A Multi-Scale Analysis of Organochlorine Pesticide Contamination in Raptor Populations: Research Effort, Historical Trends, and Current Concentrations

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DECLARATIONS

This thesis reports original research that I conducted while enrolled as a PhD student at the FitzPatrick Institute of African Ornithology, Department of Biological Sciences, Faculty of Science, University of Cape Town, South Africa. All assistance received has been fully acknowledged. This work has not been submitted in any form for a degree at another university.

I know the meaning of plagiarism and hereby declare that all the work in this thesis except for those properly acknowledged are authentic research work carried out by me. I have followed all the guidelines for preparing a thesis and now presenting it for examination for the award of Doctor of Philosophy.

Kailen Padayachee

December 2024

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TABLE OF CONTENTS

ABBREVIATIONS – Throughout this thesis I use technical language related to ecotoxicology and chemical analyses, therefore, this section serves to provide a comprehensive list of shortened forms and acronyms used in the document, facilitating clarity and understanding for readers unfamiliar with such specialized terminology.

CFC – chlorofluorocarbon

dm - dry mass

DDD – congener of dichlorodiphenyldichloroethane

DDE – congener of dichlorodiphenyldichloroethylene

DDT - congener of dichlorodiphenyltrichloroethane

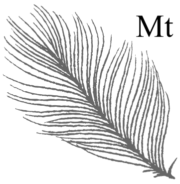
DDT – total DDT which is the sum concentration of all DDT metabolites and isomers

IRS – internal residual spraying

kt – metric kilotonnes

lw - lipid weight

Mt - metric megatonnes



ng/g - nanograms per gram

o,p’DDD - ortho para dichlorodiphenyldichloroethane isomer

o,p’DDE - ortho para dichlorodiphenyldichloroethylene isomer

o,p’DDT - ortho para dichlorodiphenyltrichloroethane isomer

OCP – organochlorine pesticide

PBDE - polybrominated diphenyl ether

PCB - polychlorinated biphenyl

POP – persistent organic pollutant

p,p’-DDD - para para dichlorodiphenyldichloroethane isomer

p,p’-DDE - para para dichlorodiphenyldichloroethylene isomer

p,p’-DDT - para para dichlorodiphenyltrichloroethane isomer

ppm - parts per million

µg/L – micrograms per litre

µg/g– micrograms per gram

UNEP – United Nations Environmental Program

wm - wet mass

WHO - World Health Organisation

THESIS SUMMARY

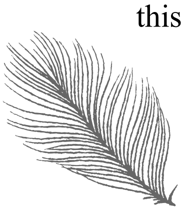
Pesticide contamination and the associated impacts on biodiversity, have been the focus of extensive research and substantial concern for environmental and conservation scientists over many decades. The environmental consequences of organochlorine pesticides, particularly dichlorodiphenyltrichloroethane (DDT), was made famous by Rachel Carson's book, *Silent Spring* in the early 1960s. Their impacts on environmental and human health were subsequently widely recognised and led to their bans and/or restricted use. DDT and dieldrin are two of the most historically significant pesticide compounds ever manufactured, being included on a list of organochlorine pesticides (OCP) of global concern by the Stockholm Convention on Persistent Organic Pollutants (POPs). Their effectiveness in controlling pest species has come with a substantial negative impact on the global environment. These OCPs have consequently been strictly controlled and managed globally by various legislation, treaties, and conventions, some of which have been in place for many decades. These bans and restrictions have led to a decline in the production and use of DDT and dieldrin throughout most parts of the world. However, despite their bans, or in the case of DDT, strict restrictions on use, have their concentrations fallen or are they still present in the environment at elevated concentrations because of their persistent nature?

The biomagnification of DDT and dieldrin in the environment, at higher trophic levels is well documented in the literature. These pesticides are ingested by potential prey species at lower trophic levels, which consume contaminated vegetation, water, or invertebrates. These prey species are subsequently consumed by species at higher trophic guilds and apex predators. The concentrations of these pesticides consequently increase in tissues of organisms at successively higher levels of the food web. This process of bioaccumulation and biomagnification means that species at higher trophic levels, like raptors, can act as valuable indicators of environmental pollutants. Raptors are a typical example of apex predators, occupying top levels of the food web in various ecosystems globally. Due to the well-known negative impacts of these pesticides on global raptor populations, this group of predatory birds have played an important role as indicator species in the monitoring of DDT and dieldrin contamination in both aquatic and terrestrial ecosystems. Consequently, raptors may be an optimal candidate to undertake a comprehensive global-scale assessment to evaluate the extent of DDT and dieldrin monitoring and to assess whether the implementation of worldwide bans and restrictions on use has led to a decline in these pesticide concentrations.

Chapter 1 of this thesis introduces pesticides and the role they played in the success of agricultural development over centuries. We discuss the various natural, non-toxic pest deterrents developed throughout history and how these deterrents gradually advanced into more powerful, synthetic pesticides such as DDT and dieldrin. We demonstrate that while these chemicals did offer a benefit to humankind, evidence began to surface demonstrating the more harmful effects of these chemicals on both environmental and human health. We outline the history of these chemicals and delve into how these pesticides were used in different contexts. Chapter 1 concludes by demonstrating how, over time, raptors became an effective group of indicator species for monitoring these pesticides in various ecosystems.

In Chapter 2, We explore DDT and dieldrin monitoring in raptors globally over time and space. Through reviewing the extensive number of published studies assessing DDT and dieldrin in raptors, we describe the patterns in global research efforts focused on the evaluation of these pesticides in raptors. This monitoring spans from the widespread use of these pesticides in the 1950s to the period following the implementation of worldwide restrictions. We then contrast these patterns of monitoring between regions, species, and time, describing how the biases uncovered in this thesis are another example of the contrast in scientific knowledge production between the Global North and Global South. In this thesis, the Global North and Global South refer to developed and developing or least developed countries respectively (UNCTAD, 2022).

In Chapter 3, we assess the efficacy of local legislation and international agreements to manage environmental contamination by DDT. We once again used the abundance of published literature to describe the spatial and temporal patterns in DDTs in raptors across the globe, specifically looking at the modelled DDT-complex slope, which includes all DDT congeners (DDT; DDD; DDE) and isomers (*p,p'*-DDT; *p,p'*-DDE; *p,p'*-DDD; *o,p'*-DDT; *o,p'*-DDE; *o,p'*-DDD) in the most commonly sampled tissues following global bans and restrictions in DDT use. We not only describe how these pesticides have changed over time but also how these changes differ amongst environments. We demonstrate a clear decline in DDT in the Global North, while demonstrating how the lack of monitoring in the Global South has led to insufficient data to assess whether declines are globally representative. We also found that rates of decline depend on multiple variables such as precipitation and dietary guild as well as historical usage patterns. The declines in the Global North, provide evidence that legislation and mitigation efforts, in concert with increased monitoring in the Global South, may benefit this region. Thus, the key finding from this chapter, is the welcome demonstration that



international conventions, when implemented correctly can have the desired effect. The Montreal Protocol is an example that helped reduce the depletion of the ozone layer, curbing harmful solar ultraviolet radiation by banning chemicals such as CFCs (chlorofluorocarbons). This study provides support that more recent international agreements, such as the Minamata Convention on Mercury, can achieve similar results in reducing the widespread use of mercury, which has seen similar Global North-South differences in use and restrictions (Canham et al., 2021). Furthermore, these success stories suggest that other global crises such as climate change and biodiversity loss can benefit from well planned and implemented global agreements.

Given the reduced concern about these contaminants, especially in the Global North, and limited data from the Global South, Chapter 4 examined contemporary DDT and dieldrin concentrations in a single raptor species. Various tissues were sampled from multiple migratory Amur Falcons (*Falco amurensis*), collected during a mass mortality event at two roost sites in the KwaZulu-Natal Province of South Africa. This chapter actively addresses some of the knowledge gaps identified in Chapter 2 (namely the lack of data on DDT and dieldrin trends from the Global South). The concentrations of ΣDDT detected in these falcons were generally low, echoing the downward trend in Global North DDT contamination described in Chapter 3. However, two fat samples exhibiting the highest ΣDDT concentrations in raptors in the last decade suggest cause for caution in the face of limited Global South data. This work also directly contributes to the limited toxicological data available for Amur Falcons in particular, representing the first samples of DDT and dieldrin concentrations in this species to my knowledge. While this study found low DDT concentrations in these migratory raptors, the dieldrin concentrations were indicative of a potential worrying, recent exposure to a pesticide that has been completely banned globally since the late 1980s.

Chapter 5 of this thesis ties together all the chapters and synthesises the key findings from each of them. It provides a global perspective on the decline in DDT and dieldrin in raptors, taking into consideration the considerable sample bias in research on this topic towards the Global North. It also highlights the efficacy of international agreements and local legislation and implementation in addressing and curbing global issues such as OCP contamination of the environment. This final chapter also discusses that, while contemporary DDT concentrations generally echo historical measurements, they may not necessarily confirm a global decline in this pesticide. We conclude this chapter by exploring potential future research opportunities that have emerged as a result of this thesis.

This thesis provides the first global-scale review of how DDT and dieldrin has been studied and assessed in raptors, providing direct evidence that DDT in the Global North is declining. This suggests that legislation in this region has been largely successful in mitigating environmental contamination by this pesticide. However, insufficient data from the Global South post the 2006 DDT reintroduction affirms the bias in monitoring and research to the Global North. Furthermore, it highlights an urgency to generate sufficient data from countries still using DDT in order to assess whether the decline in DDT can be regarded as globally representative. It is tempting to suggest that low contemporary concentrations of DDT in a raptor wintering in a country with restricted DDT use supports the notion that DDT may also be declining in the Global South. However, the record high concentrations in fat from two individuals may indicate the contrary, that declines in the Global North do not necessarily translate to declines in the Global South. The dieldrin concentrations found in Amur Falcons in South Africa, also raises concern that there may be illegal and illicit use of a banned pesticide in South Africa. This result necessitates an urgent need to monitor dieldrin in KwaZulu-Natal, South Africa. By combining my findings across the chapters, we provide robust evidence that local findings further indicate an urgent need to improve monitoring of DDT and dieldrin in the Global South in order to determine whether declines in these pesticides from the Global North can be considered globally representative.

Chapter 1

Introduction

A 1947 advertisement for the pesticide DDT in Time Magazine. This advert promoted DDT as an ‘amazing insecticide’ and claimed that ‘it is now possible for everyone to enjoy the comfort, health, and safety through the insect killing powers of DDT’. These types of adverts promoted using DDT in all facets of life, whether on crops or in homes to protect against a variety of insect pests. This kind of advertising exposed millions of people to DDT since the end of World War II. Credit: Collectors Weekly

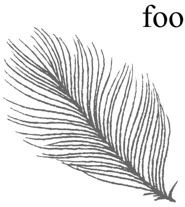
THE HISTORY OF PESTICIDES

A pest can be described as a living organism that has some degree of negative impact on human life and/or activity (Kaushik and Kaushik, 2007). These negative impacts include catastrophic crop losses and historical disease outbreaks, which have in the past, led to both incredible loss of life and economic devastation for entire countries (Matthews, 2018; Howard, 1931). For example, in 1866, Algeria experienced a historical famine believed to have been caused by locusts, which resulted in the death of approximately 5% of the country's population (Howard, 1931). In addition, one of history's most disastrous pandemics, the bubonic plague or *Black Death*, was spread to humans through the bite of infected rat fleas (Glatter and Finkelman, 2021). The plague was responsible for decimating an estimated 30-60% of the population in Europe, within a brief span of five years from 1347 and 1352 (Matthews, 2018; Zahler, 2009).

Throughout history, humanity has been engaged in a continuous struggle against various pest species. Whether these organisms threaten food security or are vectors of devastating diseases, we have searched for and implemented a variety of ever more imaginative ways to control their numbers and impact. The first recorded pesticide use was by the Sumerians, around 2500 B.C., where they used sulphur to control pest invertebrates (Dent and Binks, 2020; Pedigo et al., 2021). Similarly, before biblical times, civilisations such as the Chinese and Egyptians were making use of various botanical insecticides to control invertebrate pests to protect their crops (Dent and Binks, 2020; Pedigo et al., 2021). In 79 A.D., Pilny suggested that arsenic be used as an effective "insect-killer", while even Homer described using sulphur as a helpful deterrent of both disease and insects in his poem, *The Odyssey* (Bostock and Riley, 1855; Homer, 1961). During the 1700s, more benign remedies for the control of certain pests began to surface. Concoctions of water boiled with common rue (*Ruta graveolens*) or powdered tobacco, mixed with lime and applied to branches and leaves were said to be sufficient to rid plants of several plant pests (Matthews, 2018).

THE RISE AND FALL OF PERSISTENT ORGANIC POLLUTANTS

Prior to the early 20th century, even with an increase in inorganic pesticide compounds such as copper acetoarsenite and lead arsenate (Edwards, 1993), pest control was still dominated by traditional and mechanical methods and often supplemented by organic and inorganic chemicals originating from minerals, animals, and plants (Ujváry, 2002). By the mid 20th century, the human population was beginning to boom, requiring an urgent increase in global food production, which was dubbed the "green revolution" (Khush, 1999; Carvalho, 2017).



Traditional insecticides used up until this point became inadequate for meeting the needs of this intensive farming, with insufficient supplies and often low efficacy (Ujváry, 2002). The increasing human population and the need for food, coupled with improvements in science, particularly in the chemical industry, gave rise to the development of synthetic pesticides (Carvalho, 2017; Ujváry, 2002). The first synthetic pesticides were introduced in the early 1930s, defining this period as the birth of chlorinated hydrocarbon insecticides, a group of chemicals known as persistent organic pollutants (POPs).

Perhaps the most infamous of these POPs were Dichlordiphenyltrichloroethanes (DDT) (Costa, 1987). Although it was first synthesised in 1873, the exceptional insecticidal properties of DDT were only discovered some 70 years later, in 1939, by Swiss chemist, Paul Müller (Blus, 2003; Jarman and Ballschmiter, 2012). The discovery of DDT's insecticidal properties was hailed as one of science's greatest achievements, leading to Müller being awarded a Nobel Prize in physiology in 1945 (Dash et al., 2007). This pesticide was successfully used during World War II to combat malaria and typhus, spread by mosquitoes and body lice respectively (Bishopp, 1945) (Figure 1).

Figure 1: Spraying interior of Italian houses with 10% DDT and kerosene for malaria control. 32nd Field Hospital, Unit B Installation. 02/26/1945. World War 2. Otis Historical Archives National Museum of Health and Medicine.

With the end of World War II in 1945, DDT became widely available to the public as an agricultural pesticide and an effective insecticide to protect against insect-borne diseases (Ruus et al., 2010; Jarman and Ballschmiter, 2012). As a result of DDT's incredible efficacy, it was seen as a miracle chemical, even being applied to bedding and directly to children's skin (Charbonneau-Dahlen et al., 2016; Potter, 2018) (Figure 1). DDT was sprayed over agricultural soil and crops throughout the world starting in the mid-1940s (Ruus et al., 2010; Jarman and Ballschmiter, 2012), with an estimated total of 2.6 Mt (Metric Megatons) being used solely for agriculture between 1950 and the mid 1990s (Li and Macdonald, 2005). The top three countries that used the most DDT for agriculture were the USA (590 kt – Metric Kilotons) between 1947 and 1972, the Former Soviet Union (320 kt) between 1952 and 1971, and China (260 kt) between 1952 and 1983 (Li and Macdonald, 2005; Li and Bidleman, 2003). Today DDT is used primarily for public health, where it is applied to walls and under eves of houses during indoor residual spraying (IRS) operations in the Global South to fight malaria (van den Berg, 2009; Oxborough et al., 2014). The overall use of this pesticide has been drastically reduced from an estimated 6 269 tonnes of DDT (active ingredient) produced globally in 2005, to 1 071 tonnes in 2020 (UNEP, 2023). India remains the largest user of DDT and the only producer of this pesticide since 2008 (UNEP, 2023).

Figure 2: Promotions for bed bug products containing DDT were common and often entertaining. The cartoonist for this 1928 advertisement was Theodore Geisel (Dr Suess). Credit: Standard Oil Company of New Jersey.

Within a few years of its widespread use, scientists began to report potentially hazardous environmental impacts of DDT (US Environmental Protection Agency, 1975). In fact, the first restrictions of DDT were implemented in the USA dairy industry as early as 1948 (American

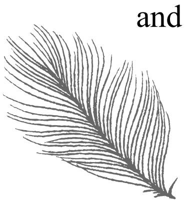
Journal of Public health, 1949). However, it was *Silent Spring*, a book published by Rachel Carson in 1962 that synthesised the irrefutable danger posed by this pesticide (Carson, 1962). This controversial piece of literature sparked incredible public outcry (Carson, 1962; Jarman and Ballschmiter, 2012), which culminated in the complete ban of DDT during the 1970s and 80s in many developed countries such as the USA, UK, and other European countries, (Grier, 1982; Blus, 2003; Jaga and Dharmani, 2003).

In the 1940's, dieldrin another organochlorine pesticide (OCP) was formulated. Ironically its creation and adoption were in part, a response to the growing evidence against DDT (Honeycutt and Shirley, 2014). Similarly, to DDT, dieldrin was used both as an agricultural pesticide as well as a domestic insecticide (Honeycutt and Shirley, 2014). Dieldrin was quite a versatile pesticide, being used in the United Kingdom as a grain and seed treatment to protect cereal grains against pests such as bulb fly (*Delia coarctata*) and in other regions such the USA and Africa as a timber treatment against termites (Brown, 1965; Stanley and Bunyan, 1979; Newton et al., 1992; Hanley, 2002). This pesticide was also applied as a soil treatment to control crop pests and a topical treatment for cattle to control ectoparasites (El Beit et al., 1981). While DDT was applied to fabrics like bed linen to combat bed bugs (Charbonneau-Dahlen et al., 2016; Potter, 2018), dieldrin was also used to treat fabrics such as wool as a moth-proofing agent (Lipson and McPhee, 1958; Honeycutt and Shirley, 2014). While all uses of dieldrin were cancelled in the USA by 1970 due to its extreme toxicity, the US Environmental Protection Agency approved its use against termites in the timber industry until its complete ban in 1987 (Honeycutt and Shirley, 2014). Most European countries, on the other hand, decided to ban dieldrin by 1990 (Jorgenson, 2001).

The continued research and monitoring of these pesticides, and advances in science since the mid 1990s, resulted in a greater understanding of the true threat posed to human and environmental health by these OCPs (Lallas, 2001). These OCPs have been positively linked to a variety of health complications in humans including endocrine dysfunction, immune suppression, and even cancer (Gerber et al., 2016). A review of the global use, risks and benefits of DDT by van den Berg (2009), suggests that exposure to this pesticide in humans may lead to a loss in fertility, miscarriage, and low sperm quality in men. In addition, cancers such as leukaemia and pancreatic cancer have been linked to DDT in parts of the Global North during the peak of its use in the 1960s (van den Berg, 2009). More recent studies suggest that woman exposed to DDT at younger ages may be more susceptible to breast cancer (Cohn et al., 2007). Similarly, dieldrin has also been linked to cancer in humans. Caldwell et al., (1981) found that people in the USA living close to cotton fields treated with dieldrin displayed higher incidences of child-hood colorectal cancer. In addition to its carcinogenic properties, dieldrin has also been classified as an endocrine disruptor (Jorgenson, 2001), appearing to reduce the testicular testosterone production in human foetuses by as much as 50% (Murray et al., 1999).

This improved understanding and awareness of the threats posed by these pesticides, prompted the need to establish an international effort and strategy to address POPs globally (Lallas, 2001). This and the growing evidence of long-range transportation of POPs such as DDT to the Arctic and the contamination of these remote ecosystems (Muir et al., 1988), gave rise to the formation of the Stockholm Convention on Persistent Organic Pollutants, which came into force in 2004 (Stockholm Convention, 2024). The convention formally recognised DDT and dieldrin as two of the twelve initial persistent organic pollutants of particular global concern (Stockholm Convention, 2004). It should be noted, however, that DDT and dieldrin had already been banned and restricted in much of the world by the early 1990s with countries like the USA completely banning DDT and dieldrin 32 and 17 years respectively, prior to the Stockholm Convention coming into force globally (Jaga and Dharmani, 2003; Honeycutt and Shirley, 2014). Once signed into force, the Stockholm Convention formally brought more countries together on the topic of banning and restricting many POPs like DDT and dieldrin, paving the way for further global-scale restrictions and bans on the production and use of these pesticides throughout most parts of the world (Stockholm Convention, 2024). However, in 2006, the World Health Organization supported the reintroduction of DDT specifically and only for the control of malaria in certain tropical countries (van den Berg, 2009; Mansouri et al., 2017). Characterised by their tremendous persistence in the environment, DDT and dieldrin's bioaccumulative properties and ability to be transported long distances via atmospheric and oceanic currents has made these chemicals ubiquitous in the global environment (Chen et al., 2009; Ali et al., 2014; Wild et al., 2022). The persistence of a chemical is dependent on how easily it is eliminated from the environment by either bio- or photodegradation (Hellou et al., 2013). This degradation process is reflected by the chemicals half-life in various environmental matrices (water, soil, air, animal tissue etc.), or how long it takes for concentrations to decrease to one half of its original concentration (Hellou et al., 2013).

Although DDT and dieldrin are persistent organic pollutants, they are still ultimately degraded and eliminated from the environment, although this elimination may be over an extended



period (Kesic et al., 2021). Both correlative and experimental evidence have shown that microbes like bacteria and fungi contribute to the degradation of these pesticides from the soil through metabolic activities (Wurster, 1971; Ghadiri et al., 1995; Aislabie et al., 1997; Foght et al., 2001). This mechanism of elimination of dieldrin has recently gained attention as a promising tool when considering remediation efforts for areas with a history of extensive dieldrin contamination (Pang et al., 2022). Temperature can also play a pivotal role in determining the half-life of DDT and dieldrin, with warmer climates, such as the tropics, leading to higher volatility and shorter half-lives compared to colder, temperate regions (Wurster, 1971; Wania and Mackay, 1993; van den Berg, 2009). In tropical soils, DDT degrades quickly, with half-lives as short as three to seven months, while in colder temperate regions, half-lives can extend up to 15 years or longer (van den Berg, 2009). Besides temperature, soil invertebrates, microbial activity and even whether the soil has been tilled or not can all have an influence on the degradation of DDT in the environment (Harris et al., 2000; Kesic et al., 2021). In the United States, after being applied to various crops, dieldrin was observed to persist in soil over an extended period, with a half-life of nine years (Luckmann and Decker, 1960; Nash and Woolson, 1967). When introduced to soil, DDT and dieldrin strongly bind to organic material and exhibit very weak solubility in water (van den Berg, 2009). Although marginal, runoff from terrestrial habitats containing contaminated organic material can also contribute to the elimination of DDT and dieldrin from terrestrial ecosystems and, simultaneously, increase concentrations in aquatic ecosystems (Arias et al., 2011; Mansouri et al., 2017). Once in the aquatic environment or air, whether through runoff or volatilization, DDT and dieldrin become susceptible to long-range transportation to colder, temperate regions via air and ocean currents. In these regions, these pesticides may accumulate, and experience significantly longer half-lives compared to the tropics (Wania and Mackay, 1993; van den Berg, 2009).

Owing to their high fat solubility, DDT and dieldrin tend to accumulate in the adipose tissue of both humans and wildlife (Geyer et al., 1993; Lee et al., 2017). However, how organisms metabolise these pesticides differs among species, leading to varying rates of accumulation and elimination (Beckvar and Lotufo, 2011). For instance, in humans, DDT has an estimated half-life of over four years, whereas in birds, its elimination can occur as rapidly as 47 days, depending on factors like body mass, body condition, and level of exposure (Furusawa and Morita, 2000; van den Berg, 2009; Espín et al., 2016). In general, dieldrin has an estimated half-life of about one year in vertebrates (World Health Organisation, 1989). A common

elimination pathway for DDT and dieldrin in both sexes is via excreta (Street and Chadwick, 1967; van Velzen et al., 1972; Beckvar and Lotufo, 2011). Additional elimination pathways in female mammals include lactation, as the lipid-rich composition of milk can lead to the accumulation of these lipophilic compounds (Smith, 1999; Sana et al., 2021; Chikuni et al., 1997). Similarly, in female birds, these pesticides can be eliminated through egg laying, where these compounds accumulate in the yolk and shell of the egg (Lamb et al., 1967; Katagi and Fujisawa, 2021). Another potential elimination process in birds is feather moult, where pesticides sequestered in feathers during the growth period are shed when the bird moults, thereby reducing the accumulation of these chemicals in the body (Espín et al., 2016).

THE COMPLEX TRADE-OFF BETWEEN PEST-CONTROL BENEFITS AND ENVIRONMENTAL DEGRADATION

The first records of DDT's negative impact on wildlife were from research on birds in North America and Europe (Hotchkiss and Pough, 1946; Robbins and Stewart, 1949; Blus, et al., 1971). However, there seemed to be a large degree of variation in species sensitivity to DDT (Blus, 2011). Furthermore, when DDT enters the environment, it often degrades to form multiple metabolites, namely dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), which accumulate at varying concentrations in different tissues (Blus, 2011). For this reason, Stickel et al., (1970) developed a weighting system using DDT equivalents to determine lethality of DDT across tissues and determined that while death can occur at concentrations as low 10 DDT equivalents in bird brains, most animals (birds or mammals) die from DDT equivalents above 20 (Stickel et al., 1970; Blus, 2011). Using Mallard Ducks (*Anas platyrhynchos*), Heath et al., (1969) were the first to experimentally prove that DDE, the major metabolite of DDT, caused eggshell thinning in birds and that this thinning was associated with reduced reproductive success. Besides nest failure due to generally poorer quality eggs and eggs with thinner shells breaking during incubation, DDE was found to reduce survival of young, post hatching (Helander et al. 2002; Blus, 2011). Since this early experiment, many more studies both correlative and experimental, have linked DDT, specifically DDE, to reduced reproductive success in birds (Porter and Wiemeyer, 1969; Cooke et al., 1982; Blus and Henny, 1997; Fry, 1995; Grasman et al., 1998; Elliott and Harris, 2001).

Dieldrin on the other hand is a strong neurotoxin linked to severe behavioural impairment, which often leads to direct injury, mortality, and reduced productivity (Walker, 2003; Elliott

and Bishop, 2011). Dieldrin inhibits GABA (Gamma-Aminobutyric Acid) receptors in the vertebrate brain (Walker, 2003; Elliott and Bishop, 2011). GABA receptors act as control switches in the brain, helping to calm and control nerve cell communication, which plays a crucial role in relaxation, anxiety reduction, and maintaining a balanced state of brain activity (Allen et. al., 2023). Lower, sub-lethal concentrations of contamination in experimental birds have resulted in a variety of different behavioural effects including suppression of avoidance behaviour, which could prove detrimental in wild birds, exposing them to predation (Kreitzer and Heinz, 1974; Heinz and Johnson, 1981). Additionally, Elliot and Bishop (2011), discussed the anorexic effect observed in birds contaminated by dieldrin, as concerning particularly for migratory species. A common symptom of acute dieldrin contamination is convulsions, with dead birds often found with clenched feet (Walker, 2003). An experiment conducted by Baxter et al., (1969) where Common Pheasants (*Phasianus cochicus*) were fed dieldrin over a period of weeks demonstrated that this pesticide also has a marked effect of reproductive success, reducing egg production, fertility, and hatchability of eggs, while lowering overall body condition over time. However, it should be noted that in a review by Elliot and Bishop (2011), no suitable evidence was found to support any direct effect of dieldrin on avian reproduction. Laboratory experiments on different bird species suggest that concentrations exceeding 10 µg/g or more in the liver can be considered lethal, where concentrations of between 3 – 9 µg/g would potentially have sub-lethal effects on birds (Walker et al., 1967; Walker, 2003). However, when considering lethality of dieldrin in birds, concentrations in the brain are most important, with concentrations as low as 5.8 µg/g considered lethal in birds (Linder et. al., 1970; Elliot and Bishop, 2011).

While not a pesticide, polychlorinated biphenyls (PCBs) have a similar chemical structure to DDT and were also included in the original 12 persistent organic pollutants (POP) covered by the Stockholm Convention (Friend and Franson, 1999; Stockholm Convention, 2024). Similarly to DDT, PCBs have been linked to reproductive failure in various wildlife species including birds (Gilbertson et al., 1991; Rattner, 2009). Captive American Kestrels (*Falco sparverius*) exhibited abnormalities at various stages of reproduction when exposed to dietary and in-ovo exposure to PCBs (Fernie et al., 2003). In wild raptor populations, such as the Bald Eagles (*Haliaeetus leucocephalus*) of the Great Lakes region of the USA, PCBs have been linked to a syndrome named Great Lakes Embryo Mortality Edema and Deformities Syndrome (GLEMEDS) (Gilbertson et al., 1991; Best et al., 2010). This syndrome in birds is associated with embryonic and chick mortality, growth impairment, oedema and deformities (Gilbertson

et al., 1991). Although PCBs have often been included in assessments of Organochlorine Pollutants (OCPs) in birds of prey, PCBs are categorised as industrial chemicals (Fernie et al., 2003). For the purposes of this thesis the focus will be only on organochlorine pesticides, and therefore will only discuss DDT and dieldrin.

In concert, DDT and dieldrin have been found to have contributed to some of the most catastrophic bird population declines globally with raptors as top predators being amongst the most affected (Newton and Bogan, 1978; Blus, 2003). The impacts of DDT on raptors were first described in Peregrine Falcons (*Falco peregrinus*) from the UK, with studies linking eggshell thinning in this species to this pesticide (Ratcliffe, 1967). The thinner eggshells led to eggs breaking under the weight of the incubating females, which resulted in significant nest failure and historic declines in the United Kingdom of not only Peregrine Falcons but also the Eurasian Sparrowhawk (*Accipiter nisus*) (Ratcliffe, 1967; Newton and Bogan, 1978). Not long after these findings in the UK, researchers from other parts of the world began describing similar trends in other raptor species (Enderson et al., 1982; Olsen et al., 1993; Rejt, 2001; Andreasen et al., 2018). While not associated with eggshell thinning, dieldrin's severe neurotoxicity, even at sublethal concentrations, had a negative impact on raptor survival due to impaired hunting ability and increasing the risk of collisions with infrastructure and vehicles (Newton et al., 1992; Walker, 2003). The effects on eggshell quality, combined with the sublethal neurotoxic impact of dieldrin on raptor nervous systems, converged to cause one of history's most disastrous raptor declines, nearly annihilating species such as Peregrine Falcons from parts of their Global North range or severely reducing the size of their breeding populations (Hickey and Anderson, 1968; Mizera and Sielicki, 2009). In fact, some of these populations are still in the process of recovery (Nygård et al., 2019).

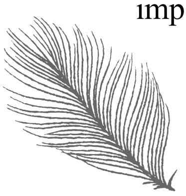
RAPTORS - A VALUABLE GROUP OF INDICATOR SPECIES

Raptors are widespread predatory birds that occupy the top of the food web across diverse ecosystems, occurring on every continent except Antarctica (Willette et al., 2009). These birds of prey are often long lived, occupy both terrestrial and aquatic ecosystems, and feed on a wide variety of prey species across all trophic levels (Willette et al., 2009; Gomez-Ramirez et al., 2014). These characteristics make raptors among the most suitable taxa to use as biomonitors or indicators in ecological research. (National Research Council, 1991; Gómez-Ramírez et al., 2014; Espín et al., 2016). Indicator species act as a type of early-warning tool to help researchers identify potential impacts of contaminants to both the environment and humans

(Gomez-Ramirez et al., 2014). The value placed on raptors as indicator species is supported by the many environmental monitoring programs, particularly in the Global North, established to monitor environmental contamination (Gomez-Ramirez et al., 2014). Examples of such programs include the Predatory Bird Monitoring Scheme in the United Kingdom (Walker et al., 2008), the National Environment Monitoring Programme in Sweden (Helander et al., 2008), and the Bird Monitoring Programme in Finland (Koskimies, 1989). The global ubiquity of raptors and their proven efficacy as indicator species in the Global North, indicates their potential to shed light on pesticide contamination in less studied regions of the Global South. This thesis aims to synthesise the current information on DDT and dieldrin in raptors, to expand our understanding on pesticide contamination in a raptor species from the Global South and ultimately provide a holistic, global understanding of DDT and dieldrin in raptors.

THESIS OUTLINE AND RESEARCH AIMS

With the recognition of the considerable danger posed by DDT and dieldrin to both humans and wildlife, came considerable amounts of research and monitoring of these pesticides in the environment and in wildlife. Globally, there has been a notable absence in effort to consolidate the extensive data on organochlorine pesticide concentrations in wildlife, particularly for raptors, highlighting the rarity of such comprehensive syntheses despite the wealth of available information. We recognised this as a research gap, with the potential to better understand how these pesticides have been monitored and to retrospectively explore how they have declined following the restrictions in their usage. Organochlorine pesticides such as DDT and dieldrin, pose a global challenge with considerable local consequences, as evidenced by the local extirpation of specific raptor species from their historical ranges in the Global North (Ratcliffe, 1958; 1965; 1967). Furthermore, while global policy proscribed the widespread restrictions and bans on DDT and dieldrin, the enforcement of legislation and degree of implementation vary greatly at a local and regional scale. This implementation will inevitably influence the concentrations of these pesticides in the environment, which in turn shapes how we interpret the efficacy of global policies and mitigation efforts such as the Stockholm Convention. Thus, global scale trends do not necessarily represent local scale research efforts and their findings. This is particularly important when comparing the Global North to the Global South as it is well established that most research effort and scientific knowledge is biased toward the former (King, 2004; Reidpath and Allotey, 2019). Therefore, trends in the Global North may not necessarily be fully representative of patterns in the rest of the globe, emphasising the importance of considering regional scale analyses in global scale reviews. The converse may



be equally true, while concentrations of DDT and dieldrin could be increasing in certain areas but would not necessarily reflect the global patterns of these pesticides. My thesis illustrates the way grand challenges manifest at different scales, as discussed by Dittrich (2022). It underscores the significance of evaluating grand challenges on a global as well as local scale, as it equips scientists, academics, and decision-makers with the tools to better comprehend these complex issues and take appropriate actions to tackle them (Dittrich, 2022).

