% of the world's Manx Shearwaters (*Puffinus puffinus*), 68% of Northern Gannets (*Morus bassanus*), and 60% of Great Skuas (*Stercorarius skua*). About 34,000 pairs of Northern Fulmars breed in Ireland (Mitchell et al., 2004). Seabirds provide robust environmental monitoring information because they are long-lived, philopatric species and top predators that feed on a variety of levels of the food chain (Furness and Camphuysen, 1997). In order to investigate the feasibility of implementing a marine litter programme that could contribute to reporting for OSPAR and MSFD the work described here intended to: (1) provide a baseline assessment of the prevalence of marine litter affecting multi-species populations of seabirds in Ireland and to discuss the implications of said data; (2) investigate the implementation of the EcoQO for marine litter monitoring in Ireland.

2. Materials and methods

2.1. Sampling

The Republic of Ireland Beached Bird Survey (RIBBS) was a project created in January 2014 to collect dead seabirds along the shore and use them in an attempt to describe the ingestion of marine litter by seabird species in Ireland. Sampling for the current analysis continued to April 2016 and thus covers just over two years of effort. Two Fulmars collected during a preliminary survey in 2012 have been added to the results. Volunteers walked their selected beaches regularly and collected or reported the presence of dead seabirds of any species for subsequent return to the co-ordinator (Fig. 1). Birds were kept frozen (−20 °C) at the Marine & Freshwater Research Centre at the Galway-Mayo Institute of Technology, in Galway, until dissection.

2.2. Dissections

Dissections were performed following the methodology of Van Franeker (2004) to allow for data comparability. Birds were scored for general condition index (0–9) according to the sum of subcutaneous fat, breast muscle and intestinal fat scores. Each organ was also scored for health condition. Age (juvenile, immature and adult) and sex were determined according to plumage and the maturity of sexual organs.

After dissection, stomach contents were washed and sieved through a 1 mm mesh following methods in Van Franeker et al. (2011). All solids were retained and air-dried overnight (Fig. 2). Contents were then examined under a Stereo microscope (MicrosAustria, 0.6x - 5x) and separated into categories according to Van Franeker et al. (2011). Litter items were divided into sub-categories (within plastic and non-plastic litter). As the focus of this study is plastic litter, plastic items only were weighed per sub-category to the nearest 0.0001 g.

2.3. Statistical analysis

Multi-species modelling was performed using R Core Team (2015) (package: lme4 version 1.1–12 (Bates and Mächler, 2016);); through a two-step approach (Duan et al., 1984; Min and Agresti, 2002), in which we assume that the data are generated by two underlying processes. The first process is modelled by a Bernoulli model which determines presence/absence ('prevalence') of litter in birds' stomachs. Conditionally on the positive outcome, the second process is modelled by a Gamma model and determines the amount of litter. This two-step approach is needed because the data are zero inflated (73% of the data is composed of zeroes). For both steps a Generalized Linear Mixed Model (GLMM) was used. GLMM is an extension of Generalized Linear Models (GLM), which includes both fixed and random effects (hence mixed models) in a linear predictor, via maximum likelihood.

On the first step, the data was analysed for presence/absence ('prevalence') of plastic litter in birds' stomachs. A linear predictor for 'Litter Presence' is the combination of the fixed and random effects. 'Family' was included as a random effect allowing for random intercept for each family. This is because birds within families are expected to correlate, whereas birds between families do not. All other variables were included as a fixed effect. This first step was modelled with a logit link function for having zero (no plastics) or positive values (plastics present), and included all variables assumed to influence the presence/absence of plastic litter. The fixed explanatory variables were: 'Sex', 'Age' and 'Feeding Source'. The model specification was: Litter.

Fig. 1. Beached Northern Fulmar (*Fulmarus glacialis*) at Connemara, Co. Galway, 2014 collected during a beached bird survey.

Fig. 2. Stomach contents of beached Northern Fulmar portrayed in Fig. 1. Foam and hard plastic fragments are the main components of sample.

Presence ~ (1|Family) + Sex + Age + Feeding Source. This model included 104 observations as 17 were deleted due to missing values in one or more of the explanatory variables (usually sex or age, as it was not possible to determine these for every individual). Coefficients for 'Age' were very similar to each other as well as their standard errors. This suggests that age group was not of importance to litter presence. To test whether age was useful as a variable, it was then omitted from the model, refit and then compared to the original model according to the change in AIC. The same way, the model was tested by removing 'Family' as a random effect. The model fit was assessed using AIC values.

On the second step, conditionally on the positive outcome of the first step, the amount of plastic litter was modelled using log link function. This step modelled positive values (plastics present), by evaluating plastic litter mass as a function of the same variables as in the first step of the model. Again, 'Family' was taken as a random effect to account for statistical independence of such variable. The model specification was: Litter.Mass ~ (1|Family) + Sex + Age + Feeding Source. Due to aforementioned absence of explanatory data for 9 observations, this analysis was performed with 24 (positive) observations. Additionally, the second step of the model was applied on only the variable ("Family") found to be significant in the previous model to verify for any variation within the family itself and any additional influence by relevant variables. The model specification was: Litter.Mass ~ Species + Sex + Age. Significance level was set at <0.05.

Birds were aggregated into families due to the small sample size for some of the individual species. The variable "Feeding Source" was a factor with 3 levels and it included the species listed in Table 1 with the corresponding sources. The 'Marine' feeding source, included species known to feed mainly offshore; 'Mixed' included species that have a mixed diet that consists of items found in coastal and terrestrial environments (including landfills); and lastly, 'Klepto' included species that are known for kleptoparasitism (Ashmole, 1971).

As birds with no litter (zeroes) represent actual outcomes of the data, they have to be incorporated in the averaged results. Thus averages for number and mass of plastics in stomachs are given as 'population averages', in which all zero values are included with data variability given as standard error (±se) (Van Franeker et al., 2011).

3. Results

For the present study, 121 seabirds were analysed, comprising 16 different species described in Table 2. Specimens were collected in the following years: 2012 (2 – archived samples), 2014 (36), 2015 (62) and 2016 (21) in 12 different counties and four coastal islands (Fig. 3), in Ireland. Of the 121 birds collected, 33 individuals (27.3%) had ingested plastic litter. This represented 12 (75%) of the 16 species collected. The species specific prevalence and abundance by number and mass of ingested plastic litter is listed per species in Table 3.

Plastic ingestion was most prevalent in Northern Fulmars. Among the 14 Fulmar stomachs sampled, there was a 93% prevalence with an average number of 65 ± 33 plastic particles and average mass of 1.1 ± 0.6 g of plastic per individual bird. The 13 Fulmars that contained plastic in their stomachs exceeded the threshold of 0.1 g of plastic as used by OSPAR and EU for defining policy targets of ecological or environmental quality (Fig. 4). The averaged data was strongly affected by a single bird having more than 8 g of plastic in the stomach (Fig. 5). The geometric mean mass of plastics in Fulmars was 0.3367 g. By category of plastic, the average Fulmar had 1.14 industrial particles (0.032 g) and 64 user plastic particles (1.0739 g). Within user plastics sub-category, foam (Av. number = 33, Av. mass = 0.2407 g) and fragments (Av. number = 26, Av. mass = 0.8024 g) were the most frequent items.

Further data for species with sample size exceeding 10 individuals showed contrast between Common Guillemot (12% prevalence) and Razorbill (0%) and plastic ingestion in 27% of Northern Gannets and 32% of Herring Gulls. For species with sample size of 10 or less, see Table 3 for details.

Multispecies samples consisted of 45.4% females (n = 55), 42.1% males (n = 51) and 12.3% of unknown sex (n = 15); 20.7% juveniles (n = 25), 35.5% immature (n = 43), 33.0% adults (n = 40) and 10.7% of unknown age (n = 13). Out of the 33 birds that had ingested plastics, 45.4% (n = 15) were females, 27.3% (n = 9) were males and 27.3% (n = 9) were of unknown sex.

Results from the first step of the multispecies model (GLMM Bernoulli distribution with logit link function) analysis, found the reduced version (excluding 'Age') to be more adequate by comparing AIC values (108.6 × 105.5). Feeding source 'Mixed' is significant in both models, with a stronger significance ($p = 0.0451$) in the reduced model. This suggests that feeding source has an effect on litter presence. Since the responses modelled directly were using a logit link, an inverse of the link function $\exp(x)/(1 + \exp(x))$ was needed to extract and back transform the fixed effect terms and interpret the model. Such approach has shown that the significant value for 'Mixed' feeding source needs to be taken with caution as the predicted probability of litter presence in a bird with a mixed feeding type is 18.46%. When looking at 'Family'

Table 1
Feeding source aggregation as well as family grouping are described by species' scientific and common names. Due to the small sample size for some species, these were grouped into families to make statistical analysis possible. Definitions are provided in 'Material and Methods' section.

Species (common name)	Scientific name	Feeding source	Family grouping
Black Guillemot	*Cepphus grylle*	Marine	Alcidae
Black-legged Kittiwake	*Rissa tridactyla*		Laridae
Common Guillemot	*Uria aalge*		Alcidae
European Shag	*Phalacrocorax aristotelis*		Phalacrocoracidae
Manx Shearwater	*Puffinus puffinus*		Procellariidae
Northern Fulmar	*Fulmarus glacialis*		Procellariidae
Northern Gannet	*Morus bassanus*		Sulidae
Razorbill	*Alca torda*		Alcidae
Sabine's Gull	*Xema sabini*		Laridae
Atlantic Puffin	*Fratercula arctica*		Alcidae
Black-headed Gull	*Larus ridibundus*	Mixed	Laridae
Herring Gull	*Larus argentatus*		Laridae
Iceland Gull	*Larus glaucoides*		Laridae
Parasitic Jaeger	*Stercorarius parasiticus*	Klepto	Stercorariidae
Great Black-backed Gull	*Larus marinus*		Laridae
Lesser Black-backed Gull	*Larus fuscus*		Laridae

Table 2
Sample description (sex and age not always known); ordered by sample size.

Species' common name	Sample size (n)	Sex Male/Female	Age Juvenile/Immature/Adult
Common Guillemot	25	13/12	5/10/9
Northern Gannet	15	4/6	2/0/9
Razorbill	15	7/7	1/8/5
Northern Fulmar	14	3/7	3/2/5
Herring Gull	13	5/6	6/4/2
European Shag	10	6/4	1/7/2
Black-headed Gull	9	3/5	1/4/3
Great Black-Backed Gull	4	2/1	0/2/1
Black-legged Kittiwake	4	0/4	2/1/1
Manx Shearwater	3	2/1	0/1/2
Atlantic Puffin	3	3/0	1/2/0
Lesser Black-backed Gull	2	1/0	0/1/1
Parasitic Jaeger	1	1/0	1/0/0
Black Guillemot	1	1/0	1/0/0
Iceland Gull	1	0/1	0/1/0
Sabine's Gull	1	0/1	1/0/0

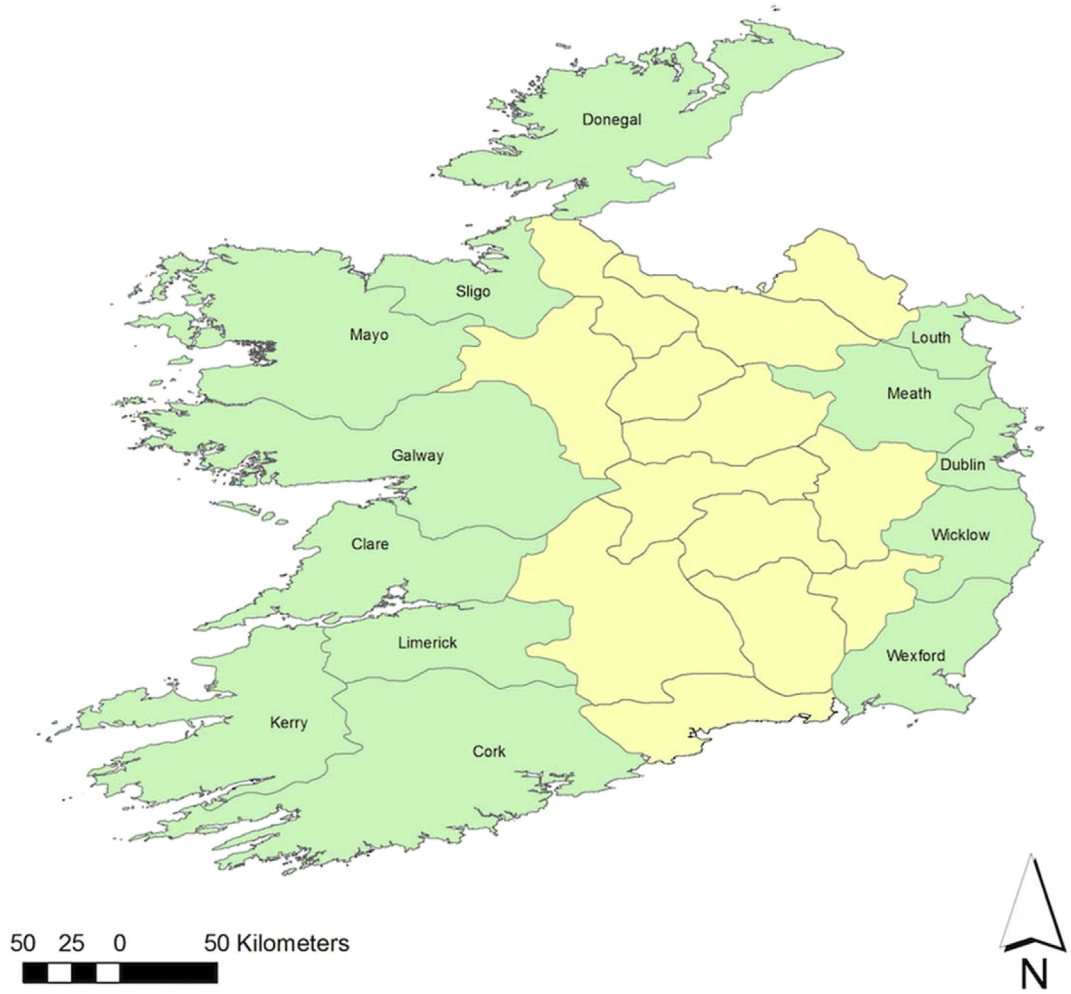


Fig. 3. Counties in green colour denote sampled sites, along with coastal islands off counties Donegal, Dublin and Kerry. Sites on the west are on the Atlantic coast, whilst sites on the east coast are surrounded by the Irish sea. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as a random effect, the estimated variability in the intercept of the random effect is 1.51, which is distinguishable from zero, meaning therefore that the random effect 'Family' is of importance to the model. The among 'Family' standard deviation is 1.23 and the variance is $1.23^2 = 1.51$. To assess model fit, 'Family' was also removed as a random effect and by comparing AIC values (105.5×115.04), it was confirmed that the GLMM was more adequate than a regular GLM. When interpreting the random effect analysis, the family 'Procellariidae' appears to have a much higher effect on positive litter presence than other families from this study

Table 3
Plastic litter abundance per species (ordered by sample size; population averages are provided and included zero values).

Species	Sample (n)	Prevalence (%)	Average number of particles n ± se	Average mass g ± se
Common Guillemot	**25**	12%	0.12 ± 0.06	0.0001 ± 0.0001
Northern Gannet	**15**	27%	0.46 ± 0.23	0.0225 ± 0.0175
Razorbill	**15**	0%	0	0
Northern Fulmar	**14**	93%	65.35 ± 32.67	1.1147 ± 0.5681
Herring Gull	**13**	32%	1.3 ± 1.22	0.0011 ± 1.1147
European Shag	**10**	10%	0.2 ± 0.2	0.0001 ± 0.0001
Black-headed Gull	**9**	22%	1.33 ± 0.94	0.0063 ± 0.0054
Black-legged Kittiwake	**4**	50%	2 ± 1.41	0.0069 ± 0.0066
Great Black-backed Gull	**4**	25%	9 ± 9	0.0200 ± 0.02
Manx Shearwater	**3**	33%	0.33 ± 0.33	0.0004 ± 0.0004
Atlantic Puffin	**3**	33%	1.33 ± 1.33	0.0077 ± 0.0077
Lesser Black-backed Gull	**2**	100%	1 ± 0	0.4324 ± 0.2786
Parasitic Jaeger	**1**	100%	30	0.0460
Sabine's Gull	**1**	0%	0	0
Black Guillemot	**1**	0%	0	0
Iceland Gull	**1**	0%	0	0

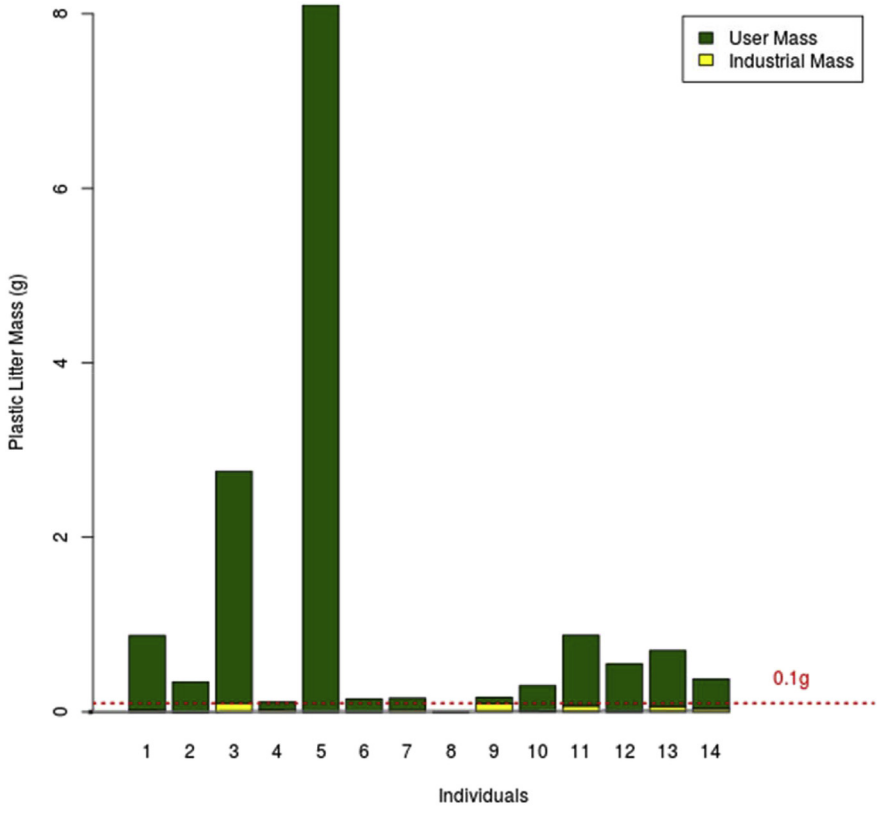


Fig. 4. Individual Fulmars plotted against plastic litter mass. All birds with plastics surpass the EcoQO threshold of 0.1 g. User mass is the main type of plastic litter found, although industrial plastic litter (nurdles) is occasionally present in samples. Individual number 5 is an extreme example, with over 8 g of plastic litter mass. Individual number 8 was the only one that contained no plastics.