Despite the near universal usage of these pesticides, and the fact that measures to then tackle them were implemented at a global scale, to the best of my knowledge Smith (1999) is the only study that has attempted to describe changes in DDT concentrations over time at a global scale. That study focused on human breast milk and showed declines in concentration following restrictions indicating that global bans of DDT were successful in reducing contamination in humans (Figure 3). While the trends described in Smith (1999) are insightful, they are limited by various factors including the use of a single species (humans), which tend to eat similar things across a limited trophic breadth and a relatively small sample size (only 130 estimates). Within my thesis, we have explored these questions for raptors, including multiple raptor species, which occupy a greater diversity of habitats and feed on a wider variety of prey. Furthermore, we have been able to collate data from more than 250 studies, thereby providing a more nuanced understanding of DDT and dieldrin trends in the environment.

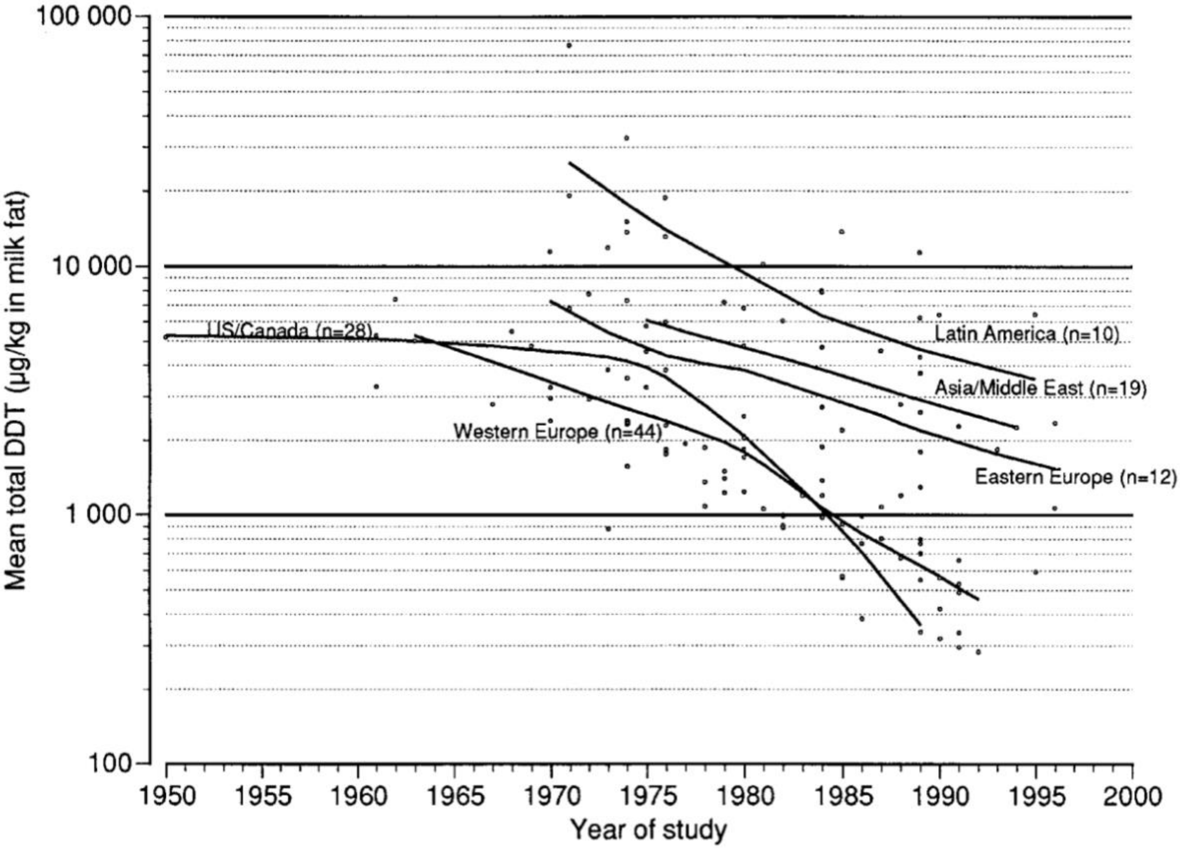


Figure 3: Smith (1999) demonstrated both a spatial and temporal decline in DDT concentrations in human breast milk globally since this pesticide was banned or strictly restricted.

Given that Smith's (1999) study was on humans, it is not clear whether these declining trends would also reflect in more natural systems. Thus, my thesis sought to produce data similar to Smith (1999), but quantifying DDT in global raptor populations to determine whether similar declines in DDT exist in natural systems around the world. Raptors are the most obvious candidate with which to explore these patterns in wildlife, given their widespread distribution and the prevalence of their use in monitoring programs. However, as of yet, there has been no attempt to quantify the changes in DDT and dieldrin concentrations amongst raptors at a global scale, nor to describe the research and monitoring effort awarded to this global environmental issue. Most studies exploring changes in concentrations of DDT and dieldrin in the environment have been at a relatively local scale and have concentrated on species and ecosystems exclusively from the Global North (Olsson and Reutergårdh, 1986; Muir et al., 1999; Helander et al., 2008). These studies tend to suggest that DDT and dieldrin have declined in the environment since they were banned, even before the implementation of the Stockholm Convention (Westöö, 1974; Muir, et al., 1999; Jorgenson, 2001; Helander et al., 2008). For example, Helander et al. (2008) showed that the banning of DDT in Sweden played a pivotal role in the recovery of White-Tailed Sea Eagles (*Haliaeetus albicilla*). By monitoring DDE, the main metabolite of DDT, in eggs of this species between 1965 (around the peak use of DDT in that region) to 2006 (36 years after the ban), Helander et al. (2008) conclusively demonstrated that as DDE concentrations decreased in eggshells of White-Tailed Sea Eagles, populations began to recover (Figure 4).

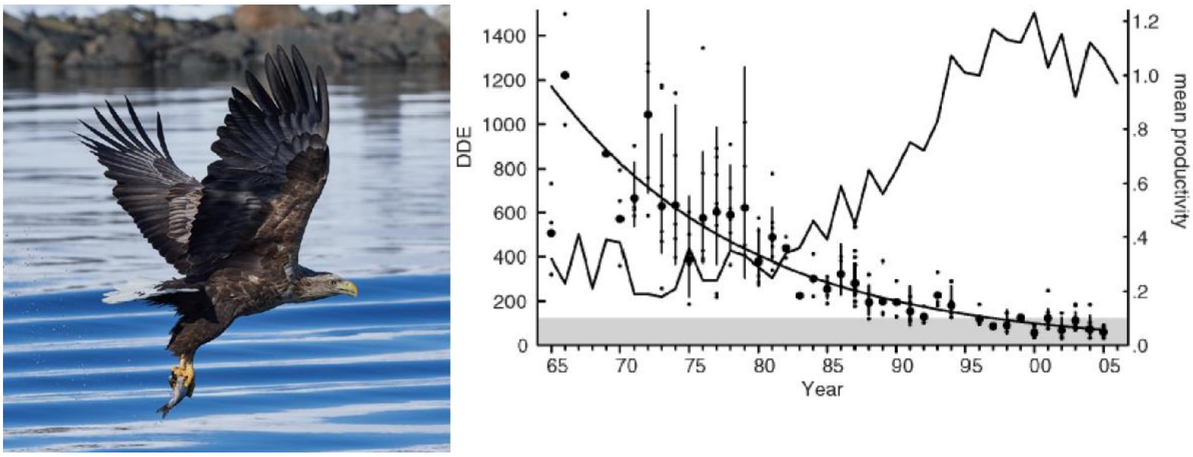


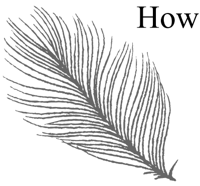
Figure 4: Graph by Helander et. al. (2008) that demonstrates that, as DDE concentrations in eggs of White-Tailed Sea Eagle decreased between 1965 and 2006, there was a corresponding increase in mean productivity of these eagles in this region. White-Tailed Sea eagle (*Haliaeetus albicilla* – Photo by Christoph Müller).

Similar to the patterns observed for DDT, Newton et. al. (1992) showed similar declining patterns for dieldrin in the United Kingdom. They found that due to the use of dieldrin as a seed treatment, raptors specialising in avian prey were most exposed, as the bird prey would feed on contaminated grain during sowing. Dieldrin was used extensively in the United Kingdom from 1956 to 1962 but withdrawn from agricultural use from 1976 and completely banned in 1986 (Newton et. al., 1992; Meijer et al., 2001). Newton et. al. (1992) demonstrated a decline in raptor mortality that coincided with this gradual decline in dieldrin application, with no dieldrin-associated raptor deaths recorded at all after dieldrin was banned in 1986. They have even suggested that banning dieldrin in the United Kingdom possibly played a bigger role in the recovery of raptor populations than the banning of DDT in this region.

Like Smith's (1999) study on human breast milk, these longer-term studies on raptors have all demonstrated a decline in these pesticides. However, while they do focus on natural ecosystems, they tend to concentrate on a limited number of species, which ultimately represent only one or two distinct ecosystems and regions. These raptor studies are also only focused on countries within the Global North where these pesticides have been largely banned for many years. Despite the Global South being considered by some as a hotspot for OCP contamination, there has been less monitoring of these pesticides in this developing region where restricted use is still allowed (UNEP, 2023; Makgoba et al. 2024). DDT and dieldrin contamination have been a pressing global environmental concern for decades and this thesis aims to comprehensively analyse these pesticides in raptors from around the world. Furthermore, we aim to assess how these pesticides have changed over time and across geographical expanses. Specifically, we synthesise measures of these pesticides from the extensive published literature, providing a historical retrospective of monitoring effort on an environmental topic that is pan-global in nature. We primarily wanted to determine where the bulk of available information pertaining to DDT and dieldrin originates from and whether monitoring of these pesticides has been applied equally throughout the world or has been biased toward certain regions, for example where more resources are available to environmental monitoring.

The crux of this thesis lies in evaluating the efficacy of legislative interventions on POPs such as DDT and dieldrin, even before the implementation of the Stockholm Convention, which proscribed the use of DDT and dieldrin throughout most of the world after 2004. On a global scale, we quantify and dissect the spatial and temporal distribution of DDT and dieldrin monitoring in raptors, delving into the disparities in monitoring efforts between the Global North and Global South. Furthermore, we then extract the concentrations of DDT from these literature sources to describe and quantify the change in DDT across time and space, evaluating the efficacy of local and international policy. By gauging the representativeness of monitoring efforts, we sought to unveil any biases that may skew our understanding of the effects and changes in DDT and dieldrin across diverse environments.

The Global North has, over many years, aimed at eradicating DDT and dieldrin from their environments (Grier, 1982; Jaga and Dharmani, 2003). This socio-geographical region has made substantial use of their access to superior resources to conduct extensive research and monitoring and generate substantial amounts of information (King, 2004; Okune et al., 2016; Allik et al., 2020), which has been used to inform the implementation of sweeping bans on these pesticides. This wealth of information, though potentially biased, has played an instrumental role in shaping international policies designed to mitigate the impacts of DDT and dieldrin. In this thesis, we assess the extent of bias within this knowledge base and determine whether the foundations upon which global pesticide policies rest are truly representative of global ecosystems. Most studies from the Global North have presented a narrative of success in relation to policy interventions, with recorded declines in DDT and dieldrin in raptor populations since they were banned in this region (Newton et al., 1992; Helander et al., 2008). However, it is less clear if the situation in the Global South, where pesticide use is restricted



(not banned) and legislative enforcement is often lacking, is different from the more well documented trends in the Global North (Dietz and Adger, 2003). In Addition to my chapters exploring historical monitoring of these pesticides, we undertake a field study to provide a contemporary understanding of DDT and dieldrin concentrations in a migratory raptor species. We analysed these pesticides in a large sample of Amur Falcons (*Falco amurensis*) recently collected in South Africa. By comparing these findings with data from diverse geographic locations and spanning different periods, this thesis contextualizes the influence of international policy on environmental contamination in South Africa, a country still using DDT and grappling with the management of obsolete pesticides like dieldrin (Naidoo and Buckley, 2003).

CHAPTER STRUCTURE

This thesis is compiled as a series of chapters formatted to facilitate publication (Chapters 2 – 4). Therefore, each of these chapters consist of an abstract, introduction, methods, results, and discussion section. Due to this format, some repetition was unavoidable in the introduction, methods, and discussion sections to ensure the readability of each chapter. We have, however, endeavoured to reduce this repetition as far as possible. In each data chapter, I use the term “we” as there are multiple co-authors (Arjun Amar, Chevonne Reynolds and Rafael Mateo).

Chapter 2 has been published (Published: https://doi.org/10.1016/j.scitotenv.2022.159734). I was the principal investigator in all chapters, including the published Chapter 2 and was responsible for all field work, literature review, statistical analysis, writing, and manuscript compilation. For this publication Prof. Arjun Amar and Prof. Chevonne Reynolds provided project supervision and guidance in the research development and statistical analysis, while Prof. Rafael Mateo assisted with the toxicological guidance.

Chapter two reviews the patterns in global monitoring of DDT and dieldrin in raptors across the globe. In this chapter we analysed the number of studies conducted and samples collected across time and space, while identifying which species were most selected for such monitoring projects. This helped us understand whether the species selected accurately represented all global environments inhabited by raptors. In addition, this chapter identifies the most analysed tissues when monitoring DDT and dieldrin in raptors, which, in addition to concentrations reported, were used to guide the analysis in Chapter 3 (where we select the most commonly sampled tissues). The consolidation and synthesis of the global literature conducted in this chapter revealed a considerable geographical bias in DDT and dieldrin monitoring in

raptors towards the Global North, particularly North America and Europe. While this review included 114 species from around the world, samples were dominated by only three species, (Eurasian Sparrowhawk *Accipiter nisus*, Bald Eagle *Haliaeetus leucocephalus*, and Peregrine Falcon *Falco peregrinus*). This species bias further demonstrates the lack of global ecosystem representation in historic monitoring and research.

Chapter three examines changes in DDT in raptors extracted from the consolidated literature sourced in Chapter 2. This pesticide was chosen over dieldrin for analysis, as Chapter 2 revealed that it was more commonly monitored in raptors. Considering the bans and restrictions on DDT in many countries before any formal, global agreement, we investigated whether DDT, particularly in raptors, has continued to decrease following these bans. Simultaneously, we also aimed to assess the overall trend in DDT in global raptor populations over time. The DDT concentrations in the most sampled raptor tissues (liver and muscle) and egg, identified in Chapter 2, were analysed to determine whether DDT had shown a decline over time since its ban. We also evaluate whether DDT trends vary among species from different dietary guilds and if trends differ in tropical versus more temperate regions or in areas with varying levels of precipitation. All of which might be predicted to alter the rate at which this compound may decay in the environment.

Chapter four analyses recent DDT and dieldrin concentrations in a migratory raptor species, the Amur Falcon (*Falco amurensis*). This species uses South Africa as its non-breeding range, migrating from central Asia during the austral summer. We exploit a mass mortality event (a severe hailstorm) to examine concentrations of DDT (currently in restricted use in South Africa) and dieldrin (completely banned in South Africa), in this insectivorous migratory raptor. By analysing these pesticides in liver and muscle, two of the most analysed tissues identified in Chapter 2, it provides an opportunity to compare concentrations of these two pesticides with contemporary (i.e. over the last decade) concentrations extracted from the data used in Chapter 3. Ethics approval for this chapter was approved by the Science Faculty Animal Ethics Committee at the University of Cape Town. The Animal Ethics approval number is: 2019/V9/AA.

Chapter five presents a synthesis of the key findings of Chapters 2 to 4. It provides an overview of how DDT and dieldrin has been studied globally in raptors as well as discusses how the change in DDT corresponds to these biased trends in global monitoring. This chapter further discusses why historic modelled DDT slopes and contemporary DDT and

dieldrin concentrations discussed in Chapters 3 and 4 respectively, can be considered a sufficient proxy of the success of global-scale initiatives, even before the establishment of the Stockholm Convention, in controlling and mitigating environmental contamination by anthropogenic chemicals. Additionally, it serves as a strong motivator for increased monitoring effort in countries allowing restricted use of these pesticides. While confirming certain assertions regarding these pesticides, this chapter discusses my key findings and their implications, including how they may influence current pesticide monitoring efforts, specifically in the Global South.

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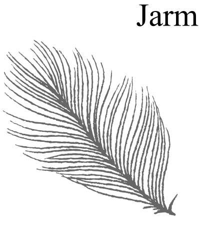

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Chapter 2

A global review of the temporal and spatial patterns of DDT and dieldrin monitoring in raptors

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The three most sampled raptor species when monitoring DDT globally: Bald Eagle (*Haliaeetus leucocephalus* - photo by Andy Morffew), Eurasian Sparrowhawk (*Accipiter nisus* – photo by Bohus Cicel), and Peregrine Falcon (*Falco peregrinus* - photo by Mykola Swarnyk).

ABSTRACT

Concentrations of organochlorine pesticides have been extensively monitored in birds, particularly from higher trophic guilds such as raptors. Whilst monitoring of raptors has been ongoing for decades, patterns from monitoring activities have never been summarised on a global scale. In this study, we undertake a review to better describe the monitoring of two widespread organochlorine pesticides monitored globally in raptors, DDT and dieldrin. We provide a historical retrospective on the monitoring effort of a global environmental issue. Sampling was heavily biased geographically to the Global North, with more than 90% of studies conducted in this socio-geographic region, most from Europe and North America. Although monitoring occurred from at least 114 species, most samples came from relatively few species, with three species (Eurasian Sparrowhawk *Accipiter nisus*, Bald Eagle *Haliaeetus leucocephalus*, and Peregrine Falcon *Falco peregrinus*) comprising 50% of samples. The types of raptors sampled have changed over time, with avian and mammal specialists dominating samples until the 1970s, but more diverse dietary guilds monitored in later decades, and greater proportions of samples coming from generalist species. The three most sampled tissues (egg, liver, and plasma) comprised 84% of all samples. Eggs were the earliest tissue examined, and the only tissue sampled in all decades. The geographical bias in monitoring effort and relatively narrow species focus, suggests that patterns in these pesticides are unlikely to be fully representative of all global environments occupied by raptors. Whilst DDT has been banned throughout most of the Global North, it remains in use in the Global South, yet monitoring effort in the south, does not match that of the north. While monitoring remains prevalent in the Global North, contemporary monitoring is limited in the Global South with less than 10% of raptors sampled in Asia, Africa, and South America, over the last 3 decades.

Keywords: DDT; dieldrin; organochlorine pesticides; avian predator; Global North; Global South

INTRODUCTION

Pesticides are chemicals used to control, kill, or deter pest plant and/or animal species (Mahmood et al., 2016). They have been used to safeguard crops against destructive agricultural pests and protect humans against vector-borne diseases for centuries (Shepard, 1939; Costa, 1987). The first synthetic pesticides became widely available in the early 1940's, and whilst benefiting agriculture, many had an unexpected negative impact on the environment and human health (Carson, 1962; van der Werf, 1996). Organochlorine pesticides had a particularly severe effect on the environment (Jayaraj et al., 2016; Rani et al., 2017). These pesticides are well known for their persistence in the environment (Blus, 2003) and were also identified as being responsible for acute neurological damage and endocrine disorders in wildlife and humans (Jayaraj et al., 2016; Buah-Kwofie et al., 2018; Gerber et al., 2021), and more specifically dichlorodiphenyltrichloroethane (DDT) in birds causing breeding failure by reducing eggshell thickness (Ratcliffe, 1967). Much data exists, both correlative and experimental, demonstrating that high concentrations of organochlorine pesticides lead to reproduction failure and adult mortality, and are positively linked to population declines in animals at higher trophic levels (Blus, 2003). This is particularly true for birds of prey, which have shown declines in populations because of organochlorine pesticide exposure (Porter and Wiemeyer, 1969; Ware, 1975; Olsen et al., 1993; Blus, 2003; Garcıa-Fernández, 2014). The focus of this review is on the monitoring in raptors of DDT and its congeners (i.e., dichlorodiphenyldichloroethane - DDD and dichlorodiphenyldichloroethylene - DDE) and dieldrin, from here on, collectively referred to as DDT and/or dieldrin.

DDT was first synthesised in 1873 (Jarman and Ballschmiter, 2012). The compound was used to combat vector-borne diseases such as malaria and typhus during World War II (Bishopp, 1945). After the war, DDT became widely available for commercial use in agriculture and vector-borne disease control (Ruus et al., 2010). While scientists had raised concerns over the potential hazards posed by DDT as early as the 1940's (US Environmental Protection Agency, 1975), wider public recognition of these dangers followed the publication of *Silent Spring* (Carson, 1962; Jarman and Ballschmiter, 2012). With growing concern and mounting evidence, the USA, United Kingdom, and other European countries banned DDT in the 1970s and 80s (Grier, 1982; Jaga and Dharmani, 2003). Dieldrin was created in the late 1940s as an alternative to DDT (Honeycutt and Shirley, 2014), with its use peaking in the 1960s and 70s (Jorgenson, 2001). Because of dieldrin's severe toxicity and threat it posed to human health

and the environment, it was banned in the USA in 1987 (Honeycutt and Shirley, 2014), with most of Europe following suit by 1990 (Jorgenson, 2001). However, DDT and dieldrin are still produced and used in parts of the developing world (National Research Council, 2012; Kaur et al., 2019; Islam et al., 2021).

More than a decade after DDT and dieldrin were banned in most of the Global North, the Stockholm Convention on persistent organic pollutants was adopted by over 90 nations (Lallas, 2001; Stockholm Convention, 2024). While the initial banning and restrictions of these two pesticides resulted in encouraging declines in concentrations in the environment, the convention aimed to further protect humans and the environment over a larger geographic range from persistent organic pollutants, with DDT and dieldrin being two of 12 persistent organic pollutants of global concern (Stockholm Convention, 2024). However, in 2006, the World Health Organization (WHO) supported the reintroduction of DDT use for the control of vector-borne diseases in certain tropical countries, particularly from the Global South (van den Berg, 2009; Mansouri et al., 2017). This resulted in the legal production, distribution, and use of DDT by various countries in this region (van den Berg et al., 2017).

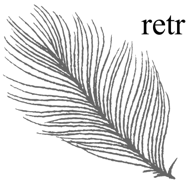
Despite the wealth of research on organochlorine pesticides, there have been very few reviews attempting to synthesise the monitoring of organochlorine pesticides in the global environment. Those that do exist, have focused only on certain regions, species, or countries. For example, Muir et al. (1999) used information on marine species of the Canadian Arctic, gathered over decades, to review the current state of knowledge of organochlorine pesticides in marine biota, concluding that information on DDT is strongly region and species specific. Loganathan and Kannan (1994) undertook a qualitative review of the temporal trend of organochlorine pesticide contamination in both human tissue and broader environmental contamination. They found that considerably less organochlorine pesticide monitoring is conducted in the Global South than Global North (Loganathan and Kannan, 1994).

Kutz et al. (1991) and Smith (1999) collated DDT concentrations in human adipose tissue and breast milk respectively, from multiple studies between the 1950s and 1990s to fit global trends for DDT levels. They found that samples were disproportionately from the Global North, from just over 13,000 samples, less than 10% were from the Global South (Smith, 1999). While Global South countries are considered by some as hotspots for organochlorine pesticide contamination, limited information and long-term contaminant monitoring has been conducted in these regions where restricted use of DDT in particular is still allowed (UNEP, 2023; Makgoba et al. 2024). Recent reviews have analysed multiple studies, over multiple decades

from Africa, South America, and Asia. These reviews report declines in organochlorine pesticide contamination over time in the Global North but increasing contamination in Global South countries still using these organochlorine pesticides (Ali et al., 2014; Taiwo, 2019), highlighting the importance of continued monitoring in this region. Biomagnification of organochlorine pesticides through the food web, means that the impacts of DDT and dieldrin may be particularly detrimental for species occupying higher trophic guilds (Grove et al., 2009). This has been seen with predatory bird species, such as raptors, where DDT and/or dieldrin have been responsible for negative demographic effects at a global scale (Gervais and Anthony, 2003; Goutte et al., 2014; Salice et al., 2014). Sublethal effects in raptors have been linked to DDE, the major metabolite of DDT (Blus, 2003) and associated with eggshell thinning and nesting failure. The first lethal impact of DDT on birds was noted in robins in the USA during the late 1950s (Carson, 1962). DDE-induced eggshell thinning and the associated reproductive failures was soon documented in other species, particularly raptors, globally (Ratcliffe, 1967; Enderson et al., 1982; Olsen et al., 1993; Rejt, 2001; Andreasen et al., 2018). Such eggshell thinning reduced productivity and drove declines in multiple raptor populations (Elliott and Martin, 1994; Lundholm, 1997; McCarty and Secord, 1999; Peakall, 1993).

Dieldrin has also been linked to declines in global raptor populations. Dieldrin does not induce eggshell thinning (Blus et al., 1972; Henny et al., 1977) but with LD_{50s} ranging between 27 mg/kg to 381 mg/kg in various bird species (Mcewen and Brown, 1966; Tucker et al., 1971), this highly toxic pesticide decreases neurotransmitters, such as serotonin and dopamine (Frank and Lutz, 1999). High exposure to dieldrin can impair cognitive and motor skill development (Frank and Lutz, 1999), increasing mortality due to accidents, disease, and starvation (Olsen et al., 1993; Frank and Lutz, 1999). Therefore, while DDT is the main cause for organochlorine pesticide induced eggshell thinning and resultant reproductive failure, precipitous declines in raptor populations were thought to be too sudden and rapid to be solely caused by such reproductive failure alone (Olsen et al., 1993; Blus, 2003). Thus, it has been suggested that global raptor population declines may have been caused through a combination of DDT and dieldrin, with eggshell thinning induced by DDE, in concert with higher mortality caused by dieldrin (Newton and Bogan, 1978).

Despite the well-established threat these compounds pose to raptors, as far as we are aware, there has never been a comprehensive global review on the patterns of DDT and dieldrin monitoring in raptors. In this paper, we attempt to address this gap and provide a historical retrospective on monitoring effort on an environmental topic that is pan-global in nature. We



undertake a global review of published studies that have quantified DDT and dieldrin levels in raptor tissues and eggs. Our aim is to quantify, at a global scale, how DDT and dieldrin monitoring in raptors has been distributed spatially, temporally, between species and foraging guilds, and between tissue types. We hope to illuminate how monitoring of this global issue has unfolded across the world and identify potential sampling biases. For example, we were particularly interested in exploring any disparities in sampling effort in the Global North vs the Global South, and whether monitoring is sufficient in countries still using DDT and dieldrin, and/or lacking stringent legislative implementation of DDT and dieldrin contamination control. Understanding whether monitoring of DDT and dieldrin in raptors is representative of geographic areas will also allow us to better understand whether conclusions on the effects or changes in DDT and dieldrin are likely to be fully representative of different global environments.

METHODS

Literature review

We undertook a literature search of all Web of Science databases for published literature on 29 October 2020, focusing on organochlorine pesticide contamination in raptors, irrespective of language and date published, using the following keywords: Raptor AND (DDT OR DDE OR DDD OR Dieldrin OR Organochlorines). The time span of our Web of Science search was from 1950 to 2020. We extracted information on DDT and its congeners and dieldrin but did not choose to report on endrin (a stereoisomer of dieldrin) and aldrin as these were less frequently reported compared to the congeners of DDT. We first scanned the title of all papers returned from these search terms. Papers were excluded if they did not indicate that DDT, its congeners and/or dieldrin were examined in raptors (n=241). We then examined the abstracts of the remaining papers and excluded papers that did not examine concentrations of DDT, its congeners and/or dieldrin in wild raptors (n=16). We then examined these remaining papers in full. Any potential additional references cited in the selected literature were also reviewed for eligibility and included (n=32). The final 256 papers were selected according to a strict set of inclusion criteria: papers had to have analysed DDT and/or its congeners and/or dieldrin in tissues (including eggs) of wild raptors and report descriptive statistics of their concentrations (e.g., means).

Data collection

For our selected papers we extracted the year in which raptors were sampled. Where the means include samples taken over multiple years, we selected the midpoint of these multiple years and rounded down to the nearest year. Where papers included previous work (e.g., syntheses or reviews), we extracted the data from the original source material. We extracted the country from which raptors were sampled, as well as the species and number of individuals sampled. A few papers (n=3) included samples traversing multiple continents, and these were excluded from the summaries examining studies in each continent. Similarly, two papers from 2020 were excluded when examining information on studies in each decade. Certain papers (n=8) examined samples from multiple countries, and two papers failed to specify the countries from which samples were collected, providing only the region for these samples, and were therefore excluded from the summaries examining studies in each country. Where concentrations were not reported per tissue type, we categorised the tissue type as "combined tissue". For cases where entire carcasses were homogenised, tissue type was categorised as "carcass".

Each species was assigned a dietary guild using the dietary traits adapted from the Elton Trait Database (Wilman et al., 2014). Foraging guild categories included: piscivores, mammal specialists, avian specialists, reptile specialists or invertebrate specialists where 70% of their diet was made up from these different prey items. Alternatively, species were categorised as generalists, where their diets were represented by multiple categories without a specific category representing more than 70% of the diet; vertebrate generalists, where vertebrate prey represented 70% of their diet; or scavengers, where carcasses, offal and/or garbage represented 70% of their diet. For a few species (n=4) that were not included in the Elton Trait Database, we assigned their dietary guild using information from The Peregrine Fund, Global Raptor Information Network and related literature and applied the Elton Traits methodology (Wilman et al., 2014).

RESULTS

General Publication Information

Our Web of Science search produced 481 papers. After examining the titles, 241 were deemed not to be relevant, leaving 240 whose abstracts were read in full. This identified a further 16 studies deemed not to be relevant. All 224 remaining papers were examined in full and deemed suitable for inclusion in this review. An additional 32 studies, cited in the selected literature were also identified as suitable, giving a final total of 256 papers that met our criteria. The 256 papers were published between 1966 and 2020, providing data on DDT and/or dieldrin in 27 563 raptors, from 114 different species spanning 115 years, from 1901 to 2016 (data published online). Samples collected in the first half of the 20th century were exclusively from eggs that were subsequently sampled from historic egg collections. For the remainder of the results, we focused on samples as our primary unit of measurement. From the raptors sampled, DDT and dieldrin were examined simultaneously in just over half of these samples (54%; n=14 751), whereas DDT and dieldrin were examined in isolation in 45% (n=12 408) and 1% (n=404) of raptors sampled respectively. Thus, DDT was monitored more frequently (99% of raptors; n=27 159) than dieldrin (55% of raptors; n=15 155).

Distribution of samples by time, space, and between species

The number of raptors sampled changed over time (Figure 2). Between the 1900s and 1930s, 169 raptors were sampled cumulatively. Whilst samples appear in this dataset from the pre-1940s, they all come from two studies exploring DDT in Peregrine Falcon eggs from museum and private collections (Peakall et al., 1976; Peakall and Kiff, 1979). Sample numbers began to increase from the 1940s, however, systematic monitoring only started from the 1960s onwards, peaking in the 1970s with 7 682 raptors sampled. From the 1980s sample numbers decreased, eventually falling to 1 718 raptors in the 2010s. Samples were collected from 48 different countries (Figure 1); however, most raptors were sampled from Europe (51%) and North America (44%) (Figure 2), and there was considerable bias in sampling toward certain species.

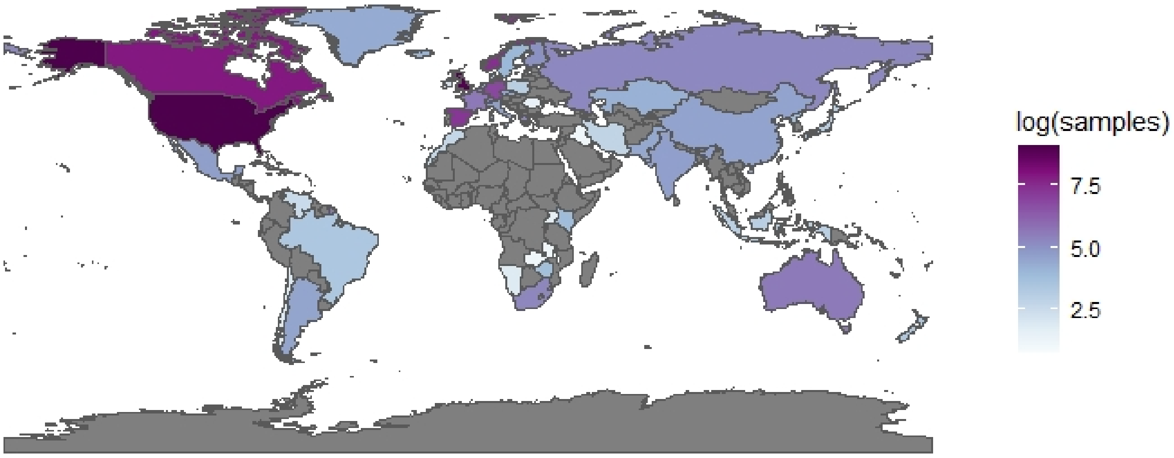


Figure 1: World map illustrating the countries from which all raptors sampled in this review originated. The darker the shade of the country, the more raptors were sampled from that country. Countries shaded in grey were not represented in this review.

For example, although we recorded samples from 114 species, the top three species (Eurasian Sparrowhawk (*Accipiter nisus*), Bald Eagle (*Haliaeetus leucocephalus*), and Peregrine Falcon (*Falco peregrinus*) alone, made up half (50%) of all samples, with the 10 most sampled species accounting for 77% of all samples. In Europe, the three most sampled species, were the Eurasian Sparrowhawk (33% of raptors sampled in Europe), the Common Kestrel (*Falco tinnunculus*) (13% of raptors sampled in Europe) and Merlin (*Falco columbarius*) (10% of raptors sampled in Europe). In North America, samples were dominated by Bald Eagle (44% of raptors sampled in North America), Peregrine Falcon (21% of raptors sampled in North America) and Osprey (*Pandion haliaetus*) (13% of raptors sampled in North America) (Figure 3). Peregrine Falcons, being a very widely distributed species, had samples coming from all continents, albeit in small numbers from Africa (n=52), Asia (n=113), and South America (n=6).