(intercept = 0.8692). For a complete list of statistical outputs, see Tables 4A and B.

For the second step of the model, which analysed the positive values for litter presence and investigated the influence of additional explanatory variables such as "Litter Mass", the best fitting model was Gamma with a log link: Litter Mass ~ (1|Family) + Sex + Age + Feeding Source. This model also identified significant effects of the feeding source 'Mixed' ($p = 0.0243$) and 'Marine' ($p = 0.0060$), suggesting that feeding source could have an influence on the amount of plastic litter ingested. Also in accordance with the first step of the model, this part identified significant effects for the family 'Procellariidae'. It was necessary to back-transform random effect using exp(x), which resulted in an intercept = 94.1868, meaning that birds in the family 'Procellariidae' were found to have ingested more plastic litter than the birds from other families analysed. Additional analysis, in which the second part of the model was run using only the Family Procellariidae, which contained only two species (Northern Fulmar and Manx Shearwater), showed a significant difference between these two species regarding the amount of ingested litter ($p < 0.0001$). The variables 'Age' and 'Sex' however did not show significant influence. Caution should be taken when interpreting

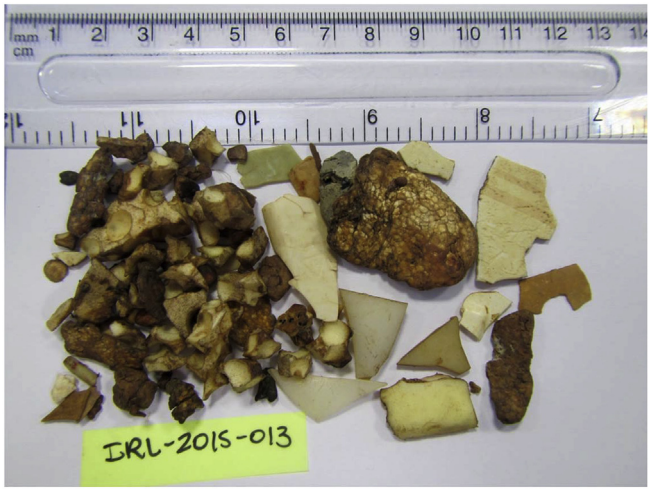


Fig. 5. Stomach contents of a beached Northern Fulmar, which amounted to 8 g of plastic litter. Foam and hard fragments are prevalent.

Table 4A
Model output from fixed effects on Step 1. Values are given on a logit scale.

	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	0.9540	1.3250	0.720	0.4715
SexM	−0.7298	0.5837	−1.250	0.2112
FeedingMarine	−1.8235	1.2491	−1.460	0.1443
FeedingMixed	−2.4389	1.2174	−2.003	0.0451*

Table 4B
Model output from random effects on Step 1. Values have been back-transformed using exp(x)/(1 + exp(x)).

	(Intercept)
Alcidae	0.2892417
Laridae	0.5028966
Phalacrocoracidae	0.3604330
Procellariidae	0.8692135
Stercorarius	0.6217054
Sulidae	0.3393089

results from this study due to limited sample size. Outputs are listed in Tables 5A and B.

4. Discussion

This study intended to provide baseline data for marine litter in seabirds in Ireland. Our results have shown that at least 12 out of the 16 analysed species have ingested plastic litter. In agreement with other studies globally, Alcids (Guillemots, Razorbills and Puffins) are shown to ingest low levels of plastic litter (9.3%) (Laist, 1997; Provencher et al., 2010; Robards et al., 1995). Procellariiformes, such as e.g. Fulmars and Shearwaters, in accordance with

Table 5A
Model output from fixed effects on Step 2. Values are given on log scale.

	Estimate	Std. Error	t value	Pr(>|z|)
(Intercept)	−0.6871	1.7774	−0.387	0.69906
SexM	−0.5229	0.9628	−0.543	0.58707
Age.L	0.0252	0.5711	0.044	0.96480
Age.Q	−0.3774	0.7880	−0.479	0.63205
FeedingMarine	−3.4094	1.5145	−2.251	0.02437*
FeedingMixed	−3.9973	1.4560	−2.745	0.00604**

Table 5B
Model output from random effects on Step 2. Values have been back-transformed using exp(x).

	(Intercept)
Alcidae	0.4881587
Laridae	0.8400705
Phalacrocoracidae	0.1294125
Procellariidae	94.1868416
Stercorarius	0.2555198
Sulidae	0.5313960

other studies, have high levels of plastic ingestion (82.3%) (Gall and Thompson, 2015; Provencher et al., 2009; Provencher et al., 2014a; Trevail et al., 2015; Van Franeker et al., 2011; Kühn et al., 2015). Based on the current results (n = 14 Fulmars) in Ireland there is a 93% prevalence of plastic litter. Since all individual Fulmars with ingested plastic exceeded the threshold of 0.1 g of plastic (Fig. 4), the current EcoQO performance for Ireland is 93%. This, at the moment, exceeds the OSPAR target of below 10%. This value is similar to that seen in the English-French Channel (99%), which is the highest in the North Sea (62%) (Van Franeker and SNS Fulmar Study Group, 2013; Van Franeker et al., 2011; Van Franeker and Law, 2015). Currently, in the Netherlands, 57% of the Fulmars (n = 171) exceed the EcoQO between 2010 and 2014 (Van Franeker, 2014). Procellariiformes were statistically significantly (Table 4) more prone to ingesting litter than other families included in this study. Reasons behind the amounts of litter found in Procellariiformes could relate to their surface feeding habits (Mallory, 2006; Van Franeker et al., 2011), which would overlap with positively buoyant plastic debris. Additionally, the narrow connector between the proventriculus and the gizzard, which prevents efficient regurgitation, could perhaps facilitate longer retention times (Ryan, 2015; Van Franeker and Law, 2015). However, when comparing Procellariiformes in this study, there was also a significant difference in the amount of plastic litter ingested by Fulmars and Manx Shearwaters ($p < 0.0001$), though the small sample size of Manx Shearwaters may have contributed to the result. Literature indicates that there are high prevalence and amounts of plastic litter ingested by both species as they share similar gastrointestinal tract morphology (Acampora et al., 2014; Bond et al., 2014; Kühn et al., 2015; Lavers et al., 2014); however Fulmars are reported to be the species with the highest number of individuals ingesting debris (Gall and Thompson, 2015).

For the Suliformes (Gannets and Shags), most studies have reported nest incorporation of debris rather than ingestion (Bond et al., 2012; Montevecchia, 1991), as ingestion seems to be low for this order (Codina-García et al., 2013; Laist, 1997). However a study has reported death by starvation of a Northern Gannet by the occlusion of the digestive tract by debris (Pierce et al., 2004). The reported prevalence in Suliformes from the current study (26.7%) is similar to the 23.9% reported for Pelecaniformes by Kühn et al. (2015), but higher than the 13% reported for Northern Gannets alone in the Mediterranean (Codina-García et al., 2013).

Birds from the family Laridae ingested less litter (26.5%) than expected as some of these species have mixed diets, and are known to feed from terrestrial areas such as landfills (Belant et al., 1998; Duhem et al., 2003; Lindborg et al., 2012), for instance. However, birds that regurgitate their stomach contents, such as most gulls, likely eject indigestible matter at least once a day (Barrett et al., 2007). Thus stomach contents from necropsies might be a reflection of this emptying. The family Laridae are not suitable candidates for oceanic marine litter monitoring, but could be the subject of other types of studies, such as occurrence, type of debris, retention times and, more appropriately, the monitoring of coastal areas.

Ingested litter in the stomach of beached birds reflects temporal trends and/or spatial difference of plastic litter abundance at sea (Van Franeker et al., 2011; Van Franeker and Law, 2015), but there is no way of inferring what the amount of ingested litter represents in terms of the quantitative abundance of plastic litter at sea. An individual bird could have been carrying a larger amount of litter and may have passed some of it either through regurgitation, faeces, or through feeding of chicks. For species that regurgitate indigestible matter, perhaps a better way to collect information about these would be through the collection of boluses at breeding colonies (Avery-Gomm et al., 2013; Hammer et al., 2016; Ryan and Fraser, 1988). For birds that cannot regurgitate, it is necessary to assess how much these birds can carry as extra weight without affecting their regular activities. For instance, research that involves satellite or other tracking devices has come to the conclusion that birds can carry approximatelyan additional 3–5% of their body mass (Adams et al., 2009) without having their regular niche activities negatively affected. However, recent studies have shown that even when the 3–5% rule is applied, some tagged birds have taken longer in regular activities, and took more extensive foraging trips or reduced chick provisioning (Adams et al., 2009; Heggøy et al., 2015). The amounts of marine litter ingested by seabirds reported in this study suggest that except for possible incidental cases (e.g. Fulmar with more than 8 g), they did not die directly from plastic ingestion. If seabirds are however, unable to regurgitate or excrete ingested plastic there may be indirect lethal effects. Several authors have suggested indirect impacts such as reduced foraging efficiency, or a reduced feeding rate due to feeling satiated as the stomach is full (Azzarello and Van Vleet, 1987; Ryan, 1988, 1990).

In addition to gathering baseline data, it was possible with the help of volunteers to collect an amount of birds to investigate presence/absence of litter in birds and to run a pilot marine litter monitoring project. Engaging citizens in environmental work has benefits for society by raising awareness (Smith et al., 2014), for the environment by the large collection of data more effectively (Silvertown, 2009) and allows for local research with international impact. It has become common to involve citizens in beach cleaning efforts (Ribic et al., 1997) and species surveys (Camphuysen, 1998; Parrish et al., 2007; Sullivan et al., 2009); these could be extended to becoming a beached bird survey without greater effort.

The second aim of the current study was to investigate the implementation of the EcoQO for marine litter monitoring in Ireland. Results from the current study suggest that implementation of a programme utilising OSPAR's and MSFD's Common Indicator (Vinet & Zhedanov, 2010) for marine litter can be achieved in Ireland. Although numbers of beached Fulmars can be unpredictable, they can provide information and comparability with data collected by other countries in the North East Atlantic. To date, 12 specimens between 2014 and early 2016 (January–April), along with 2 more provided from 2012 before the start of the project, were analysed. This could be considered a small sample. However, according to Van Franeker and Meijboom (2002), a sample of 40 birds is enough to provide one with a reliable figure for plastic ingestion, and in the Irish case such a sample size seems realistically possible for the 5-year time frame used in EcoQO monitoring. Fulmars collected in Ireland had high levels of plastic ingestion, with one Fulmar alone containing over 8 g of plastics.

In order for a species to be considered a good monitor for marine litter, there are some aspects to be considered: 1) monitoring location: offshore or coastal as that will define what species can be considered; 2) local species abundance, through either breeding pairs or migration routes; 3) stranding occurrence; and 4) likely accumulation of ingested marine litter. In addition, certain areas could be difficult to access, thus restricting surveying effort, or the presence of scavengers could reduce carcass availability.

Based on the criteria above and the data gathered in this study, we would not recommend another candidate monitoring species other than Northern Fulmar. An exception could be other Procellariiform species, such as Shearwaters, which have similar internal anatomy permitting the accumulation of debris in the digestive tract. However, some species of Shearwaters appear to feed more at the sub-surface than Fulmars, which are surface feeders (Mallory, 2006). Perhaps this results in Shearwaters encountering litter/plastic less frequently than Fulmars, as most plastics are positively buoyant, at least before they are colonized by organisms (Wright et al., 2013). The higher rate of plastic ingestion by Fulmars compared to Manx Shearwaters seen in this study could also be attributed to regional or species-specific differences, as some species of Shearwaters, such as Great, Sooty and Short-tailed Shearwaters have among the highest rates of ingestion of marine litter (Provencher et al., 2014b).

5. Conclusion

The prevalence of plastic ingestion by seabirds in Ireland is at similar levels to other parts of the world. Additionally, current data indicates the marine litter monitoring through Fulmars in Ireland to be possible. The preliminary data suggest high levels of prevalence of plastic litter ingestion, as well as high litter mass. Although it is important to comply with policy to focus on the Fulmar as a priority monitoring species, this study has shown that different species with different habitats and biology are prone to being affected by marine litter. It is relevant that all occurrences, even at low levels are reported so a better understanding of marine litter is gained globally, which allows for optimal management and mitigation of plastic pollution.

Acknowledgements

This work was supported by Science Without Borders (CAPES, Brazil) and the Department of Housing, Planning, Community and Local Government (DHPCLG, Ireland). We thank all volunteers who have embraced the Republic of Ireland Beached Bird Survey. Without you this project would not be possible. Many thanks to all at BirdWatch Ireland and Clean Coasts. Special thanks to Rosemary Hill, Kieran Campbell, Sean O'Gallaghan, Steve Newton, Niall Keogh, Richard Cronin, Annabel Fitzgerald, Rick Officer, Simon Berrow and Roisin Nash.

References

Acampora, H., Schuyler, Q.A., Townsend, K.A., Hardesty, B.D., 2014. Comparing plastic ingestion in juvenile and adult stranded short-tailed shearwaters (*Puffinus tenuirostris*) in eastern Australia. Mar. Pollut. Bull. 78 (1–2), 63–68.

Adams, J., Scott, D., McKechnie, S., Blackwell, G., Shaffer, S. a, Moller, H., 2009. Effects of geolocation archival tags on reproduction and adult body mass of sooty shearwaters (*Puffinus griseus*). N. Z. J. Zoology 36 (3), 355–366. http://dx.doi.org/10.1080/03014220909510160.

Ashmole, N.P., 1971. Seabird ecology and the marine environment. Avian Biol. 1, 223–286.

Avery-Gomm, S., Provencher, J.F., Morgan, K.H., Bertram, D.F., 2013. Plastic ingestion in marine-associated bird species from the eastern North Pacific. Mar. Pollut. Bull. 72 (1), 257–259. http://dx.doi.org/10.1016/j.marpolbul.2013.04.021.

Azzarello, M., Van Vleet, E., 1987. Marine birds and plastic pollution. Mar. Ecol. Prog. Ser. 37, 295–303. http://dx.doi.org/10.3354/meps037295.

Barrett, R.T., Camphuysen, K., Anker-Nilssen, T., Chardine, J.W., Furness, R.W., Garthe, S., Veit, R.R., 2007. Diet studies of seabirds: a review and recommendations. ICES J. Mar. Sci. 64 (9), 1675–1691. http://dx.doi.org/10.1093/icesjms/fsm152.

Bates, D., Mächler, M., 2016. Package "lme4.". Retrieved from. https://cran.r-project.org/web/packages/lme4/lme4.pdf (accessed 14.03.16).

Belant, J.L., Ickes, S.K., Seamans, T.W., 1998. Importance of landfills to urban-nesting herring and ring-billed gulls. Landsc. Urban Plan. 43 (1–3), 11–19. http://dx.doi.org/10.1016/S0169-2046(98)00100-5.

Bond, A.L., Montevecchi, W.A., Guse, N., Regular, P.M., Garthe, S., Rail, J.F., 2012.

Prevalence and composition of fishing gear debris in the nests of northern gannets (Morus bassanus) are related to fishing effort. Mar. Pollut. Bull. 64 (5), 907–911. http://dx.doi.org/10.1016/j.marpolbul.2012.03.011.
Bond, A.L., Provencher, J.F., Daoust, P.Y., Lucas, Z.N., 2014. Plastic ingestion by fulmars and shearwaters at sable island, Nova Scotia, Canada. Mar. Pollut. Bull. 87 (1), 68–75. http://dx.doi.org/10.1016/j.marpolbul.2014.08.010.
Camphuysen, K., 1998. Beached bird surveys indicate decline in chronic oil pollution in the North Sea. Mar. Pollut. Bull. 36 (7), 519–526. http://dx.doi.org/10.1016/S0025-326X(98)80018-0.
Codina-García, M., Militão, T., Moreno, J., González-Solís, J., 2013. Plastic debris in Mediterranean seabirds. Mar. Pollut. Bull. 77 (1–2), 220–226. http://dx.doi.org/10.1016/j.marpolbul.2013.10.002.
Duan, N., Manning, W.G., Morris, C.N., Newhouse, J.P., 1984. Choosing between the sample-selection model and the Multi-Part Model. J. Bus. Econ. Statistics 2 (3), 283–289. http://dx.doi.org/10.1080/07350015.1984.10509396.
Duhem, C., Vidal, E., Legrand, J., Tatoni, T., 2003. Opportunistic feeding responses of the Yellow-legged gull Larus michahellis to accessibility of refuse dumps: the gulls adjust their diet composition and diversity according to refuse dump accessibility. Bird. Study 50, 61–67. http://dx.doi.org/10.1080/00063650309461291. April.
Furness, R.W., Camphuysen, C., 1997. Seabirds as monitors of the marine environment. ICES J. Mar. Sci. 54, 726–737.
Galgani, F., Hanke, G., Maes, T., 2015. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Cham: Springer International Publishing, pp. 29–56. http://dx.doi.org/10.1007/978-3-319-16510-3_2.
Gall, S.C., Thompson, R.C., 2015. The impact of debris on marine life. Mar. Pollut. Bull. http://dx.doi.org/10.1016/j.marpolbul.2014.12.041.
Hammer, S., Nager, R.G., Johnson, P.C.D., Furness, R.W., Provencher, J.F., 2016. Plastic debris in great skua (*Stercorarius skua*) pellets corresponds to seabird prey species. Mar. Pollut. Bull. http://dx.doi.org/10.1016/j.marpolbul.2015.12.018.
Heggøy, O., Christensen-Dalsgaard, S., Ranke, P.S., Chastel, O., Bech, C., 2015. GPS-loggers influence behaviour and physiology in the black-legged kittiwake Rissa tridactyla. Mar. Ecol. Prog. Ser. 521, 237–248. http://dx.doi.org/10.3354/meps11140.
Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science 347 (6223).
Kühn, S., Bravo Rebolledo, E.L., Franeker, J.A., 2015. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Cham: Springer International Publishing, pp. 75–116. http://dx.doi.org/10.1007/978-3-319-16510-3_4.
Laist, D., 1997. In: Coe, J.M., Rogers, D.B. (Eds.), Marine Debris. Springer, Society. New York, NY. http://dx.doi.org/10.1007/978-1-4613-8486-1.
Lavers, J.L., Bond, A.L., Hutton, I., 2014. Plastic ingestion by flesh-footed shearwaters (Puffinus carneipes): implications for fledgling body condition and the accumulation of plastic-derived chemicals. Environ. Pollut. 187, 124–129. http://dx.doi.org/10.1016/j.envpol.2013.12.020.
Lindborg, V.A., Ledbetter, J.F., Walat, J.M., Moffett, C., 2012. Plastic consumption and diet of Glaucous-winged Gulls (*Larus glaucescens*). Mar. Pollut. Bull. 64 (11), 2351–2356. http://dx.doi.org/10.1016/j.marpolbul.2012.08.020.
Lusher, A.L., Burke, A., O'Connor, I., Officer, R., 2014. Microplastic pollution in the Northeast Atlantic ocean: validated and opportunistic sampling. Mar. Pollut. Bull. 88 (1–2), 325–333. http://dx.doi.org/10.1016/j.marpolbul.2014.08.023.
Lusher, A.L., Hernandez-Milian, G., O'Brien, J., Berrow, S., O'Connor, I., Officer, R., 2015. Microplastic and macroplastic ingestion by a deep diving, oceanic cetacean: the True's beaked whale Mesoplodon mirus. Environ. Pollut. 199, 185–191. http://dx.doi.org/10.1016/j.envpol.2015.01.023.
Mallory, M.L., 2006. The Northern Fulmar (*Fulmarus glacialis*) in Arctic Canada: ecology, threats, and what it tells us about marine environmental conditions. Environ. Rev. 14 (3), 187–216. http://dx.doi.org/10.1139/a06-003.
Min, Y., Agresti, A., 2002. Modeling nonnegative data with clumping at zero: A survey models for semicontinuous data. Jirss 1 (1), 7–33.
Mitchell, P.I., Newton, S.F., Ratcliffe, N., Dunn, T.E., Poyser, a D., May, L. (Eds.), 2004. Seabird Populations of Britain and Ireland: Results of the Seabird 2000 Census. JNCC, Poyser, London (August).
Montevecchi, W.A., 1991. Incidence and types of plastic in gannets' nests in the northwest Atlantic. Can. J. Zoology 69, 295–297. http://dx.doi.org/10.1139/z91-047.
Moriarty, M., Pedreschi, D., Stokes, D., Dransfeld, L., Reid, D.G., 2016. Spatial and temporal analysis of litter in the Celtic sea from groundfish survey data: lessons for monitoring. Mar. Pollut. Bull. http://dx.doi.org/10.1016/j.marpolbul.2015.12.019.
OSPAR., 2010. The Ospar System of Ecological Quality Objectives for the North Sea, p. 16.
Parrish, J.K., Bond, N., Nevins, H., Mantua, N., Loeffel, R., Peterson, W.T., Harvey, J.T., 2007. Beached birds and physical forcing in the California Current System. Mar. Ecol. Prog. Ser. 352, 275–288. http://dx.doi.org/10.3354/meps07077.
Pierce, K.E., Harris, R.J., Larned, L.S., Pokras, M.A., 2004. Obstruction and starvation associated with plastic ingestion in a northern Gannet morus bassanus and a greater shearwater puffinus gravis. Mar. Ornithol. 32 (2), 187–189.
Provencher, J.F., Bond, A.L., Hedd, A., Montevecchi, W.A., Muzaffar, S. Bin, Courchesne, S.J., Mallory, M.L., 2014a. Prevalence of marine debris in marine birds from the North Atlantic. Mar. Pollut. Bull. 84 (1–2), 411–417. http://dx.doi.org/10.1016/j.marpolbul.2014.04.044.
Provencher, J.F., Bond, A.L., Mallory, M.L., 2014b. Marine birds and plastic debris in Canada: a national synthesis, and a way forward. Environ. Rev. 1–13. http://dx.doi.org/10.1139/er-2014-0039.
Provencher, J.F., Gaston, A.J., Mallory, M.L., 2009. Evidence for increased ingestion of plastics by northern fulmars (*Fulmarus glacialis*) in the Canadian Arctic. Mar. Pollut. Bull. 58 (7), 1092–1095. http://dx.doi.org/10.1016/j.marpolbul.2009.04.002.
Provencher, J.F., Gaston, A.J., Mallory, M.L., O'hara, P.D., Gilchrist, H.G., 2010. Ingested plastic in a diving seabird, the thick-billed murre (Uria lomvia), in the eastern Canadian Arctic. Mar. Pollut. Bull. 60 (9), 1406–1411. http://dx.doi.org/10.1016/j.marpolbul.2010.05.017.
Ribic, C.A., Johnson, S.W., Cole, C.A., 1997. In: Coe, J.M., Rogers, D.B. (Eds.), Marine Debris: Sources, Impacts, and Solutions. Springer New York, New York, NY, pp. 35–47. http://dx.doi.org/10.1007/978-1-4613-8486-1_5.
Robards, M.D., Piatt, J.F., Wohl, K.D., 1995. Increasing frequency of plastic ingested by seabirds in the Subarctic North pacific. Mar. Pollut. Bull. 30 (2), 151–157 doi: 0025-326X(94)00121-9.
Ryan, P.G., 1988. Effects of ingested plastic on seabird feeding: evidence from chickens. Mar. Pollut. Bull. 19 (3), 125–128.
Ryan, P.G., 1990. The effects of ingested plastic and other marine debris on seabirds. In: Second International Conference on Marine Debris, pp. 2–7.
Ryan, P.G., 2015. How quickly do albatrosses and petrels digest plastic particles? Environ. Pollut. 207, 438–440. http://dx.doi.org/10.1016/j.envpol.2015.08.005.
Ryan, P.G., Fraser, M.W., 1988. The use of great skua pellets as indicators of plastic pollution in seabirds. Emu 88 (July), 16–19.
Silvertown, J., 2009. A new dawn for citizen science. Trends Ecol. Evol. (Personal Ed. 24 (9), 467–471. http://dx.doi.org/10.1016/j.tree.2009.03.017.
Smith, S.D.A., Gillies, C.L., Shortland-Jones, H., 2014. Patterns of marine debris distribution on the beaches of Rottnest Island, Western Australia. Mar. Pollut. Bull. 88 (1–2), 188–193. http://dx.doi.org/10.1016/j.marpolbul.2014.09.007.
Sullivan, B.L., Wood, C.L., Iliff, M.J., Bonney, R.E., Fink, D., Kelling, S., 2009. eBird: A citizen-based bird observation network in the biological sciences. Biol. Conserv. 142 (10), 2282–2292. http://dx.doi.org/10.1016/j.biocon.2009.05.006.
Trevail, A.M., Gabrielsen, G.W., Kühn, S., Van Franeker, J. a., 2015. Elevated levels of ingested plastic in a high Arctic seabird, the northern fulmar (*Fulmarus glacialis*). Polar Biol. http://dx.doi.org/10.1007/s00300-015-1657-4.
Van Franeker, J.A., 2004. Save the North Sea Fulmar-Litter-EcoQO Manual Part 1: Collection and Dissection Procedures, p. 38. Retrieved from. http://edepot.wur.nl/40451.
Van Franeker, J.A., Meijboom, A., 2002. Marine litter Monitoring by Northern Fulmars: a Pilot Study, p. 72.
Van Franeker, J.A., SNS Fulmar Study Group, 2013. Fulmar Litter EcoQO Monitoring along Dutch and North Sea Coasts. Update 2010 and 2011, (May), p. 61.
Van Franeker, J.A., 2014. Fulmar Litter EcoQO Monitoring in the Netherlands. IMARES, Wageningen UR.
Van Franeker, J.A., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., Turner, D.M., 2011. Monitoring plastic ingestion by the northern fulmar *Fulmarus glacialis* in the North Sea. Environ. Pollut. 159 (10), 2609–2615. http://dx.doi.org/10.1016/j.envpol.2011.06.008.
Van Franeker, J.A., Law, K.L., 2015. Seabirds, gyres and global trends in plastic pollution. Environ. Pollut. 203, 89–96. http://dx.doi.org/10.1016/j.envpol.2015.02.034.
Vinet, L., Zhedanov, A., 2010. A "missing" family of classical orthogonal polynomials. J. Phys. A: Math. Theor. 1, 1–5. http://dx.doi.org/10.1088/1751-8113/44/8/085201.
Wright, S.L., Thompson, R.C., Galloway, T.S., 2013. The physical impacts of microplastics on marine organisms: a review. Environ. Pollut. Barking, Essex 1987 178, 483–492. http://dx.doi.org/10.1016/j.envpol.2013.02.031.

Marine Pollution Bulletin 119 (2017) 171–174

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Opportunistic sampling to quantify plastics in the diet of unfledged Black Legged Kittiwakes (*Rissa tridactyla*), Northern Fulmars (*Fulmarus glacialis*) and Great Cormorants (*Phalacrocorax carbo*)

Heidi Acampora[a,*], Stephen Newton[b], Ian O'Connor[a]

[a] Galway-Mayo Institute of Technology, Marine & Freshwater Research Centre, Dublin Rd, Galway, Ireland
[b] BirdWatch Ireland, Unit 20, Block D, Bullford Business Campus, Kilcoole, Co. Wicklow, Ireland

ARTICLE INFO

Keywords:
Seabird chicks
Plastic pollution
Marine litter
Regurgitate
Ingestion

ABSTRACT

Seabirds can interact with marine litter, mainly by entanglement or ingestion. The ingestion of plastics can lead to starvation or physical damage to the digestive tract. For chicks, it could additionally lead to reduced growth, affecting survival and fledging. This study quantified the ingestion of plastics by seabird chicks via an opportunistic sampling strategy. When ringing is carried out at colonies, birds may spontaneously regurgitate their stomach contents due to the stress or as a defence mechanism. Regurgitates were collected from nestlings of three different species: Black-legged Kittiwake (*Rissa tridactyla*, n = 38), Northern Fulmar (*Fulmarus glacialis*, n = 14) and Great Cormorant (*Phalacrocorax carbo*, n = 28). Plastic was present in all species, with the highest frequency of occurrence (FO) in Northern Fulmar chicks (28.6%), followed by Black-legged Kittiwakes (7.9%) and Great Cormorants (7.1%). The observed load of plastics on chicks, which have not yet left the nest, highlights the pervasive nature of plastic pollution.

Marine litter has been recognised as a threat to wildlife and the marine environment (Bergmann et al., 2015; Derraik, 2002; Gall and Thompson, 2015). Kühn et al. (2015) report that 557 species, including 50% of all seabird species, are affected by marine litter. Seabirds are affected by marine litter through two main ways: ingestion and entanglement. Ingestion can block an animal's digestive tract, cause ulcers or perforations, produce a false satiation feeling, causing the bird not to feed, leading to impairment or starvation (Derraik, 2002; Ryan, 1988a, 1988b). There are also possible effects originating from compounds either added to plastics during production processes or adsorbed by them when drifting at sea (Koelmans, 2015; Tanaka et al., 2015). Entanglement can cause injuries or trap animals, impairing their ability to search for food (Laist, 1997), or if used in nest construction, ensnare young and prevent them from fledging (Bond et al., 2012; Lavers et al., 2013).

Ingestion of plastic debris has been widely reported globally for adult seabirds (Avery-Gomm et al., 2013; Gall and Thompson, 2015; Kühn et al., 2015; Provencher et al., 2016; Provencher et al., 2014; Roman et al., 2016; Van Franeker and Law, 2015), but there has been fewer reports in the peer-reviewed literature for chicks (Bond et al., 2010; Carey, 2011; Cousin et al., 2015; Rodríguez et al., 2012; Ryan, 1988a, 1988b), except for albatross chicks, which have high levels of plastic litter in their digestive tract and have been extensively studied (Sievert and Sileo, 1993; Sileo et al., 1990; Young et al., 2009). Chicks are not able to feed by themselves, so they receive their food from their parents, in many species via regurgitation. Chick survival can be dependent on a range of factors including: predation, thermal stress and, food availability. The fact that seabirds are long lived species, with delayed sexual maturity, that lay small clutch sizes compounds the potential impact that an additional threat, such as plastic litter could have on seabird populations.

Dietary studies through the collection of expelled boluses and spontaneous regurgitation are minimally invasive, and yet can provide an insight into the presence/absence of plastic litter in 'healthy' seabirds, as opposed to beached birds and carcasses found in breeding colonies (Hammer et al., 2016; Lindborg et al., 2012). During the course of demographic research activities such as ringing, many birds spontaneously regurgitate stomach contents as a response to the stress of being handled or as a defence mechanism. Regurgitation does not always expel the entire stomach contents, sometimes permitting that only the upper stomach contents to be expelled (Barrett et al., 2007; Bond and Lavers, 2013). However, regurgitates provide an opportunity to sample the diet of seabirds in situ and alive, as opposed to laboratory experiments and the examination of carcasses. Understanding trends in

* Corresponding author.
E-mail address: heidi.acampora@research.gmit.ie (H. Acampora).

http://dx.doi.org/10.1016/j.marpolbul.2017.04.016
Received 30 January 2017; Received in revised form 3 April 2017; Accepted 10 April 2017
Available online 26 April 2017
0025-326X/

Table 1
Regurgitate sample description per species ordered by year of collection and location.

Species	Year	Regurgitates (n)	Location
Great Cormorant (*Phalacrocorax carbo*)	2011	25	St. Patrick's, Co. Donegal & Great Saltee, Co. Wexford
	2012	3	Ireland's Eye, Co. Dublin
Great Cormorant total		28	
Black-legged Kittiwake (*Rissa tridactyla*)	2013	17	Rockabill, Co. Dublin
	2015	21	Rockabill, Co. Dublin
Black-legged Kittiwake total		38	
Northern Fulmar (*Fulmarus glacialis*)	2015	14	Great Saltee, Co. Wexford
Northern Fulmar total		14	
Sample total		80	

ingestion of plastic litter by different species has the potential to inform policy and generate mitigation measures.

This study aimed to provide baseline data for the ingestion of plastics by seabird chicks in Ireland. Spontaneous regurgitates were collected at four different breeding colonies during ringing and demographic colony work, from three different species: Black-Legged Kittiwake (*Rissa tridactyla*), Northern Fulmar (*Fulmarus glacialis*) and Great Cormorant (*Phalacrocorax carbo*). Through the examination of chick regurgitates, it is possible to obtain insight into the diet of seabird chicks and how they interact with plastic pollution and, consequently into the same interactions in breeding adults when considering seabird populations in Ireland as a whole.

Regurgitate samples were collected from 80 individuals at four different colonies in the years 2011, 2012, 2013 & 2015 (Table 1) via opportunistic sampling while chicks were ringed in the nest during colony work. Samples were collected in plastic bags and frozen until further analysis. After thawing overnight, each sample was washed through a 1 mm mesh sieve and every solid item retained in petri dishes. Solid contents were air dried overnight and examined under a Stereo microscope (MicrosAustria, 0.6 ×–5 ×). They were separated into food and non-food categories according to Van Franeker et al. (2003). Litter items were weighed to the nearest 0.0001 g and food items were identified and counted.

Statistical analysis was carried out using R studio version 0.98.1102 (2009–2014, R Studio, Inc.). Data were non-normal, skewed and zero-inflated. For that reason, non-parametric tests such as Mann-Whitney and Kruskal-Wallis were used. The variables 'Litter Presence' and 'Litter Mass' were tested against relevant variables such as 'Food Presence' and the main food categories using a Mann-Whitney-Wilcoxon Test. A Kruskal-Wallis test was used to investigate if the variables 'Litter Presence' and 'Litter Mass' were influenced by the variable 'Species'.

The present study analysed 80 individual regurgitates from chicks of 3 different species. Samples were collected from 2011 to 2015 at 4 different breeding colonies along the coast of Ireland, described in Table 1. Due to the opportunistic nature of this sampling, sample sizes were limited and spatial and temporal differences were not taken into account in this particular work. Instead, all colonies and years were considered together in order to improve the power of statistical analysis. From all regurgitates analysed (n = 80), 11.3% (n = 9) contained plastic litter (Fig. 1). Regurgitates from all 3 studied species contained plastic litter, from 3 different colonies: Black-legged Kittiwakes (n = 3), Great Cormorants (n = 2) and Northern Fulmars (n = 4). Plastic categories were fragments (44.4%), sheet (33.3%) and foam (22.2%). Two individuals (1 Black-legged Kittiwake and 1 Great Cormorant) contained also non-plastic litter (fragments of paraffin wax).

Plastic litter ingestion was higher in Northern Fulmar chicks, with a 28.6% frequency of occurrence (FO), an average mass of 0.0129 g (Range: 0–0.1043 g. SD ± 0.0317) and an average number of particles of 0.50 (Range: 0–3. SD ± 0.90); followed by Black-legged Kittiwakes

Fig. 1. Sample containing plastic litter (type: sheet) found in regurgitate from a Black-legged Kittiwake chick.
Rockabill, Co. Dublin, 2013.

with 7.9% FO, 0.0001 g average plastic mass (Range: 0–0.0045 g. SD ± 0.0007) and 0.08 average number of particles (Range: 0–1. SD ± 0.26); and lastly, Great Cormorants with 7.1% FO, an average mass of 0.0123 g (Range: 0–0.3450 g. SD ± 0.0640), average number of particles of 0.21 (Range: 0–5. SD ± 0.93) (Table 2).

When testing if species had any effect on the mass of plastic litter, we found no significant differences among all three study species ($p = 0.075$). No significant difference was found when testing if food presence, or any of selected food items had an influence on the presence of plastic litter.

This study aimed to investigate ingestion of plastics by chicks of three species of seabird in Ireland and set baseline data by using an opportunistic sampling method (spontaneous regurgitation). Our results have shown that chicks are ingesting litter, mainly plastics. These birds have not left the nest and yet, have been contaminated by the ingestion of anthropogenic debris fed to them via parents.

Our results show that the frequency of plastic occurrence in chick regurgitates of Northern Fulmars was higher (28.6%) than Black-legged Kittiwakes (7.9%) and Great Cormorants (7.1%). Ingestion of plastics has been connected to foraging strategy by various studies (Azzarello and Van Vleet, 1987; Ryan, 1988a, 1988b; Shephard et al., 2015). Surface seizing birds would be more likely to come across positively buoyant plastics (Moser and Lee, 1992). Birds with a generalist diet are more prone to mistaking plastics for food items (Moser and Lee, 1992). Northern Fulmars are both surface feeders and generalist feeders (Burg et al., 2003; Mallory, 2006), with our results thus reinforcing such connection between plastic ingestion and feeding strategy and diet. Previous authors have reported that young birds have more plastics in their stomachs than adults (Acampora et al., 2014; Carey, 2011). This could be explained by parental delivery when feeding chicks, or perhaps because young birds could be more naïve when feeding by themselves. In the case of the birds in this study, the former would apply as samples were collected from chicks, which were still completely dependent on parents for their food requirements. When comparing prevalence of plastic litter in adult birds from the same region, Acampora et al. (2016) found a higher prevalence (93%) in corpses of Northern Fulmars, with an equal sample size (n = 14) to the chick regurgitates from this study. The same was true for stomach contents of Black-legged Kittiwakes, with a 50% prevalence, but in a smaller sample size (n = 4). Previous work on Great Cormorants in Ireland found a 3.2% plastic prevalence in boluses (Acampora et al., 2017).