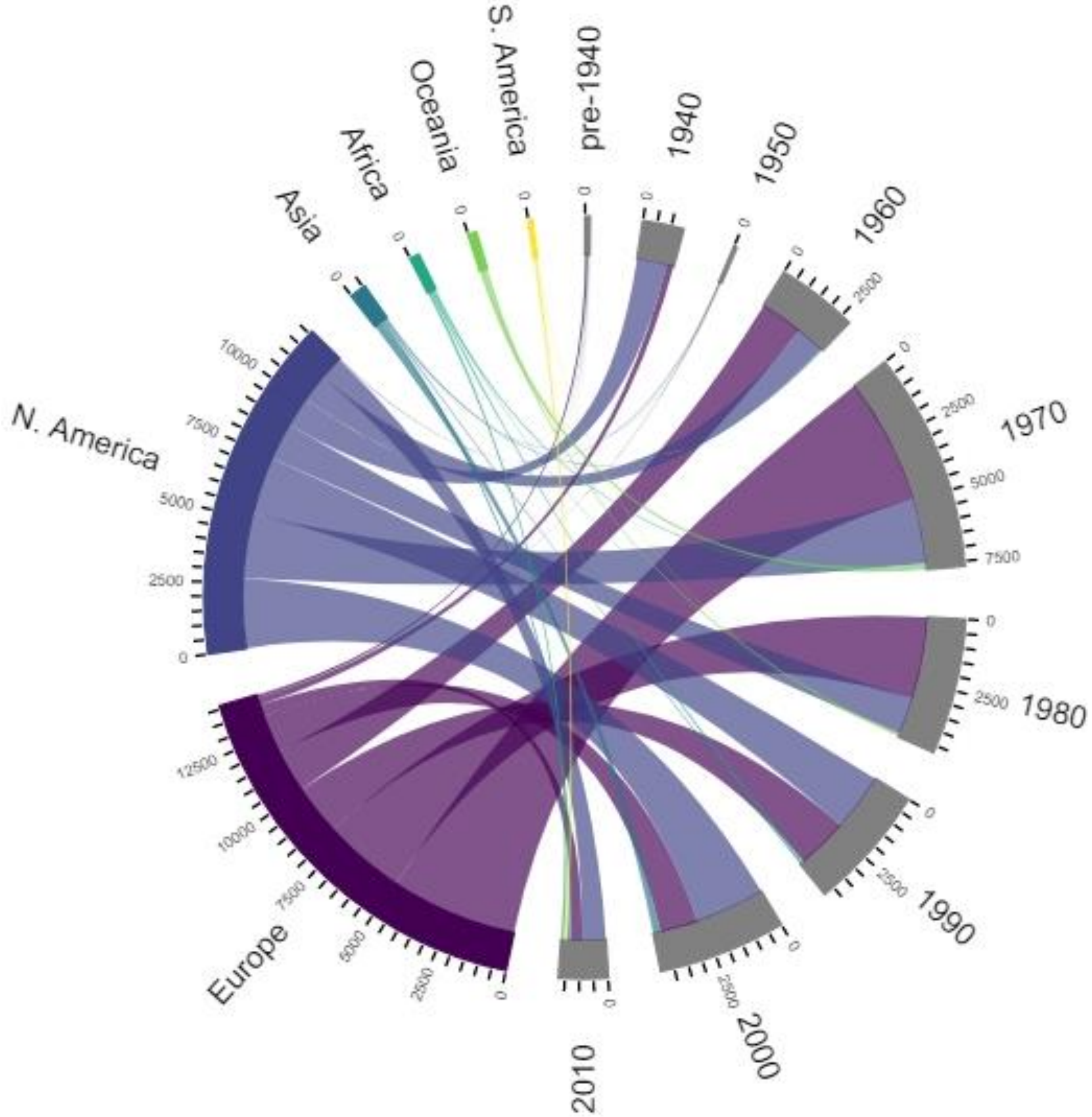


Figure 2: Chord diagram illustrating the number of raptors sampled from six continents, and their distribution by decade. The width of connection strands between continents and decades is proportionate to the number of raptors sampled from that continent during that decade.

Over time the species sampled for monitoring DDT and dieldrin changed. Peregrine Falcons were the only species to be sampled until the 1940s (Figure 4). In the 1960s, a relatively broad range of species were sampled, with no species dominating. In the 1970s and 1980s, Eurasian Sparrowhawks formed a large part of the samples (34% and 29% respectively). The proportion of Bald Eagles sampled increased considerably in the 1990s and 2000s (Figure 4).

Changing patterns of DDT and dieldrin in different foraging guilds

Most raptors sampled for DDT and/or dieldrin were avian specialists (42%), generalists (24%) or mammalian specialists (23%). On the other hand, species feeding on reptiles (0.03%) and

invertebrate specialists (2%) were sampled to a far lesser extent (Figure 5). Over time, the dietary guild of raptors sampled changed. The largely historical samples, from the 1900s through to the 1950s consisted exclusively of avian specialists (Figure 5), which from Figure 4, we know to be exclusively peregrine falcons. Since the 1970s the proportion of avian and mammalian specialists sampled have declined, with more samples coming from more diverse dietary guilds and a greater proportion coming from generalist species (Figure 5).

Tissues sampled in time and space

We found DDT and/or dieldrin concentrations explored in 17 different tissue types (data published online). The three most sampled tissues included egg (40%), liver (25%) and plasma (19%), thus, comprising 84% of all tissues sampled. The most common DDT congener reported across the top three tissues was DDE (75%). Eggs were the oldest tissue assessed for DDT and/or dieldrin and were the only tissue measured between the 1900s and 1950s (Figure 6). Other tissues emerged in samples from the 1960s, and while in recent decades, plasma seems to have been the preferred tissue for analysis, egg continues to be the only tissue sampled in all decades.

Monitoring of DDT and dieldrin post-banning

Most DDT and dieldrin bans in Europe and North America occurred during the 1970s and 80s, however, when examining studies outside these two continents during the last three decades, 4%, 2%, and 1% of samples were collected from Asia, Africa, and South America respectively (Figure 2), yet these are the continents in which these compounds are still used or in which usage data is limited. Half of all raptors were sampled in countries before their country banned DDT (49%), whereas 62% of raptors were sampled before dieldrin bans (Figure 7). However, these patterns mask country specific patterns which were very different from each other. For example, in the USA most raptors (79%) were sampled after their DDT ban, whereas, in the United Kingdom most raptors (87%) were sampled prior to their DDT ban. Conversely, for dieldrin, in both the USA and the United Kingdom, more raptors were sampled before than after the ban (61%, and 84%, respectively) (Figure 7).

DISCUSSION

DDT and dieldrin contamination in wild animals have been the focus of extensive research around the globe since concerns about their environmental impacts were first raised in the mid 21st century. In this global review, we provide the first temporal and spatial syntheses of monitoring that has occurred for these compounds in birds of prey. Within the published

literature, we identified more than 27 000 individual samples collected from 114 species of raptors across six continents, with DDT and/or dieldrin concentrations reported in over 250 studies from samples spanning more than 100 years. However, we also identified extensive bias in when, where and which species were monitored. We found that raptor sampling increased dramatically between the 1960s and 70s, but decreased from the 1980s onward, with the 2010s accounting for only 6% of all samples compared to 28% of samples collected during peak sampling in the 1970s. Areas outside North America and Europe comprise less than 5% of all samples. Similarly, despite the wealth of samples, the raptors identified in our review represented only 21% of global raptor species (McClure et al., 2018), with 50% of all samples coming from just three species, of which only one is found in both Global North and South countries. Likewise, although we identified more than 10 tissue types used when examining DDT and dieldrin, eggs were by far the most sampled tissue globally accounting for 40% of all samples. Furthermore, of the two pesticides, DDT was assessed far more in raptors than dieldrin. Our review demonstrates that most of the monitoring of DDT and dieldrin in raptors has occurred in the Global North with 95% of raptors sampled from North America and Europe alone. Furthermore, three countries (USA; United Kingdom; Canada) accounted for 75% and 85% of samples collected for DDT and dieldrin monitoring respectively.

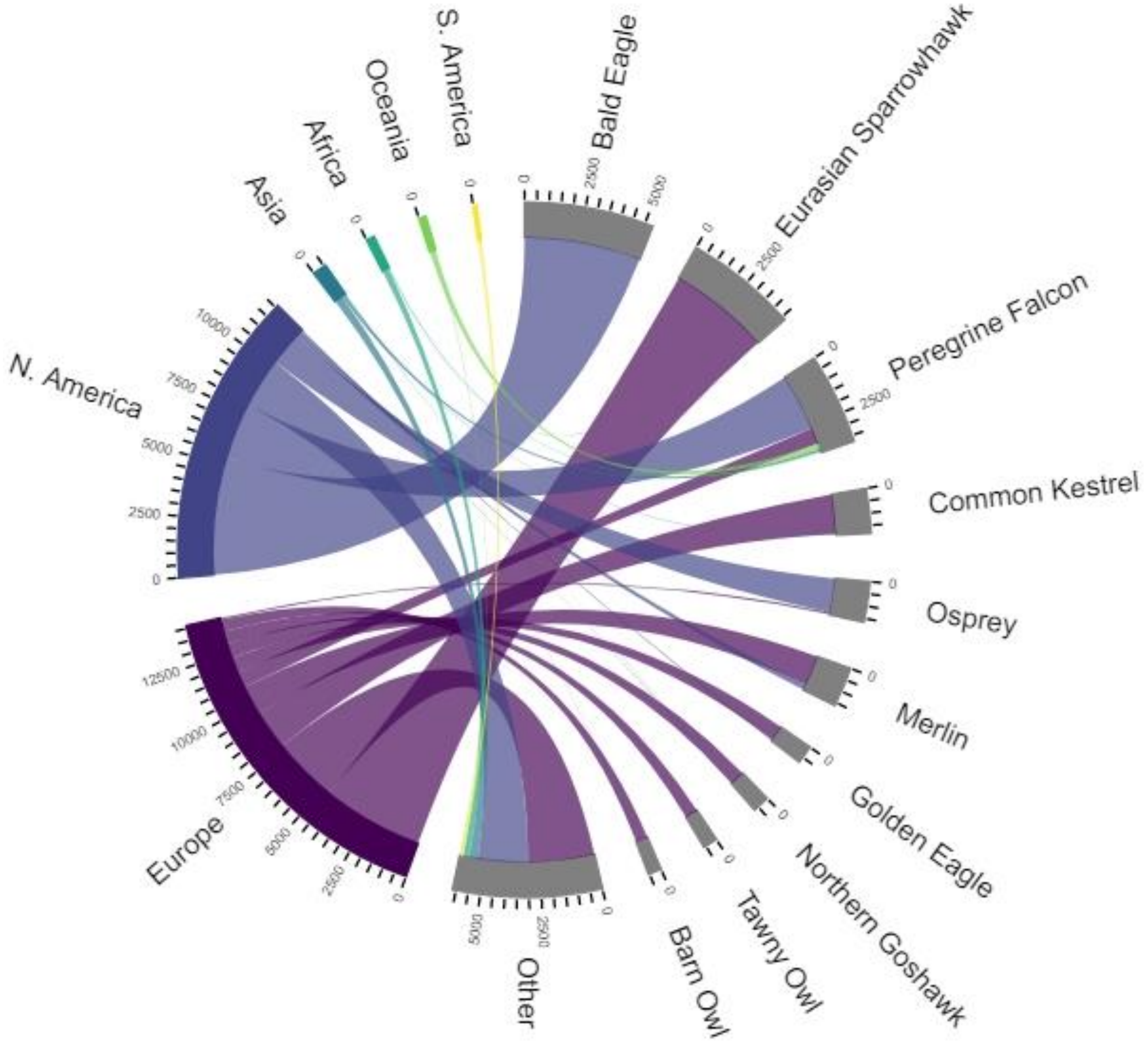


Figure 3: Chord Diagram illustrating the ten most sampled species of raptor (and other) and their respective numbers sampled globally, distributed across six continents. The width of each connection strand between continents and species is proportionate to the number of individuals from that species sampled from a particular continent.

DDT and dieldrin monitoring in time

We found an increase in the number of raptors sampled between the 1960s and 70s, reflecting the growing concern over the impact of DDT and dieldrin on the environment during this period (Bouwman et al., 2013). This concern was sparked by an increased awareness surrounding these organochlorine pesticides, particularly emanating from the publication of Carson (1962). Conversely the decrease in raptors sampled from the 1980s onward, coincided with the banning of DDT and dieldrin in the Global North, which suggests that concern surrounding these organochlorine pesticides in raptors decreased as bans were implemented. Furthermore, as species began to recover post-ban, resources available for monitoring these "recovered" species began to decline, inevitably reducing the monitoring effort in this region. However, it is important to note that pre-1965 DDT may be over reported (Jensen, 1972). This is because, after PCBs were identified in 1964 , it became apparent that there was a high probability that PCB interference played a role in DDT detection pre-1965 (Jensen, 1972). Therefore, DDT residues reported in this study from before 1966 may be a combination of DDTs and PCBs (Jensen, 1972). We expected DDT to be assessed far more in raptors than dieldrin, as historically, DDT has been in existence considerably longer than dieldrin and is still currently used in many countries which have banned dieldrin. Furthermore, DDT's link to raptor declines has been better documented than that of dieldrin (Ratcliffe, 1967; Enderson et al., 1982; Olsen et al., 1993; Rejt, 2001; Andreasen et al., 2018; Dagen, 2020).

Monitoring of DDT and dieldrin post-ban

The USA and United Kingdom accounted for most of the world's DDT and dieldrin monitoring, which might be expected, given that the impacts of DDT and dieldrin on birds were first revealed in research on birds from these countries (Carson, 1962; Ratcliffe, 1967; Busbee, 1977). The United Kingdom has been a major pioneer of diagnostic research in concentrations of DDT and dieldrin in raptors with most samples collected before their respective bans, whereas the high level of monitoring of raptors within the USA after their bans, suggest that raptors are being used here as indicator species for monitoring the temporal trends of these compounds and to assess the effectiveness of the regulatory actions. This shifting pattern is further highlighted by comparisons in the sampling of raptors in Europe with North America over time. We found that 70% of all samples came from Europe in the 1960s-1980s, but this fell to only 26% of samples in the 2010s. In contrast, between 1960s-1980s only 26% of studies came from North America, but this increased to 53% of global samples in the 2010s.

A geographical bias in monitoring of DDT and dieldrin

The contrast, including but not limited to, the available funding, appropriate infrastructure, and requisite training, has resulted in considerable disparity in scientific knowledge production between the Global North and south, with the Global South facing many challenges and difficulties in relation to scientific research and monitoring (King, 2004; Okune et al., 2016; Reidpath and Allotey, 2019; Allik et al., 2020). As such, it is perhaps unsurprising that 95% of raptors were sampled from the Global North, and that most of the DDT and dieldrin monitoring effort has been biased toward this region. However, this geographical bias is concerning, since most, if not all countries still using and/or producing DDT and dieldrin are in the under-sampled Global South. This suggests limited monitoring in countries where these compounds are still in use. The fact that only 175 and 94 raptors were sampled from Russia and China

respectively since 1960 further demonstrates this lack of monitoring in regions of the Global South. This is in the face of extensive DDT use by these countries between the 1950s and 1980s, with the Former Soviet Union and China being responsible for 320 kt and 260 kt of DDT use respectively (Li and Li 2004; Li and Bidleman, 2003). This trend continues in recent times with the three countries responsible for the highest DDT use globally for public health purposes (India, Indonesia, and Brazil) (Chapter 1) representing some of the lowest samples globally. Only 106 raptors from India and 28 from Brazil sampled since the 1960s, and none sampled from Indonesia during this period. Our findings are consistent with the global trends in organochlorine pesticide monitoring described by Loganathan and Kannan (1994), and Jaga and Dharmani (2003) while studying organochlorine pesticides in terrestrial, aquatic, and marine ecosystems as well as human tissue, suggesting that despite being a hotspot for organochlorine pesticide contamination, the Global South still receives comparatively less monitoring of DDT and dieldrin.

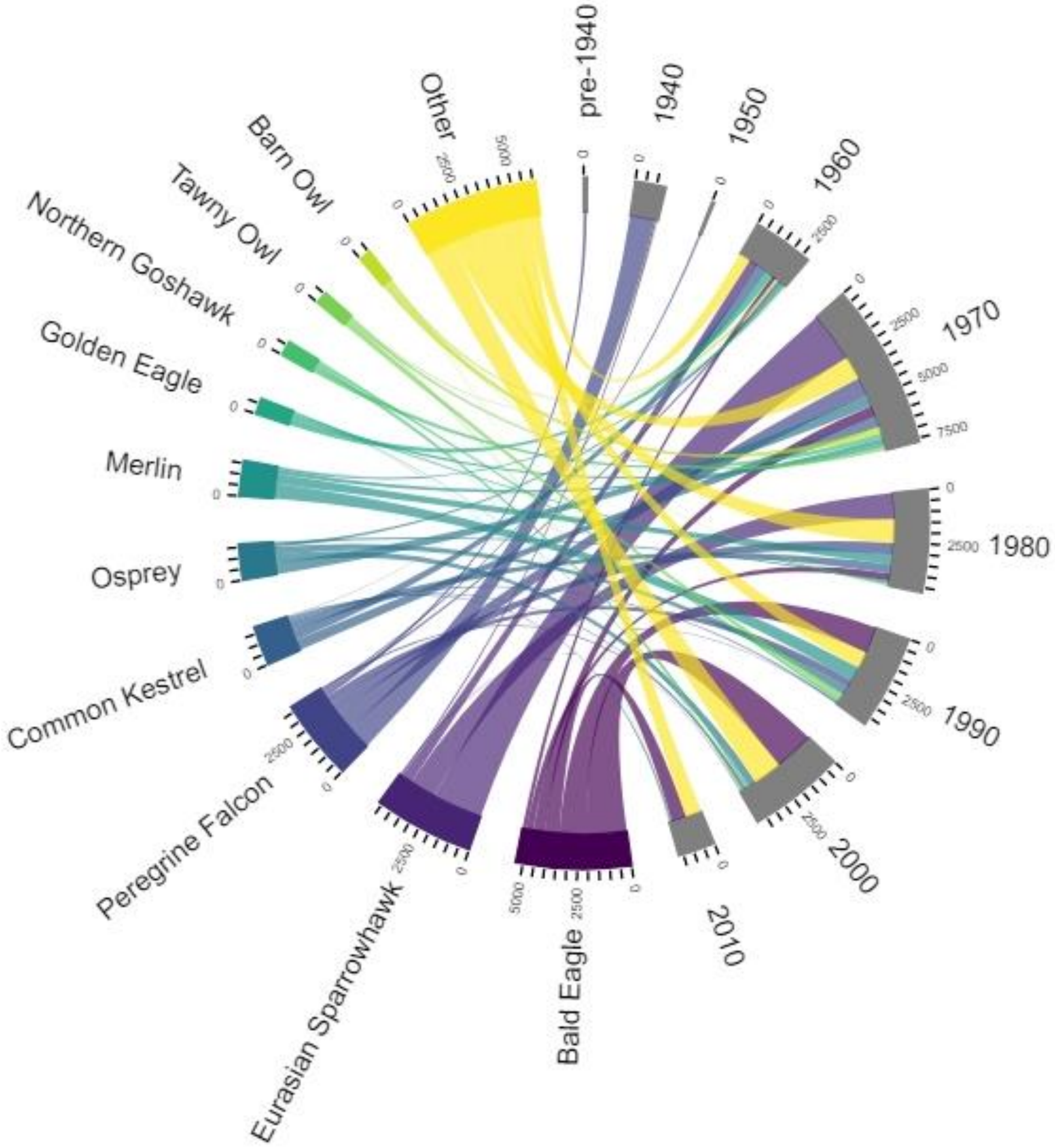


Figure 4: Chord diagram illustrating the ten most sampled species of raptor (and other), and their sampling distribution by decade. The width of each connection strand between the species and decades is proportional to the number of individuals from that species sampled from a particular decade.

DDT and dieldrin as a current or historic concern

The dramatic decline we observed in sampling of raptors between the 2000s and 2010s could reflect a reduced concern about these contaminants in the Global North due to substantial reductions in DDT and dieldrin concentrations observed in individual studies. For example, Nygård et al. (2019) reported a sharp decline in DDT and dieldrin concentrations in Peregrine Falcon eggs coinciding with their strong population recovery in Norway. Similarly, Sun et al.,

(2020) reported a declining trend in these organochlorine pesticides across northern Europe based on White-Tailed Sea Eagle feathers. This reduced concern originates from the Global North, representing areas where strict bans have been implemented and enforced. However, our review shows that the Global South has been and continues to be relatively under-monitored for DDT and dieldrin in raptors. Despite this relatively low level of monitoring, researchers in the Global South continue to identify high concentrations of DDT and dieldrin in countries where they have been banned, as well as in countries that continue to allow their restricted use. For example, recent research by Garcia-Heras et al. (2018) and Aver et al. (2020) reported high levels of DDTs in South African ($\underline{x}$=3.06 ng/ml) and South American ($\underline{x}$=4.13 µg/g) raptors respectively. Additionally, reviews of Ali et al. (2014) and Taiwo (2019) have both reported high levels of DDT and/or dieldrin in different environmental matrices from parts of South Asia (DDT - 7.64 – 59.88 ng/g; dieldrin – 5.49 - 81.8 ng/g in soil) and West Africa (DDT – 125.00 µg/L; dieldrin – 17.50 µg/L in surface water samples). While the presence of these organochlorine pesticides may, in part, be attributed to extensive historical use, it may also be due to continued illegal use (van den Berg et al., 2017; Chen et al., 2020; Buah-Kwofie and Humphries, 2021), which is plausible, given that the Global South often has less effective legislative enforcement and is well known for not meeting deadlines proposed by international conventions (Dietz and Adger, 2003). Our finding that Africa, Asia, and South America combined account for only 3% of all samples collected between the 1960s and 2010s, and the continued use of these organochlorine pesticides (legal and illegal) in this region further highlight the bias in DDT and dieldrin monitoring information and suggests that these compounds are still worthy of current concern in the Global South, where monitoring should be increased.

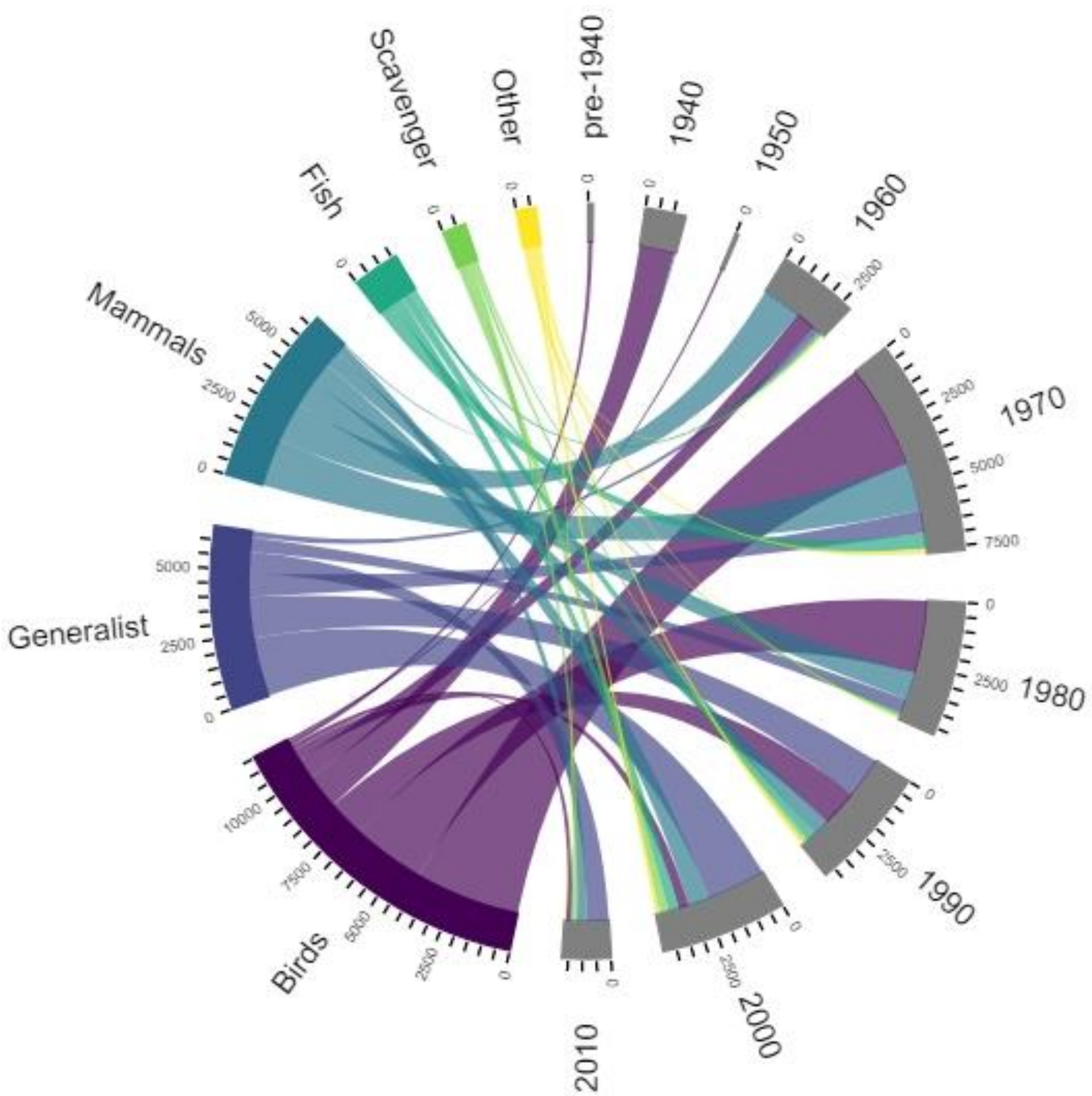


Figure 5: Chord Diagram illustrating the different foraging guilds (bird specialists; generalists; mammal specialists; piscivore; scavengers; and other) and the number of raptors sampled from each guild distributed between decades. The width of each connection strand between the foraging guild and decade is proportional to the number of individual raptors from that foraging guild sampled in a particular decade.

Species bias in the monitoring of DDT and dieldrin

We found that DDT and dieldrin monitoring showed a strong bias toward a relatively narrow range of species, with a few species making up the bulk of the samples. However, even for well sampled species, the distribution of monitoring is often spatially constrained. For example, although European Sparrowhawks were the second most sampled species, 90% of these data were collected from the United Kingdom. We found that the diversity of foraging guilds sampled appeared to have increased in recent decades, however, it was also clear that some guilds remain relatively under sampled, which may reduce our ability to understand sources of

local contamination. For example, it has been suggested that non-migratory, insectivorous passerines are good indicators of local contamination (Dauwe et al., 2006). Thus, the low numbers of samples (less than 2% of all samples) from invertebrate specialists specifically, may influence our ability to assess and monitor local contamination. Furthermore, the shift from sampling more avian species to sampling more generalist species with diverse diets from the 1990s, may pose a challenge when interpreting the trend of organochlorine pesticide contamination (Gabrielsen et al., 1995). This may be particularly challenging for species which use both aquatic and terrestrial ecosystems, and both scavenge and hunt e.g., Bald Eagles and African Fish Eagles (*Haliaeetus vocifer*) (Ewins and Andress, 1995; Stewart et al., 1997).

Reporting of DDT and dieldrin in tissues: need for unification

The choice of tissue for contaminant monitoring is dependent on several factors, including the contaminant/s of interest, resources available and ethical and legal considerations (Espín et. al., 2016). Our review revealed that DDT and dieldrin has been assessed in more than 10 different tissues, from both dead and live raptors. The use of these different tissues creates challenges when comparing between sites, or species or over different periods of time. Different tissues may indicate different levels of temporal contamination, for example adipose tissue is a good indicator of chronic exposure whereas liver may indicate more recent exposure (Espín et al., 2016). Furthermore, starvation, intoxication, and moulting in individual birds may result in high variation in contaminant load amongst individuals. Therefore, we should be cautious when comparing contaminant levels in tissues collected from live birds with those collected post-mortem (Acampora et al., 2017). While eggs are regarded as a suitable tissue to reduce variability in organochlorine pesticide contamination associated with age, sex, and season, they only represent a short-term contaminant history of egg-laying females, which can also vary according to their dietary exposure (Lundstedt-Enkel et al., 2006; Hellou et al., 2013). While our review has revealed egg as the most sampled tissue, in recent decades, plasma seems to have become the preferred tissue. This could indicate the increasing need for less destructive sampling methods, particularly for raptors, many of which are protected (Espín et al., 2016), as well as an improvement in technology to allow for detection of DDT and dieldrin in smaller quantities of plasma. An additional challenge in comparing between samples, beside the different tissues used, is the fact that there is also considerable variation in which metabolite and isomer concentration are reported.

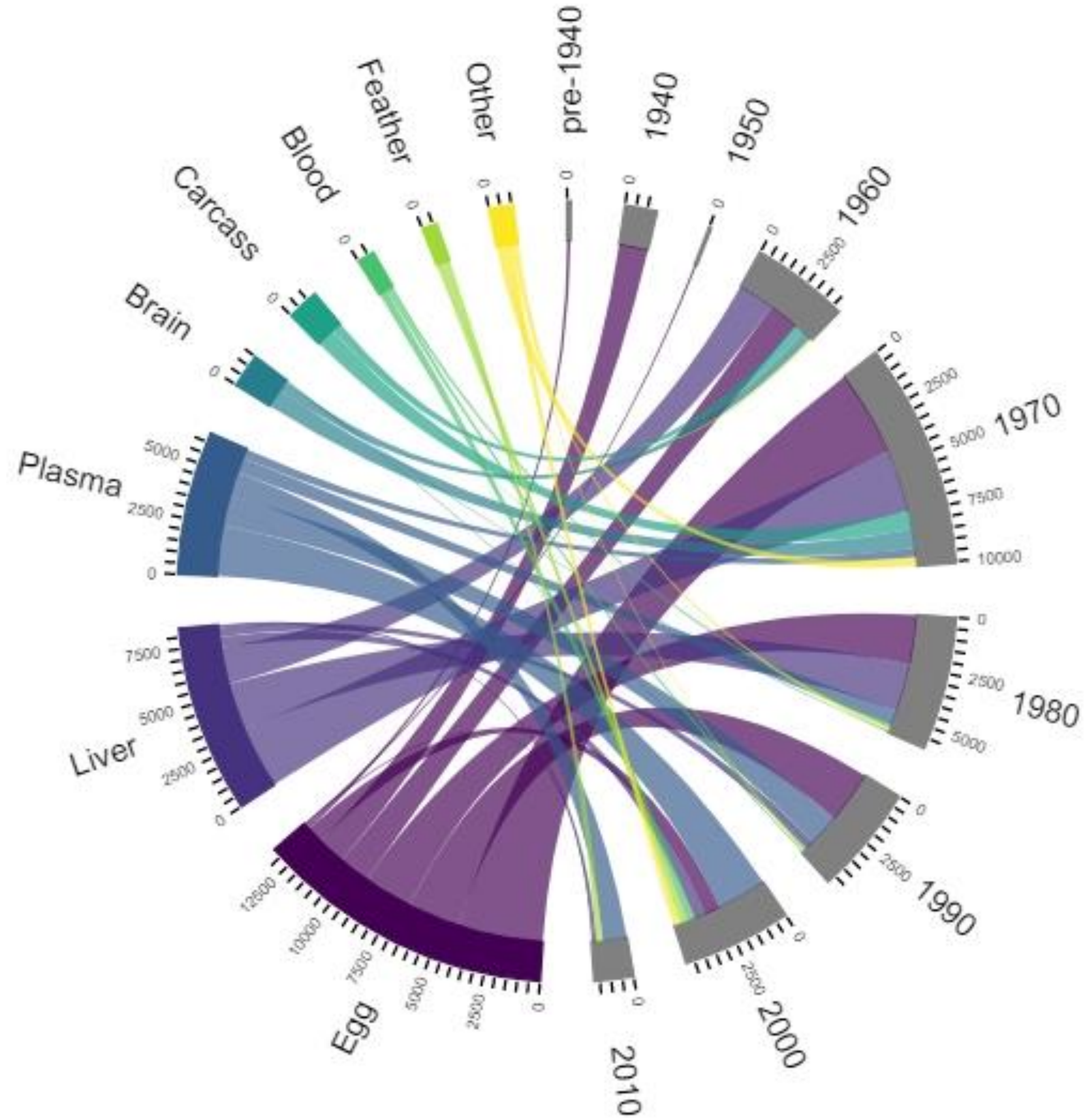
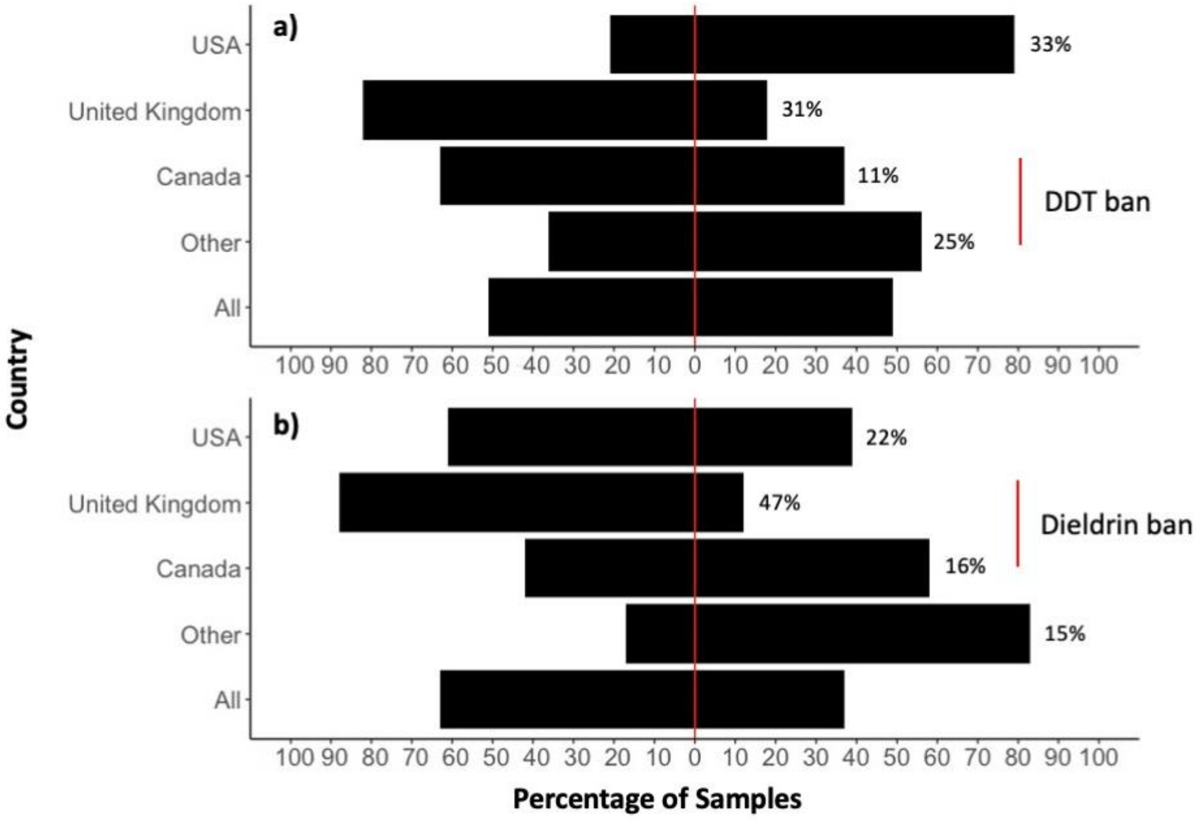


Figure 6: Chord Diagram illustrating the seven most sampled tissues (and other) and their sampling distribution by decade. The width of each connection strand between tissue and decade is proportionate to the number of samples of that tissue sampled during a particular decade.

While we chose to only report on monitoring of dieldrin (not its metabolites), DDT was often separated into its respective congeners (DDD; DDE and DDT) and isomers (*p,p'*-DDE; *o,p'*-DDE; *p,p'*-DDD; *o,p'*-DDD; *p,p'*-DDT; and *o,p'*-DDT). Studies did not follow a set reporting strategy with some reporting total DDT while others reported only a subset of DDT congeners and/or isomers. To improve the comparability of data in time and space, it would be advisable to have unified monitoring practices and criteria for tissues and reporting of DDT and dieldrin in raptors and other species. The need for a more unified and standardised approach to reporting highlighted from this review, applies to both future monitoring of DDT and dieldrin, and to other contaminant monitoring, if we want to facilitate cross comparisons between studies over space and time. Whilst we do not provide recommendations on standardising guidelines, we believe it is something worthy of consideration by the ecotoxicological community. For example, a data archiving facility, similar to how MoveBank hosts tracking data (Kranstauber et al., 2011), could be a potential option.

Implications of this review on DDT and dieldrin monitoring

The geographical sampling bias to Europe and North America will also lead to an inherent bias in environmental conditions. Temperate environments dominate these regions, whereas most tropical countries have received far less monitoring. Therefore, our understanding on how DDT and dieldrin accumulates or degrades will be based principally from temperate environments and may not translate as well to estimates for tropical regions. The continued use of DDT and dieldrin in the Global South, a region which is home to most of the world's biodiversity (Lenzen et al., 2012; Adenle et al., 2015), and the lack of monitoring identified in this review presents an ongoing risk to global biodiversity in that region. While DDT may be important for vector control to protect human health in many of these poorer regions, these findings support the importance of monitoring to inform effective and efficient contaminant management decisions for organochlorine pesticides and other emerging persistent organic pollutants.



Note: In both cases, 3% and 1% of raptors sampled for DDT and Dieldrin respectively, came from countries which either had no available information on ban dates or have not completely banned these compounds.

Figure 7: Percentage of raptors sampled before and after the banning of a) DDT and b) dieldrin in each respective country (date of ban varies among countries). The percentage beside each bar indicates the percentage of raptors sampled in the corresponding country for that compound. Included are the top three countries in which most raptors were examined for DDT and dieldrin concentrations.

To our knowledge, this is the first review to focus on efforts of monitoring of DDT and dieldrin in raptors globally. Similar reviews on birds, bats, sea turtles and even air have showed similar patterns, that studies on persistent organic pollutants such as DDT and dieldrin are critically geographically biassed, with information originating primarily from the Global North, particularly North America and Europe (Bogdal et al., 2013; Muñoz and Vermeiren, 2020; Hao et al., 2021; Torquetti et al., 2021). This trend is not restricted to wildlife but has also been detected in humans by Smith (1999), who found that less than 10% of human breast milk samples were collected from the Global South from a total sample size of 13 000. Hao et al., (2021) also found that studies focused on a limited number of species and tissues for analysis and discovered patterns which suggest that the declines in organochlorine pesticides such as DDT and dieldrin in the Global North coincided with respective regulations implemented in these countries. Similar to our findings, Torquetti et al.,’s (2021) review on the exposure of bats to pesticides between 1951 and 2020 also found that most research was conducted in the 1970s and 80s, which further suggests that most concern was centred around the peak use of

DDT and dieldrin in the Global North and has decreased with the implementation of bans in this region. There seems to be a growing interest in reviewing contaminants in raptors, Chen and Hale (2010) and Plaza and Lambertucci (2019) conducted reviews on polybrominated diphenyl ether flame retardants (PBDEs) in birds and lead in vultures, respectively. Both reviews interestingly showed very similar patterns to some of our findings, with a bias towards sampling in the more developed countries of the northern hemisphere. Furthermore, they revealed that most information on some of these contaminants came from a limited number of species (Plaza and Lambertucci, 2019). These reviews therefore suggest that our findings are not limited to DDT and dieldrin and that these organochlorine pesticides as well as other contaminants tend to be sampled far more frequently in the Global North and findings are not always representative of all environments.

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Chapter 3

Global declining trends of DDT concentrations in raptors: an analysis using historic measurements

Two Bald Eagles in the USA that were assessed for pesticide residues in 1963, soon after the publication of Rachel Carson's *Silent Spring*. Seney National Wildlife Refuge - 1963

ABSTRACT

While synthetic chemicals have profoundly benefited humankind, many of them have had unintended negative effects on the environment, with their use subsequently banned or restricted. The pesticide, dichlorodiphenyltrichloroethane (DDT), is one such chemical which has had a particularly severe effect on the environment. Awareness of the environmental damage by DDT came principally via avian bioindicators, such as birds of prey. Subsequent to and following the local bans and restrictions on DDT, raptors were extensively monitored for DDT across the globe, with such monitoring slowing drastically over the last few decades. However, despite this extensive monitoring, changes in DDT concentrations in raptors following the bans and restrictions have never been analysed on a global scale. This study examines changes in DDT in the tissues (liver and plasma) and eggs of wild raptors over the last six decades, extracted from the published literature. Our aim was to evaluate whether the historic declines in DDT realised in the Global North during the early 1970s and 80s have continued after the implementation of the Stockholm Convention, which paved the way for further restrictions of DDT in much of the rest of the world. We describe how this pesticide has changed both spatially (e.g. between continents, in relations to latitude, or precipitation), and in relation to raptor foraging guilds (aquatic or terrestrial). We found a decline in DDT in raptors from the Global North following its ban. Declines were similar between continents, but DDT concentrations differed, with higher concentrations in North America than in Asia. Declines were also similar irrespective of the latitude of the samples, but concentrations were higher, closer to the equator. Declines differed depending on raptor diet, with declines being steeper for raptors eating mainly terrestrial species, versus those with more aquatic diets. Declines also differed depending on the levels of precipitation, with steeper declines in areas with higher levels of precipitation. Our results from using raptors as bioindicators of DDT concentrations, suggests that the rate in which DDT degrades in the environment does vary. However, while we did detect an overall decline in DDT, the lack of monitoring in the Global South has resulted in insufficient data from countries allowing restricted DDT use after its reintroduction in 2006. This impedes our ability to affirm the declines of the Global North as globally representative. Nevertheless, these findings can be viewed as a success story, giving hope that, with sufficient implementation and monitoring, similar declines can be achieved in the Global South.

Keywords: DDT; organochlorine pesticides; pesticides; raptor; avian predator; decline

INTRODUCTION

Many synthetic chemicals have had profound benefit for humankind, for example, chlorofluorocarbons (CFCs) have enabled safe, effective food refrigeration (de Wildt et al., 2022), polybrominated diphenyl ethers (PBDEs) protected humans and property from fire as a component of flame retardants (Abbasi et al., 2015), and polychlorinated biphenyl's (PCBs) played an integral role in multiple industrial applications (Abramowicz, 1995). However, while benefiting humankind, these, and many other synthetic chemicals have had unintended, negative impacts on the environment and humankind itself (Newman et al., 2009; Abbasi et al., 2015; de Wildt et al., 2022). CFCs are linked to the depletion of the ozone layer, resulting in increased solar ultraviolet radiation, which, as a known carcinogen, negatively impacts humans and wildlife (Gallagher and Lee, 2006; Slominski and Pawelek, 1998), while PBDEs and PCBs, are linked to endocrine disorders and reduced fertility in humans and wildlife (Kelly et al., 2007; Abbasi et al., 2015). These negative impacts have often prompted local and regional bans to control environmental contamination (Abbasi et al., 2015). However, when the environmental threat needs uniform cooperation from multiple states, international agreements in the form of conventions and treaties are required (Munday, 1978; Hoel, 1992). These conventions are tools used to help promote cooperation among multiple countries in the protection of the environment at a global scale (Hoel, 1992), but the efficacy in achieving their aims and understanding why different states comply (or not) is not always easy to assess (Raustiala, 2000; World Meteorological Organization, 2022).

Dichlorodiphenyltrichloroethane (DDT) is a good example of a useful anthropogenic chemical that became a global human and environmental health concern and was subsequently controlled by an international convention. As a pesticide, DDT became widely available during the mid 1940s (Kamel et al., 2015; Zeng et al., 2022). While it proved valuable in increasing agricultural yields and protecting humans against vector-borne diseases (Kamel et al., 2015; Zeng et al., 2022), it is toxic and resistant to environmental degradation, persisting in the environment for decades (Chopra et al., 2011; Singh and Singh, 2017). High concentrations of DDT can cause neurological damage and endocrine disorders in both humans and wildlife (Blus, 2003; Jayaraj et al., 2016; Buah-Kwofie et al., 2018; Gerber et al., 2021). DDT’s negative impact on wildlife has been extensively studied and monitored globally, in multiple species, for decades (Loganathan and Kannan, 1994; Muir et al., 1999). Scientists were first alerted to the impacts of DDT on wildlife by studies on birds conducted in Europe and North America as early as the 1950s (Cooke et al., 1982; Tesfahunegny, 2016). The publication of

Rachel Carson’s book, *Silent Spring* in 1962 sparked public recognition of the dangers posed by DDT, which prompted governments in the USA, United Kingdom, and other European countries to prohibit its use in the 1970s and 80s (Carson, 1962; Grier, 1982; Jaga and Dharmani, 2003; Jarman and Ballschmiter, 2012). The use of DDT was widely restricted throughout most of the world by the time the Stockholm Convention on Persistent Organic Pollutants (POP) was adopted in 2001, the convention only came into force in 2004 (Stockholm Convention, 2024). However, in 2006, the World Health Organization (WHO) supported the reintroduction of DDT in many developing tropical countries to control the vectors of malaria (van den Berg, 2009; Mansouri et al., 2017).

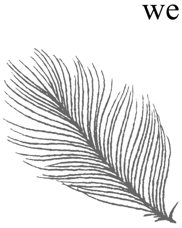
DDT’s persistence in the environment resulted in bioaccumulation in wildlife and biomagnification at higher trophic levels (Chen et al., 2009; Zacharia, 2019; Fremlin et al., 2020; Valters et al., 2022). Raptors are apex predators that occupy the top of the food web in various ecosystems globally (Espín et. al., 2016; Gómez-Ramírez et al., 2019). As such, raptors became instrumental as indicator species to monitor DDT, as seen in Chapter 2 where 27,000 raptors from 114 species, were sampled across more than 6 decades. This level of widespread raptor monitoring, both before and after various international restrictions of DDT, provides an ideal opportunity to explore how DDT has declined following the ban, and whether these declines have been uniform across regions, environmental conditions and habitats.

In this study, we examine changes in DDT (and its congeners) in the tissues (liver and plasma) and eggs of wild raptors since the late 1960s, extracted from the published literature. Our aim was to use these raptors to evaluate whether DDT has continued to decrease following various bans and restrictions implemented since the late 1900s. We use these data to explore how DDT has changed both spatially (i.e. between continents or in relations to latitude), in relation to environmental conditions (precipitation) and in relation to raptor foraging guilds (aquatic or terrestrial). Since DDT has been banned or severely restricted in most parts of the world, we hypothesise that, if adherence to this legislation has been strong, we would see substantial and continued declines in DDT in raptors following the implementation of various legislation. Some studies have suggested that DDT declines at a slower rate in terrestrial ecosystems than aquatic ecosystems (Dimond et al., 1968; Loganathan and Kannan, 1994). However, most of the information on aquatic DDT since the 1970s has come from measurements in fish (Hellou et al., 2013). These aquatic organisms often have short lifespans, experience rapid contamination, and exhibit a faster clearance rate than larger, longer-lived terrestrial predators such as raptors, which exhibit a much slower clearance rate (Loganathan and Kannan, 1991).

Therefore, we hypothesise that declines in DDT will be steeper in raptors which prey on predominantly aquatic species than species with more of a terrestrial prey base. Some studies have suggested that DDT may break down quicker in warmer, tropical environments compared to colder temperate regions (Karlsson et al., 2000; Bouwman, 2004). Closer to the equator, in the tropics, areas tend to experience hotter, wetter conditions, with greater productivity (MacArthur, 1969; Taborda et al., 2022). All these processes are likely to lead to an increase in DDT degradation (Loganathan and Kannan, 1994; Singh and Agarwal, 1995; Guerin, 1999; Foght et al., 2001). Additionally, high levels of rainfall can help to increase the rate of volatilization of DDT in soils, which may accelerate its breakdown or even wash away pesticides from their point of application (Loganathan and Kannan, 1994; Singh and Agarwal, 1995; Anju et al., 2010). We therefore predicted that DDT in raptors may decline more rapidly in tropical regions (e.g. those closer to the equator) and regions with higher precipitation rates.

METHODS

For this study we used literature which provided data on DDT concentrations in wild raptors from a literature search derived from Clarivate *Web of Science* (© Copyright Clarivate 2020, All rights reserved), conducted in Chapter 2. We used the database from Chapter 2, which provided information on the location, the tissue, the species (and their dietary guild) of the samples monitored. This literature search covered the period from 1950 to 2020 and used Raptor AND (DDT OR DDE OR DDD OR Dieldrin OR Organochlorines) as search terms, irrespective of language and date published. The search result also included literature on dieldrin contamination in raptors (n=256), however, for this study we included only papers that reported on DDT (including all congeners and isomers) contamination in wild raptors (n=208). The inclusion criteria for these papers were that they reported descriptive statistics (e.g., means, or individual values) of DDT concentrations in egg, plasma, or liver. In Chapter 2, we demonstrated that these tissues were the most frequently sampled raptor tissues between the 1960s and 2010s, comprising 84% of all tissues sampled during this period, making them the most suitable tissues to assess in this chapter. Egg was the only tissue assessed for DDT before 1960, but we only analysed data from samples collected post 1959 (n=2185). Together with the estimate of DDT concentration, we also extracted the year and country from which raptors were sampled, as well as the species and number of individuals sampled. For the year of sampling, when samples were collected over multiple years, we selected the midpoint of these multiple years and rounded down to the nearest year. If more than one sample was collected, we identified which measure of central tendency was used for the data (geometric



mean, arithmetic mean or mode). We also extracted information on the weight basis of samples (i.e. whether the sample was measured as wet weight, dry weight, or lipid weight) and compound (to account for the different DDT congeners). All DDT, DDE, and DDD concentrations were analysed, including the isomers of each DDT congener (*p,p'*-DDT; *p,p'*-DDE; *p,p'*-DDD; *o,p*'-DDT; *o,p'*-DDE; *o,p'*-DDD). When a study reported all congeners or isomers, concentrations were extracted as total DDT and was analysed as the sum of all metabolites.

Each species was assigned a dietary guild using the dietary traits adapted from the Elton Trait Database (Wilman et al., 2014). For a few species (n=4) that were not included in the Elton Trait Database, we assigned their dietary guild using information from The Peregrine Fund's Global Raptor Information Network and related literature and applied the Elton Traits methodology (Wilman et al., 2014). For ease of analysis, each dietary guild was further categorised to either an aquatic or terrestrial dietary guild. Piscivores were assigned to the aquatic dietary guild, whereas raptors relying on all other foraging sources, were assigned to the terrestrial dietary guild.

To assess the change in DDT between tropical and temperate regions, we extracted the country or region (e.g. state, province, etc.) from which samples were collected and then used Google Earth® to determine latitudinal coordinates of the centre point for each of those regions. Similarly, to determined average precipitation for countries (excluding USA and Canada) in which samples were collected, we used average precipitation per annum (mm) over a 50-year period from the Food and Agriculture Organization of the United Nations - World Bank (2022) via Our World in Data, which reported average precipitation per country. However, due to the geographical and climatological expanse of the USA and Canada, for samples collected in these countries, we extracted the city name, or the state/province, and used Google Earth® to determine latitudinal coordinates of the state capital. To determined average precipitation for samples collected in the USA and Canada, we used average precipitation per annum over a 50-year period from the Food and Agriculture Organization of the United Nations - World Bank (2022) via Our World in Data, which reported average precipitation per state/province. When reporting latitude, we converted all true latitudes into absolute latitude to express all values as distance from the equator. To assess changes in DDT following their respective bans or restrictions, we extracted the year that DDT was either completely banned or restricted per country and recorded the prohibition status for each country (restricted or banned).

This data was retrieved from country national implementation plans prepared for the Stockholm Convention on Persistent Organic Pollutants where available (Chapter 3, Table S1). Alternatively, information on DDT bans and restrictions was retrieved from published literature in particular countries lacking an implementation plan. These data were used to calculate the time between sample collections and banning or restriction of DDT. To visualise the data in a manner that allowed all the various factors to be incorporated, we modelled all the data from 15 years before DDT was formally banned and/or restricted, to 40 years after these bans and restrictions (Figure 5). However, for the formal trend analysis exploring the trend in DDT across the different variables and to standardise the data, we used the year in which DDT was banned or formally restricted in each country as 0 and excluded samples collected before the bans or restrictions (n=11 177). However, as there was limited data available from Oceania (n=27 samples), this continent was excluded from models comparing concentrations between continents.

There is a difference of opinion regarding critical DDT (DDE specifically) thresholds in eggs, which lead to eggshell thinning-induced reproductive failure in raptors (Blus, 2011). Investigations by Fyfe et al. (1988) and Noble and Elliott (1990) suggest that individual egg DDE concentrations of between 1.2 to 30 µg/g (wet weight) are associated with eggshell thinning-induced reproductive failure. We therefore contrasted the mean total DDT concentrations of egg samples collected between the 1960s and 2000s (only samples measured in wet weight), to the individual threshold concentrations described by Fyfe et al. (1988) and Noble and Elliott (1990) to determine the proportion of samples that fell above these critical thresholds. While lethal concentrations of DDT in plasma have not been as scrutinised to the extent they have been in egg and lipid rich tissue such as liver, DDE concentration in bird plasma has been found to be significantly correlated to concentrations in the brain (Henny and Meeker, 1981). While some investigations suggest that DDE concentrations in brains exceeding 300 µg/g (wet weight) can be regarded as lethal to various bird species (Stickel et al., 1984), concentrations as low as 223 µg/g were found to cause death in American Kestrels (*Falco sparverius*) (Henny and Meeker, 1981).

Statistical analysis

All statistical analysis and visualisation were conducted using R 3.6.1 (R Core Team 2019). We used a linear mixed effects model from the package lme4 (Bates et al., 2015) to analyse the changes in DDT. All concentrations were converted to parts per million (ppm) as this measurement was most frequently used in historic studies when reporting concentrations. However, ppm is an outdated measurement unit, therefore, all concentrations were reported in µg/g. In studies where measurements were reported in volume (n=12), we have assumed a density close to one (1 ml=1 g). These concentrations were then logarithmically (natural log) transformed to approximate a normal distribution. The (square root) sample size of each concentration was included in the model as a weight; this was done to ensure that high concentrations that were from only a small sample size did not have an undue influence on the analysis, and that more reliable concentrations which are derived from a larger sample size carry more weight in the analysis. Where raw data was used and displayed, we chose to keep all zero values and adjust them by 0.001 to produce a log value. These zero values represent a tangible absence of pesticide concentration in tissue samples, which is what international efforts, both before and after the implementation of the Stockholm Convention, ultimately sought to achieve. While it varied amongst studies, most authors included non-detections as zeros, and we used the mean values to explore the decline in DDT.

The models included five random terms to account for the variance associated with each of these, and the associated influence they may have on the overall patterns detected. These random terms included: species, mass basis of samples (whether the sample was measured as wet weight, dry weight or lipid weight), tissue (egg, liver, or plasma), central tendency measure (arithmetic/geometric mean or median), and compound (DDT, DDE, DDD, *p,p'*-DDT; *p,p'*-DDE; *p,p'*-DDD; *o,p'*-DDT; *o,p'*-DDE; *o,p'*-DDD); to account for the different DDT congeners and isomers. Because we use compound as a random term, all modelled DDT slopes reported in this chapter refers to total DDT-complex or ©DDT. Including these terms as random terms allowed us to combine these different measures into one analysis and allowed us to examine for the slope in relation to time (no. years after the ban) after accounting for the measurement coming from these different types of data. We used five models to test the changes in DDT, fitting time since DDT was banned or restricted, as a permanent fixed effect to each model as well as its interaction with each relevant predictor. Within each model, if there was no significant interaction between our different predictors, we removed the interaction and looked only at the main effects. Our response variable in all models was on the log scale which also allowed us to examine for curvi-linear effects. We inspected diagnostic plots for all models to ensure models were well fitted, ensuring residuals were approximately normally distributed. Model one (M1) explored whether DDT had declined overall globally following its prohibition, this model included only time since ban as a fixed effect. Model two (M2) explored whether declines in DDT differed between continents and included time and the interaction with continent. Model three (M3) explored whether declines in DDT differ between raptors from terrestrial and aquatic dietary guilds and include time and its interaction with dietary guilds. Model four (M4) explored whether declines in DDT differ across a gradient from tropical and temperate regions and included time and its interaction with absolute latitude (i.e. irrespective of whether the site was in the northern or southern hemisphere). Model five (M5) explored whether declines in DDT differ according to average annual precipitation and included time and the interaction with average annual precipitation. Due to the complexity of the models, we used marginal means when testing changes in DDT. Marginal means are means extracted from each of the models that represent averages of all response variables for each level of a predictor variable. Estimated marginal means help provide a more accurate understanding of predictor effects by adjusting for all the different variables in the model. This approach controls for confounding factors and random terms while also accounting for different interactions between variables, providing clearer, unbiased comparisons and interpretations. Prior to running these last two models we examined whether latitude and precipitation were correlated, using Pearson’s Correlation, which suggested only a relatively weak correlation (coefficient: -0.34), and thus both models were run. After running the first model, we additionally conducted a time-series analysis using a suitable subset of data (n=19 studies) from the original data (n=208 studies) used for model M1. For this time-series analysis, we extracted studies (n=19) that reported a minimum of three concentrations from the same region, conducted on the same species, spanning over a minimum of five years, after DDT was banned. This was done as a means of validating our more complex and full analyses, with a conservative number of studies allowing us to compare their slope to the overall trend we found in model M1. We used a mixed model similar to model M1, again using the number of years since ban as a fixed effect which estimated the overall trend in DDT across those studies. In this time-series analysis, we included ‘study’ as a random term in the model to account for variability between studies in DDT concentrations (random intercept) and to allow the effect of ‘year since ban’ on the response variable to vary across studies (random slope). Specifically, the random effects structure (1 + year | study) models a unique intercept and slope for each study, capturing both

inter-study differences in the overall level of the response variable and how these levels change over time (Chapter 3, Figure S1).

RESULTS

As a result of the filtering process discussed above, 96 studies were excluded from Chapter 2, leaving 160 studies, covering 73 species from the original 114 species. We excluded 12 555 raptor samples and extracted data from a total of 15 008 samples. This provided 1 450 estimates of DDT concentrations from three tissue types, with eggs (n=1 011, 70%) being the most frequent, followed by plasma (n=232, 16%) then liver (n=207, 14%). Estimates chosen for the analyses were collected from all continents except Antarctica and South America, between 1969 and 2013, with 370 estimates from Europe and 981 estimates from North America (Figure 1).

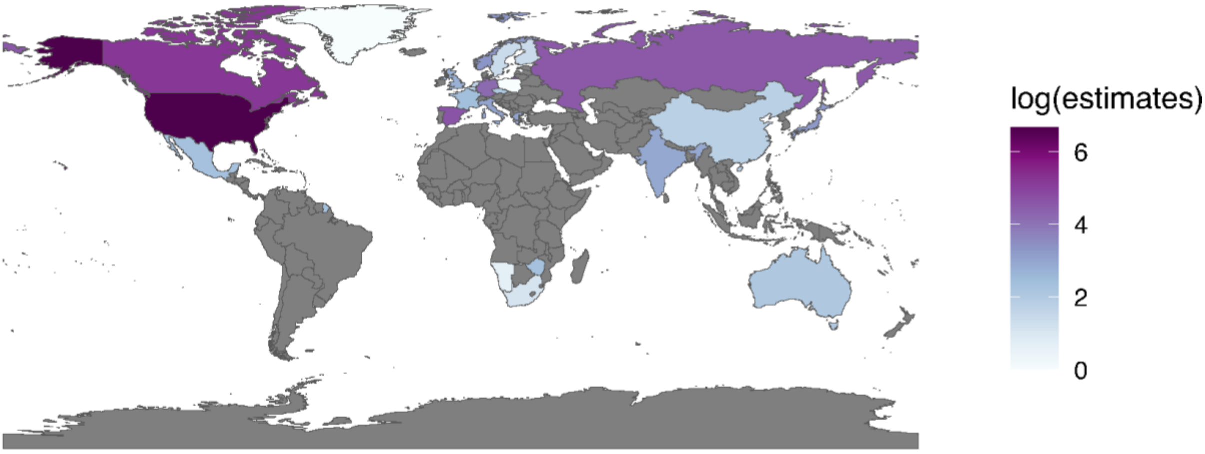


Figure 1: World map illustrating the countries from which all raptor estimates used in this analysis originated. The darker the shade of the country, the more estimates were collected from that country. Countries shaded in grey were not represented in this analysis.

Estimates peaked in 1990, with 530 raptor estimates observed in the 1990s across all continents analysed (Figure 2). Eggs were the most sampled tissue between 1960-1990 with plasma samples becoming the preferred tissue between the 2000s and 2010s (Figure 3).

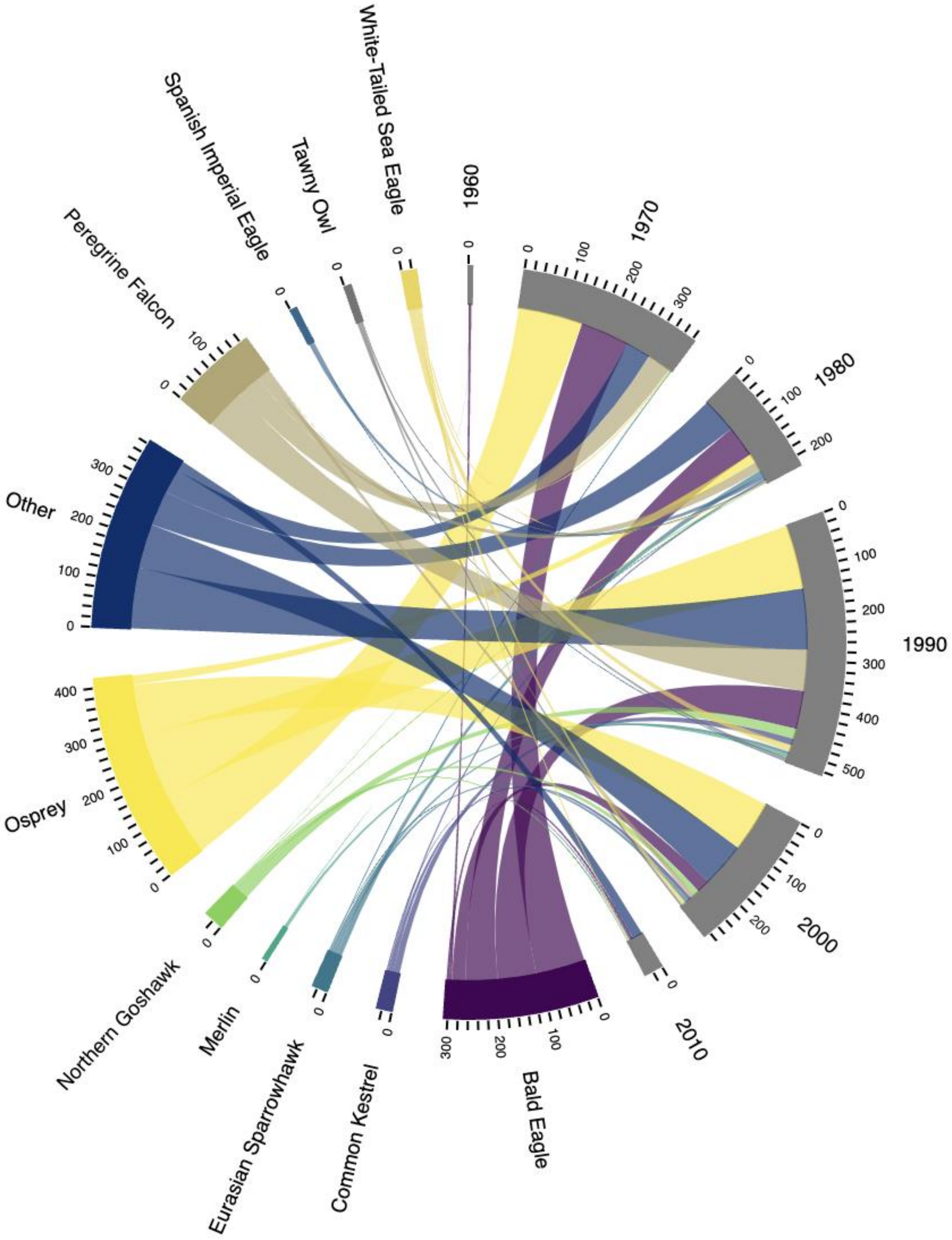


Figure 2: Chord diagram illustrating the ten most sampled species of raptor (and other), and their estimates distributed by decade. The width of each connection strand between the species and decades is proportional to the number of estimates from that species in a particular decade.

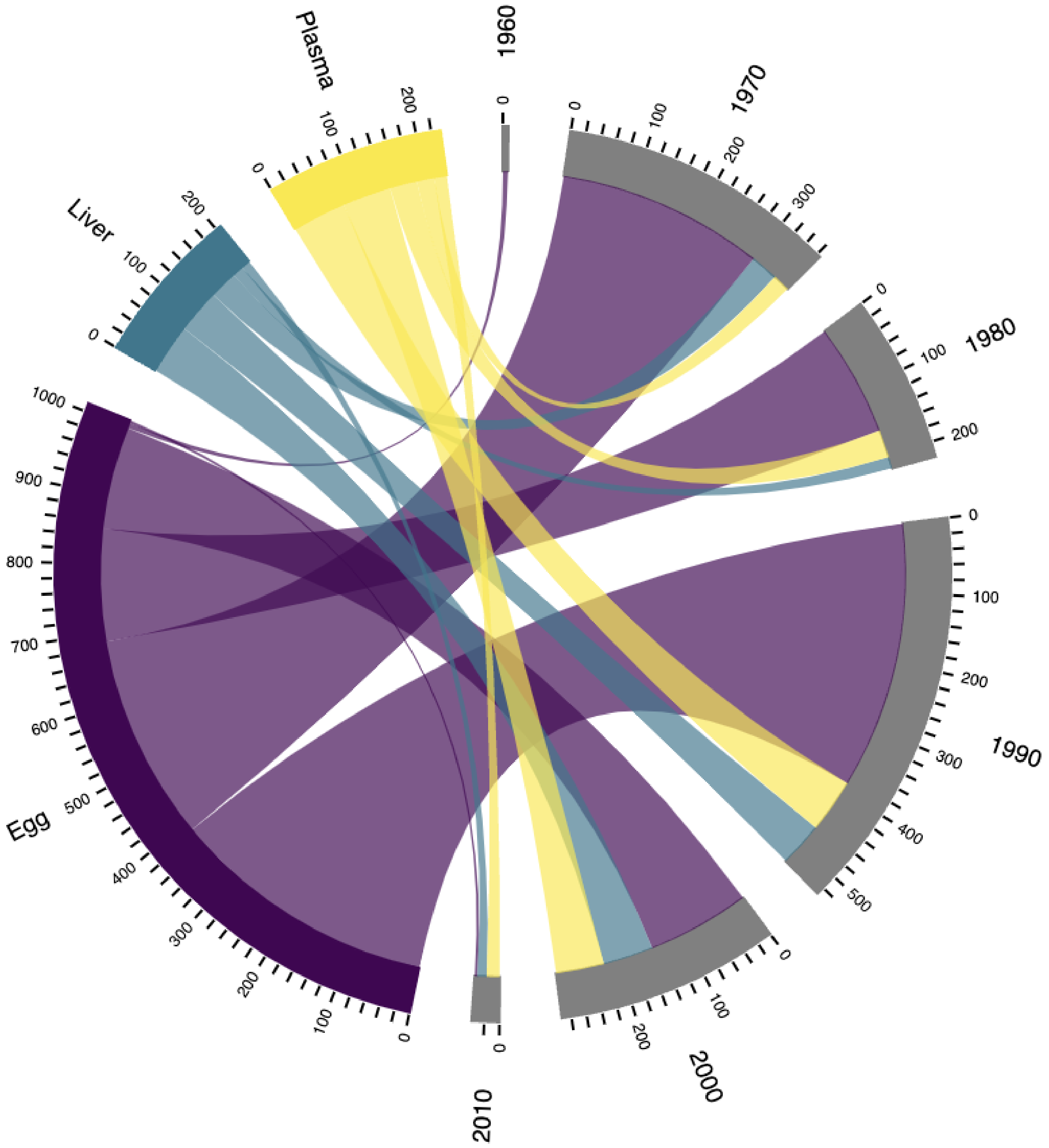


Figure 3: Chord diagram illustrating how the number of tissue estimates have been distributed by decade. The width of each connection strand between tissue types and decades is proportional to the number of tissue estimates observed in that particular decade.