When using this type of dietary analysis, comparison between species should be done with caution, taking species' biology regarding

Table 2
Plastic litter abundance per species (ordered by sample size; population averages are provided and included zero values). CI = Confidence interval, SD = standard deviation.

Species	Sample (n)	Frequency of occurrence (%) – 95% CI	Average number of particles (n) ± SD	Average mass (g) ± SD
Black-legged Kittiwake	38	7.9	0.08 ± 0.26	0.0002 ± 0.0007
Great Cormorant	28	7.1	0.21 ± 0.93	0.0123 ± 0.0640
Northern Fulmar	14	28.6	0.50 ± 0.90	0.0129 ± 0.0317

accumulation and regurgitation into consideration (Lindborg et al., 2012). For instance, Procellariiform birds have a restricted regurgitation ability due to the constriction between their proventriculus and their gizzard (Azzarello and Van Vleet, 1987), so even when they regurgitate their stomach contents as a defence mechanism (stomach oil), they would only be able to regurgitate the upper part of the stomach (proventriculus), but not the part that accumulates the hard, indigestible matter (gizzard) (Karnovsky et al., 2012). Therefore, sampling regurgitates from such species only provides a snapshot of what their stomach contents are. This has to be taken into account in both stages: when the parent delivers the food to the chick and when the chick regurgitates as a response to disturbance. Yet in this study, Northern Fulmars had the highest prevalence of plastic ingestion.

Although Black-legged Kittiwakes chicks had a lower rate of plastic litter ingestion in this study, the FO (7.9%) is similar to that reported by Robards et al. (1995) of 7.8% and by Poon et al. (2017) of 9% for adult birds. However, plastic litter has been reportedly used as nesting material for Black-legged Kittiwakes in 57% of nests in Danish colonies (Hartwig et al., 2007), perhaps providing chicks with opportunities for accidental ingestion or entanglement.

For birds that regurgitate indigestible matter daily (Cormorants) or after each meal (Gulls and Skuas) (Barrett et al., 2007), there may be a lower probability of detecting plastics in their stomachs via necropsies of dead birds, as particles could have been previously expelled via a bolus. However, in our study adults have delivered plastics to chicks and, while at low levels, in the case of Great Cormorants (7.1%), chicks' regurgitates also represent a reflection of the parents' diet, even if the plastics quantified in this study only reflect the last ingested meal or meals throughout the day in which the samples were collected (Johnstone et al., 1990). Additionally, it is necessary to take into account that colony sampling means adults could be feeding chicks differently than they would feed themselves outside of the chick rearing period (Bearhop et al., 2001). Nevertheless, chicks are being exposed to plastic litter via regurgitation through their parents, which could affect growth and fledgling survival.

The majority of the Irish populations of Northern Fulmar and Black-legged Kittiwake (30 largest colonies in the country, comprising about 90–95% of the population in year 2000) were resurveyed in the summer of 2015 (Newton et al., 2015, unpublished report to National Parks & Wildlife Service). These showed that Northern Fulmars had declined by 12% and Black-legged Kittiwakes by 33% over a 15 year period. The most likely explanations for this are declining prey fish stocks, perhaps related to climate change, overfishing or diminishing discarding. This study, along with the growing body of literature on plastic pollution, has demonstrated that populations of seabirds are vulnerable to interactions with plastics throughout their life cycle, thus more research into the prevalence and impacts of plastics is needed to investigate as to whether ingested plastics could yet be another factor involved in such demographic decline. A diet containing plastics could prevent seabird chicks from getting adequate body condition prior to fledging, which is essential for fledgling survival (Arizaga et al., 2015; Lavers et al., 2014).

The presence of plastics in chick's diet confirms that plastics are present in many seabird species throughout their life cycle. The use of chick regurgitates has proved to be a valid approach, when consideration is taken related to anatomic differences in species. Our previous work (Acampora et al., 2016) has utilised beached birds as a tool for multispecies monitoring of marine litter. Different approaches of monitoring, rather than a single one, offer more reliable information and, with such compilation of data, it is expected in the future to be able to infer a health status for seabird populations in Ireland.

Acknowledgments

This work was supported by Science Without Borders scheme (CAPES, Brazil, BEX 1269/2013-05). We thank all at BirdWatch Ireland. Special thanks to John Lusby, Niall Tierney, Helen Boland, Niall Keogh, Brian Burke and Andrew Power for collection and help in the field. Thanks to Jan van Franeker for an early review of this manuscript. We also thank the input of anonymous reviewers, which helped to improve the manuscript.

References

Acampora, H., Berrow, S., Newton, S., O'Connor, I., 2017. Presence of plastic litter in pellets from Great Cormorant (Phalacrocorax carbo) in Ireland. Mar. Pollut. Bull. 117 (1), 512–514.

Acampora, H., Lyashevska, O., Van Franeker, J.A., O'Connor, I., 2016. The use of beached bird surveys for marine plastic litter monitoring in Ireland. Mar. Environ. Res. 120, e87–e91. http://dx.doi.org/10.1016/j.marenvres.2016.08.002.

Acampora, H., Schuyler, Q.A., Townsend, K.A., Hardesty, B.D., 2014. Comparing plastic ingestion in juvenile and adult stranded short-tailed shearwaters (*Puffinus tenuirostris*) in eastern Australia. Mar. Pollut. Bull. 78, 63–68.

Arizaga, J., Herrero, A., Aldalur, A., Cuadrado, J.F., Oro, D., 2015. Effect of pre-fledging body condition on juvenile survival in Yellow-legged Gull *Larus michahellis*. Acta Ornithol. 50, 1–9. http://dx.doi.org/10.3161/00016454AO2015.50.2.002.

Avery-Gomm, S., Provencher, J.F., Morgan, K.H., Bertram, D.F., 2013. Plastic ingestion in marine-associated bird species from the eastern North Pacific. Mar. Pollut. Bull. 72, 257–259. http://dx.doi.org/10.1016/j.marpolbul.2013.04.021.

Azzarello, M., Van Vleet, E., 1987. Marine birds and plastic pollution. Mar. Ecol. Prog. Ser. 37, 295–303. http://dx.doi.org/10.3354/meps037295.

Barrett, R.T., Camphuysen, K., Anker-Nilssen, T., Chardine, J.W., Furness, R.W., Garthe, S., Hüppop, O., Leopold, M.F., Montevecchi, W.a., Veit, R.R., 2007. Diet studies of seabirds: a review and recommendations. ICES J. Mar. Sci. 64, 1675–1691. http://dx.doi.org/10.1093/icesjms/fsm152.

Bearhop, S., Thompson, D.R., Phillips, R.A., Waldron, S., Hamer, K.C., Gray, C.M., Votier, S.C., Ross, B.P., Furness, R.W., 2001. Annual variation in great skua diets: the importance of commercial fisheries and predation on seabirds revealed by combining dietary analyses. Condor 103, 802–809. http://dx.doi.org/10.1650/0010-5422(2001)103[0802:avigsd]2.0.co;2.

Bergmann, M., Gutow, L., Klages, M., 2015. Marine anthropogenic litter. In: Marine Anthropogenic Litter, http://dx.doi.org/10.1007/978-3-319-16510-3.

Bond, A.L., Jones, I.L., Williams, J.C., Byrd, G.V., 2010. Auklet (Charadriiformes: Alcidae, *Aethia* spp.) chick meals from the Aleutian Islands, Alaska, have a very low incidence of plastic marine debris. Mar. Pollut. Bull. 60, 1346–1349. http://dx.doi.org/10.1016/j.marpolbul.2010.05.001.

Bond, A.L., Lavers, J.L., 2013. Effectiveness of emetics to study plastic ingestion by Leach's Storm-petrels (*Oceanodroma leucorhoa*). Mar. Pollut. Bull. 70. http://dx.doi.org/10.1016/j.marpolbul.2013.02.030.

Bond, A.L., Montevecchi, W.A., Guse, N., Regular, P.M., Garthe, S., Rail, J.F., 2012. Prevalence and composition of fishing gear debris in the nests of northern gannets (*Morus bassanus*) are related to fishing effort. Mar. Pollut. Bull. 64, 907–911. http://dx.doi.org/10.1016/j.marpolbul.2012.03.011.

Burg, T.M., Lomax, J., Almond, R., Brooke, M.D.L., Amos, W., 2003. Unravelling dispersal patterns in an expanding population of a highly mobile seabird, the Northern Fulmar (*Fulmarus glacialis*). Proc. Biol. Sci. 270, 979–984. http://dx.doi.org/10.1098/rspb.2002.2322.

Carey, M.J., 2011. Intergenerational transfer of plastic debris by Short-tailed Shearwaters (*Ardenna tenuirostris*). Emu 111, 229–234. http://dx.doi.org/10.1071/MU10085.

Cousin, H.R., Auman, H.J., Alderman, R., Virtue, P., 2015. The frequency of ingested plastic debris and its effects on body condition of short-tailed shearwater (*Puffinus tenuirostris*) pre-fl edging chicks in Tasmania, Australia. Emu 115, 6–11.

Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: a review. Mar. Pollut. Bull. 44, 842–852. http://dx.doi.org/10.1016/S0025-326X(02)00220-5.

Gall, S.C., Thompson, R.C., 2015. The impact of debris on marine life. Mar. Pollut. Bull. http://dx.doi.org/10.1016/j.marpolbul.2014.12.041.

Hammer, S., Nager, R.G., Johnson, P.C.D., Furness, R.W., Provencher, J.F., 2016. Plastic debris in great skua (*Stercorarius skua*) pellets corresponds to seabird prey species. Mar. Pollut. Bull. http://dx.doi.org/10.1016/j.marpolbul.2015.12.018.

Hartwig, E., Clemens, T., Heckroth, M., 2007. Plastic Debris as Nesting Material in a Kittiwake - (*Rissa tridactyla*) - Colony at the Jammerbugt, Northwest Denmark. 54. pp. 595–597. http://dx.doi.org/10.1016/j.marpolbul.2007.01.027.

Johnstone, I.G., Harris, M.P., Wanless, S., Graves, J.a., 1990. The usefulness of pellets for assessing the diet of adult shags *Phalacrocorax aristotelis*. Bird Study 37, 37–41. http://dx.doi.org/10.1080/00063659009477030.

Karnovsky, N.J., Hobson, K.A., Iverson, S.J., 2012. From lavage to lipids: estimating diets of seabirds. Mar. Ecol. Prog. Ser. 451, 263–284. http://dx.doi.org/10.3354/meps09713.

Koelmans, A.A., 2015. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Springer International Publishing, Cham, pp. 309–324. http://dx.doi.org/10.1007/978-3-319-16510-3_11.

Kühn, S., Bravo Rebolledo, E.L., Franeker, J.A., 2015. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Springer International Publishing, Cham, pp. 75–116. http://dx.doi.org/10.1007/978-3-319-16510-3_4.

Laist, D., 1997. Marine Debris, Society, Springer Series on Environmental Management. Springer New York, New York, NY. http://dx.doi.org/10.1007/978-1-4613-8486-1.

Lavers, J.L., Bond, A.L., Hutton, I., 2014. Plastic ingestion by flesh-footed shearwaters (*Puffinus carneipes*): implications for fledgling body condition and the accumulation of plastic-derived chemicals. Environ. Pollut. 187, 124–129. http://dx.doi.org/10.1016/j.envpol.2013.12.020.

Lavers, J.L., Hodgson, J.C., Clarke, R.H., 2013. Prevalence and composition of marine debris in Brown Booby (*Sula leucogaster*) nests at Ashmore Reef. Mar. Pollut. Bull. 77, 320–324. http://dx.doi.org/10.1016/j.marpolbul.2013.09.026.

Lindborg, V.a., Ledbetter, J.F., Walat, J.M., Moffett, C., 2012. Plastic consumption and diet of Glaucous-winged Gulls (*Larus glaucescens*). Mar. Pollut. Bull. 64, 2351–2356. http://dx.doi.org/10.1016/j.marpolbul.2012.08.020.

Mallory, M.L., 2006. The Northern Fulmar (*Fulmarus glacialis*) in Arctic Canada: ecology, threats, and what it tells us about marine environmental conditions. Environ. Rev. 14, 187–216. http://dx.doi.org/10.1139/a06-003.

Moser, M., Lee, D., 1992. A 14-year survey of plastic ingestion by western North-Atlantic seabirds. Colon. Waterbirds 15, 83–94. http://dx.doi.org/10.2307/1521357.

Poon, F.E., Provencher, J.F., Mallory, M.L., Braune, B.M., Smith, P.A., 2017. Levels of ingested debris vary across species in Canadian Arctic seabirds. Anal. Methods 9, 1454–1469. http://dx.doi.org/10.1039/C6AY02419J. (Paper).

Provencher, J., Bond, A., Aver-Gomm, S., Borrelle, S., Bravo Rebolledo, E., Hammer, S., Kuhn, S., Lavers, J., Mallory, M., Trevail, A., van Franeker, J., 2016. Quantifying ingested debris in marine megafauna: a review and recommendations for standardization. Anal. Methods. http://dx.doi.org/10.1039/C6AY02419J.

Provencher, J.F., Bond, A.L., Mallory, M.L., 2014. Marine birds and plastic debris in Canada: a national synthesis, and a way forward. Environ. Rev. 1–13. http://dx.doi.org/10.1139/er-2014-0039. (in press).

Robards, M.D., Piatt, J.F., Wohl, K.D., 1995. Increasing frequency of plastic ingested by seabirds in the subarctic North Pacific. Mar. Pollut. Bull. 30, 151–157 (doi:0025-326X(94)00121-9).

Rodríguez, A., Rodríguez, B., Nazaret Carrasco, M., 2012. High prevalence of parental delivery of plastic debris in Cory's shearwaters (*Calonectris diomedea*). Mar. Pollut. Bull. 64. http://dx.doi.org/10.1016/j.marpolbul.2012.06.011.

Roman, L., Schuyler, Q.A., Hardesty, B.D., Townsend, K.A., 2016. Anthropogenic Debris Ingestion by Avifauna in Eastern Australia. pp. 1–14. http://dx.doi.org/10.5061/dryad.p48f7.

Ryan, P.G., 1988a. Effects of ingested plastic on seabird feeding: evidence from chickens. Mar. Pollut. Bull. 19, 125–128.

Ryan, P.G., 1988b. Intraspecific variation in plastic ingestion by seabirds and the flux of plastic through seabird populations. Condor 90, 446–452.

Shephard, S., van Hal, R., de Boois, I., Birchenough, S.N.R., Foden, J., O'Connor, J., Geelhoed, S.C.V., Van Hoey, G., Marco-Rius, F., Reid, D.G., Schaber, M., 2015. Making progress towards integration of existing sampling activities to establish Joint Monitoring Programmes in support of the MSFD. Mar. Policy 59, 105–111. http://dx.doi.org/10.1016/j.marpol.2015.06.004.

Sievert, P.R., Sileo, L., 1993. The effects of ingested plastic on growth and survival of albatross chicks. In: Status, Ecol. Conserv. Mar. Birds North Pacific, pp. 212–217.

Sileo, L., Sievert, P.R., Samuel, M.D., 1990. Causes of mortality of albatross chicks at Midway Atoll. J. Wildl. Dis. 26, 329–338. http://dx.doi.org/10.7589/0090-3558-26.3.329.

Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M., Watanuki, Y., 2015. Facilitated leaching of additive-derived PBDEs from plastic by seabirds' stomach oil and accumulation in tissues. Environ. Sci. Technol. 150901174241000. http://dx.doi.org/10.1021/acs.est.5b01376.

Van Franeker, J.A., Law, K.L., 2015. Seabirds, gyres and global trends in plastic pollution. Environ. Pollut. 203, 89–96. http://dx.doi.org/10.1016/j.envpol.2015.02.034.

Van Franeker, J.A., Meijboom, A., de Jong, M.L., 2003. Marine Litter Monitoring by Northern Fulmars in the Netherlands 1982–2003. Wageningen, Alterra, Alterra-rapport. 1093.

Young, L.C., Vanderlip, C., Duffy, D.C., Afanasyev, V., Shaffer, S.a., 2009. Bringing home the trash: do colony-based differences in foraging distribution lead to increased plastic ingestion in Laysan albatrosses? PLoS One 4, 11–13. http://dx.doi.org/10.1371/journal.pone.0007623.

Marine Pollution Bulletin 117 (2017) 512–514

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Presence of plastic litter in pellets from Great Cormorant (*Phalacrocorax carbo*) in Ireland

Heidi Acampora [a,*], Simon Berrow [a,b], Stephen Newton [c], Ian O'Connor [a]

[a] Galway-Mayo Institute of Technology, Marine & Freshwater Research Centre, Dublin Rd, Galway, Ireland
[b] Shannon Dolphin and Wildlife Foundation, Merchants Quay, Kilrush, Co. Clare, Ireland
[c] BirdWatch Ireland, Unit 20, Block D, Bullford Business Campus, Kilcoole, Co. Wicklow, Ireland

ARTICLE INFO

Article history:
Received 19 October 2016
Received in revised form 30 January 2017
Accepted 5 February 2017
Available online 9 February 2017

Keywords:
Marine litter
Plastics
Seabirds
Phalacrocoracidae
Pellets

ABSTRACT

Plastic pollution has been the subject of much research in the last decade. Seabirds can mistake plastic fragments for prey, which can perforate or block the digestive tract and cause ulcers. Most commonly, seabirds accumulate this indigestible matter in their stomachs, obtaining no nutrition and may die from starvation. Certain species of seabirds however, have the ability of regurgitating indigestible matter in the form of pellets. This study aimed to investigate the ingestion of plastics by live seabirds through the examination of regurgitated pellets (n = 92) from a Great Cormorant (*Phalacrocorax carbo*) breeding colony and a winter roost in Ireland. Plastic prevalence was consistently 3.2% at both sites. The presence of plastic litter highlights the fact that all species of seabird are susceptible to interact with marine litter regardless of feeding habits, although at different rates. More research is needed to understand the driving factors involved in plastic ingestion among different species.

1. Baseline

The presence of litter in the diet of marine top predators has been the subject of global research. At least 50% species of seabird species are known to interact with marine plastic litter (Kühn et al., 2015). This interaction can occur in two main ways: ingestion and entanglement. The effects of entanglement are more readily understood (Kühn et al., 2015). For ingestion however, besides physical effects such as perforation or occlusion of the digestive tract, there may be secondary effects. If seabirds ingest sufficient quantities of litter to fill their stomachs, they may have a feeling of satiation, but without nutritive benefits. This can lead to a loss of body condition and perhaps, mortality through starvation. Wilcox et al. (2015) has predicted that by 2050, all seabird species will have ingested some plastic debris.

The use of seabirds as environmental monitors has been widely documented (Burger and Gochfeld, 2004; Furness and Camphuysen, 1997; Mallory et al., 2010; Monteiro and Furness, 1995). The Northern Fulmar (*Fulmarus glacialis*) has been the main focus for monitoring ingestion of plastic litter, which has been incorporated into European environmental policies such as the Oslo-Paris Convention (OSPAR) and the Marine Strategy Framework Directive (MSFD) (Van Franeker et al., 2011). Fulmars are in the order Procellariiformes, which have a very limited ability to regurgitate indigestible matter, thus ingested litter is accumulated. Many species of seabird however, regurgitate pellets or boluses, which comprise items they cannot digest, including fish bones, otoliths, squid beaks and stones (Barrett et al., 2007). Regurgitated pellets are frequently used in dietary studies as they can be collected with minimal disturbance at colonies and can provide valuable information on seabird diet (Barrett et al., 2007). Using regurgitated pellets may underestimate the presence of soft prey (Bearhop et al., 2001), hence it is important to be cautious when interpreting results and not limit dietary studies to evidence from pellets only.

Monitoring plastic litter through seabird diet has been primarily achieved through the analysis of the stomach contents of dead birds (Acampora et al., 2014; Avery-Gomm et al., 2013; Van Franeker et al., 2011), but monitoring of live birds could also provide complementary information from species that do not always accumulate plastics in their digestive tract. Such species could be considered as being less prone to ingesting plastic litter due to the possible masking effects of pellet regurgitation. Thus, other methods, such as the use of regurgitates and pellets could provide supporting or additional information on the incidence of marine plastic litter in their diet.

The family Phalacrocoracidae comprises Cormorants and Shags which occur in both freshwater and marine environments. This study focuses on the Great Cormorant (*Phalacrocorax carbo*) (hereafter Cormorant). Whilst Shags are predominantly a marine species, Cormorants can be also found foraging and breeding in lakes and rivers. Cormorants are relatively abundant in Irish waters, with 4548 breeding pairs recorded between 1998 and 2002 during the last published national census (Mitchell et al., 2004). Cormorants feed primarily on fish, and are mainly benthic divers (Gremillet et al., 1998).

* Corresponding author.
E-mail address: heidiacampora@gmail.com (H. Acampora).

http://dx.doi.org/10.1016/j.marpolbul.2017.02.015
0025-326X/

Table 1
List of samples by year, season, and location.

Species	Year	Season	Bolus (n)	Location
Cormorant	2011	Summer	29	Great Saltee, Co. Wexford
	2014	Winter	3	Money Point, Co. Clare
	2015	Winter	60	Money Point, Co. Clare

Both macro and micro plastics are widespread in Irish waters. Lusher et al. (2014) reported an average of 2.46 microplastic particles/m^3 of seawater during sub-surface transects in the Northeast Atlantic, whilst the presence of litter was reported in 57% of trawl stations sampled in the Celtic Sea, with 84% of this litter found to be plastic (Moriarty et al., 2016). There is little information on the presence of marine litter in seabirds in Ireland. Recently, Acampora et al. (2016) investigated the presence of plastics through stomach content analysis of dead birds, and reported the ingestion of plastics by 27% of specimens examined (n = 121), however due to the opportunistic nature of such sampling methodology, no data for Cormorants were available.

This study sets a baseline for the presence of plastic litter in pellets regurgitated by breeding and non-breeding Cormorants in Ireland. This technique is believed to be complementary to data collected from dead seabirds.

In total, 92 pellets were collected between the years 2011–2015 (Table 1) from two sites: Money Point, County Clare, on the western seaboard and from Great Saltee Island, County Wexford, off the south-east coast. Cormorant pellets were collected during winter at a roost site (Money Point), and in summer during ringing operations on Great Saltee Island. Pellets were placed in plastic bags and frozen until subsequent analysis. Pellets were soaked in water in individual containers for 24 h before being washed through a 1 mm mesh sieve and every solid item retained in Petri-dishes. Solid contents were air dried overnight and examined under a stereo microscope (MicrosAustria, 0.6×–5×). They were then separated into categories according to Van Franeker et al. (2003). Only litter items were weighed, to the nearest 0.0001 g. Food items were identified to groups and counted.

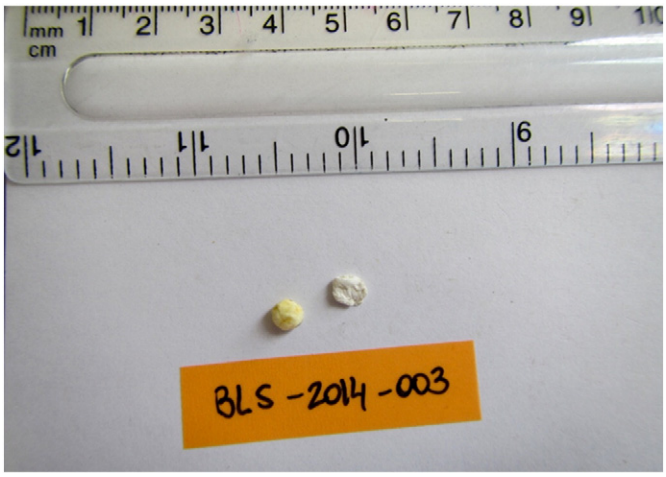


Fig. 1. Plastic fragments (foam) found in a Cormorant pellet, during the non-breeding season, in Money Point, County Clare, 2014.

Three of 92 analysed pellets (3.2%) contained plastic litter (Fig. 1). The proportion of pellets containing plastics was consistent between sampling sites (c. 3%). The average plastic mass was 0.0002 g (Range: 0–0.01, SE ± 0.0001), with a 0.043 average number of particles (Range: 0–2, SE ± 0.0263). Types of plastic litter included sheet, foam and fragment. Table 2 describes abundance of different food types in pellets.

According to Johnstone et al. (1990), plastics quantified in pellets only reflect the last ingested meal or meals consumed throughout the previous day. Cormorants are known to regurgitate pellets daily, whilst Gulls and Skuas, regurgitate after each meal (Barrett et al., 2007). Thus sampling regurgitated pellets reflects short time-scales, implying pellets are produced within hours of a meal. Additionally, collecting samples at nest sites might reflect the diet fed to chicks as adult birds could provision their chicks with different prey compared to what they would feed themselves outside of the chick rearing period (Bearhop et al., 2001). Thus, a comparison between breeding and non-breeding season is appropriate.

There are no data for the presence of plastic litter in Cormorants in Ireland, but Shags (*Phalacrocorax aristotelis*), a related species, found beached in Ireland (n = 10) had a prevalence of plastic litter of 10% (n = 10) (Acampora et al., 2016), which is higher than 3.1% found in pellets in this study. Such differences could be explained by species-specific feeding habits, small sample size, or additionally, biased towards starving birds which is the case for most beached birds. Robards et al. (1995) found a 20% prevalence in stomachs of a related species: the Pelagic Cormorant (*Phalacrocorax pelagicus*) between 1988 and 1990. Burthe et al. (2014) classified plastics as a 'low' threat to Great Cormorants.

Multiple studies have connected plastic ingestion to foraging strategy (Azzarello and Van Vleet, 1987; Ryan, 1988; Shephard et al., 2015). Diving seabirds should not be as prone to ingesting plastic litter as those feeding at the surface due to the buoyant nature of most plastic types. Such birds could, on the other hand, be prone to secondary ingestion, which means they might have obtained plastic litter from their prey. When considering such factors, birds that are able to regurgitate indigestible matter, such as plastic litter, have an effective mechanism to counter the potential accumulation or effects of plastic litter.

It is important to set a baseline for the presence of marine litter in seabirds using a variety of sampling methods, in order to obtain a more reliable and extensive record. Sampling live birds compared to dead birds, within the breeding season alongside non-breeding birds, and from a range of species, has the potential to provide a multi-dimensional record of plastic pollution in the marine environment not only in Ireland, but globally.

Acknowledgements

This work was supported by Science Without Borders (CAPES, Brazil, BEX 1269/2013-05) scheme through a doctoral scholarship awarded to Heidi Acampora. We thank all at BirdWatch Ireland. Special thanks to John Lusby, Niall Tierney and Niall Keogh for sample collection and storage in the field. Thanks to the anonymous reviewers for improving the quality of this manuscript.

Table 2
Main items found in pellets. Numbers are proportion of items in relation to total items and proportion of pellets containing said item.

	Otoliths	Lens	Bones	Crustacean	Plant	Seaweed	Stones	Parasitic worms
Proportion of items %	26.7	4.0	50.2	8.7	3.8	0.8	4.7	0.9
Proportion of pellets %	79.3	43.4	59.7	36.9	40.2	15.2	32.6	15.2

References

Acampora, H., Schuyler, Q.A., Townsend, K.A., Hardesty, B.D., 2014. Comparing plastic ingestion in juvenile and adult stranded short-tailed shearwaters (*Puffinus tenuirostris*) in eastern Australia. Mar. Pollut. Bull. 78 (1–2), 63–68.

Acampora, H., Lyashevska, O., Van Franeker, J.A., O'Connor, I., 2016. The use of beached bird surveys for marine plastic litter monitoring in Ireland. Mar. Environ. Res. 120: e87–e91. http://dx.doi.org/10.1016/j.marenvres.2016.08.002.

Avery-Gomm, S., Provencher, J.F., Morgan, K.H., Bertram, D.F., 2013. Plastic ingestion in marine-associated bird species from the eastern North Pacific. Mar. Pollut. Bull. 72 (1):257–259. http://dx.doi.org/10.1016/j.marpolbul.2013.04.021.

Azzarello, M., Van Vleet, E., 1987. Marine birds and plastic pollution. Mar. Ecol. Prog. Ser. 37:295–303. http://dx.doi.org/10.3354/meps037295.

Barrett, R.T., Camphuysen, K., Anker-Nilssen, T., Chardine, J.W., Furness, R.W., Garthe, S., ... Veit, R.R., 2007. Diet studies of seabirds: a review and recommendations. ICES J. Mar. Sci. 64 (9):1675–1691. http://dx.doi.org/10.1093/icesjms/fsm152.

Bearhop, S., Thompson, D.R., Phillips, R.A., Waldron, S., Hamer, K.C., Gray, C.M., ... Furness, R.W., 2001. Annual variation in great skua diets: the importance of commercial fisheries and predation on seabirds revealed by combining dietary analyses. Condor 103 (4):802–809. http://dx.doi.org/10.1650/0010-5422(2001)103[0802:avigsd]2.0.co;2.

Burger, J., Gochfeld, M., 2004. Marine birds as sentinels of environmental pollution. EcoHealth 1 (3):263–274. http://dx.doi.org/10.1007/s10393-004-0096-4.

Burthe, S.J., Wanless, S., Newell, M.A., Butler, A., Daunt, F., 2014. Assessing the vulnerability of the marine bird community in the western North Sea to climate change and other anthropogenic impacts. Mar. Ecol. Prog. Ser. 507, 277–295.

Furness, R.W., Camphuysen, C., 1997. Seabirds as monitors of the marine environment. ICES J. Mar. Sci. 54, 726–737.

Gremillet, D., Argentin, G., Schulte, B., Culik, B., 1998. Flexible foraging techniques in breeding cormorants *Phalacrocorax carbo* and shags *Phalacrocorax aristotelis*: benthic or pelagic feeding? IBIS 140 (May 1994), 113–119.

Johnstone, I.G., Harris, M.P., Wanless, S., Graves, J.a., 1990. The usefulness of pellets for assessing the diet of adult shags *Phalacrocorax aristotelis*. Bird Study 37 (1):37–41. http://dx.doi.org/10.1080/00063659009477030.

Kühn, S., Bravo Rebolledo, E.L., Franeker, J.A., 2015. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Springer International Publishing, Cham: pp. 75–116 http://dx.doi.org/10.1007/978-3-319-16510-3_4.

Lusher, A.L., Burke, A., O'Connor, I., Officer, R., 2014. Microplastic pollution in the Northeast Atlantic Ocean: validated and opportunistic sampling. Mar. Pollut. Bull. 88 (1–2):325–333. http://dx.doi.org/10.1016/j.marpolbul.2014.08.023.

Mallory, M.L., Robinson, S.a., Hebert, C.E., Forbes, M.R., 2010. Seabirds as indicators of aquatic ecosystem conditions: a case for gathering multiple proxies of seabird health. Mar. Pollut. Bull. 60 (1):7–12. http://dx.doi.org/10.1016/j.marpolbul.2009.08.024.

Mitchell, P.I., Newton, S.F., Ratcliffe, N., Eds, T.E.D., Dunn, T.E., Poyser, A.D., May, L., 2004. Seabird Populations of Britain and Ireland: Results of the Seabird 2000 Census. JNCC, Poyser, London (August).

Monteiro, L.R., Furness, R.W., 1995. Seabirds as indicators of mercury in the marine environment. Water Air Soil Pollut. 80, 851–870.

Moriarty, M., Pedreschi, D., Stokes, D., Dransfeld, L., Reid, D.G., 2016. Spatial and temporal analysis of litter in the Celtic Sea from Groundfish Survey data: lessons for monitoring. Mar. Pollut. Bull. 103 (1-2), 195–205.

Robards, M.D., Piatt, J.F., Wohl, K.D., 1995. Increasing frequency of plastic ingested by seabirds in the subarctic North Pacific. Mar. Pollut. Bull. 30 (2):151–157 (http://doi.org/0025-326X(94)00121-9).

Ryan, P.G., 1988. Intraspecific variation in plastic ingestion by seabirds and the flux of plastic through seabird populations. Condor 90 (2):446–452 (Retrieved from http://links.jstor.org/sici?sici=0010-5422(198805)90:2%3C446:IVIPIB%3E2.0.CO;2-R).

Shephard, S., van Hal, R., de Boois, I., Birchenough, S.N.R., Foden, J., O'Connor, J., ... Schaber, M., 2015. Making progress towards integration of existing sampling activities to establish joint monitoring programmes in support of the MSFD. Mar. Policy 59 (2015):105–111. http://dx.doi.org/10.1016/j.marpol.2015.06.004.

Van Franeker, J.A., Meijboom, A., de Jong, M.L., 2003. Marine litter monitoring by northern fulmars in the Netherlands 1982–2003. Alterra-Rapport 1093. Alterra, Wageningen.

Van Franeker, J.A., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., ... Turner, D.M., 2011. Monitoring plastic ingestion by the northern fulmar *Fulmarus glacialis* in the North Sea. Environ. Pollut. 159 (10):2609–2615. http://dx.doi.org/10.1016/j.envpol.2011.06.008.

Wilcox, C., Van Sebille, E., Hardesty, B.D., 2015. Threat of plastic pollution to seabirds is global, pervasive, and increasing. Proc. Natl. Acad. Sci., 201502108 http://dx.doi.org/10.1073/pnas.1502108112.

Environ Sci Pollut Res
DOI 10.1007/s11356-017-8931-7

RESEARCH ARTICLE

Presence of persistent organic pollutants in a breeding common tern (*Sterna hirundo*) population in Ireland

Heidi Acampora[1] · **Philip White**[1] · **Olga Lyashevska**[1] · **Ian O'Connor**[1]

Received: 30 January 2017 / Accepted: 23 March 2017

Abstract Persistent organic pollutants (POPs) are chemical compounds of environmental concern due to their toxic, persistent nature and their ability to bio-accumulate in biological tissue. Seabirds, for often being at the top of the food web, have been used as monitors of environmental pollutants. Adverse effects caused by POPs have been reported in common terns (*Sterna hirundo*) since the 1970s. Egg shell thinning, embryo and hatchling deformities have been reported for this species. Environmental legislation, such as the Oslo-Paris Convention (OSPAR), has agreed on the monitoring of concentration of POPs in common terns. This study set out to investigate contemporary concentrations of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and brominated flame retardants (BFRs) in common terns breeding in Ireland, along with congener profiles. Investigation was conducted in live (n = 15) and dead birds (n = 20) to test for the efficiency of different methodologies using preen oil and feathers versus liver and preen gland. Mean concentrations of POPs followed the order: PCB (36.48 ng/g ww feather) > PAH (30.01 ng/g ww feather) > OCP (13.36 ng/g ww feather) > BFR (1.98 ng/g ww feather) in live birds; and PAH (46.65 ng/g ww preen gland) > PCB (44.11 ng/g ww preen gland) > OCP (15.15 ng/g ww liver) > BFR (5.07 ng/g ww liver) in dead birds. Comparison of contaminant results with toxicity pre-established levels concluded that this population of common terns in Ireland is not at risk of anomalies caused by POPs. However, some levels are higher in comparison to the ones established by OSPAR's EcoQO and must be monitored periodically.

Keywords Common tern · *Sterna hirundo* · Persistent organic pollutants · PCB · PAH · OCP · BFR

Highlights • First detected levels of persistent organic pollutants (POPs) in common terns (*Sterna hirundo*) in Ireland.
• PCBs, PAHs, OCPs and BFRs were detected in feathers and preen oil of live birds (n = 15).
• PCBs, PAHs, OCPs and BFRs were detected in liver and preen gland of dead birds (n = 20).
• Comparisons were made with levels of toxicological importance and EcoQO monitoring values.

Responsible editor: Philippe Garrigues

✉ Heidi Acampora
heidiacampora@gmail.com

[1] Marine & Freshwater Research Centre, Galway-Mayo Institute of Technology, Dublin Rd, Galway, Ireland

Introduction

Persistent organic pollutants (POPs) are chemical compounds of environmental concern due to their environmentally resilient and toxic nature. Such compounds are generally man-made or the result of anthropogenic activities and have become ubiquitous in the environment (Jones and de Voogt 1999; Pariatamby and Kee 2016). POPs have been used for many purposes in industrial, commercial and agricultural activities (Stockholm Convention 2001; Van Den Brink 1997), but in past decades have been found to cause ill-effects on humans and, mainly wildlife (Jones and de Voogt 1999; Stockholm Convention 2001).