The most common species sampled globally when analysing DDT in raptors has been Bald Eagles (*Haliaeetus leucocephalus*), accounting for 29% of all raptors sampled. The top three species sampled globally, Bald eagle (n=4 411); Osprey (*Pandion haliaetus*) (n=3 100) and Peregrine Falcon (*Falco peregrinus*) (n=1 720), accounted for 62% of all raptors sampled when analysing DDT (Figure 4).

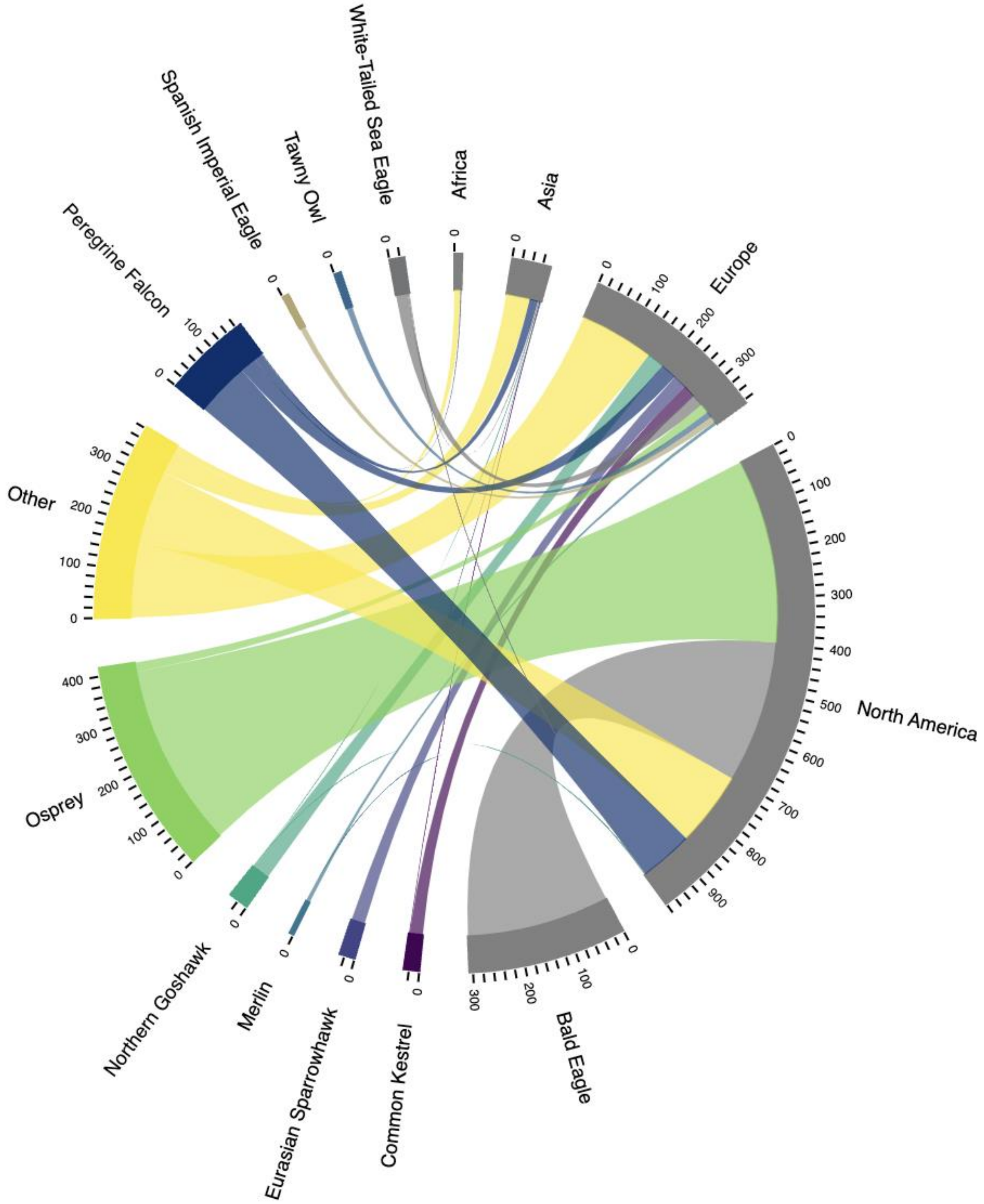


Figure 4: Chord diagram illustrating the ten most sampled species of raptor (and other) and their respective estimates observed globally, distributed across five continents. The width of each connection strand between continents and species is proportional to the number of species estimates observed from a particular continent.

Table 1: GLMM models (M1-M5) exhibiting different hypotheses on the change in DDT in raptors. These models used species, weight basis of samples (whether the sample was measured as wet weight, dry weight or lipid weight), tissue, central tendency measure, and compound (to account for the different DDT congeners and isomers) as random terms.
Time – This effect refers to the time in years since DDT was either banned or restricted.

Model	**Fixed Effects**		**Estimate**	**Std. Error**	**Chisq**	**DF**	**P**
M1	(Intercept)		-2.217	2.094			
	Time		-0.053	0.005	**106.645**	**1**	**<0.001**
M2	(Intercept)		-1.535	2.316			
	Continent	**Asia**	-1.678	1.043	**14.687**	**3**	**0.002**
		Europe	-0.718	1.003			
		North America	-0.136	1.006			
	Time		-0.051	0.005	**98.316**	**1**	**<0.001**
M3	(Intercept)		-1.014	2.223			
	Time		-0.045	0.006	**105.825**	**1**	**<0.001**
	Dietary guilds		-1.060	0.846	2.978	1	0.084
	Time * Dietary guilds		-0.023	0.012	**4.345**	**1**	**0.037**
M4	(Intercept)		-1.251	2.092			
	Time		-0.055	0.005	**111.602**	**1**	**<0.001**
	Absolute Latitude		-0.021	0.007	**8.832**	**1**	**0.003**

M5	(Intercept)	-2.513	2.130			
	Time	0.009	0.018	**101**	**1**	**<0.001**
	Precipitation	0.000	0.000	**9.147**	**1**	**0.002**
	Time*Precipitation	-0.000	0.000	**12.696**	**1**	**<0.001**

Overall, we found a significant decline in DDT following its prohibition, specifically for the Global North (Table 1 – M1, Figure 5). Our more conservative time-series analysis with a subset of the original data, (19 studies, six estimates), also revealed a similar significant declining trend in DDT (Chapter 3, Figure S1, Chapter 3, Table S3).

Initially we aimed to explore whether declines in DDT differed between countries allowing restricted use and those with complete bans. However, there was only one study conducted in countries allowing restricted use after the reintroduction of DDT in 2006. Therefore, we could not ascertain whether this region experienced similar declines to the countries where full bans were in place.

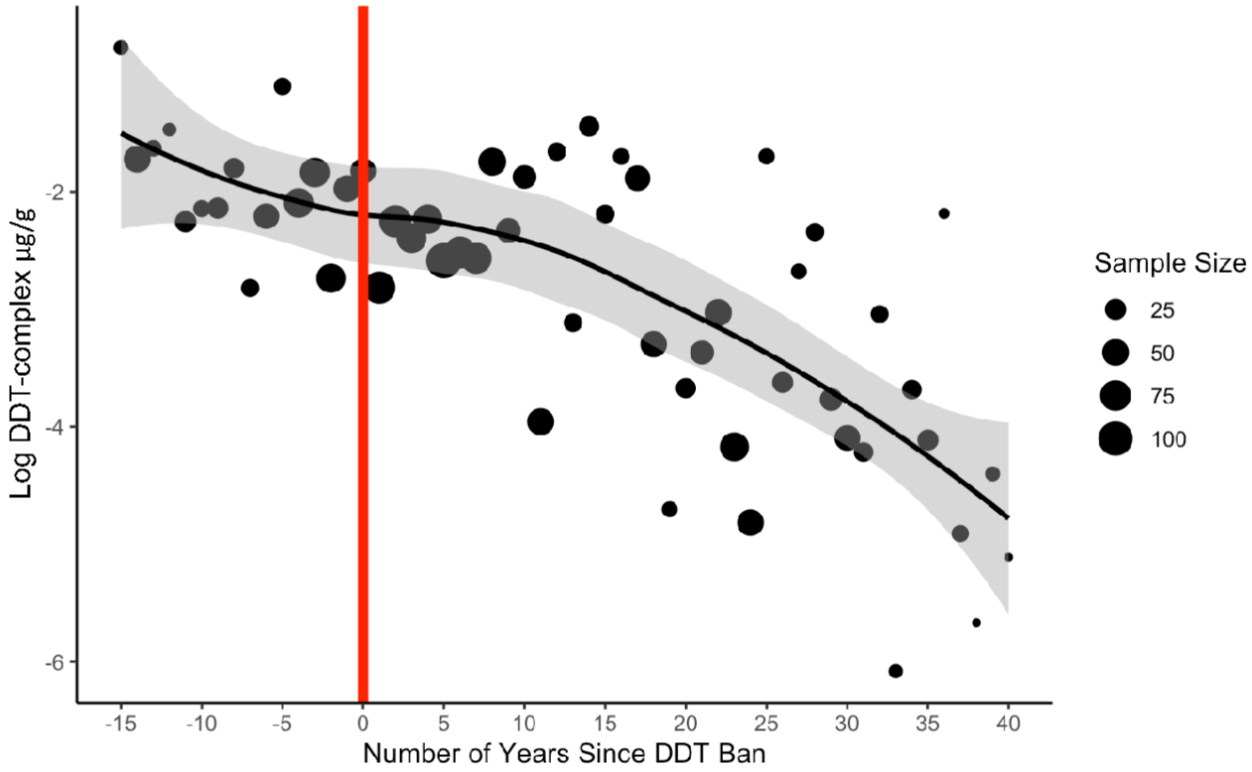


Figure 5: Marginal mean Log DDT-complex representing modelled concentrations of all DDT isomers and congeners, for each year collected from 15 years before DDT was banned to 40 years after DDT was banned globally. This graph represents all the data points used from when DDT was banned locally, irrespective of the 2004 Stockholm Convention enforcement but there are data points from countries allowing restricted use (n=1) included in this analysis. The size of the dots represents the number of samples collected during that particular period, with larger dots representing larger sample sizes. Values are the estimates from a GLMM, with species, weight basis of samples (whether the sample was measured as wet mass, dry mass or lipid mass), tissue, central tendency measure, and compound (to account for the different DDT congeners and isomers) as random terms, and time since ban as the fixed effect, using a loess method to express a best-fit line. There was a significant decline in DDT in raptors as determined via an emmeans comparison (Chapter 3, Table S2).

It took 13 years for DDT to decline by 50%, calculated from when DDT was globally banned. For DDT to further decline to 25% it took 17 years, demonstrating that these declines were non-linear (Figure 6 - inset figure).

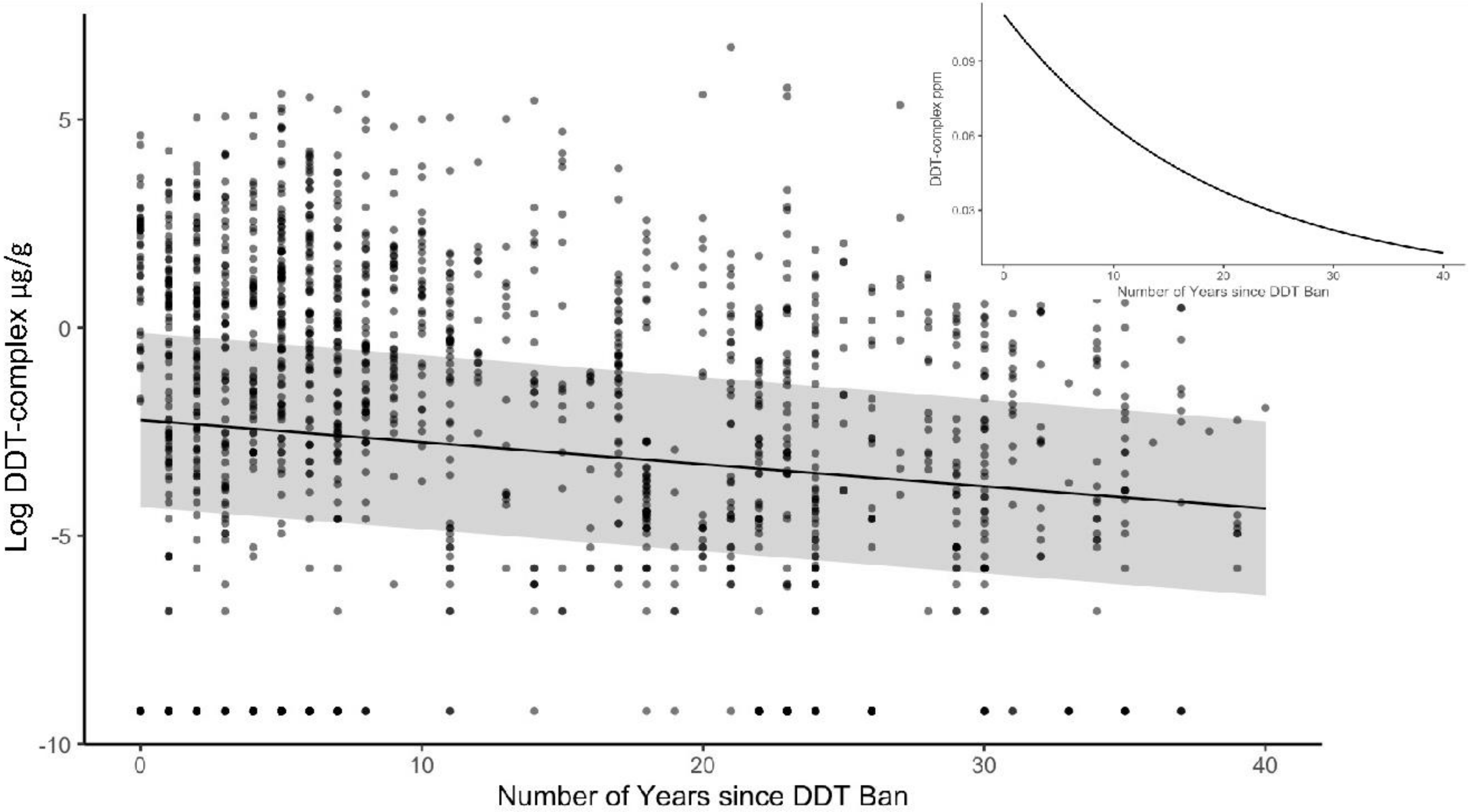
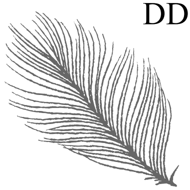


Figure 6: Temporal decline of marginal mean Log DDT-complex which represents modelled concentrations of all DDT isomers and congeners from raptors sampled over 40 years, since DDT was banned or restricted in different countries. Values are the estimate means by year from a GLMM, with species, weight basis of samples (whether the sample was measured as wet mass, dry mass or lipid mass), tissue, central tendency measure, and compound (to account for the different DDT congeners and isomers) as random terms, and time since ban as the fixed effect, using a loess method to express a best-fit line. All dots represent the raw logged data, adjusted by the addition of 0.0001. The embedded graph represents the predicted true DDT slope over 40 years using the same random terms and fixed effects.



Declines in DDT did not vary between continents, with no significant interaction found between continent and time since ban ($\chi2$=6.514; DF=3; P=0.089). However, overall DDT did vary among continents (Figure 7) (Table 1), with Asian raptors having significantly lower DDT concentrations than North American raptors (Figure 10, Chapter 3, Table S1).

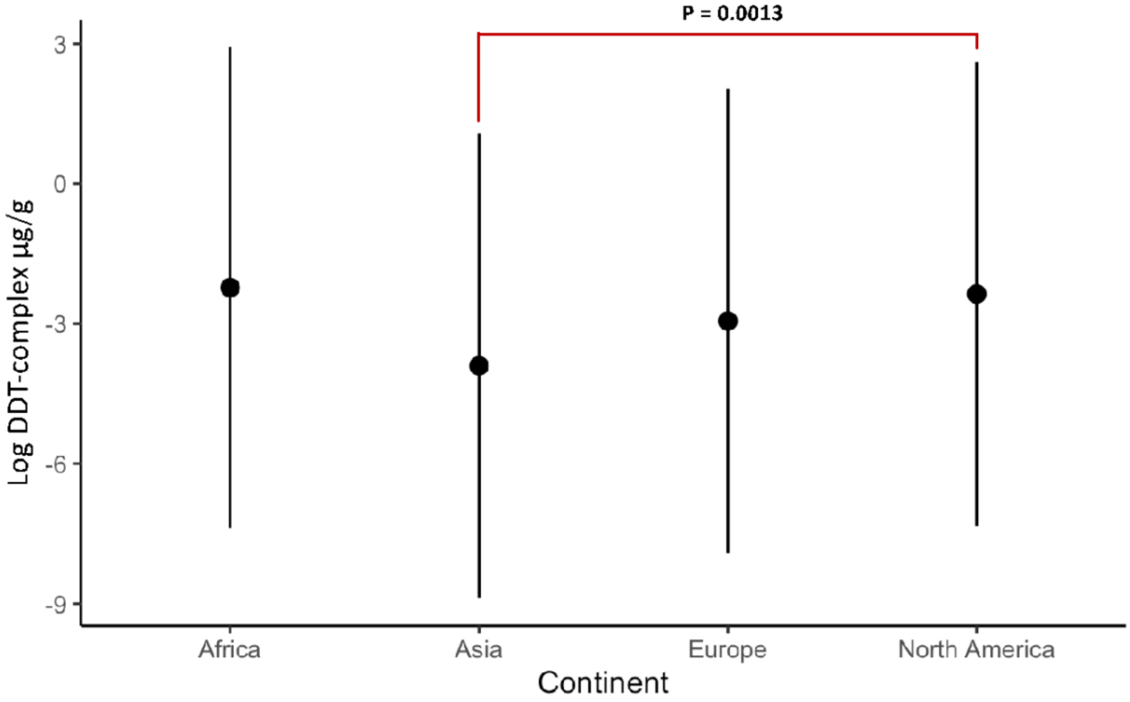


Figure 7: Estimated mean Log DDT-complex which represents modelled concentrations of all DDT isomers and congeners in raptors sampled among the different continents (with 95% CI). Values are the estimates from a GLMM, with species, weight basis of samples (whether the sample was measured as wet weight, dry weight or lipid weight), tissue, central tendency measure, and compound (to account for the different DDT congeners and isomers) as random terms, and time since ban and continent as fixed effects. There was a significant difference between Asian and North American raptors as determined via an emmeans comparison (Chapter 3, Table S1).

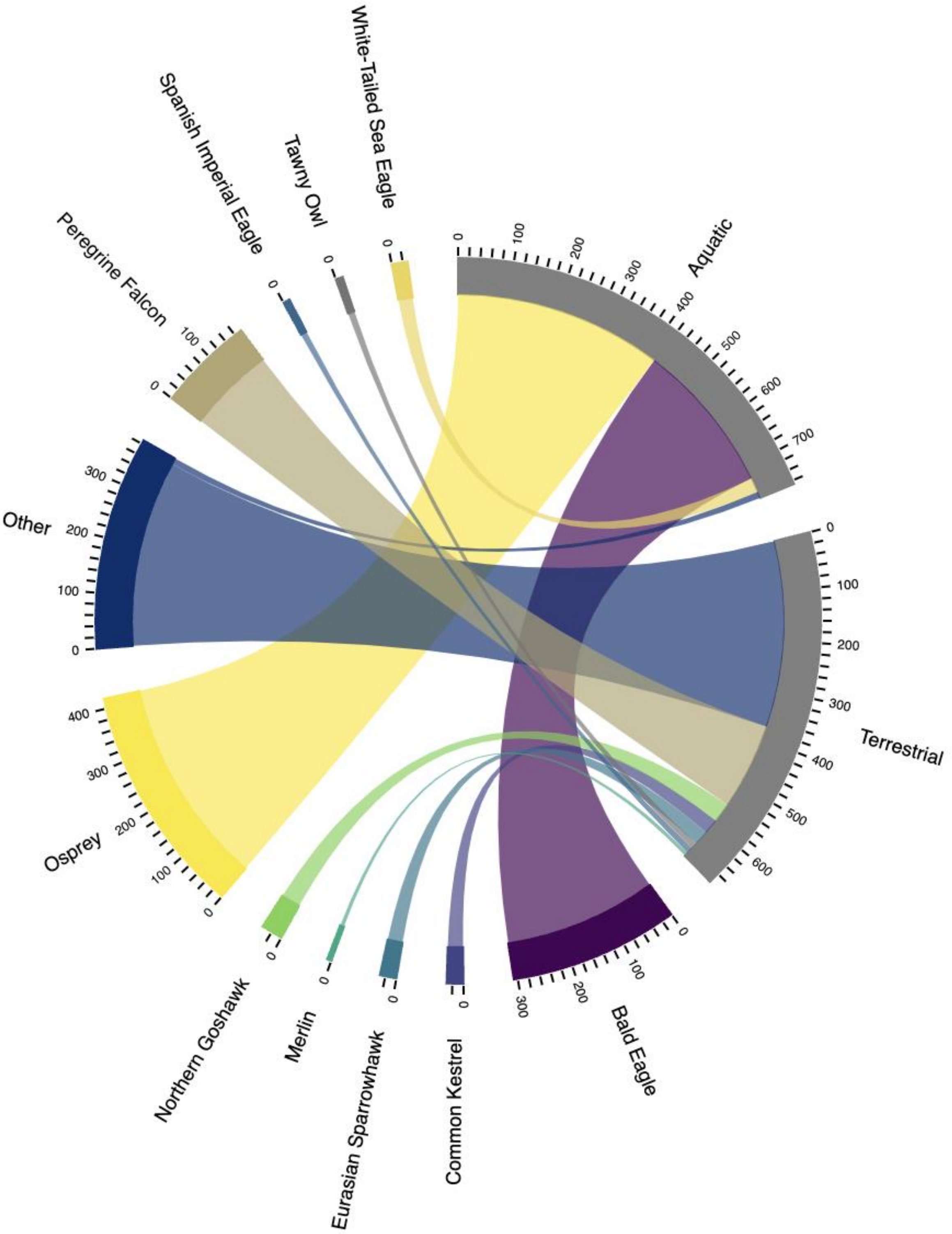


Figure 8: Chord diagram illustrating the ten most sampled species of raptor (and other) and their respective estimates, distributed across the two dietary guilds (Aquatic and Terrestrial). The width of each connection strand between dietary guild and species is proportional to the number of estimates from that species. Most estimates (92%) from the aquatic dietary guild were sampled from North America whereas 48% of estimates from the terrestrial dietary guild were sampled from Europe (Figure 9).

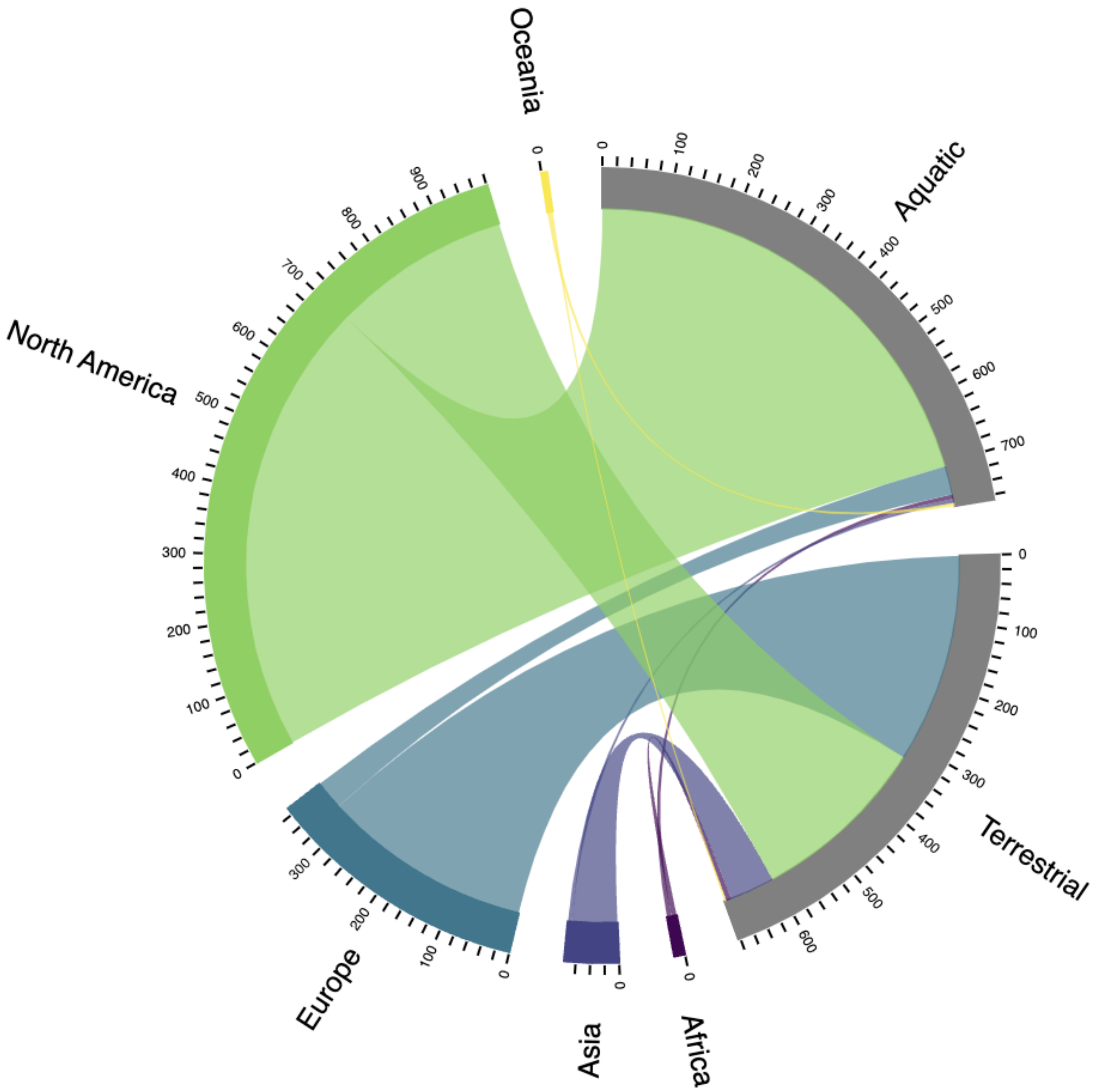


Figure 9: Chord diagram illustrating how the number of dietary guild estimates is distributed amongst five continents. The width of each connection strand between continents and dietary guilds is proportional to the number of estimates from that dietary guild sampled from a particular continent.

Declines in DDT differed between raptor species depending on their dietary guild, with those consuming predominantly terrestrial prey items showing a steeper decline than those whose main prey were predominantly aquatic (Figure 10). In this analysis, the aquatic dietary guild consisted of six species which accounted for 52% of all raptor samples, whereas the terrestrial dietary guild was more diverse, consisting of 67 species accounting for 48% of all raptor samples (Figure 8). The greatest number of aquatic dietary guild estimates was the Osprey (n=418), whereas the greatest number of terrestrial dietary guild estimates (of a single species) was from the Peregrine Falcon (n=174) (Figure 8).

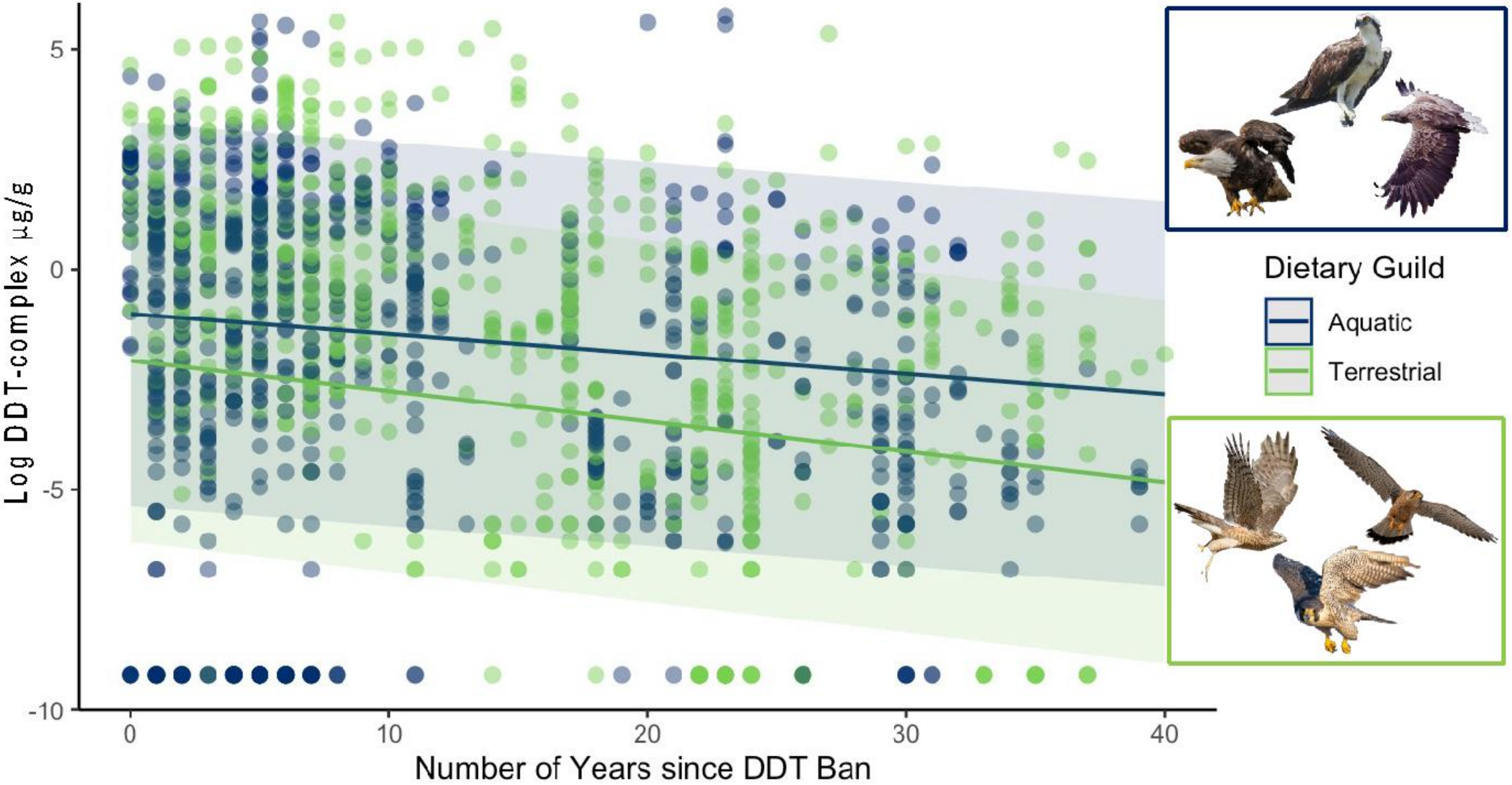


Figure 10: Comparison of estimated marginal mean Log DDT-complex, which represents modelled concentrations of all DDT isomers and congeners between raptors from the aquatic and terrestrial dietary guilds (with 95% CI). Values are the estimates from a GLMM, with species, weight basis of samples (whether the sample was measured as wet mass, dry mass or lipid mass), tissue, central tendency measure, and compound (to account for the different DDT congeners and isomers) as random terms, and time since ban and dietary guild as fixed effects (see M2 in Table 1). Species shown represent examples of the most sampled raptors from the aquatic (top) and terrestrial (bottom) dietary guilds. All dots represent the raw logged data, adjusted by the addition of 0.0001.