Persistent organic pollutants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and brominated flame retardants (BFRs) have been found to cause endocrine disruption and to have carcinogenic effects (Barron et al. 1995; UNEP 2011). These compounds can be biomagnified along the food web reaching levels of toxicological importance in top predators (Jaspers et al. 2006). In birds, for instance, PCBs were

Published online: 05 April 2017

found responsible for egg shell thinning in many raptor species in the 1970s causing concerning population decline (Tanabe et al. 1984). POPs have been correlated to low reproductive success in fish-eating birds (Giesy et al. 1994), embryonic abnormalities (Gilbertson and Fox 1977), reduced growth (Gilbertson and Fox 1977) and physiological and biochemical alterations (Elliott et al. 1989). When such severe ill-effects were brought to light by research, legislation throughout the world imposed ban or restriction to most well-known POPs (Stockholm Convention 2001). The Stockholm Convention came into force in 2004 and with it, the need to monitor concentrations and levels in all environmental matrices, including biota (Stockholm Convention 2001).

Measuring the concentration of pollutants in birds is often done through destructive sampling, where a certain number of birds were sacrificed, although sometimes found dead, and serve as proxy for a given population. Such sampling would involve the collection of internal organs such as the liver, muscle or brain (Falkowska et al. 2016; Roscales et al. 2011). Eggs are an alternative to destructive sampling (Elliott et al. 2005; Moore and Tatton 1965; Mora et al. 2016; Peck et al. 2016), but when certain species of birds lay a single egg per season, care should be taken to make sure such species would relay. Non-destructive sampling techniques became necessary and feathers started being used as a proxy for contamination levels in internal organs (Jaspers et al. 2007; Jaspers et al. 2011; Van den Steen et al. 2007). Additionally, preen oil has also been regarded as a non-destructive technique (Wang et al. 2015; Yamashita et al. 2007).

Persistent organic pollutant concentrations in common terns (*Sterna hirundo*) have been measured in many parts of the world since the 1960s (Bosveld et al. 1995; Gilbertson et al. 1976; Scharenberg 1991; Van Den Brink and Bosveld 2001; Custer et al. 2001). POPs were found to cause death, feminization of male embryos and other embryonic developmental abnormalities in this species (Becker et al. 1993; Fox 1976; Hays and Risebrough 1972; Hoffman et al. 1998; Hoffman et al. 1993; Scharenberg 1991). Since then, toxicity levels over which embryonic development would be affected have been established (Hays and Risebrough 1972; Hoffman et al. 1998; Scharenberg 1991).

Monitoring of POPs in eggs of common terns is one of the Oslo-Paris Convention's (OSPAR) Ecological Quality Objectives (EcoQO) (OSPAR 2010). EcoQOs establish threshold contaminant levels for certain species and parties must monitor levels to meet the treaty's requirements (Dittmann et al. 2012).

Common terns are highly migratory seabirds, globally distributed, with tropical wintering areas in the south and northern breeding areas (Austin 1953). Their diet consists mainly of fish (Massias and Becker 1990). In Ireland, there are over two and a half thousand pairs of breeding common terns (Mitchell et al. 2004). Main threats to common tern populations are habitat loss and pollution (Mitchell et al. 2004). To our knowledge, there are no persistent organic pollutant data for common terns breeding in Ireland. Most recent published data for closely related species such as roseate (*Sterna dougallii*) and sandwich (*Sterna sandvicensis*) terns date from 1965 (Koeman et al. 1967). Given the absence of data in Ireland for a species of conservation importance, the research presented here intended to (1) gather contemporary data on concentrations of PCBs, PAHs, OCPs and BFRs in common terns breeding in Ireland; (2) investigate congener profiles, along with destructive and non-destructive sampling methods, using preen oil and feathers in live birds, and liver and preen gland in corpses found in breeding colonies; and (3) investigate contaminant levels of toxicological importance.

Material and methods

Sampling location

Rockabill is a 0.9 ha island located 7 km off the north coast of county Dublin, Ireland (Grid Ref. O320627). Rockabill is home to approximately 2000 pairs of common terns, along with 1550 pairs (47% of the entire European population) of roseate terns (*S. dougallii*) and smaller numbers of breeding Arctic terns (*Sterna paradisaea*), black-legged kittiwakes (*Rissa tridactyla*) and black guillemots (*Cepphus grylle*) (Burke et al. 2016). The major disturbance to tern nests on the island is predation by great black-backed gulls (*Larus marinus*) (Burke et al. 2016). Common tern diet composition consists mostly of Clupeids, Sandeels and Gadoids (Burke et al. 2016).

Dead birds sampling

Necropsies

In total, 38 common tern corpses were collected at Rockabill colony, during the breeding seasons of 2015–2016. Birds were necropsied following Van Franeker (2004) methodology. When possible, sex, age class and cause of death were inferred. Preen gland and liver were collected from 20 birds for persistent organic pollutants (POP) analysis. All 38 stomachs were additionally analysed for plastic litter according to Van Franeker (2004) by sieving contents through a 1 mm mesh sieve. All retained solids were collected in petri-dishes and air-dried overnight. Only a single piece of plastic (fragment) was found in all stomachs analysed. Mass of the item was 0.1538 g and it was perforating the stomach lining, causing an ulcer.

Liver and preen gland extractions

In total, 20 livers and preen glands were analysed from necropsied birds. All utensils were previously washed using *n*-hexane (VWR Analar Normapur). Tissue samples (liver and preen gland) were cut into small pieces. Preen gland samples also had remaining feathers removed. Samples were weighed in beakers to the nearest 0.0001 g. A solvent mixture of three parts of hexane and one part of acetone (Merck SupraSolv) was added to samples (approximately 30 ml). Samples were spiked with internal standards (PAH 24D, 13C PCB and BFR, OCP Pesticide Mix 20). Samples were homogenised using an UltraTurrax (IKA T10 Basic) for 1 min, then 20 ml of pure water was added to the sample, and the mixture was homogenised again for another minute. Samples were transferred to centrifuge tubes and placed on the centrifuge (Hehich Zentrifugen Mikro 220R) for 5 min at 4000 rpm. Using disposable pipette tips, the top layer (solvent) was transferred to glass vials. The cleaning process was achieved by placing 2 g of pre-treated (300 °C for 3 h, with 5% weight by water) silica gel (Molekula) in a glass column for each sample. The solvent layer in the glass vials was then poured into the glass column followed by a solvent mixture of 60 ml of hexane and 10 ml of acetone. Clean samples were collected in a conical flask by opening the tap of the glass column. Samples were then evaporated in the TurboVap LP (Biotage) to approximately 1 ml and transferred into GC vials.

Live birds sampling

In total, 15 common terns were hand caught at Rockabill colony, county Dublin during the breeding season, under licence no. C124/2015 and C125/2015 from National Parks and Wildlife Service (NPWS), in July 2015. Birds were weighed, had their wingspan measured and were ringed if they had not been previously ringed. Preen oil cotton swabs were collected by exposing the preen gland and gently pressing it to express the oil. Swabs were placed in sterile glass jars with foil covered lids. Furthermore, six breast feathers were collected from each individual and kept in paper envelopes. Preen oil samples were kept frozen at −80 °C, whilst feather samples were kept at room temperature until analysis.

Preen oil extraction

All utensils were previously washed using methanol (Merck SupraSolv). Cotton swabs were transferred into glass beakers by using metal forceps. Sample jars were then rinsed with SupraSolv methanol to remove any remaining preen oil in the glass jar. This methanol was also poured into the beaker containing the corresponding cotton swab. In total, 150 ml of methanol was poured into each beaker (in three aliquots). Contents were stirred for 1 min each time. Samples were spiked with internal standards (PAH 24D, 13C PCB and BFR, OCP Pesticide Mix 20). Only the liquid sample was then transferred to another beaker and covered with aluminium foil. Samples were placed in a TurboVap LP (Biotage) to evaporate the volume to approximately 1 ml. Using disposable glass pipettes, the remaining sample was transferred into previously labelled GC vials. Samples were kept frozen at −80 °C until subsequent analysis using gas-chromatography/mass-spectrometry (GC/MS).

Feather extraction

All utensils were previously washed with methanol. Samples of four feathers per bird were placed in individual beakers. Feathers were washed with distilled water, using forceps to separate the barbs, and stirred. They were left soaking for 20 min and then left to dry in folded tissue paper for 2 h or until fully dried. After drying, each sample was weighed to the nearest 0.0001 g and placed inside a beaker with 15 ml of 37% HCl (Merck EMSURE) and 20 ml of a solvent mixture of two parts of hexane and one part of acetone. Samples were spiked with internal standards (PAH 24D, 13C PCB and BFR, OCP Pesticide Mix 20). Beakers were covered with aluminium foil and put in the oven at 37 °C overnight (in total for approximately 15 h). Consequently, 40 ml of a solvent mixture of three parts of hexane and one part of acetone was added to each sample. Samples were then placed within a separation funnel and shaken vigorously. The subsequent aqueous layer was removed by opening the tap on the separation funnel and pouring the liquid into a beaker. The remaining lipid layer was decanted into previously labelled glass vials. This separation procedure was repeated by placing the aqueous layer back into the separation funnel and adding 20 ml of fresh hexane/acetone solvent mixture. Samples were transferred into a TurboVap LP (Biotage) and evaporated under a nitrogen stream until approximately 1 ml remained. Samples were subsequently transferred to pre-labelled GC vials using disposable glass pipettes. Samples were kept frozen at −80 °C until subsequent analysis using GC/MS.

Gas-chromatography mass-spectrometry

Liver, preen gland, preen oil and feather solvent extractions were then analysed for polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and brominated flame retardants (BFRs) using gas-chromatography/mass spectrometry (Agilent GC-MS (5977E)) equipped with an auto-sampler. GC/MS was run in EI mode, with a J&W 30 m BD1 MS column, with helium being the carrier gas. Quality control was guaranteed by the use of blanks per batch of samples and certified reference materials (CRMs). For preen gland, preen oil and liver analysis, cod liver oil (Commission of the European

Communities, Community Bureau of Reference – BCR. Reference Material n° 349. Chlorobiphenyls in cod liver oil n° 0831) was used as a CRM and for feather analysis, fish tissue (NIST 1947 Lake Michigan Fish Tissue. U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899).

Statistical analysis

Statistical analysis was carried out using R (R Core Team 2015), version 3.2.3 and 'prcomp' package. To investigate the potential relationships between matrices, such as preen oil and feathers and liver and preen gland, Pearson's correlation was computed for each group of contaminants. This was done in two ways: through a correlation matrix at the individual level and through aggregated data. A correlation matrix was combined with hierarchical clustering using complete hierarchical clustering method. The input to a hierarchical clustering algorithm consists of the measurement of the similarity (or dissimilarity) between each pair of objects. The goal of the clustering algorithm is then to partition the objects into homogeneous groups, such that the within-group similarities are large compared to the between-group similarities. Aggregated data on the other hand uses means and standard deviations of each congener to compute correlation by homogenising individual samples.

A principal component analysis (PCA) was used to investigate which congeners contributed most to the variance in each group of contaminants. The principal components were extracted to represent the patterns encoding the highest variance in the data set. However, in many high-dimensional data sets, the most dominant patterns, i.e. those captured by the first principal components, are those separating different subgroups of the samples from each other. The first principal component (PC1) captures the maximum variance and will determine the direction of highest variability in the data. The following components (e.g. PC2, PC3, etc.) capture the remaining variance. The same analysis was then used to investigate if live sampling (e.g. preen oil and feathers) can potentially serve as a proxy for organs (e.g. liver and preen gland). Congeners with over 50% of values below the level of detection (LOD) were excluded from statistical analysis (Jaspers et al. 2008).

Results

Live birds—preen oil and feathers

In total, 16 PCBs were detected in preen oil and feathers. The mean concentration of ∑PCBs was 4.23 ng/g ww preen oil (range 1.78–9.11 ng/g ww) and 36.48 ng/g ww feathers (range 14.96–113.48 ng/g ww). The mean concentration of ∑7 PCBs was 3.45 ng/g ww preen oil and 27.25 ng/g ww feathers (Table 1). Results from the PCA showed that in preen oil, the three first components (PC1, PC2 and PC3) explained 72% of the variance, whilst in feathers, they explained 91%. In preen oil, the congeners that contributed most to PCB burden were PCBs 118, −153 and −138, whilst in feathers, highest contributions came from PCBs 101, −149 and −138.

Twelve PAH congeners were detected in preen oil and feathers. The mean concentration of PAHs was 10.52 ng/g ww preen oil (range 6.42–18.74 ng/g ww) and 30.01 ng/g ww feathers (range 18.53–53.46 ng/g ww) (Table 2). PCA results showed that in preen oil, the three first components explained 69% of the variance; and in feathers, 63%. Congeners that mostly contributed to PAH burden in preen oil were chrysene, benzo(b)fluoranthene and benzo(a)anthracene, whilst for feathers were pyrene, fluoranthene and benzo(b)fluoranthene.

Fifteen OCPs were detected in feather and preen oil. The mean concentration of OCPS was 3.69 ng/g ww preen oil (range 2.86–5.02 ng/g ww) and 13.36 ng/g ww feathers (range 6.23–25.01 ng/g ww) (Table 3). PCA results showed that the first three components retained 59% of the variance for preen oil and 94% for feathers. Congeners that had the highest contribution to PAH burden were heptachlor, dieldrin and pp-DDE in preen oil, and Endrin, a-HCH and heptachlor in feathers.

In total, six BFRs were detected in feathers and preen oil. The mean concentration of BFRs was 1.86 ng/g ww preen oil (range 1.54–2.20 ng/g ww) and 1.98 ng/g ww feathers (range 1.87–2.90 ng/g ww) (Table 4). The first three components in the principal component analysis explained 84% of the variance in preen oil, and 75% in feathers. Congeners that contributed most to BFR burden in preen oil were BFRs 47, −99 and −100, and BFRs 100, −154 and −183 in feathers.

Congener profiles differed between feathers and preen oil. That was confirmed by the correlation matrices combined with hierarchical clustering. Correlations were either negative or very low between congeners. Aggregated data on the other hand showed a strong correlation between feathers and preen oil for BFR (0.97), PCB (0.73) and PAH (0.72), and a moderate correlation for OCP (0.51).

Dead birds—liver and preen gland

In total, 16 PCBs were detected in liver and preen gland. The mean concentration of PCBs was 41.43 ng/g ww liver (range 11.01–103.93 ng/g ww) and 44.11 ng/g ww preen gland (range 4.74–115.6 ng/g ww). The mean concentration for ∑7 PCBs was 35.34 ng/g ww liver and 34.85 ng/g ww preen gland (Table 1). The three first principal components explained 82% of the variance in liver and 85% in preen gland. In liver, the congeners that contributed most to PCB burden

Table 1 PCB mean concentrations (ng/g ww) ± standard deviation (SD) separated per congener, detected in preen oil, feathers, liver and preen gland. Seven PCBs(Σ7) are −28, −52, −101, −118, −153, −138 and −180

PCB	Live common terns		Dead common terns	
	Preen oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD	Liver (ng/g ww) ± SD	Preen gland (ng/g ww) ± SD
PCB 18	0.03 ± 0.03	0.71 ± 0.74	0.07 ± 0.04	1.25 ± 4.59
PCB 28	0.07 ± 0.06	2.42 ± 1.83	0.76 ± 0.63	0.97 ± 1.14
PCB 31	0.06 ± 0.05	2.27 ± 1.94	0.65 ± 0.62	0.83 ± 0.84
PCB 52	0.20 ± 0.18	6.75 ± 3.86	1.94 ± 1.69	2.89 ± 4.48
PCB 44	0.15 ± 0.18	2.51 ± 1.40	0.98 ± 0.80	1.83 ± 4.45
PCB 101	1.13 ± 0.54	9.16 ± 7.41	5.64 ± 3.37	5.36 ± 5.51
PCB 118	0.69 ± 0.43	3.88 ± 3.67	5.51 ± 3.48	5.80 ± 5.74
PCB 105	0.08 ± 0.06	0.74 ± 0.93	0.68 ± 0.53	2.00 ± 3.17
PCB 149	0.30 ± 0.13	2.65 ± 2.59	3.10 ± 3.64	1.71 ± 2.08
PCB 153	0.68 ± 0.35	2.45 ± 2.41	11.71 ± 6.69	9.69 ± 9.43
PCB 138	0.44 ± 0.23	2.26 ± 2.13	8.25 ± 5.28	6.92 ± 6.41
PCB 156	0.09 ± 0.05	0.19 ± 0.22	0.28 ± 0.26	0.78 ± 0.71
PCB 180	0.24 ± 0.14	0.33 ± 0.24	1.53 ± 1.35	3.22 ± 3.18
PCB 170	0.04 ± 0.04	0.08 ± 0.08	0.24 ± 0.28	0.42 ± 0.53
PCB 194	0.02 ± 0.01	0.07 ± 0.06	0.07 ± 0.07	0.29 ± 0.74
PCB 209	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.02	0.15 ± 0.41
∑ all PCBs	4.23 ± 0.30	36.48 ± 2.47	41.43 ± 3.33	44.11 ± 2.68
∑ 7 PCBs	3.45 ± 0.34	27.25 ± 2.81	35.34 ± 3.69	34.85 ± 2.68

were PCBs 153, −138 and −180, whilst in preen gland, the highest contributions came from PCBs 138, −153 and −118.

Fifteen PAH congeners were detected in preen gland and only 13 in liver. The mean concentration of PAHs

Table 2 PAH mean concentrations (ng/g ww) ± standard deviation (SD) separated per congener, detected in preen oil, feathers, liver and preen gland

PAH	Live common terns		Dead common terns	
	Preen oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD	Liver (ng/g ww) ± SD	Preen gland (ng/g ww) ± SD
Acenaphthylene	1.00 ± 0.01	0.23 ± 0.12	0.19 ± 0.10	0.72 ± 0.28
Acenaphthene	ND	ND	ND	2.78 ± 1.62
Fluorene	ND	ND	ND	5.07 ± 2.20
Phenanthrene	3.89 ± 2.45	9.99 ± 3.34	7.03 ± 8.92	7.59 ± 3.36
Anthracene	0.50 ± 0.56	0.67 ± 0.26	0.88 ± 1.29	0.43 ± 0.43
Fluoranthene	0.63 ± 0.38	3.21 ± 1.53	2.17 ± 2.34	0.83 ± 0.45
Pyrene	ND	ND	3.72 ± 5.27	2.69 ± 1.23
Benzo(a)anthracene	0.43 ± 0.54	0.54 ± 0.66	0.99 ± 1.54	3.29 ± 4.33
Chrysene	0.76 ± 0.64	0.49 ± 0.60	0.39 ± 0.62	1.51 ± 1.12
Benzo(b)fluoranthene	0.45 ± 0.55	0.48 ± 0.15	2.91 ± 7.12	5.99 ± 8.27
Benzo(k)fluoranthene	0.43 ± 0.36	0.23 ± 0.08	0.85 ± 1.97	5.46 ± 15.48
Benzo(a)pyrene	0.62 ± 0.71	0.70 ± 1.27	4.06 ± 6.16	4.43 ± 4.03
Indeno(1,2,3-CD)pyrene	1.21 ± 1.09	12.67 ± 8.60	3.25 ± 4.56	0.89 ± 1.31
Dibenzo(a,h)anthracene	0.38 ± 0.41	0.62 ± 0.05	0.84 ± 0.72	1.42 ± 2.24
Benzo(g,h,i)perylene	0.22 ± 0.18	0.18 ± 0.20	0.36 ± 0.36	3.55 ± 4.11
∑PAH	10.52 ± 0.94	30.01 ± 4.06	27.64 ± 1.92	46.65 ± 2.13

ND not detected

Table 3 OCP mean concentrations (ng/g ww) ± standard deviation (SD) separated per congener, detected in preen oil, feathers, liver and preen gland

OCP	Live common terns		Dead common terns	
	Preen oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD	Liver (ng/g ww) ± SD	Preen gland (ng/g ww) ± SD
a-HCH	0.17 ± 0.15	2.78 ± 1.55	0.88 ± 1.04	0.33 ± 0.22
HCB	0.08 ± 0.05	0.09 ± 0.06	1.46 ± 2.04	0.07 ± 0.06
g-HCH	ND	ND	1.23 ± 3.67	2.43 ± 2.96
b-HCH	ND	ND	0.43 ± 1.94	0.35 ± 1.56
Heptachlor	0.17 ± 0.13	1.77 ± 2.67	0.25 ± 0.39	0.39 ± 0.20
Aldrin	0.01 ± 0.02	0.13 ± 0.19	0.12 ± 0.15	0.35 ± 0.25
Isobenzan	0.02 ± 0.02	0.11 ± 0.24	0.09 ± 0.07	0.37 ± 0.60
Isodrin	0.02 ± 0.02	0.26 ± 0.40	0.45 ± 1.06	0.20 ± 0.12
Heptachlor epoxide	0.01 ± 0.02	0.15 ± 0.29	0.34 ± 0.38	0.32 ± 0.17
op-DDE	0.20 ± 0.24	0.17 ± 0.21	0.63 ± 0.63	0.42 ± 1.36
pp-DDE	0.49 ± 0.49	0.21 ± 0.24	1.77 ± 4.34	0.14 ± 0.23
Dieldrin	0.03 ± 0.02	0.29 ± 0.33	0.91 ± 1.25	0.43 ± 1.00
pp-DDT	0.01 ± 0.02	0.39 ± 0.41	0.41 ± 0.43	0.15 ± 0.20
Endrin	0.18 ± 0.23	2.83 ± 4.97	1.28 ± 1.28	3.70 ± 6.03
Endosulphan B	0.40 ± 0.42	0.50 ± 0.81	1.16 ± 1.12	0.42 ± 0.41
pp-DDD	1.87 ± 0.01	2.84 ± 1.51	2.93 ± 1.09	2.90 ± 2.19
op-DDT	0.03 ± 0.03	0.84 ± 0.94	0.81 ± 0.92	0.51 ± 0.52
∑OCP	3.69 ± 0.45	13.36 ± 1.04	15.15 ± 0.69	13.48 ± 1.05

ND not detected

was 27.64 ng/g ww liver (range 4.49–78.76 ng/g ww) and 46.65 ng/g ww preen gland (range 12.34–124.37 ng/g ww) (Table 2). The first three components of the PCA explained 61% of the variance in preen oil and preen gland equally. Congeners that mostly contributed to PAH burden in liver were phenanthrene, fluoranthene and pyrene, whilst for preen gland were phenanthrene, acenaphthene and fluoranthene.

Seventeen OCPs were detected in liver and preen gland. The mean concentration of OCPS was 15.15 ng/g ww liver (range 4.84–38.08 ng/g ww) and 13.48 ng/g ww preen gland (range 4.80–28.85 ng/g ww) (Table 3). The three first components explained 52% of the variance in preen oil and the same in feathers. Congeners that had the highest contribution to OCP burden were dieldrin, HCB and pp-DDE in liver, and op-DDT, dieldrin and op-DDE in preen gland.

In total, seven BFRs were detected in liver and preen gland. The mean concentration of BFRs was 5.07 ng/g ww liver (range 2.04–18.81 ng/g ww) and 4.37 ng/g ww preen gland (2.06–8.53 ng/g ww) (Table 4). Principal components 1, 2 and 3 explained 83% of the variance in liver and 78% in preen gland. Congeners that contributed most to BFR burden in liver were BFRs 99, −153 and −100, and BFRs 47, −28 and −99 in preen gland.

Table 4 BFR mean concentrations (ng/g ww) ± standard deviation (SD) separated per congener, detected in preen oil, feathers, liver and preen gland

BFR	Live common terns		Dead common terns	
	Preen oil (ng/g ww) ± SD	Feathers (ng/g ww) ± SD	Liver (ng/g ww) ± SD	Preen gland (ng/g ww) ± SD
BFR 28	0.31 ± 0.02	0.30 ± 0.02	0.37 ± 0.12	0.45 ± 0.14
BFR 47	0.48 ± 0.11	0.58 ± 0.24	0.93 ± 0.66	0.84 ± 0.68
BFR 100	0.34 ± 0.04	0.33 ± 0.04	0.77 ± 0.61	0.69 ± 0.45
BFR 99	0.32 ± 0.05	0.37 ± 0.07	0.78 ± 0.97	0.61 ± 0.43
BFR 154	0.38 ± 0.10	0.37 ± 0.05	0.45 ± 0.23	0.41 ± 0.14
BFR 153	ND	ND	0.70 ± 1.65	0.52 ± 0.34
BFR 183	0.03 ± 0.02	0.03 ± 0.04	1.07 ± 0.72	0.85 ± 0.69
∑BFR	1.86 ± 0.55	1.98 ± 0.16	5.07 ± 0.22	4.37 ± 0.16

ND not detected

Results from the correlation matrices between congeners of liver and preen gland showed weak or negative correlations. Aggregated data correlation, however, showed a strong correlation between liver and preen gland for PCB (0.96) and BFR (0.94), but a weak correlation for PAH (0.6) and OCP (0.55).

Live versus dead

Results from the PCA comparing feathers as a proxy for liver (Fig. 1) and preen oil as a proxy for preen gland (Fig. 2) showed a clear separation between the two types of sample (live and dead), with much clustering in live bird samples, whilst dead bird samples show larger variance between individuals.

Discussion

To our knowledge, this is the first study to provide data on persistent organic pollutants in common terns in Ireland. Whilst there are data on POPs from sandwich and roseate terns in Ireland, this originates from the 1960s, and it is comprised of only two OCP congeners (Koeman et al. 1967).

Total PCB concentrations were ninefold higher in feathers (36.48 ng/g) than in preen oil (4.23 ng/g) in live

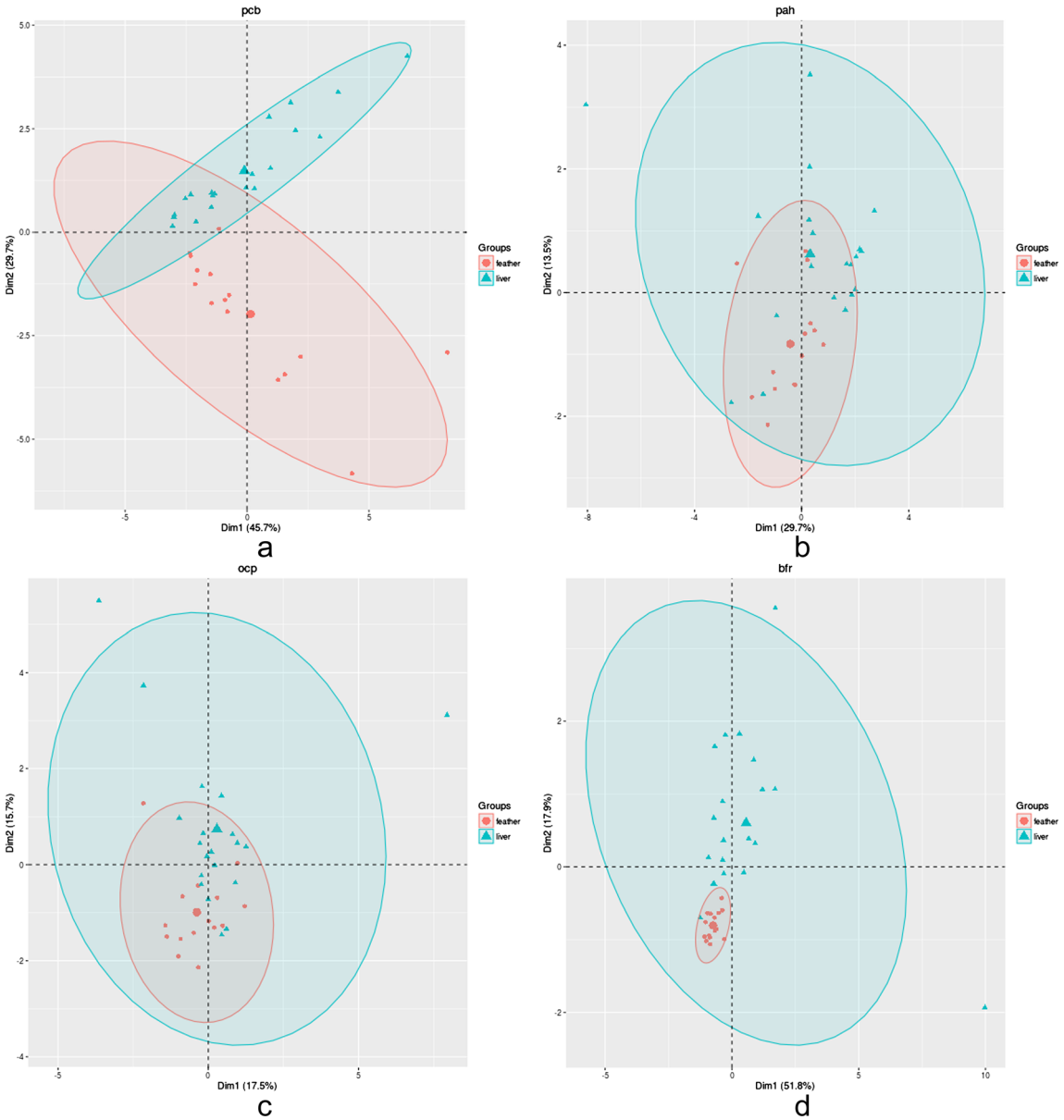


Fig. 1 Principal component analysis (*PCA*) comparing feathers (*red dots*) as a proxy for liver (*blue triangles*) for PCB (**a**), PAH (**b**), OCP (**c**) and BFR (**d**). There is a clear separation between the two groups, with feathers being much more clustered together, whilst liver samples appear to be more spread. *Ellipses* drawn around individual samples show a 95% concentration of points

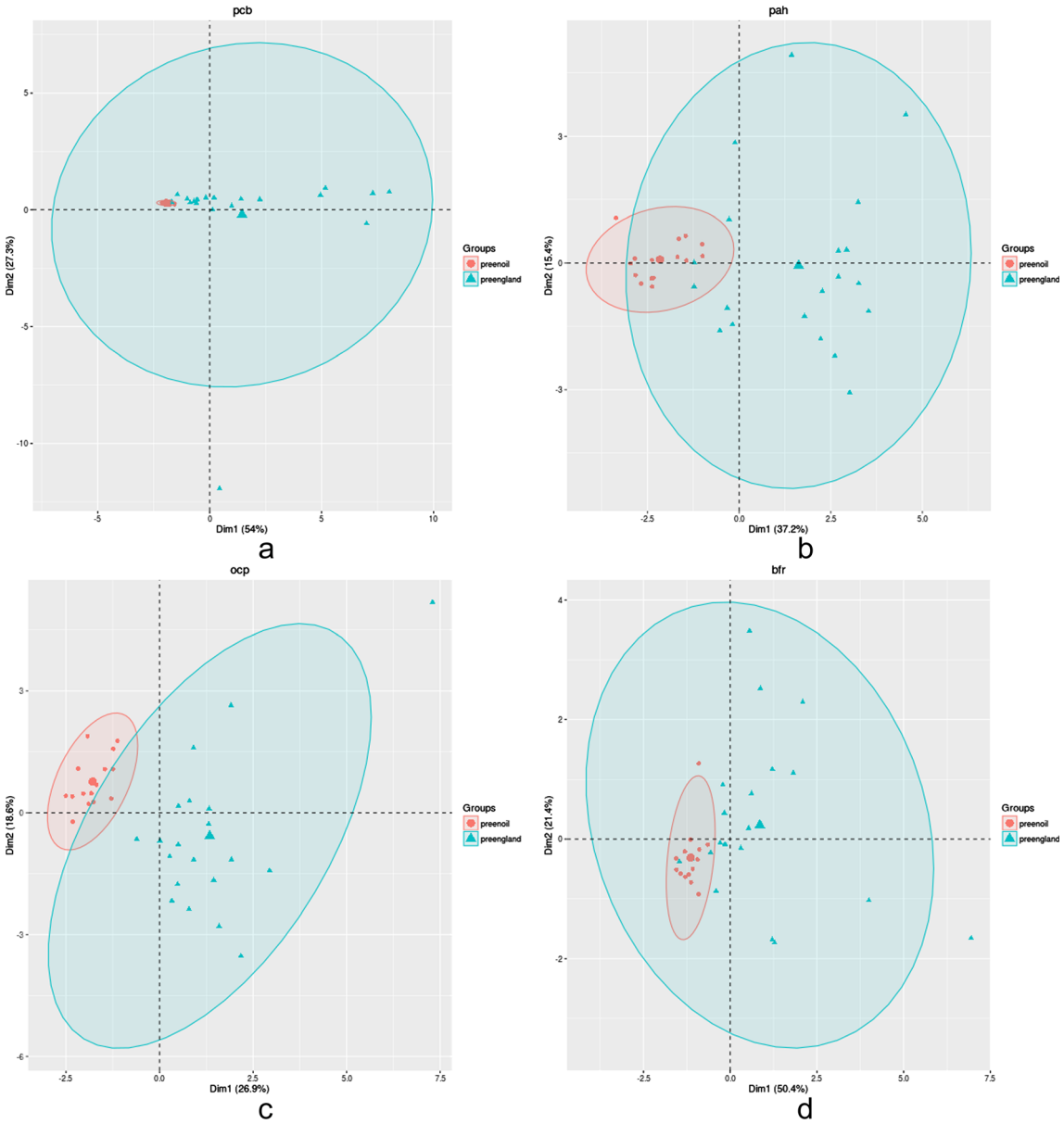


Fig. 2 Principal component analysis (*PCA*) comparing preen oil (*red dots*) as a proxy for preen gland (*blue triangles*) for PCB (**a**), PAH (**b**), OCP (**c**) and BFR (**d**). There is a clear separation between the two groups, with preen oil samples being much more clustered together, whilst preen gland samples appear to be more spread. *Ellipses* drawn around individual samples show a 95% concentration of points

birds and similar between liver (41.43 ng/g) and preen gland (44.11 ng/g) in dead birds, though a strong correlation was seen between both sets of sampling techniques: preen oil vs feathers (0.73) and liver vs preen gland (0.96). All samples were dominated by high molecular weight components, suggesting an accumulation of such congeners and potential metabolising of low molecular weight congeners. Concentrations in all matrices, apart from preen oil exceed the EcoQO for ∑ PCB, which is 20 ng/g in eggs (Dittmann et al. 2012). Research on Foster's Terns (*Sterna forsteri*) suggests that three PCB congeners (−126, −77 and −105) might contribute to 90% of toxicity in eggs (Kubiak et al. 1989). Laboratory experiments that involved the injection of PCB 126 in common tern eggs showed that all three different dosage levels given from 44 to 434 ng/g caused significant mortality (27–53%) after a week of treatment. The median lethal dose (LD_{50}) for PCB 126 in common tern eggs, based on hatching success of said study, is approximately 104 ng/g (Hoffman et al. 1998). Deformities in bills (crosses and shortened) increased with higher doses (Hoffman et al. 1998). PCBs 126 and −77 were not detected in common terns from Rockabill colony. PCB 105, however, was detected in all matrices, but at low levels (0.08–2.00 ng/g ww). The lowest observed adverse effects level (LOAEL) in common terns affected reproduction

and is reported to be 8 mg/kg (= 8000 ng/g) (Bosveld and Van den Berg 1994; Su et al. 2014).

Total PAH concentrations were threefold higher in feathers (30.01 ng/g ww) when compared to preen oil (10.52 ng/g ww), while mean concentrations in preen gland (46.65 ng/g ww) were nearly twice as high than in liver (27.64 ng/g ww). The contribution profile of congeners differs highly between preen oil and feathers, but it shows two of the same congeners for liver and preen gland. In general, PAH levels were comparable to values found in livers of Bulwer's petrels (*Bulweria bulwerii*) in the Atlantic Ocean (range 17.2–66.2 ng/g) (Roscales et al. 2011). It has been reported that PAH levels in the tissues of birds far from industrialised areas and non-contaminated sites tend to be low (Hall and Coon 1988). Additional studies have also found higher levels of PAH in tissues of birds that feed on lower trophic prey, such as invertebrates, rather than higher trophic prey, such as pelagic fish (Broman et al. 1990; Custer et al. 2001), which is the main common tern prey (Cabot and Nisbet 2013). This is possibly due to the fact that PAH tend to accumulate mostly in sediments and have been shown to have low bio-magnification properties (MacRae and Hall 1998; Nfon et al. 2008; Perugini et al. 2007; Wan et al. 2007).

Total OCP mean concentrations were fourfold higher in feathers (13.36 ng/g ww) than in preen oil (3.69 ng/g ww). Mean concentrations in liver (15.15 ng/g ww) and preen gland (13.48 ng/g ww) were similar. Heptachlor highly contributed to the burden in preen oil and feathers, whilst for liver and preen gland, dieldrin and DDE isomers were the common contributors. HCB was present in all matrices. Mean concentrations did not exceed the EcoQO of 2 ng/g for eggs, with mean values between 0.07 ng/g preen gland and 1.46 ng/g liver. ∑DDT was below the EcoQO (10 ng/g) for eggs in all matrices, with the highest mean in liver (6.55 ng/g). ∑HCH was above the EcoQO (2 ng/g) for eggs in all matrices, but preen oil, with the lowest mean at 2.54 ng/g in liver and the highest at 3.11 ng/g in preen gland. PCBs, DDT and DDE were previously associated with abnormalities in chicks. Hays and Risebrough (1972) recorded various deformities in bill, eye and foot in common and roseate terns unhatched and chicks up to a few days old. Premature feather losses (PFL) were also recorded in young chicks, sometimes preventing them from fledging. These abnormalities were similar to the chick edema disease in poultry, associated with the toxic compound chlorinated dibenzo-*p*-dioxin, a substance that has been reported to contaminate commercial PCB mixtures (Barron et al. 1995). Sublethal effects in adult birds include reduced parental attentiveness and abnormal reproductive behaviour (Barron et al. 1995).