Declines in DDT were similar irrespective of distance from the equator, with no significant interaction found between absolute latitude and time since banned or restricted. DDT concentrations were, however, significantly higher closer to the equator (i.e. in more tropical regions) (Table 1 – M4, Figure 11). In contrast to latitude, samples were collected relatively uniformly across the annual precipitation gradient (Figure 12). Most raptor samples were collected in the northern hemisphere, with sample collections peaking around 40° north of the equator (Figure 11). The amount of precipitation did influence the rate of decline in DDT over time (Table 1 - M5), with DDT declining faster in areas with more precipitation (Figure 12)

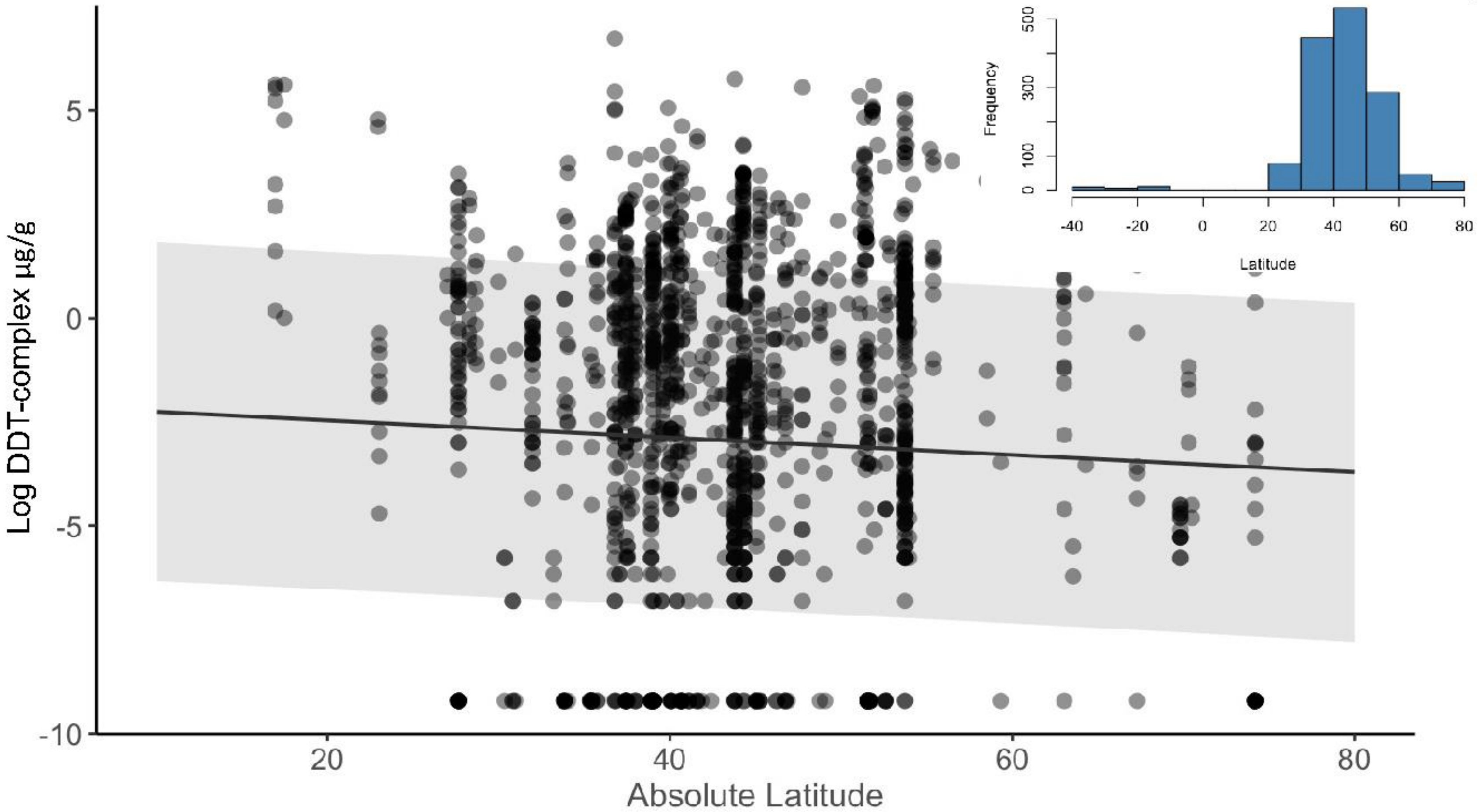


Figure 11: Estimated marginal mean Log DDT-complex which represents modelled concentrations of all DDT isomers and congeners across a latitudinal gradient. Values are the estimates from a GLMM, with species, weight basis of samples (whether the sample was measured as wet mass, dry mass or lipid mass), tissue, central tendency measure, and compound (to account for the different DDT congeners and isomers) as random terms, and time since ban and absolute latitude as fixed effects (see M4 in Table 1). DDT concentrations in raptors closer to the equator (tropical regions) are higher, than raptors further from the equator (temperate regions). The insert in the top right depicts the frequency histogram showing that most raptors were sampled in the northern hemisphere when monitoring DDT. Raptor samples peaked around 40° north of the equator. All dots represent the raw logged data, adjusted by the addition of 0.0001.

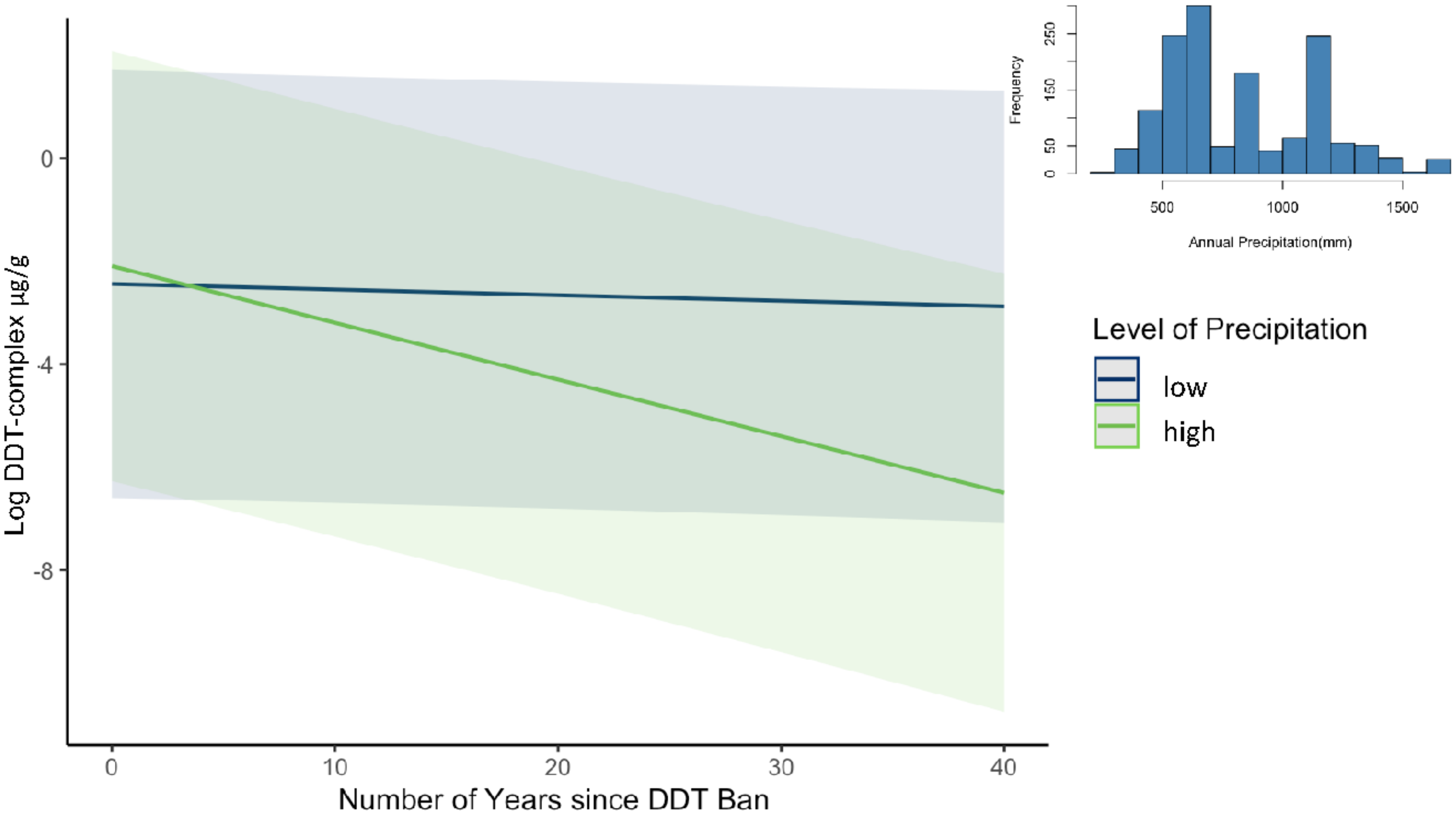
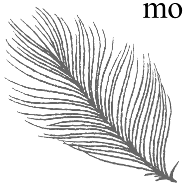


Figure 12: Estimated marginal mean Log DDT-complex which represents modelled concentrations of all DDT isomers and congeners in raptors from regions of high precipitation and low precipitation (with 95% CI). The insert in the top right depicts the frequency histogram showing that raptor samples were collected relatively uniformly across the annual precipitation gradient when monitoring DDT. Values are the estimates from a GLMM, with species, weight basis of samples (whether the sample was measured as wet mass, dry mass or lipid mass), tissue, central tendency measure, and compound (to account for the different DDT congeners and isomers) as random terms, and time since ban and precipitation as fixed effects (see M5 in Table 1). DDT in raptors decrease faster in regions with higher precipitation, with "Low" precipitation representing 285 mm or the lower 10% of modelled concentrations and "High" precipitation representing 1668 mm or the upper 10% of modelled concentrations.



The proportion of egg samples exhibiting DDT concentrations greater than 1.2 µg/g peaked in the 1970s with 44% of observations falling above the lower threshold of 1.2 µg/g. These observations declined gradually with 15% of observations falling above 1.2 µg/g in the 2000s (Figure 13). When contrasting the mean total DDT concentrations of liver samples collected between the 1970s and 2010s to individual threshold concentrations, less than 2 % of observations from the 1990s fell above 100 µg/g (wet weight), with observations from all other decades falling below this critical value (Figure 14). No plasma observations were found to exceed 200 µg/g between the 1970s and 2010s (Figure 15).

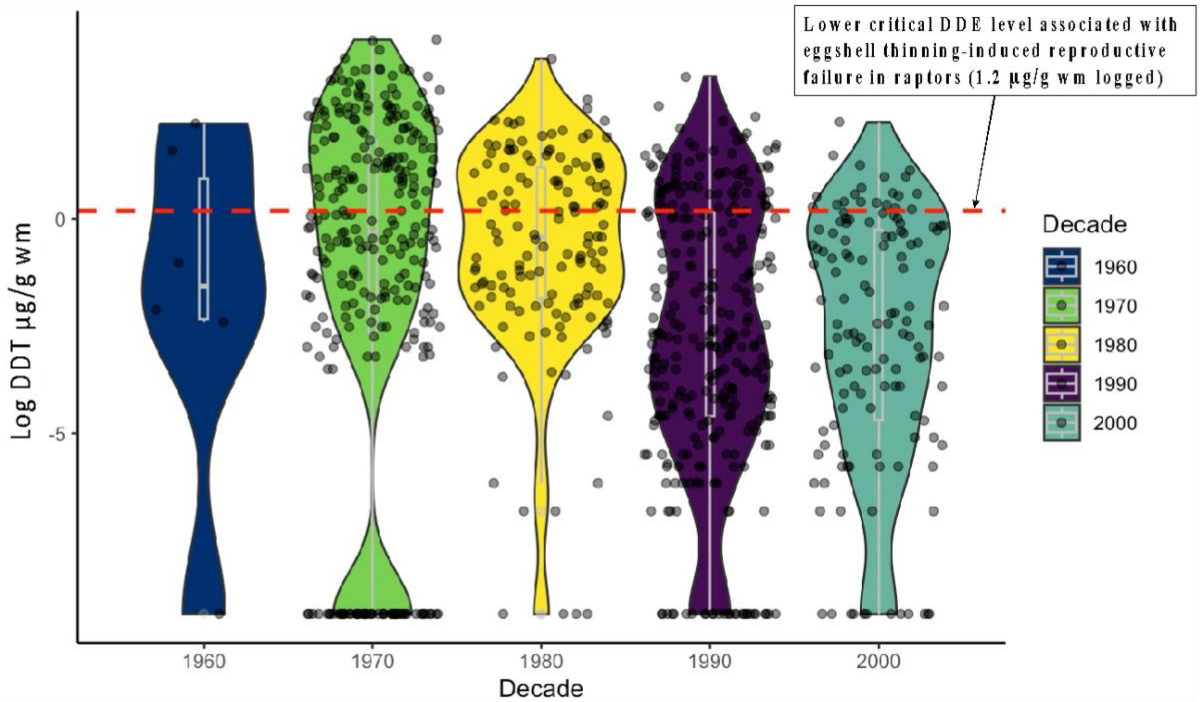


Figure 13: Violin graph showing the proportion of egg sample means with total DDT concentrations, against the lower critical value of 1.2 µg/g (wet mass) in individual eggs, associated with eggshell thinning-induced reproductive failure in raptors (red dashed line). Only mean egg samples measured in wet weight were used in this visualisation, with concentrations naturally logged and displayed per decade. All dots represent the raw logged data, adjusted by the addition of 0.0001.

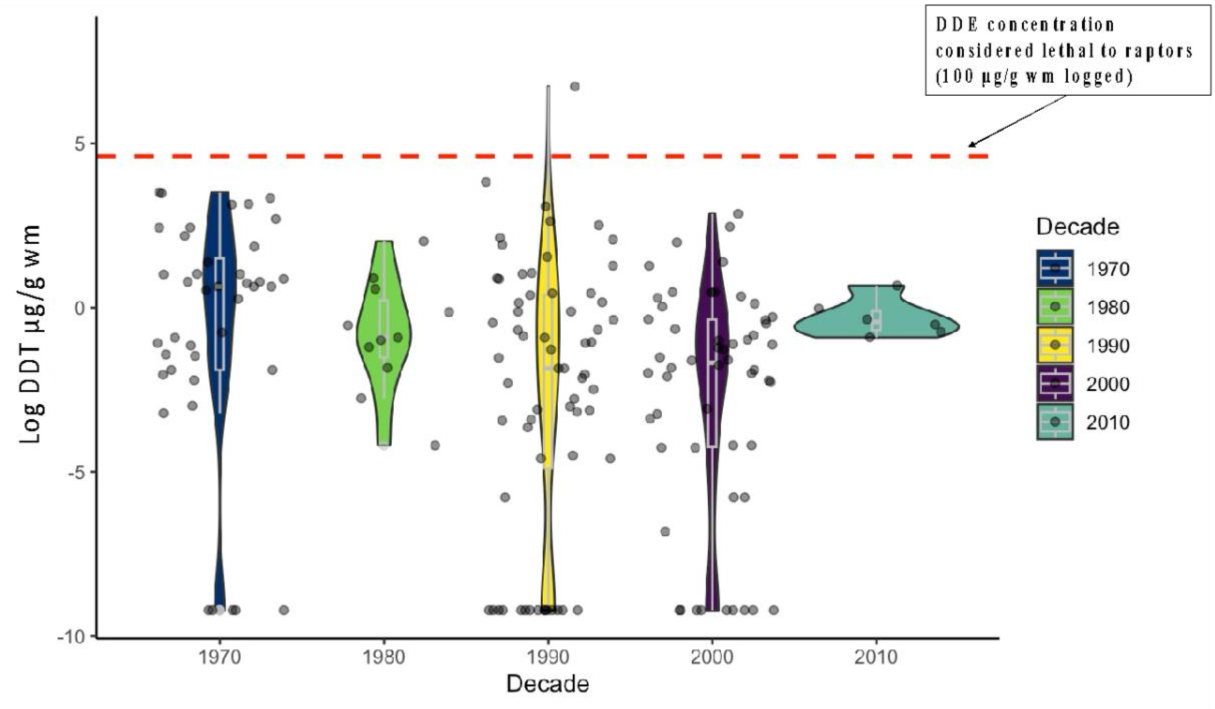


Figure 14: Violin graph showing the proportion of liver sample means with total DDT concentrations, against the critical value of 100 µg/g (wet mass) in individual livers (Cooke, 1982; Blus, 2011), considered lethal in raptors (red dashed line). Only mean liver samples measured in wet weight were used in this visualisation, with concentrations naturally logged and displayed per decade. All dots represent the raw logged data, adjusted by the addition of 0.0001.

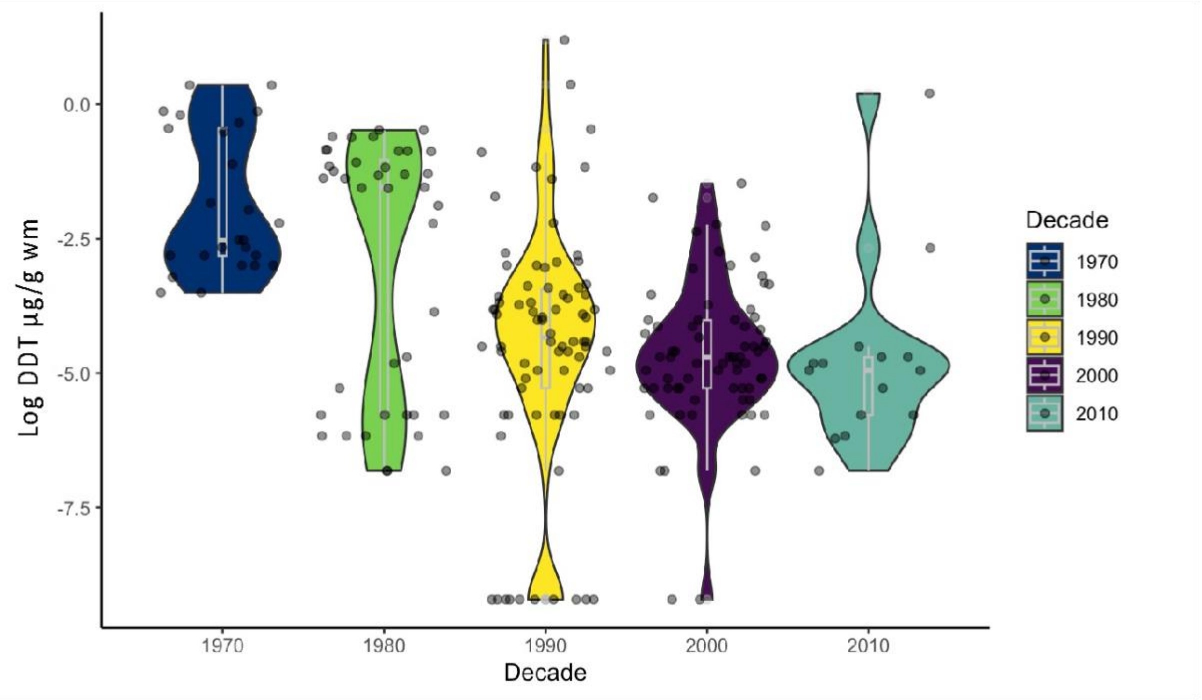


Figure 15: Violin graph showing the proportion of plasma sample means with total DDT concentrations, against the lower critical value of 223 µg/g (wet mass) in individual plasma samples, considered lethal in raptors. Only mean plasma samples measured in wet weight were used in this visualisation, with concentrations naturally logged and displayed per decade. No plasma sample means collected between 1970 and 2010 exceeded individual lethal concentrations of individual plasma samples. All dots represent the raw logged data, adjusted by the addition of 0.0001.

DISCUSSION

By analysing historic measurements, we provided the first global analysis of trends in DDT in birds of prey. From 160 studies spanning more than 40 years (Figure 2), we assessed 1,450 DDT concentration observations in more than 15,000 egg, plasma, and liver samples collected from over 70 different raptor species across four continents. Most of the samples analysed (97%) came from North America and Europe, indicating a strong bias in DDT monitoring in raptors towards this region. This bias is further demonstrated when we realise that most of the top three species, Bald Eagle, Peregrine Falcon, and Osprey, which account for 62% of global raptors sampled, were collected from just North America and Europe. Furthermore, most aquatic raptors were sampled from North America whereas most terrestrial raptors were sampled from Europe (Figure 9).

Global decline in DDT

The significant overall decline in DDT uncovered in our analysis (Table 1 – M1, Figure 5), coincides with its banning and restriction. By visually examining concentrations before and after the various national bans and restrictions on DDT, it was apparent that that higher pre-

ban concentrations persisted in the environment for many years, even after it was banned or restricted, which is reflective of the fact that DDT is a persistent chemical that is slow to break down in the environment (Snedeker, 2001), with a half-life in soils of between two to 15 years (Azzouz et al., 2021). Based on our analysis (M1, Figure 5), it appears that the slope from raptor samples reflected this half-life reasonably well, with our model estimates indicating that DDT took around 13 years to fall to about half of their modelled concentrations at the time of the ban. It is recognised that over time, equipment has become more sensitive allowing the detection of DDT at much lower levels than in the past. However, even with these advancements in technology, we have still observed a decline in DDT, suggesting the decline we have estimated can be considered as conservative. Therefore, in the first instance, our results suggest that global DDT in raptors has continued to decline after the implementation of global mitigation measures and legislation both before and after the Stockholm Convention, particularly in the Global North. However, only one study has been conducted in regions allowing restricted use of DDT following the 2006 reintroduction of this pesticide. Therefore, there is insufficient data available to conclusively testify that declines in DDT in raptors particularly, are in fact, globally representative. This finding calls for substantially more sampling in regions of the world still using DDT. This will help us determine whether DDT is in fact declining at a similar rate in countries with restricted use, as in countries with complete bans. Whilst we found no differences in the declines of DDT between continents or between latitudes, we did find significant differences in DDT, with higher concentrations nearer to the equator. This, however, did not translate to a significant interaction between distance to the equator and decline in this pesticide. We also observed higher modelled DDT concentrations in raptors from North America, compared to Asia, which may be attributed to the earlier, more intense agricultural use of DDT in North America (Li et al., 2006; Wong et al., 2005). Alternatively, it could be linked to the peak of agricultural development in North America coinciding with the period of highest DDT application in that region (Ramankutty et al., 2010). DDT in raptors were found to be significantly higher in North America than in Asia, this could be linked to higher intensity of agriculture in North America, with DDT being applied much earlier in North America than most parts of Asia (Li et al., 2006; Wong et al., 2005), or that agricultural development in North America peaked during the period of highest DDT application (Ramankutty et al., 2010). This great exposure may allow for a longer time to accumulate in that environment. More importantly, the intensive use of DDT in North America, documented by Carson (1962) is most likely responsible for the higher DDT observed in raptors from this region. The literature search for this study was restricted to English on the

Web of Science platform. We, therefore, likely missed papers which may also have had an influence on the difference detected in DDT between North American and Asian raptors, with our search revealing only 10 studies focusing on Asian raptors. Future reviews should try to include non-English literature within existing databases to add further studies in less well sampled regions. An additional limitation is that the use of "Raptor" alone as a search term for identifying literature assessing DDT and dieldrin in birds of prey may have limited the number of literatures detected in this thesis. A solution to this is to include keywords such as "Eagle" or "Falcon", or even " Bird of Prey", as important search terms.

Decline in DDT across habitats

Many studies have suggested that DDT persists longer in terrestrial environments than aquatic ones, primarily due to DDTs ability to bind to soil particles and its low solubility in water (Blaylock, 2005). The half-life of DDT in terrestrial soils can be in excess of 15 years whereas in aquatic sediments and water as little as 1 year and 28 days respectively (Blaylock, 2005; Mansouri et al., 2017; Azzouz et al., 2021). DDT's affinity to soil and insolubility in water, along with its application in agriculture and pest control, would expectedly lead to higher concentrations in terrestrial environments. The higher modelled concentrations and longer persistence of DDT in raptors using aquatic habitats seen in our study was therefore slightly unexpected. However, this finding may occur because, although half-lives of DDT in water and aquatic sediments are shorter than those of terrestrial soils, this pesticide biomagnifies up the food web, accumulating in predators (Grove et al., 2009; Hellou et al., 2013). Our results may support the idea that runoff from terrestrial to aquatic habitats can be an important contributor to aquatic DDT (Arias et al., 2011; Mansouri et al., 2017). Coastal and riverine areas are exposed to DDT through contaminated sediments (from historical and current applications) entering the system through run-off (Loganathan and Kannan, 1991; Hartwell, 2004). Potential prey species (fish and bird) exposed to this DDT; would in-turn contaminate aquatic raptors which depend on such prey. These long-lived predators have slow clearance rates and because they would be feeding on prey that are continuously exposed to DDT from both application (where allowed) and runoff, they are expected to exhibit higher DDT concentrations which then decline slower than terrestrial raptors, because they are continually topped up through runoff and may also be trapped in sediment (Veljanoska-Sarafiloska et al., 2013; Zhu et al., 2019). The biases in DDT monitoring in raptors identified in Chapter 2, however, may have a considerable influence on our results. For example, raptors representing the aquatic dietary guild were dominated by Bald Eagles, comprising 56% of the species in this

dietary guild. Bald Eagles were the second most sampled species globally, and only occur in North America, further biassing the extent to which we view and perceive the distribution of DDT data across aquatic and terrestrial raptors globally.

The influence of latitude and precipitation on DDT

Our analyses suggest that declines have not occurred equally between environments, it appears that declines have happened at a far higher rate in areas with higher precipitation. However, this was not simply explained by precipitation being higher in the tropics as no interaction between distance to the equator and declines in DDT was detected. While much of the Global North has banned the use and production of DDT, many Global South nations have continued the use of DDT in the fight against malaria (Jaga and Dharmani, 2003). Most Global South nations are found in the tropics and sub-tropics, occurring at lower latitudes (Sachs, 2001), therefore, the higher DDT slope we observed in raptors from lower latitudes may, at least in part, be attributed to continued use of DDT in these regions (Harada et al., 2016; Iwata et al., 1993). Our findings are further supported by studies showing that distribution sources of DDT have been shifting or at least expanding to lower latitudes since the early 1980s (Iwata et al., 1993). This shift coincides with the banning of DDT in much of the Global North (Iwata et al., 1993; Hao et al., 2021). The steeper decline in DDT from regions experiencing higher precipitation aligned with our expectations. High precipitation results in moist soils, which may increase revolatilization of DDT into the air (Faroon and Harris 2002). Additionally, high precipitation may lead to increased surface run-off of DDT into aquatic environments (Afful et. al., 2010). Once in the air or in the aquatic environment, DDT is more susceptible to long-range transportation away from deposition sites experiencing high precipitation (Li et al., 2007). Wetter regions also allow for higher levels of bacteria and fungi growth (Nydahl et al., 2013; Talley et al., 2002), which would also speed up the breakdown of these compounds (Aislabie et al., 1997). Furthermore, we observed that, in general, since the 1960s, the proportion of samples that exhibited DDT concentrations greater than critical values established for specific tissues have decreased.

Biases in global DDT monitoring and the value of international cooperation

While we found significant declines in DDT in raptors since it was banned, we must recognise several biases associated with these results. For example, in Chapter 2, we demonstrated that 95% of raptors have been sampled from the Global North. So, one could argue that our findings are overwhelmed by data from this region and are not necessarily global patterns. However, when controlling for continent in our models, the slopes remained similar, and although Global

South samples were far less than the Global North, we did include more than 400 samples, consisting of more than 50 estimates from this region. This is further supported by the fact that no significant interaction was identified between continents. This is, however, negated by the limited number of studies (n=1) and samples collected from the Global South after the WHO formally approved the reintroduction of DDT in 2006 to help control malaria. This lack of data from the Global South may suggest that, while we did demonstrate a significant decline in DDT, the strong bias in sampling towards the Global North, may indicate that these declines are not globally representative. Overall declining trends in DDT are a good indicator of global cooperation in the control of this organochlorine pesticide. However, our findings do still indicate an uneven decline in DDT in raptors utilising different ecosystems and from areas with differing levels of precipitation. Most localised evidence supporting these declines, even before the implementation of the Stockholm Convention, were primarily from developed countries (Muir et al., 1999; Helander et al., 2008). The benefits of using raptors as biomonitors of pesticides and other dangerous contaminants has been well documented, particularly in the Global North. Decades of using raptors as indicators have played a crucial role in shaping international conventions like the Stockholm Convention by providing essential information on the harmful effects of contaminants on the environment and humans.

While our study confirms that global efforts and regulations set forth both before the implementation of the Stockholm Convention and by the Stockholm Convention have had a significant effect on DDT in the environment, it simultaneously affirms the importance and urgency of increasing the effort afforded to monitoring DDT in the Global South where restricted use is allowed. Our study demonstrates the value of large-scale, long-term monitoring, pre and post legislative implementation to monitor the efficacy of regional and international agreements. When we consider the extent of global environmental challenges such as climate change, critical declines in biodiversity, and water scarcity, it is encouraging to demonstrate the value of international conventions dedicated to improving environmental integrity. Throughout the 20th century many conventions have been established and implemented to address global environmental challenges (Roberts et al., 2004). These conventions have often imposed ambitious, overarching goals and objectives that seem difficult to achieve at a global level (Wheeler, 1993). With a result that some international agreements, such as the Convention on Biological Diversity, have failed to meet their intended outcomes (Butchart et al., 2010; Hoffman et al., 2022). There are, however, agreements such as the Montreal Protocol on Substances that Deplete the Ozone Layer, that have been successful in their mandate (McKenzie et al., 2019). By effectively banning chemicals such as CFCs, the Montreal Protocol has helped reduce the depletion of the ozone layer, curbing harmful solar ultraviolet radiation (McKenzie et al., 2019). This chapter can be considered as a valuable contribution to Article 11 of the Stockholm Convention in terms of research on DDT (UNEP, 2023). Furthermore, findings from this chapter correspond to the declines in DDT reported in the 2023 Stockholm Convention Effectiveness Evaluation in the environment over the last three decades (UNEP, 2023.), suggesting that parties to the Stockholm Convention are largely adhering to Article 3 of the Stockholm Convention, and are continuing to adopt measures to control POPs such as DDT (UNEP, 2023). Our findings confirm that DDT bans have been successful in reducing DDT contamination of the environment and wildlife of the Global North, even before the enforcement of the Stockholm Convention on Persistent Organic Pollutants. Therefore, the strict controls outlined by the Stockholm Convention can potentially provide some hope that environmental contamination by DDT and other POPs can be successfully curtailed in the Global South too.

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Chapter 4

Assessing organochlorine pesticide contamination in the migratory Amur Falcon (*Falco amurensis*) in South Africa

Animal Ethics approval number: 2019/V9/AA.

Female Amur Falcon (*Falco amurensis*) being dissected at the Durban Natural Science Museum, to collect fat, muscle, and liver samples for DDT and dieldrin analysis.

ABSTRACT

Organochlorine pesticides such as dichlorodiphenyltrichloroethane (DDT) and dieldrin have been extensively studied in global raptor populations, revealing strong links to various endocrine disorders and reproductive failures. Despite global bans, these synthetic pesticides persist in the environment and accumulate in top predators such as raptors. While resident raptors have been valuable in monitoring local pesticide contamination, migratory raptors offer insights into broader geographic contamination. Most studies have focused on species migrating between North and South America, while far fewer studies have examined raptors migrating between Asia and Africa. We analysed ΣDDT (*p,p’*-DDT; -*p,p′*-DDD; -*p,p′*-DDE) and dieldrin concentrations in fat, liver, and muscle from 100 Amur Falcons (*Falco amurensis*) killed at two roosts by severe hailstorms in their South African non-breeding grounds. We provide the first detailed description of ΣDDT and dieldrin concentrations in the Amur Falcon, while also describing the differences in these pesticide concentrations between tissue, sex, age, and roosting site. We also place these estimates in a global context by comparing the concentrations found in this study with those found in other studies around the globe since 2010. We used a linear mixed effects model (GLMM) to analyse the ΣDDT and dieldrin concentrations between ages, sexes, and tissues of Amur Falcons at the two roost sites. For ΣDDT we found a strong interaction between sex and site, where male falcons from Mooi River exhibited significantly higher ΣDDT concentrations than females. Unlike ΣDDT, we detected a strong site and age difference in dieldrin concentrations, with juvenile falcons collected in Mooi River exhibiting significantly higher average dieldrin concentrations than falcons collected in Newcastle. Dieldrin concentrations in all tissue types were much higher at the Mooi River roost, which is surrounded by more intensive agriculture. Comparison of DDT and dieldrin concentrations with historical measures suggested that the mean concentrations found in this study were generally at the lower end of the range of recent recorded concentrations elsewhere around the globe. While the concentrations of both pesticides were not considered high enough to have lethal effects, the strong site and age differences in dieldrin concentrations may be an indication of potential recent exposure in an area with intensive agriculture to a pesticide that has been banned in South Africa since the late 1980s.

Keywords: DDT; dieldrin; organochlorine pesticides; migratory raptor; Amur Falcon; pesticides

INTRODUCTION

Pesticides have been used for generations to improve agricultural yields and protect humans and animals from diseases (Shepard, 1939; Costa, 1987). The increased urgency to improve food production and safeguard human health during the mid-late 20th century, brought about a surge in the development and production of synthetic pesticides (Tudi et al., 2021; Carvalho, 2017). By the end of World War II, organochlorine pesticides such as DDT and dieldrin became widely available to the public and were used indiscriminately throughout much of the world (Zitko, 2003). While successful at controlling agricultural pests and disease carrying insects, these pesticides had an extremely negative impact on environmental and human health (Carson, 1962; Jayaraj et al., 2016; Rani et al., 2017).

High DDT and dieldrin concentrations can disrupt endocrine, immune, and nervous systems in both humans and wildlife, while also causing reproductive failure, particularly in birds (Deribe et al., 2011; Jayaraj et al., 2016; Gerber et al., 2021). DDT has been negatively correlated to eggshell quality in various raptor species globally, resulting in reduced reproductive success and associated population declines (Ratcliffe, 1967). Dieldrin is a persistent neurotoxic pesticide of particular concern due to its prolonged neurotoxic action (Walker, 2003). Besides the risk of death linked directly to dieldrin contamination (Walker et al., 1967), raptors in Great Britain and elsewhere have been reported suffering from behavioural impairment, deterioration of hunting skills, reduced feeding rate, collision with structures due to sublethal neurotoxic effects (Newton et al., 1992; Elliot and Bishop, 2011). These sublethal effects have the potential of causing reduced reproductive success or death as an indirect result of dieldrin contamination. These OCPs are exceptionally resistant to environmental degradation and persist in the environment for decades (Chopra et al., 2011; Singh and Singh, 2017). Furthermore, DDT and dieldrin are highly lipophilic, accumulating in fat and lipid rich tissues of organisms (Lee et al., 2017). Strong lipophilicity and resistance to environmental degradation allow these OCPs to bioaccumulate in wildlife and magnify up the food web, resulting in their accumulation in top predatory species such as raptors (Deribe et al., 2011; Fremlin et al., 2020).

Due to their place at the top of the food web in various ecosystems, raptors have been successfully used for decades as indicator species to assess DDT and dieldrin globally (Gomez-Ramirez et al., 2014; Espín et al., 2016; Fremlin et al.,2020). While resident raptors are useful in monitoring local contaminant concentrations, most pesticide concentrations in migratory raptors will represent exposure to these chemicals not only on breeding grounds but also, non-

breeding grounds and along migration routes (Hong et al., 2014). While there have been many investigations on OCP contamination in migratory raptors, most have been conducted in North America on species migrating within North America and between North and South America, testing contamination between these regions (Cade et al., 1971; Johnston, 1978; Henny et al., 1982; Becker and Sieg, 1987; Elliott and Shutt, 1993; Elliot et al., 2007). In comparison, there have been far fewer investigations into OCP contamination in raptors migrating between Africa and Asia and even fewer in species overwintering in Southern Africa. In fact, in Chapter 2, we found only four studies assessing DDT and dieldrin in raptors in South Africa in the last 60 years. Steppe Eagles (*Aquila nipalensis*), Pallid Harriers (*Circus pygargus),* and Montagu's Harriers (*Circus macrourus*) are examples of migrants from Asia that over winter in north Africa (Henny, 1998; Espín et al., 2018). While OCPs have been investigated in these species, they were only investigated on their breeding grounds in Asia, with no investigations focusing on potential contamination sources in their African range (Henny, 1998; Espín et al., 2018). We are unaware of any studies that have been conducted on pesticide contamination in migratory raptor species during their wintering period in southern Africa. Furthermore, the habits of migratory species make it particularly difficult to attribute contamination to a specific area (Hong et al., 2014), however, due to the variation in how contaminants are deposited in different tissues, analysing concentrations across different tissue types may provide some insight into when contamination may have taken place (Espín et al., 2016).

The Amur Falcon is a small raptor, which breeds in central Siberia, Mongolia, and northern China and over-winters in eastern and southern Africa during the austral summer (Schäfer, 2003; Symes and Woodborne, 2010; Ganpule, 2011; Bouwman et al., 2012; Meyburg et al., 2017). This falcon species undertakes one of the longest migrations of any raptor species, with a one-way migration of more than 13 000 km (Symes and Woodborne, 2010; Meyburg et al., 2017). Amur Falcons have been studied throughout its migration route from Asia to Africa (Pietersen and Symes, 2010; Symes and Woodborne, 2010; Meyburg et al., 2017; Kaur et al., 2024; Tamir, et al., 2024; Mellone, 2021), however, contaminant data on this species remains limited throughout its range. A large part of the Amur Falcon's diet when breeding and as juveniles, consists of vertebrates but shifts to mainly invertebrates (specifically agricultural pests) in their non-breeding range (Schäfer, 2003; Pietersen and Symes, 2010; Bouwman et al., 2012; Alivizatos and Kassinis, 2021). Thus, we expect that these birds could exhibit some degree of pesticide contamination linked to their agricultural invertebrate diet when in South Africa.

The death of more than 1 000 individuals during severe hailstorms in their non-breeding range, provided a valuable opportunity to contribute to the lack of data on this species but also raptors in the Global South in general (see Chapter 2). This event provided us with in-built controls, with a large dataset for our study (100 individual birds, 3 tissue samples per bird), equally distributed across both sexes and age groups (juvenile and adult), coming from two distinct roost sites. Accumulation and elimination rates of contaminants differ substantially between tissue types; therefore, different tissues should provide information on the accumulation of such contaminants over different time periods (Gomez-Ramirez et al., 2014). For example, Lipophilic contaminants such as OCPs tend to bind to lipids and accumulate in lipid-rich tissues (Lee et al., 2017). As fat contains more lipids than liver and muscle, it is expected that fat samples would exhibit higher concentrations of ΣDDT and dieldrin compared to liver and muscle samples. Fat normally represents an accumulation of contaminants stored over time, with these contaminants being transferred to the bloodstream when birds mobilise fat reserves during periods of high stress, for example, during migration (Espín et al., 2010; 2016). Therefore, concentrations in fat are more likely to represent long-term exposure, which in migratory species, could originate from multiple regions. Concentrations of ΣDDT and dieldrin in blood, however, are generally more representative of recent exposure than those detected in fat (Espín et al., 2010; 2016). Therefore, although liver and muscle are relatively lipid-rich tissues, unlike fat, they represent more recent exposure due to the higher, more consistent transfer of contaminants from the bloodstream, potentially inferring local contamination (Jaspers et al., 2006; 2007; Voorspoels et al., 2006; Espín et al., 2010; 2016). Therefore, by analysing ΣDDT and dieldrin in different tissues we could, at least broadly, narrow down potential contamination sources.

The primary aim of this study was to provide the first detailed account of ΣDDT and dieldrin concentrations in migratory Amur Falcons. As far as we could tell, this study is only the second to assess DDT levels in raptors from countries in the Global South where its use remains restricted (Chapter 3). We expected concentrations of these pesticides to differ between tissues, with fat exhibiting higher concentrations than liver and muscle. We also expected concentrations to differ between age groups due to younger birds having a shorter period in which to accumulate these pesticides than adult birds, which would have experienced multiple migrations to and from their non-breeding grounds. We expected that, should there be a difference in ΣDDT and dieldrin concentrations between sexes, this would most likely be in adults due to female falcons depositing DDT in eggs during the egg-laying process (Lamb et al., 1967; Katagi and Fujisawa 2021). This is particularly the case for the isomer *p.p'* DDE, which is more persistent in the environment than *p.p'*-DDT and *p.p'*-DDD suggesting a longer-term exposure (Yohannes et al. 2017; Naso et al.,2003). However, we did not expect sex-related differences in these pesticides in juveniles, as both sexes exhibit similar diet choice when on the non-breeding grounds (Pietersen and Symes, 2010). Lastly, we expected higher ΣDDT concentrations in falcons from the Mooi River roost, as there is more intensive agriculture surrounding the Mooi River roost than the Newcastle roost (Figure 1). This suspicion arises from evidence of illegal DDT use in South African agricultural areas into the 1990s (Wells and Leonard, 2006). Recent studies on Black Harriers in the Western Cape by Garcia-Heras et al. (2018) has also suggested the possibility of recent illegal use. Furthermore, whilst there may be some localised movements in non-breeding grounds, as suggested by Symes and Woodborne (2010), if most birds remain around the same roost, as the limited tracking data suggests, we might expect differences in contamination levels, linked to local differences in DDT application levels (past or present).

METHODS

Sample collection and study area

We collected tissue samples from Amur Falcons that were killed at two roosts in two separate hailstorms in the KwaZulu-Natal province, South Africa. The first roost near Mooi-River (29.21° S, 30.00° E) was struck on 9 March 2019, killing 836 birds and the second roost near Newcastle (27.72° S, 30.00° E) struck on 21 March 2019, killing 1 155 birds (Figure 1). While these numbers are high, they still represent only a small fraction of the global population, which is estimated at 1 000 000 individuals by Symes and Woodborne (2010). Therefore, this mortality event accounted for only 0.2% of the global population and 1.8% of the total population believed to over-winter in South Africa. India, as the only known DDT producer currently (UNEP, 2023), may influence contamination in these birds as it forms part of the Amur Falcon's migration route and is an important stop-over point before continuing their migration south to Africa (Kaur et al., 2024; Tamir, et al., 2024). These falcons are particularly vulnerable to the large-scale land transformation and pesticide use associated with the agricultural sector in their South African range (Symes and Woodborne, 2010; Alexander and Symes, 2016; BirdLife International, 2023). This economic sector in South Africa utilises a wide variety of pesticides, which historically included DDT and dieldrin (Quinn et al., 2011). While these OCPs have been banned or severely restricted in South Africa, their persistence in the environment, continued use (specifically DDT for malaria control), and potential illegal

use, has led to continued contamination in wildlife, including raptors (Wells and Leonard, 2006; Garcia-Heras et al., 2018; Gerber et al., 2021; Leighton et al., 2022; Bornman et al., 2022).

We used a South African country shapefile (igismap.com) on which we overlaid the South African National Landcover (SANLC) 2020 raster to create a land cover map for the two roost sites, which characterised the land uses surrounding each roost (Figure 1). All data for the map is in GCS datum EPSG:4326 WGS84 CRS (Coordinate Reference System). Using Movebank (movebank.org), we visually inspected movements of satellite tracked Amur Falcons around known roost sites in South Africa, to determine how far from these roosts the birds can be expected to forage. Most fixes were clustered at approximately 25 km around known roost sites; therefore, we established a 25 km buffer around each roost site to identify the most prominent land cover type surrounding each roost. While both roost sites were dominated by grasslands within the 25 km buffer (60% for Newcastle and 52% for Mooi River), they differed in other aspects of land cover, specifically the proportion of cultivated croplands. The Newcastle roost was surrounded by less cultivated cropland (12% cropland cover within the 25 km buffer) than the Mooi River roost (19% cropland cover within the 25 km buffer) (Figure 1).

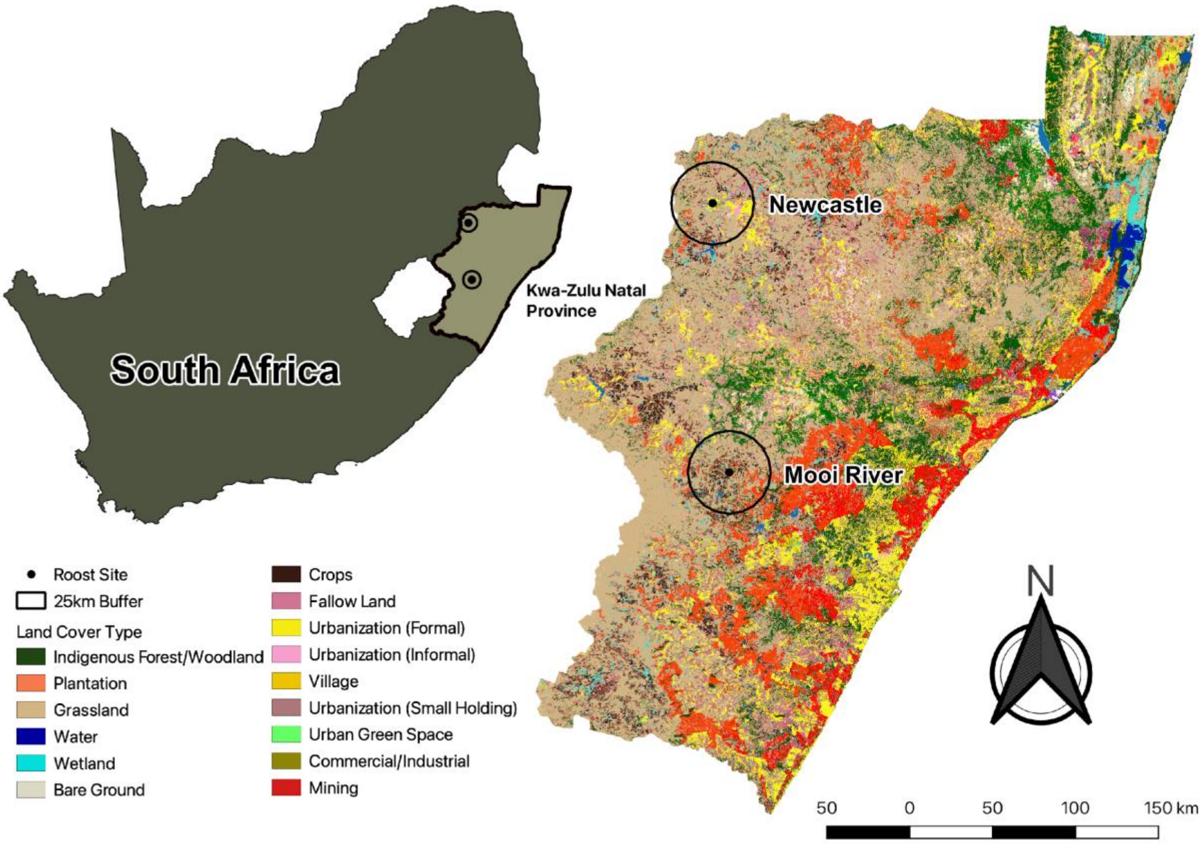

Figure 1: Map of South Africa indicating the two Amur Falcon roost sites in the KwaZulu-Natal province affected by severe hailstorms during March 2019. The 25 km radius buffer around each roost site was calculated from the majority of GPS fixes from satellite tracked Amur Falcons around a roost site while in South Africa. The enlarged portion of the map shows the land cover of the KwaZulu-Natal Province, with the Newcastle roost surrounded by a higher proportion of natural grass cover and a lower proportion of cultivated cropland than what is found around the Mooi River roost. The land cover data for this map was retrieved from the South African Department of Forestry, Fisheries and the environment (last accessed 23 January 2024).

Carcasses were collected from each roost within 48 hours after each storm by members of the FreeMe Wildlife rehabilitation team and the Durban Natural History Museum. Carcasses were transported to the Durban Natural Science Museum in KwaZulu-Natal, where all dirt and debris was washed from the carcasses using tap water. Carcasses were thoroughly dried using hair dryers, thereafter, packed individually into plastic bags and then into plastic lined cardboard boxes and frozen within 24 hours of collection, until tissue extraction, which was conducted

within two months of freezing. Amur Falcons are highly sexually di-chromatic (Piross et al., 2015), making it easy to differentiate between sexes using plumage. We sampled carcasses that were aged and measured in the study by Adekola et al. (2021) and therefore, used the two age classes from that study (adult and juvenile). We selected 100 Amur Falcon carcasses for this study, which were divided equally across site, sex, and approximately equally between age classes (Table 1).

Table 1: Mean, standard deviation and range of mass and wing lengths of 100 individual Amur Falcons distributed approximately evenly across site, sex, and age.

Site	Sex	Age	Mass mean ± SD range	Wing Length mean ± SD range	Number of Individuals
Mooi River	Male	Juvenile	140.23 ± 9.12 121.30 – 154.90	232.08 ± 5.20 220.00 – 242.00	12
Mooi River	Male	Adult	146.72 ± 9.33 134.60 – 171.50	239.23 ± 5.39 231.00 – 248.00	13
Mooi River	Female	Juvenile	150.60 ± 11.43 130.00 – 173.90	234.86 ± 4.84 228.00 – 243.00	13
Mooi River	Female	Adult	160.58 ± 8.78 136.60 – 173.20	241.00 ± 6.32 229.00 – 250.00	12
Newcastle	Male	Juvenile	136.72 ± 12.58 109.70 – 152.80	233.23 ± 6.80 220.00 – 245.00	13
Newcastle	Male	Adult	139.32 ± 8.73 125.10 – 155.10	239.59 ± 5.26 228.00 – 245.00	12
Newcastle	Female	Juvenile	137.65 ± 7.84 125.90 – 152.80	238.09 ± 4.63 231.00 – 245.00	12
Newcastle	Female	Adult	152.60 ± 8.04 140.10 – 167.10	238.75 ± 5.89 230.00 – 245.00	13
TOTAL					**100**

Sample processing and organochlorine pesticide determination

Fat, liver, and muscle samples were collected from each Amur Falcon carcass for ΣDDT and dieldrin analyses (Espín et al., 2016; Quadri-Adrogué et al., 2021) (Table 2).

Fat was collected from around the stomach, liver, and abdominal cavity using a sterile scalpel and tweezers. The fat was then stored in labelled polyethylene containers. The entire liver was excised from each bird and divided roughly in half. One half was stored, uncovered, in labelled polyethylene containers and the other half was used in a different analysis. The same process was followed for pectoral muscles, of which one lobe (left or right) was collected. Once excised and packaged, all samples were weighed to determine wet weight, and then were frozen at -20º C until virus inactivation and drying was achieved as per the requirements of the Spanish Ministry of Agriculture, in an attempt to minimise the spread of potential diseases across international borders (Jaspers et al., 2006; Taggart et al., 2006; Ansara-Ross et al., 2013). Additionally, samples were heated at 56º C for 60 minutes as per instructions from the Spanish Ministry of Agriculture to ensure potential virus inactivation (Table 2). After virus inactivation, the samples were again kept frozen at -20º C until lyophilisation. Samples were lyophilised using a VirTis Benchtop Pro Freeze Dryer (SP Scientific). The frozen samples were placed in the lyophiliser in labelled glass containers and the cover put in place. The condenser temperature was -60º C at vacuum and the samples were lyophilised for 48 hours. After 48 hours, the vacuum was released, and each sample was weighed again to determine dry weight before being stored in labelled polyethylene containers at room temperature until analysis (Table 2).

Table 2: Average sample masses across both sample sites (Newcastle and Mooi River), in grams wet mass (wm) before heating for virus inactivation and in grams dry mass (dm) after lyophilisation.

Tissue	Average Sample Mass Before Drying (g wm)	Standard Deviation	Average Sample Mass After Drying (g dm)	Standard Deviation
Fat	4.53	2.31	3.81	1.75
Liver	1.50	0.41	0.84	0.24
Muscle	7.97	1.07	2.75	0.48

* g wm – grams wet mass, g dm – grams dry mass

Organochlorine Analysis and Quality Control

ΣDDT and dieldrin concentrations were determined following the extraction method described by Dulsat-Masvidal et al. (2023). Prior to analysis, the dried muscle and liver samples were homogenised with a ball mill (MM400, Retsch) (Buck et al., 2020) to produce a homogenous powder. Fat samples were homogenised using a glass tissue homogenizer, because this tissue becomes oily once lyophilized and thus the most efficient way to dissolve this oily fat is with friction caused between the external glass tube and embolus. Samples containing 0.5 g liver, 0.5 g muscle, were subjected to extraction with 10 ml hexane: dichloromethane at a ratio of 1:1 each. Each sample was then vortexed for 1 minutes and ultrasonicated for 10 minutes - this procedure was repeated 3 times without changing the solvent. Thereafter, the samples were centrifuged for 10 minutes at 1 034 rcf and the supernatant was collected. In the case of fat, the extract from 0.2 g of homogenised sample and internal standards solution was centrifuged and collected. Extracts were concentrated to 1 ml of hexane: dichloromethane (1:1). The following clean-up procedure was the same for the extracts obtained from muscle, liver and, fat tissues which consisted of the purification with Bond Elut Florisil cartridges (1 g/6 ml, Agilent Technologies) using 5 ml of hexane:dichloromethane (1:1) as conditioning solvent. Then, the concentrated extract (1 ml) was passed through the cartridge and eluted twice with 5 ml hexane:dichloromethane (1:1). Finally, 0.5 ml of iso-octane were added to the sample extract before solvent evaporation under N_2 stream at 37° C and redissolved in 600 µl of cyclohexane: ethyl acetate (9:1) and transferred to a chromatography vial. This extract was analysed by gas chromatography coupled to a triple quadrupole mass spectrometer (7 000D TQ series Agilent Technologies). The transitions used are described in Chapter 4, Table S1. Blanks (without sample) and chicken liver and muscle samples spiked with Pesticide Mix 13 (Dr Ehrenstorfer)

were processed in each batch of extractions to determine the precision and accuracy of the method. Calibrations we performed with two pesticide mixtures (Pesticide Mix 13, Dr Ehrenstorfer; and Certified Reference Material nº 47 426). The average recovery obtained for DDTs and dieldrin were within the range of 87 - 113% (Chapter 4, Table S2), additionally, the LOD and/or LQ per isomer has been reported in the appendices, Chapter 4, Table S2.

Statistical analysis

All DDT and dieldrin concentrations were originally measured and recorded in nanograms per gram of sample (ng/g), using dry mass (dm) as the weight basis of the sample. In addition to DDT and dieldrin concentrations, we recorded the lipid fraction for each sample. The lipid fraction of a sample represents the components of the sample that are not water-soluble and includes triglycerides, fatty acids and of particular importance for our analysis, lipids (Cox and García-Palmieri, 1990). When analysing DDT, we combine all isomers (*p,p′*-DDT; *p,p′*-DDD; *p,p′*-DDE), and report the findings as ΣDDT. However, it is important to note that the analysis is principally a *p,p′*-DDE analysis, with *p,p′*-DDE concentrations making up the majority of the ΣDDT concentration from both sexes and both sites (Table 3, Figure 2). Results from the Amur Falcons were converted from ng/g dm to µg/g dm as the most contemporary measurement in toxicology (1 ng/g = 0.001 µg/g). The falcon carcasses were collected at different times of day, and over multiple days. This increased the risk of carcasses losing fluid at varying rates, thus introducing variation in wet mass of the samples. For this reason, the decision was made to express all concentrations in dry mass in order to avoid variability. However, when comparing ΣDDT and dieldrin concentrations in Amur Falcons to historical data from raptors from other parts of the world, only historical concentrations reported in lipid mass (lm) were used. Historical samples reported in anything other than µg/g were converted to µg/g to allow comparison between our Amur samples and historical samples (see Chapter 3).

All statistical analysis and visualisation were conducted using R 3.6.1 (R Core Team 2019). We used linear mixed effects models from the package lme4 (Bates et al., 2015) to analyse the interactions between ages, sexes, tissues, and sites for ΣDDT and *p,p′*-DDE separately. However, due to more than 90% of *p,p′*-DDT and *p,p′*-DDD values being zero, we were unable to model the interactions of the above variables for these two isomers. All concentrations were logarithmically (natural log) transformed before modelling to approximate a normal distribution.

We determined a body condition score for each falcon using a mass-to-wing length ratio by applying residuals of a linear model of the body mass of each falcon, regressed on the length of the left wing (Labocha and Hayes, 2012; Jirinec et al., 2021). This method helps to control for differences in pesticide concentrations potentially driven by body condition between sexes (Labocha and Hayes, 2012; Jirinec et al., 2021), as we found females to be in better condition than males. The models included individual as a random term to account for the multiple tissues coming from the same individual bird, and the associated influence it may have on the overall patterns detected. We used a single model for each ΣDDT, dieldrin, and *p,p'*-DDE analysis. Each model investigated the interactions between the relevant pesticide concentration in each Amur Falcon and the different predictors (sex, age, tissue type, and sample site) while controlling for body condition of each falcon and lipid fraction of each sample (as fixed effects). Controlling for lipid fraction can be important, as individual falcons may have varying amounts of lipids, and this may result in differences in the distribution of lipophilic pesticides (Elliott and Norstrom, 1998). Furthermore, different samples from individual falcons are likely to have varying amounts of lipids, particularly as a result of fat mobilisation (Ulfstrand, 1972; Ishikawa, et al., 2015), potentially skewing the results if not controlled for. We inspected diagnostic plots for all models, which indicated a good model fit, as residuals were normally distributed. It is important to note that all non-detects were recorded as zero. Additionally, to ensure these non-detects were appropriately incorporated into the models, the zeros were transformed by adding the detection limit, thus allowing for their inclusion in the statistical analysis. When providing descriptive statistics, we excluded samples from two falcons, both from Newcastle, which were large outliers, exhibiting approximately 100 times higher ΣDDT concentrations than all other falcons. However, these outliers were included in the overall analysis.

Historical ΣDDT Comparison

We compared the mean concentrations of ΣDDT in the Amur Falcon samples collected in 2019 with historical mean concentrations from the same tissues in raptors worldwide, collected between 2000 and 2011 (12 years) as analysed in Chapter 3. This historical range was chosen as it was the most recent record of both DDT and dieldrin concentrations in raptors, measured in a manner comparable to the Amur Falcon samples (samples measured using lipid mass as the weight basis). To enable a meaningful comparison, we converted all our Amur Falcon tissue samples to a lipid weight basis to match the historical samples, which were captured in lipid weight. The conversion method used was as follows:

$$DDT\ concentration\ (\mu g/g\ lm)\ =\ \frac{DDT\ concentration\ \mu g/g\ dm}{Lipid\ Fraction}$$

Any historical samples measured in either ng/g (nanograms per gram) or mg/kg (milligram per kilogram) were converted to µg/g (microgram per gram) (1 ng/g = 0.001 µg/g; 1 mg/kg = 1 µg/g).

RESULTS

All birds and all tissue samples with the exception of three liver samples from Mooi River contained quantifiable concentrations of ΣDDT. We recorded a mean ΣDDT concentration of 0.43 µg/g dm (SD=0.64) across all tissues in Amur Falcons from Newcastle and a mean ΣDDT concentration of 0.57 µg/g dm (SD=0.84) across all tissues in Amur Falcons from Mooi River, with *p,p'*-DDE concentrations making up the majority of the ΣDDT concentrations (Table 3, Figure 2). In addition, nearly 90% of all birds contained quantifiable dieldrin concentrations (Table 4). Whereas all falcons sampled from Mooi River contained quantifiable dieldrin concentrations across at least one of the three tissues sampled, with a mean of 0.28 (SD=0.10) across all tissues, whereas in Newcastle, 80% of falcons contained quantifiable dieldrin concentrations across tissue samples, with a mean of 0.01 (SD=0.06).

Table 3: Mean *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT concentrations ± standard deviation measured in µg/g d/m from 100 individual Amur Falcons, divided roughly between male, female, juvenile, and adult birds between Mooi River and Newcastle roost sites. Two outliers were excluded from this table. Two outliers were excluded from this table. One juvenile male and one adult female, both from Newcastle. The juvenile male exhibited *p,p'*-DDE concentrations in fat of 101.05 µg/g d/m and the adult female exhibited *p,p'*-DDE concentrations of 63.83 µg/g d/m.

***Site**	**Tissue**	**n**	**Adult Female**			**n**	**Juvenile Female**			**n**	**Adult Male**			**n**	**Juvenile Male**		
			p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT		*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT		*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT		*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT
			X ± SD	X ± SD	X ± SD		X ± SD	X ± SD	X ± SD		X ± SD	X ± SD	X ± SD		X ± SD	X ± SD	X ± SD
MR	Fat	12	0.94 ± 0.86	0.06 ± 0.12	0	13	1.34 ± 0.66	0.07 ± 0.14	0	13	1.84 ± 1.49	0.04 ± 0.07	0	12	2.07 ± 1.95	0.05 ± 0.07	0 ± 0.01
MR	Liver	12	0.02 ± 0.02	0	0	13	0.03 ± 0.02	0	0	13	0.05 ± 0.05	0	0	12	0.05 ± 0.06	0	0
MR	Muscle	12	0.05 ± 0.03	0	0	13	0.06 ± 0.04	0	0	13	0.07 ± 0.05	0	0	12	0.10 ± 0.08	0	0

NC	Fat	13	1.06 ± 0.72	0.02 ± 0.06	0.01 ± 0.03	12	1.31 ± 1.21	0	0.01 ± 0.02	12	1.25 ± 0.71	0.02 ± 0.05	0.01 ± 0.03	13	1.27 ± 0.86	0.02 ± 0.08	0
NC	Liver	13	0.02 ± 0.01	0	0	12	0.02 ± 0.01	0	0	12	0.02 ± 0.01	0	0	13	0.02 ± 0.01	0	0
NC	Muscle	13	0.03 ± 0.01	0.02 ± 0.02	0.02 ± 0.01	12	0.03 ± 0.02	0.01 ± 0.02	0.02 ± 0.01	12	0.03 ± 0.01	0.02 ± 0.02	0.02 ± 0.01	13	0.03 ± 0.02	0.01 ± 0.02	0.01 ± 0.01

*MR – Mooi River; NC - Newcastle

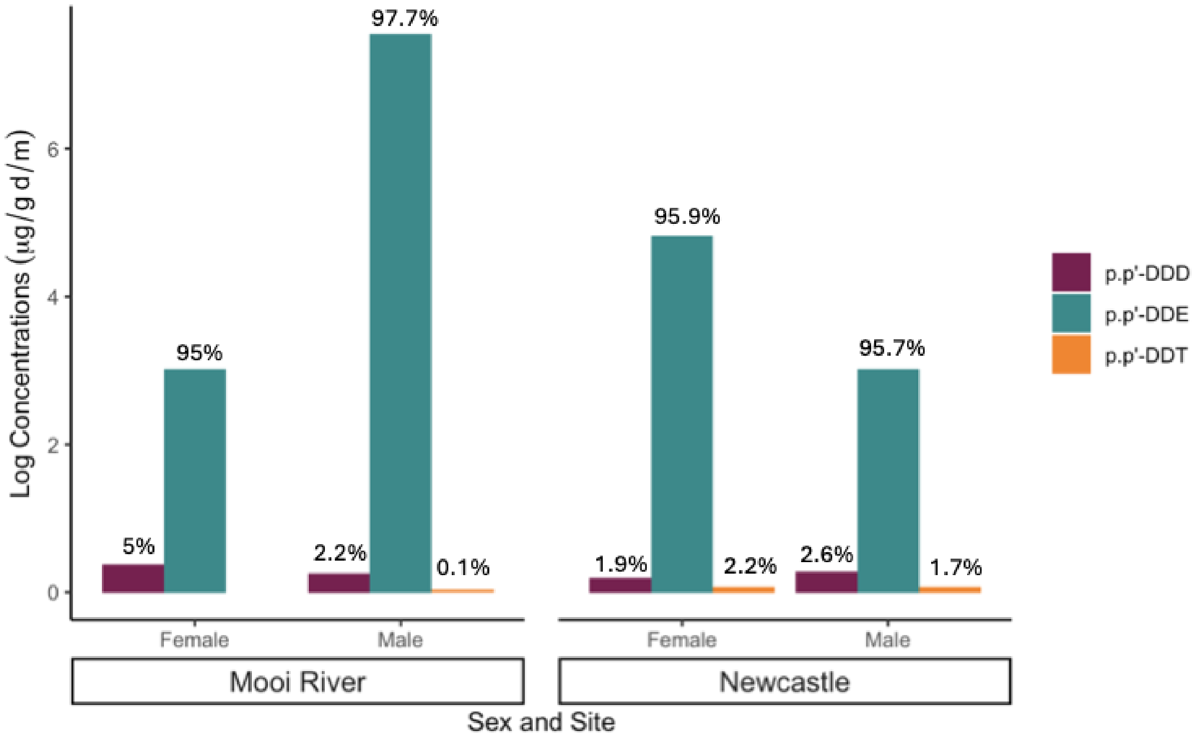

Figure 2: The three DDT isomer concentrations (*p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT) analysed across male and female Amur Falcons from Mooi River and Newcastle and across all tissues (fat, liver, and muscle). The percentages above each bar represents the proportion of that respective isomer constituting the ΣDDT concentration. This graph emphasises the role of *p,p'*-DDE as the principal isomer in this study. Two outliers were excluded from this figure. One juvenile male and one adult female, both from Newcastle. The juvenile male exhibited *p,p'*-DDE concentrations in fat of 101.05 µg/g d/m and the adult female exhibited *p,p'*-DDE concentrations of 63.83 µg/g d/m.

Table 4: Mean dieldrin concentrations ± standard deviation, and range measured in µg/g d/m from 100 individual Amur Falcons, divided roughly between male, female, juvenile, and adult birds between Mooi River and Newcastle roost sites

***Site**	**Tissue**	**n**	**Adult Female**	**n**	**Juvenile Female**	**n**	**Adult Male**	**n**	**Juvenile Male**
			dieldrin		dieldrin		dieldrin		dieldrin
			X ± SD		X ± SD		X ± SD		X ± SD
MR	Fat	12	**0.24** ± 0.13	13	**1.09** ± 2.87	13	**0.56** ± 0.19	12	**0.69** ± 0.65
MR	Liver	12	**0.09** ± 0.12	13	**0.24** ± 0.45	13	**0.11** ± 0.13	12	**0.20** ± 0.18
MR	Muscle	12	**0.01** ± 0.01	13	0.04 ± 0.08	13	**0.02** ± 0.01	12	**0.04** ± 0.04
NC	Fat	13	**0**	12	**0.01** ± 0.04	12	**0.06** ± 0.14	13	**0.04** ± 0.11
NC	Liver	13	**0.02** ± 0.04	12	**0.02** ± 0.03	12	**0.01** ± 0.02	13	**0.01** ± 0.02
NC	Muscle	13	**0**	12	**0**	12	**0**	13	**0**

*MR – Mooi River; NC - Newcastle

Age did not influence ©DDT or dieldrin concentrations (Table 1). Unsurprisingly, there was a significant difference in ©DDT concentrations among tissue types (fat, liver, and muscle), across both sample sites, with fat exhibiting the highest concentrations (Figure 3; Table 5).

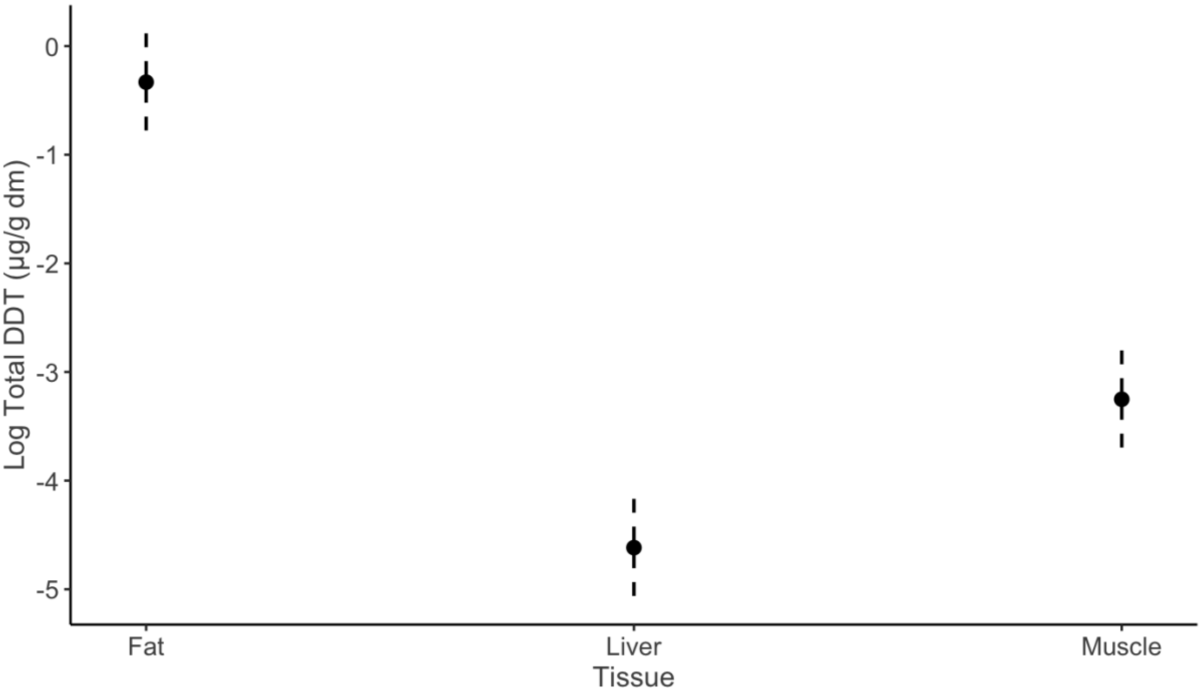

Figure 3: Naturally logged ©DDT concentrations amongst tissue types in µg/g dry mass, with fat containing the highest ©DDT concentrations. The error bars represent the 95% Confidence Intervals. Concentrations for this visualisation were combined across both sample sites (Mooi River and Newcastle).