Total BFR mean concentrations were similar between matrices for both preen oil (1.86 ng/g ww) and feathers (1.98 ng/g ww), and liver (5.07 ng/g ww) and preen gland (4.37 ng/g ww). Feathers and liver appear to have a higher contribution from high molecular weight congeners, whilst preen oil and preen gland appear to have lower molecular weight congeners. Common tern carcasses in the north Atlantic have reported a much higher ∑BFR concentration (121 ± 25 ng/g lipid weight) (Jenssen et al. 2007) compared to values from this study in liver and preen gland. The same is true for the Arctic tern (*S. paradisaea*) (95.4 ± 36 and 40.9 ± 8.4 ng/g lipid weight) (Jenssen et al. 2007). BFRs from our study were just above the level of quantification (LOQ). BFRs are applied in industry to combustible materials to meet safety regulations (Jenssen et al. 2007). Such additives can leach out of products in certain conditions and have become of environmental importance due to their persistent and toxic nature. In experimental conditions, BFRs have been shown to leach out of plastic products 20–50 times more in stomach and fish oil than in seawater (Tanaka et al. 2015). Due to the ubiquity of plastic pollution at sea, BFR dispersal and bioaccumulation has become of greater concern (Derraik 2002).

In general, feathers have demonstrated more similar concentrations to internal organs than did preen oil. That could be explained by the fact that feathers tend to carry a higher burden due to the various sources of contaminant input: the blood stream when feathers are grown, external contamination (although that has been claimed to be irrelevant by Jaspers et al. 2008) and additionally, preen oil, due to the constant act of preening of the feathers. In the case of common terns, they undergo a post-breeding moult (Ginn and Melville 1983), which means that in the case of these samples, collected during the breeding season, birds would still be carrying contaminants acquired during winter and southern migration. Preen oil on the other hand is constantly produced and is more likely to reflect local contamination (Jacob and Ziswiler 1982), like eggs in the case of income breeders (Arnold et al. 2004; Janke et al. 2015).

Pollutant concentrations in seabirds depend on a variety of factors. Moulting influences the uptake of contaminants onto feathers by the blood stream (Jaspers et al. 2006; Van den Steen et al. 2007). Migration can alter contaminant burden in two ways: by exposing the birds to more or less contaminated areas and by the mobilisation of lipids to cope with energy expenditure. Such mobilisation affects contaminant load in starving birds in the same way (Barron et al. 1995; Jaspers et al. 2008). Breeding affects the burden of female birds, which are known to pass from 4 to 45% (45% in Arctic terns) of their burden to their eggs (Lemmetyinen et al. 1982; Tanabe et al. 1984), contaminating unborn chicks. Variation in contaminant load and different congener profiles can be attributed to species specific metabolism and elimination and congener-specific toxicokinetics (Barron et al. 1995; Brunström et al. 1990; Hoffman et al. 1998; Hoffman et al. 1996; Smith et al. 1990).

Results from the PCA analysis between dead and live common terns revealed that the utility of organs (e.g. dead birds) for POP monitoring might bring biased results due to great variation among individuals. If death is accidental, birds might have recently experienced starvation, migration, moulting or

even intoxication. These unknown factors result in great individual variation.

POPs in common terns in Ireland are not at toxicological levels to cause embryonic deformities, or reproductive failure. However, some levels are higher than recommended by European policy, such as OSPAR's EcoQO in eggs (OSPAR 2010). In reality, effects of certain compounds are difficult to properly quantify as biota and environmental media is pre-contaminated with various pollutants, thus it is recommended to keep periodic monitoring of concentrations and potential effects.

Acknowledgments This work was supported by Science Without Borders (CAPES, Brazil, BEX: 1269-13-5). Many thanks to all at BirdWatch Ireland. Thanks to Steve Newton. Special thanks to Rockabill wardens Brian Burke and Andrew Power. Thanks to Niall Keogh for assistance in the field. Thanks to Danilo Hirota, Killian Coakley and Bill Delee for assistance in the lab. Thanks to anonymous reviewers for improving the quality of this manuscript.

References

Arnold JM, Hatch JJ, Nisbet ICT (2004) Seasonal declines in reproductive success of the common tern *Sterna hirundo*: timing or parental quality? J Avian Biol 35(1):33–45

Austin OL (1953) The migration of the common tern (*Sterna hirundo*) in the western hemisphere. Bird-Banding:39–55

Barron MG, Galbraith H, Beltman D (1995) Comparative reproductive and developmental toxicology of PCBs in birds. Comp Biochem Physiol C: Pharmacol Toxicol Endocrinol 112(1):1–14

Becker PH, Schuhmann S, Koepff C (1993) Hatching failure in common terns (*Sterna hirundo*) in relation to environmental chemicals. Environ Pollut 79:207–213

Bosveld ATC, Van den Berg M (1994) Effects of polychlorinated biphenyls, dibenzo-p-dioxins, and dibenzofurans on fish-eating birds. Environ Rev 2(2):147–166

Bosveld ATC, Gradener J, Murk AJ, Brouwer A, Van Kampen M, Evers EHG, Van den Berg M (1995) Effects of PCBs, PCDDs and PCDFs in common tern (*Sterna hirundo*) breeding in estuarine and coastal colonies in the Netherlands and Belgium. Environ Toxicol Chem 14(1):99–115

Broman D, Näuf C, Lundbergh I, Zebühr Y (1990) An in situ study on the distribution, biotransformation and flux of polycyclic aromatic hydrocarbons (pahs) in an aquatic food chain (seston-Mytilus edulis L.-Somateria mollissima L.) from the baltic: an ecotoxicological perspective. Environ Toxicol Chem 9(4):429–442

Brunström B, Andersson L, Nikolaidis E, Dencker L (1990) Non-ortho- and mono-ortho-chlorine-substituted polychlorinated biphenyls—embryotoxicity and inhibition of lymphoid development. Chemosphere 20(7–9):1125–1128

Burke B, Kinchin-Smith D, Somers S, Newton S (2016) Rockabill Tern Report 2016. BirdWatch Ireland Seabird Conservation Report. BirdWatch Ireland Seabird Conservation Report

Cabot D, Nisbet I (2013) Terns. In: Corbet SA, West R, Streeter D, Silvertown J (eds) Journal of Field Ornithology (Vol. 85). HarperCollins Publishers, London

Custer TW, Custer CM, Dickerson K, Allen K, Melancon MJ, Schmidt LJ (2001) Polycyclic aromatic hydrocarbons, aliphatic hydrocarbons, trace elements, and monooxygenase activity in birds nesting on the North Platte River, Casper, Wyoming, USA. Environ Toxicol Chem 20(3):624–631

Derraik JGB (2002) The pollution of the marine environment by plastic debris: a review. Mar Pollut Bull 44(9):842–852. doi:10.1016/S0025-326X(02)00220-5

Dittmann T, Becker PH, Bakker J, Bignert A, Nyberg E, Pereira MG et al (2012) Large-scale spatial pollution patterns around the North Sea indicated by coastal bird eggs within an EcoQO programme. Environ Sci Pollut Res 19(9):4060–4072

Elliott JE, Butler RW, Norstrom RJ, Whitehead PE (1989) Environmental contaminants and reproductive success of great blue herons *Ardea herodias* in British Columbia, 1986–1987. Environ Pollut 59(2):91–114

Elliott J, Wilson LK, Wakeford B (2005) Polybrominated diphenyl ether trends in eggs of marine and freshwater birds from British Columbia, Canada, 1979–2002. Environmental Science & Technology 39(15):5584–5591

Falkowska L, Reindl AR, Grajewska A, Lewandowska AU (2016) Organochlorine contaminants in the muscle, liver and brain of seabirds (Larus) from the coastal area of the southern Baltic. Ecotoxicol Environ Saf 133:63–72. doi:10.1016/j.ecoenv.2016.06.042

Fox GA (1976) Eggshell quality: its ecological and physiological significance in a DDE-contaminated common tern population. The Wilson Bulletin 88(3):459–477

Giesy JP, Ludwig JP, Tillitt DE (1994) Dioxins, dibenzofurans, PCBs and colonial, fish-eating water birds. In: Schecter A (ed) Dioxins and health. Springer US, Boston, pp 249–307. doi:10.1007/978-1-4899-1462-0_9

Gilbertson M, Fox GA (1977) Pollutant-associated embryonic mortality of Great Lakes herring gulls. Environmental Pollution (1970) 12(3):211–216

Gilbertson MMRD, Morris RD, Hunter RA (1976) Abnormal chicks and PCB residue levels in eggs of colonial birds on the lower Great Lakes (1971-73). Auk 93(3):434–442

Ginn HB, Melville DS (1983) Moult in birds: BTO guide. British Trust for Ornithology

Hall RJ, Coon NC (1988) Interpreting residues of petroleum hydrocarbons in wildlife tissues. US Fish and Wildlife Service

Hays H, Risebrough RW (1972) Pollutant concentrations in abnormal young terns from Long Island sound. Auk 89(1):19–35

Hoffman DJ, Smith GJ, Rattner BA (1993) Biomarkers of contaminant exposure in common terns and black-crowned night herons in the Great Lakes. Environ Toxicol Chem 12(6):1095–1103. doi:10.1002/etc.5620120615

Hoffman DJ, Rice CP, Kubiak TJ (1996) PCBs and dioxins in birds. Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations, 165–207

Hoffman DJ, Melancon MJ, Klein PN, Eisemann JD, Spann JW (1998) Comparative developmental toxicity of planar polychlorinated biphenyl congeners in chickens, american krestels, and common terns. Environ Toxicol Chem 17(4):747–757

Jacob J, Ziswiler V (1982) The uropygial gland. Avian Biology 6:199–324

Janke AK, Anteau MJ, Markl N, Stafford JD (2015) Is income breeding an appropriate construct for waterfowl? J Ornithol 156(3):755–762. doi:10.1007/s10336-015-1200-y

Jaspers VLB, Oorspoels S, Covaci A, Eens M (2006) Can predatory bird feathers be used as a non-destructive biomonitoring tool of organic pollutants? Biol Lett 2(2):283–285. doi:10.1098/rsbl.2006.0450

Jaspers VLB, Voorspoels S, Covaci A, Lepoint G, Eens M (2007) Evaluation of the usefulness of bird feathers as a non-destructive biomonitoring tool for organic pollutants: a comparative and meta-analytical approach. Environ Int 33(3):328–337. doi:10.1016/j.envint.2006.11.011

Jaspers VLB, Covaci A, Deleu P, Neels H, Eens M (2008) Preen oil as the main source of external contamination with organic pollutants onto

feathers of the common magpie (*Pica pica*). Environ Int 34(6):741–748. doi:10.1016/j.envint.2007.12.002

Jaspers VLB, Rodriguez FS, Boertmann D, Sonne C, Dietz R, Rasmussen LM et al (2011) Body feathers as a potential new biomonitoring tool in raptors: a study on organohalogenated contaminants in different feather types and preen oil of West Greenland white-tailed eagles (*Haliaeetus albicilla*). Environ Int 37(8):1349–1356

Jenssen BM, Sørmo EG, Bæk K, Bytingsvik J, Gaustad H, Ruus A, Skaare JU (2007) Brominated flame retardants in north-East Atlantic marine ecosystems. Environ Health Perspect 115(SUPPL1):35–41. doi:10.1289/ehp.9355

Jones KC, de Voogt P (1999) Persistent organic pollutants (POPs): state of the science. Environ Pollut 100(1–3):209–221. doi:10.1016/S0269-7491(99)00098-6

Koeman JH, Oskamp AAG, Veen J, Brouwer E, Rooth J, Zwart P et al (1967) Insecticides as a factor in the mortality of the sandwich tern (*Sterna sandvicensis*). Meded Rijksfac Landbouwwetenschappen Gent 32:841

Kubiak TJ, Harris HJ, Smith LM, Schwartz TR, Stalling DL, Trick JA et al (1989) Microcontaminants and reproductive impairment of the Forster's tern on Green Bay, Lake Michigan-1983. Arch Environ Contam Toxicol 18(5):706–727. doi:10.1007/BF01225009

Lemmetyinen R, Rantamäki P, Karlin A (1982) Levels of DDT and PCB's in different stages of life cycle of the Arctic tern *Sterna paradisaea* and the herring gull *Larus argentatus*. Chemosphere 11(10):1059–1068

MacRae JD, Hall KJ (1998) Biodegradation of polycyclic aromatic hydrocarbons (PAH) in marine sediment under denitrifying conditions. Water Sci Technol 38(11):177–185

Massias A, Becker PH (1990) Nutritive value of food and growth in common tern *Sterna hirundo* chicks. Ornis Scand:187–194

Mitchell PI, Newton SF, Ratcliffe N, Eds TED, Dunn TE, Poyser AD, May L (2004) Seabird populations of Britain and Ireland: results of the Seabird 2000 census. JNCC, Poyser, London., (August)

Moore NW, Tatton J (1965) Organochlorine insecticide residues in the eggs of sea birds

Mora MA, Durgin B, Hudson LB, Jones E (2016) Temporal and latitudinal trends of p,p'-DDE in eggs and carcass of North American birds from 1980-2005. Environ Toxicol Chem 35(6):1340–1348. doi:10.1002/etc.3360

Nfon E, Cousins IT, Broman D (2008) Biomagnification of organic pollutants in benthic and pelagic marine food chains from the Baltic Sea. Sci Total Environ 397(1):190–204

OSPAR (2010) The Ospar system of ecological quality objectives for the North sea, 16

Pariatamby A, Kee YL (2016) Persistent organic pollutants management and remediation. Procedia Environmental Sciences 31:842–848. doi:10.1016/j.proenv.2016.02.093

Peck LE, Gilchrist HG, Mallory CD, Braune BM, Mallory ML (2016) Persistent organic pollutant and mercury concentrations in eggs of ground-nesting marine birds in the Canadian high Arctic. Sci Total Environ 556(March):80–88. doi:10.1016/j.scitotenv.2016.02.205

Perugini M, Visciano P, Giammarino A, Manera M, Di Nardo W, Amorena M (2007) Polycyclic aromatic hydrocarbons in marine organisms from the Adriatic Sea, Italy. Chemosphere 66(10):1904–1910

R Core Team. (2015) A language and environment for statistical computing. Vienna: R Foundation for Statistical Computing. Retrieved from https://www.r-project.org

Roscales JL, Gonzalez-Solis J, Calabuig P, Jimenez B (2011) Interspecies and spatial trends in polycyclic aromatic hydrocarbons (PAHs) in Atlantic and Mediterranean pelagic seabirds. Environ Pollut 159(10):2899–2905. doi:10.1016/j.envpol.2011.04.034

Scharenberg W (1991) Prefledging terns (*Sterna paradisaea*, *Sterna hirundo*) as bioindicators for organochlorine residues in the German Wadden Sea. Arch Environ Contam Toxicol 21(1):102–105

Smith LM, Schwartz TR, Feltz K, Kubiak TJ (1990) Determination and occurrence of AHH-active polychlorinated biphenyls, 2, 3, 7, 8-tetrachloro-p-dioxin and 2, 3, 7, 8-tetrachlorodibenzofuran in Lake Michigan sediment and biota. The question of their relative toxicological significance. Chemosphere 21(9):1063–1085

Stockholm Convention, 2001 (2001) Stockholm Convention on Persistent Organic Pollutants (p. http://chm.pops.int/)

Su H, Wu F, Zhang R, Zhao X, Mu Y, Feng C, Giesy JP (2014) Toxicity reference values for protecting aquatic birds in China from the effects of polychlorinated biphenyls. In Reviews of Environmental Contamination and Toxicology volume (pp. 59–82). Springer

Tanabe S, Tanaka H, Tatsukawa R (1984) Polychlorobiphenyls, $Σ$DDT, and hexachlorocyclohexane isomers in the western North Pacific ecosystem. Arch Environ Contam Toxicol 13(6):731–738. doi:10.1007/BF01055937

Tanaka K, Takada H, Yamashita R, Mizukawa K, Fukuwaka M, Watanuki Y (2015) Facilitated leaching of additive-derived PBDEs from plastic by seabirds' stomach oil and accumulation in tissues. Environmental Science & Technology . doi:10.1021/acs.est.5b01376150901174241000

United Nations Environment Programme. Division of Early Warning, and Assessment. UNEP Year Book 2011: Emerging Issues in Our Global Environment. UNEP/Earthprint, 2011

Van Den Brink NW (1997) Directed transport of volatile organochlorine pollutants to polar regions: the effect of the contamination pattern of Antarctic seabirds. Sci Total Environ 198(1):43–50. doi:10.1016/S0048-9697(97)05440-5

Van Den Brink NW, Bosveld ATC (2001) PCB concentrations and metabolism patterns in common terns (*Sterna hirundo*) from different breeding colonies in The Netherlands. Mar Pollut Bull 42(4):280–285. doi:10.1016/S0025-326X(00)00151-X

Van den Steen E, Covaci A, Jaspers VLB, Dauwe T, Voorspoels S, Eens M, Pinxten R (2007) Experimental evaluation of the usefulness of feathers as a non-destructive biomonitor for polychlorinated biphenyls (PCBs) using silastic implants as a novel method of exposure. Environ Int 33(2):257–264

Van Franeker JA (2004) Save the North Sea fulmar-Litter-EcoQO manual part 1: collection and dissection procedures., 38. Retrieved from http://edepot.wur.nl/40451

Wan Y, Jin X, Hu J, Jin F (2007) Trophic dilution of polycyclic aromatic hydrocarbons (PAHs) in a marine food web from Bohai Bay, North China. Environmental Science & Technology 41(9):3109–3114

Wang J, Caccamise SAL, Woodward LA, Li QX (2015) Polychlorinated biphenyls in the plasma and preen oil of black-footed albatross (*Diomedea nigripes*) chicks and adults on midway atoll, North Pacific Ocean. PLoS One 10(4):e0123041. doi:10.1371/journal.pone.0123041

Yamashita R, Takada H, Murakami M, Fukuwaka MA, Watanuki Y (2007) Evaluation of noninvasive approach for monitoring PCB pollution of seabirds using preen gland oil. Environ Sci Technol 41(14):4901–4906. doi:10.1021/es0701863