We found no difference in ©DDT between sites however, we did observe a strong interaction between site and sex with a significant difference in ©DDT between sexes at Mooi River (Figure 4, Table 4). Male falcons from Mooi River exhibited significantly higher ©DDT concentrations than females. Conversely, we found no significant difference in ©DDT concentrations between sexes from Newcastle (Figure 4). While the results between the ΣDDT and *p,p'*-DDE models were similar, a new significant interaction emerged between site and tissue when modelling *p,p'*-DDE (Chapter 4 Table S3; Figure S1).

Table 5: GLMM models exhibiting the important predictors influencing the differences in ΣDDT and Dieldrin concentrations in Amur Falcon sampled in Newcastle and Mooi River, KwaZulu-Natal, South Africa. These models used sample name as a random term. Values in **bold** indicate significance.

Model	Predictors	Chisq	DF	P
ΣDDT	Site	0.23	1	0.63
	Age	0.95	1	0.33
	Sex	**7.58**	**1**	**0.01**
	Tissue	**1159.95**	**2**	**0.00**
	Body Condition	0.52	1	0.47
	Lipid Fraction	1.05	1	0.31
	Site*Age	3.21	1	0.07
	Sex*Site	**5.06**	**1**	**0.03**
	Site*Tissue	0.51	2	0.78
	Age*Sex	0.48	1	0.49
	Age*Tissue	1.02	2	0.60
	Sex*Tissue	2.98	2	0.23
Dieldrin	**Site**	**270.26**	**1**	**0.00**
	Age	2.97	1	0.09
	Sex	**5.94**	**1**	**0.02**
	Tissue	**47.08**	**2**	**0.00**
	Body Condition	1.95	1	0.16
	Lipid Fraction	0.12	1	0.75
	Site*Age	1.54	1	0.22
	Site*Sex	0.33	1	0.57
	Site*Tissue	**84.33**	**2**	**0.00**

Age*Sex	0.00	1	0.96
Age*Tissue	**6.37**	**2**	**0.04**
Sex*Tissue	2.95	2	0.22

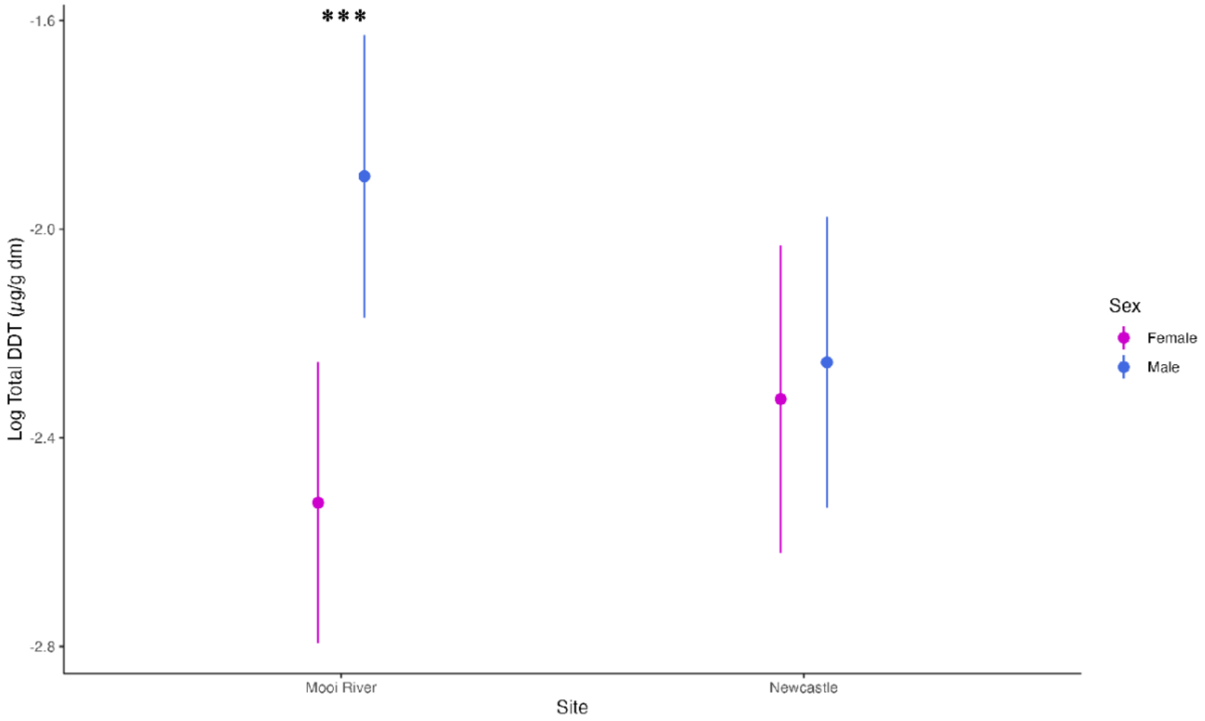

Figure 4: Estimated marginal means of (log) ©DDT concentrations µg/g dry mass by sex and site showing the strong interaction between sex and site. ©DDT concentrations for male Amur Falcons from Mooi River were significantly higher than those in female falcons from Mooi River. Conversely, concentrations between sexes from Newcastle are statistically indistinguishable. Concentrations for this visualisation have controlled for different tissue values (fat, liver, and muscle).

For dieldrin concentrations, in contrast to ©DDT, we found a strong interaction between tissue and sample site, with dieldrin concentrations in tissue types varying between sample sites. Falcons from Mooi River exhibited significantly higher dieldrin concentrations in all tissues than falcons from Newcastle (Figure 5).

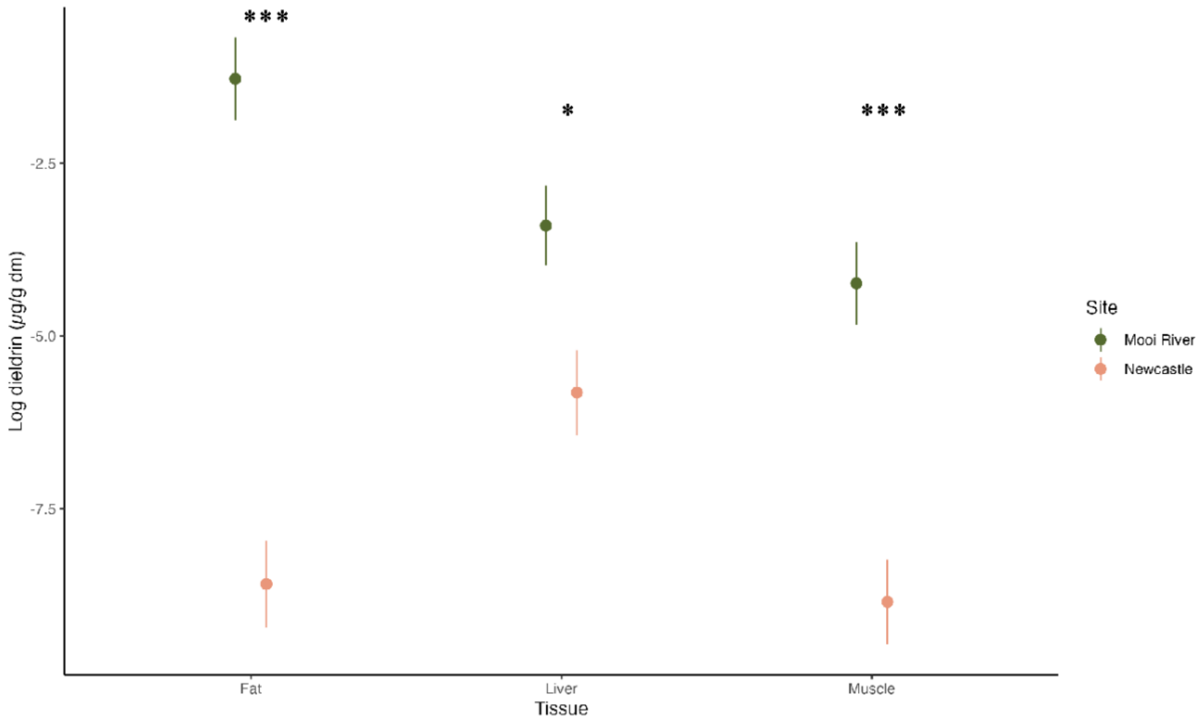

Figure 5: Estimated marginal means of (log) dieldrin concentrations in µg/g dry mass, showing the strong interaction between tissue and site. Dieldrin concentrations were significantly different amongst tissues as well as between Mooi River and Newcastle.

In addition to a strong interaction between tissue and sample site, I found a strong interaction between tissue and age, with dieldrin concentrations in the liver varying between ages. Juvenile Falcons exhibited significantly higher dieldrin concentrations in liver samples than adult falcons (Figure 6).

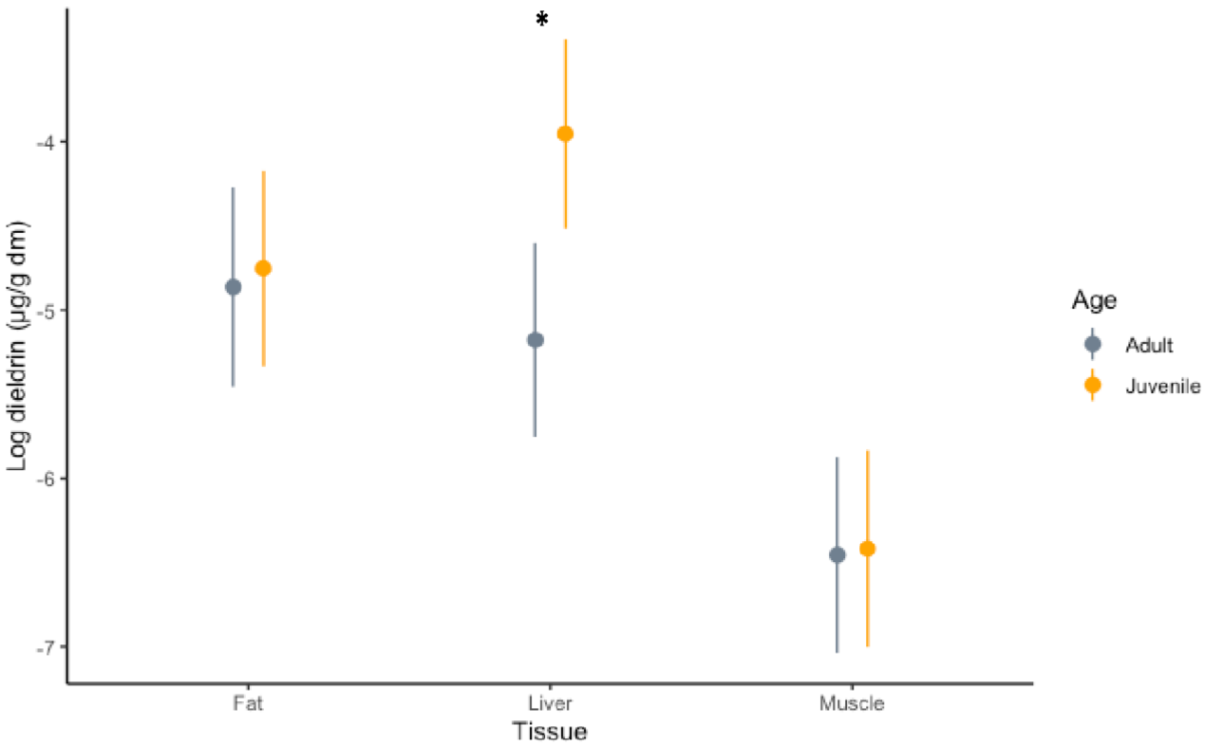

Figure 6: Estimated marginal means of (log) dieldrin concentrations in µg/g dry mass, showing the strong interaction between tissue and age. Dieldrin concentrations were significantly different between livers of adult and juvenile birds.

We found ΣDDT concentrations in liver and muscle from our Amur Falcon samples were lower than the average recent historical concentrations. Only five estimates were available for historical dieldrin concentrations in raptors from 2000 onwards and these were only for liver samples. Similarly to ΣDDT concentrations, Amur Falcons exhibited marginally lower dieldrin concentrations than these recent historical concentrations (Figure 7). We found that ΣDDT concentrations from our Amur Falcon fat samples were higher than the only fat sample available for comparison over the last decade. In fact, two of the values had the highest ΣDDT concentrations in the fat of any raptor recorded over the last two decades (Figure 7).

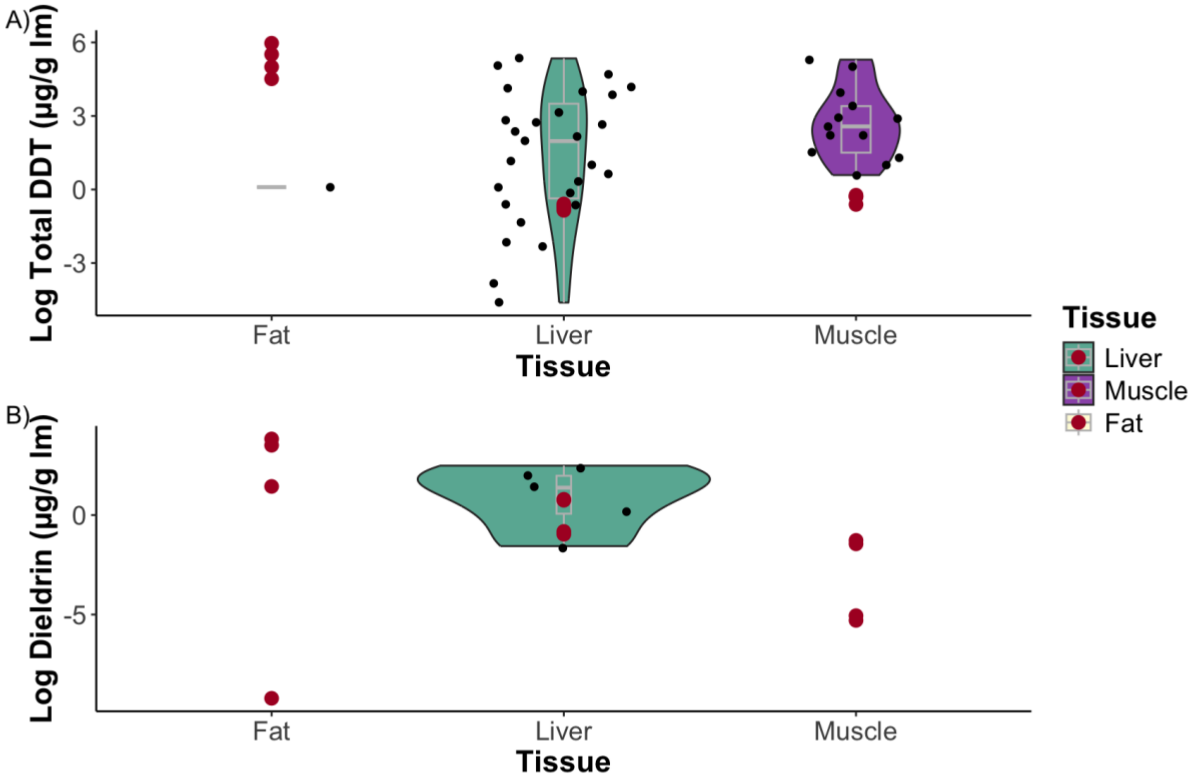

Figure 7: This violin graph compares the log mean ΣDDT concentrations measured in Amur Falcons, expressed in lipid weight, collected in 2019, with historical mean ΣDDT concentrations measured in various raptor species from 2000 onwards. Only historical sample means measured in lipid weight were included in this visualisation, and if not measured in µg/g, they were converted to µg/g before comparison. Concentrations were naturally logged and displayed per tissue. The red dots represent mean concentrations for male and female Amur Falcons (one each from each sample site) while black dots represent historical sample mean values. Only a limited number of dieldrin measurements were available for this period in lipid mass (five estimates), and these measurements were from liver samples only.

DISCUSSION

While DDT and dieldrin has been the focus of many raptor contamination studies and monitoring schemes globally (Espín et al., 2016), such research has been relatively limited in migratory raptors to Africa in general and southern Africa, specifically. In this study we made use of samples collected from 100 Amur Falcons to provide the first detailed analysis of DDT and dieldrin concentrations of this raptor in their non-breeding grounds. There was a strong interaction between sample site and sex for ΣDDT, where males from Mooi River exhibited significantly higher ΣDDT concentrations than females (Table 3; Table 5). Whereas, with dieldrin, there was a strong interaction between tissue and sample site, with birds from Mooi River exhibiting significantly higher dieldrin concentrations in all tissues than birds from Newcastle (Table 4; Table 5). Additionally, we found a significant difference in both pesticide concentrations amongst all tissue types across both roost sites. While overall ΣDDT and dieldrin concentrations were relatively low and not cause for concern when comparing them to

the lethal levels discussed in Chapter 3, page 63, two birds displayed ΣDDT concentrations in fat that were amongst the highest recorded over the last two decades. As discussed in Chapter 3, ΣDDT concentrations in raptor livers exceeding 100 µg/g wet mass is considered critical (Cooke et al., 1982), whereas dieldrin concentrations exceeding 10 µg/g wet mass in raptor livers is considered lethal (Benson, 1975). None of the Amur Falcons sampled exhibited liver concentrations higher than these critical concentrations.

Differences in ΣDDT and dieldrin concentrations between tissues

These Amur Falcons were sampled shortly before their return migration and therefore had begun to store fat in preparation for this journey. As lipophilic chemicals, ΣDDT and dieldrin are deposited in fat, however, this tissue type represents chronic exposure and therefore makes for a less reliable tissue when attempting to identify precise (space by time) contamination sources in migratory species (Tanabe et al., 1998; Espín et al., 2016). The higher concentrations detected in our analysis of this tissue could therefore be a combination of accumulated contaminants from their breeding grounds, along their migration route, as well as in their non-breeding grounds (Tanabe et al., 1998; Espín et al., 2016). Analysis of POPs in other migratory bird species, particularly ones that breed in the temperate northern hemisphere, suggest that POP concentrations in such migratory birds may be linked to their breeding grounds rather than over wintering grounds (Leat et al., 2013; Miller et al., 2020). Additionally, concentrations in liver generally indicates a longer-term contamination exposure (Espín et al., 2016), suggesting contamination from their breeding grounds in northern China or even parts of India, which these falcons use as an important stop-off point both during their southward and northward migrations (Kaur et al., 2024; Tamir, et al., 2024). This would be supported, considering India’s history and current status as the world’s largest user and only producer of DDT in particular (UNEP, 2023). However, considering the difficulty in pinpointing a precise contamination source for migratory birds (Tanabe et al., 1998; Espín et al., 2016), and the complexity behind the pharmacokinetics of these POPs, any assessment from methods used in this study would be highly speculative (Tanabe et al., 1998; Espín et al., 2016).

Sex related differences in ΣDDT concentrations

As with most OCPs, DDT bioaccumulates in wildlife and magnifies up trophic levels, accumulating in predators (Deribe et al., 2011; Fremlin et al., 2020). Therefore, ΣDDT concentrations in Amur Falcons are expected to be linked to their diet. While DDT is still being applied in parts of the Kwa-Zulu Natal Province, both roost sites occur upriver and well outside

DDT-sprayed areas (Bouwman et al. 2015). Furthermore, tracking data of these falcons show most GPS fixes from satellite tracked Amur Falcons to be no more than 25 km from roost sites while in South Africa. Therefore, although DDT concentrations reported in other birds from the Kwa-Zulu Natal region, such as Little Egret (*Egretta garzetta*) and African Openbill Stork (*Anastomus lamelligerus*) may signify a threat to predatory birds adjacent to sprayed areas (Bouwman et al. 2019), the DDT concentrations in the Amur Falcons from this study in particular are not expected to be linked to currently sprayed areas of South Africa. The strong interaction between sex and site observed in ΣDDT concentrations is an indication of potential sex-related diet segregation in this species, particularly from Mooi River. While sex-related diet segregation has been assessed in many bird species, in raptors it has been far less studied due to the difficulty in assigning diet composition to specific sexes when using traditional methods such as pellet analysis (Catry et al., 2016, Panter & Amar, 2021, 22). Such segregation in raptors could be explained by different energetic requirements experienced by males and females during different periods of the breeding cycle (egg-laying or incubation etc.) (Ludynia et al., 2013; Weimerskirch et al., 2009). The observed difference in ΣDDT between male and female falcons may be influenced by the deposition of DDT in eggs during the egg-laying process (Lamb et al., 1967; Katagi and Fujisawa 2021). This phenomenon could lead to variations in ΣDDT concentrations between the sexes. However, this explanation fails to explain why there were no significant differences in ΣDDT concentrations between male and female falcons from Newcastle, but there were sex differences from Mooi River.

An alternative hypothesis is that female falcons in the Mooi River region originate from a distinct area within their breeding ground. However, this explanation is also unlikely, as previous research by Symes and Woodborne (2010), has indicated that this falcon species demonstrates weak migratory connectivity. This means that birds from different parts of their breeding grounds tend to mix when they arrive in South Africa, making it improbable that females from Mooi River exclusively come from a separate region.

Alternatively, and in our view the most likely explanation links to a combination of a different diet between the sexes and different exposure levels between the two sites. Larger females in species with reversed sexual size dimorphism may feed on larger prey while smaller, more agile males feed on smaller prey (Newton, 2010, Panter & Amar 2021). We did find a slight difference in weight between male ($\underline{x}$=141, SD=10.8) and female ($\underline{x}$=151, SD=12.2) falcons, with females being roughly 7% heavier on average, and exhibiting a negligible difference in average wing lengths, which corresponded with the size differences of this species described by Ferguson-Lees and Christie (2001). Thus, female falcons from Mooi River may be exposed to varying concentrations of DDT if their diet differs compared to males. This divergence could arise from differences in the species of insects they feed on, which might be more exposed to DDT, or from variations in the geographical locations where they hunt, which may be less contaminated by DDT. This latter scenario gains credibility when we consider that ΣDDT concentrations in females and males from Newcastle did not differ significantly from those in males from Mooi River. Furthermore, while many studies have examined the diet of Amur Falcons on their non-breeding grounds, none explored whether a sex-related difference in diet exists (Kopij, 2010; Symes and Woodborne, 2010; Alexander and Symes, 2016). Even when investigating the diet of a similar migratory falcon species to South Africa, the Lesser Falcon (*Falco naumanni*), no sex-related dietary differences were found (Anderson et al., 1999), suggesting this is less likely to be the cause of the varying DDT concentrations between sexes. As per my finding in Chapter 3, male falcons from Mooi River in particular, could be targeting prey species from more aquatic environments, where DDT has not decayed as much as in terrestrial ecosystems. Further investigation into dietary differences between sexes and areas are needed to support this hypothesis. This could be easily achieved via stomach dissections of the dead falcons which remain in storage.

Site and age-related differences in Dieldrin concentrations

The most reliable indication of local contamination originating from the Amur Falcon non-breeding grounds in South Africa, is the strong interactions not just between site and tissue, but between age and tissue observed in dieldrin concentrations. This suggests that it is particularly juvenile birds from Mooi River that are exhibiting higher concentrations of dieldrin than any other group in this study. There will always be a degree of variability associated with ΣDDT and dieldrin concentrations in lipids of fat, liver, and muscle samples, with the possibility of these OCPs remobilizing from fat deposits into the bloodstream during periods of stress (Espín et al., 2016). This variability makes it difficult to reliably distinguish an exact contamination source among breeding grounds, along migration routes, and on non-breeding grounds when using these tissues alone. However, the significantly higher dieldrin concentrations in juveniles from Mooi River in comparison to all birds from Newcastle may indicate a potential contamination source within the former region. While none of the birds exhibited concentrations on an individual basis that exceeded those that result in death (<10 µg/g) or even sublethal effects (3 – 9 µg/g) in raptors (Walker et al., 1967; Walker, 2003), it is still of particular concern that 100% of birds at this site registered quantifiable concentrations of dieldrin, as this pesticide has been completely banned in South Africa since 1983 (Naidoo and Buckley, 2003; Gomez-Ramirez et al., 2019).

Dieldrin is often formed from the degradation of another toxic POP, aldrin, both of which were historically used in South Africa to control termites, particularly in pasture lands, which could account for historical contamination (Dippenaar et. al., 1978; Naidoo and Buckley, 2003; Deck et al., 2015; Gerber et al., 2021). While dieldrin has been banned in South Africa since 1983, the use of aldrin was only banned in 2013 (Gerber et al., 2021). Aldrin, however, rapidly changes to dieldrin in the environment and in animals (Gerber et al., 2021). Except for nine falcons (all from Mooi River), there was a marked lack of aldrin detected (unpublished results), suggesting that, while there is a significant difference in local dieldrin contamination between juveniles from Mooi River and all other falcons from Newcastle, this contamination cannot conclusively be linked to recent aldrin application but may be linked to historical use. This point, however, is negated by the fact that aldrin and dieldrin have a half-life in vertebrates of about one year (World Health Organisation, 1989). Africa in general and South Africa in particular have suffered with the accumulation of obsolete pesticides for decades, with stockpiles of banned, unwanted, or unidentified pesticides, such as dieldrin (Naidoo and Buckley, 2003). These stockpiles of dieldrin are sometimes stored incorrectly and used illegally, leading to environmental contamination (Naidoo and Buckley, 2003; Gomez-Ramirez et al., 2019). Similar legacy dieldrin contamination of Helmeted Guineafowl (*Numida meleagris*) was identified in the same region as this study in the late 1990s (Ratcliffe et al., 2000), suggesting that legacy dieldrin contamination may also be responsible for the identified contamination in Amur Falcons. The type of land use varies between the two sample sites, with Mooi River dominated by dairy, horse stud, maize, and potato farms, and Newcastle dominated by mining, industry, manufacturing, and livestock farming (Pero and Crowe, 1996; Bhikraj-Kallicharan, 2010; Humphries et al., 2016; Nolakana, 2016). The dieldrin contamination in Mooi River could therefore be linked to agricultural application in that region (Gomez-Ramirez et al., 2019). Furthermore, with the higher precipitation in Mooi River, we can expect greater run-off from contaminated soil into aquatic environments resulting in greater accumulation of dieldrin in these ecosystems (Matsumoto et al., 2009; Afful et al., 2010), which would potentially contaminate aquatic invertebrates (World Health Organisation, 1989; LeBlanc, 1995). The Amur Falcons from Mooi River may feed on invertebrates which have been exposed to dieldrin accumulated over time in water bodies adjacent to agricultural areas, accounting for the significantly higher concentrations in juvenile Amur Falcons from Mooi River. Additionally, this would have been the juvenile falcons first migration to their non-

breeding grounds, and with a half-life of approximately a year (World Health Organisation, 1989), the dieldrin contamination in this age group could conceivably have been accumulated at least in part, from their outward migration to South Africa, from parts of India where termites form an important part of their diet (Williams, 2013). While dieldrin has been banned for use in India since 2003 (Sharma et al., 2017), this OCP was extensively used for many years in the region to control termites in the agricultural sector (Paul et al., 2018). Therefore, legacy dieldrin contamination may remain in parts of India, which are used as an important stop-off point for Amur Falcons during their migration.

Similarly, the strong interactions we observed in *p.p’*-DDE between site and tissue and between site and sex (Chapter 4 Table S3), both suggest potential legacy contamination, as *p.p’*-DDE is more persistent in the environment than *p.p’*-DDT and *p.p’*-DDD and is regarded as a good indicator of historical contamination (Yohannes et al. 2017; Naso et al.,2003). Additionally, the substantially lower *p.p’*-DDT than *p,p’*-DDE concentrations detected (Table 3) simultaneously suggests a lack of contemporary DDT input in this region (Yohannes et al. 2017; Naso et al.,2003). Substantively, the results were similar when analysing ©DDT or only *p,p’*-DDE (Table 5, Chapter 4 Table S3, Figure S1). The only exception being that the interaction between site and tissue went from non-significant (p=0.78, DF=2, F=0.25) when analysing ©DDT, to strongly significant, when analysing and *p,p’*-DDE (Table 5, Chapter 4 Table S3, Figure S1). This strong interaction can be explained by the combination of (1) the conversion of DDT to DDE in the environment (Cecil et al., 1972), both at lower and higher trophic levels, resulting in more *p,p’*-DDE in these birds than other isomers, (2) the higher persistence of *p.p’*-DDE than the other isomers in the environment (Yohannes et al. 2017; Naso et al.,2003), and (3) the lipophilicity of DDT (Fremlin et al., 2020), leading to the lipid-rich fat samples of this study contained higher concentrations of DDT in general than the other tissues analysed. This study has provided the first comprehensive description of persistent organic pollutant concentrations for this species on its non-breeding ground. While concentrations of both OCPs were not found to be high enough to be considered lethal, the ©DDT concentrations in fat samples from two birds exceeded historical measures (Figure 6) and may be an indication of contamination occurring on breeding grounds or along the migration route from Asia to South Africa. This is further supported by historical studies on other bird species such as Helmeted Guineafowl from the same region exhibiting DDT and dieldrin concentrations low enough to be considered historical rather than recent contamination as far back as the late 1990s (Ratcliffe et al., 2000). In the study by Ratcliffe et al. (2000), they

detected *p.p'*-DDE in only six of the 36 Guineafowl liver samples, in comparison with this study which detected *p.p'*-DDE in 96 of the 100 falcon livers sampled. However, when comparing the range of *p.p'*-DDE concentrations they detected (8 - 208 ng/g ww),we recorded concentrations far lower (0 – 50 ng/g ww), further suggesting that these concentrations may be linked primarily to historical application of this pesticide rather than contemporary contamination. The higher dieldrin concentrations detected in the Mooi River area, however, may indicate the need to increase monitoring efforts for this OCP, as a banned pesticide, to identify potential contamination sources.

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Chapter 5

Synthesis & Conclusions

The White-Tailed Sea Eagle (*Haliaeetus albicilla*- photo by Christoph Müller) and Western Osprey (*Pandion haliaetus* – photo by Dr Raju Kasambe) are examples of raptor species from the northern hemisphere, that have recovered once OCPs such as DDT were banned throughout their Global North range.

DISCUSSION

I would describe the findings from my thesis as encouraging (Figure 1). We have shown that local legislation and international agreements (e.g. The Stockholm Convention) when applied effectively and universally can be used to address a global crisis. Our findings provide notable insights that may assist environmentalists in addressing current environmental challenges (e.g. climate change and biodiversity loss). This thesis should also serve as motivation to monitor and assess various other POPs listed by the Stockholm Convention. Particularly the newer POPs of concern such as endosulfane, dicofol, and lindane, which are all persistent pesticides still in use in certain countries around the world (UNEP, 2023). These pesticides, just like DDT and dieldrin, persist in the environment and bioaccumulate up trophic levels, leading to various toxic effects in humans and animals (Deribe et al., 2011; Fremlin et al., 2020). This study therefore indicates the potential that contamination from these, and other recent POPs of concern can be addressed with similar concerted bans and restrictions. The second effectiveness evaluation of the Stockholm Convention, pursuant to Article 16 of the convention has found that the Stockholm Convention has been successful in its mandate to regulate and reduce the environmental presence of POPs in general and DDT in particular (UNEP, 2023). It has, however, highlighted limitations to evaluating the effectiveness of the convention that are similar to those identified within this thesis, primarily the limited data available from national reports and implementation plans for various member states (UNEP, 2023).

In this thesis, I examined how monitoring efforts afforded to DDT and dieldrin in raptors were distributed over time, space and between species. Additionally, I also investigated the trends in DDT in raptor populations globally, from the period of peak use to after it was banned or restricted throughout most of the world. I explored the global representation of the general consensus that these pollutants are declining across all ecosystems, while considering that this consensus is based on data mostly derived from the Global North. Lastly, a substantial sample of recently collected raptor tissue from South Africa, provided me with an opportunity to describe contemporary DDT and dieldrin concentrations in an understudied migratory raptor that winters in the Global South. This thesis offers evidence that supports the common consensus that DDT has declined in the Global North. However, due to lack of sufficient data from countries allowing restricted use after the reintroduction of DDT in 2006, such declines cannot conclusively be considered globally representative. Furthermore, low

contemporary concentrations of DDT in Amur Falcons wintering in a country with restricted DDT use may support the opinion that DDT could be declining in the Global South. However, the high concentrations in fat from two of these individuals, mentioned in Chapter 4, page 119, may indicate that declines in the Global North do not necessarily translate to declines in the Global South. While the research (Chapter 4) may not be able to conclusively support the notion of global DDT declines, it does contribute contemporary data to the well documented lack of information in the Global South highlighted previously (Chapter 2).

SUMMARY OF KEY FINDINGS

The consolidation and synthesis of the global literature, spanning more than 100 years of monitoring (Chapter 2), revealed a substantial geographical bias in DDT and dieldrin monitoring in raptors towards the Global North. Initially, with 114 raptor species being included in monitoring of DDT and dieldrin globally, it was expected that most ecosystems throughout the world were well represented. This, however, was not the case, as while the species selected for monitoring these pesticides have diversified over time, most of the DDT and dieldrin monitoring data in raptors have originated from just three species (Peregrine Falcon, Bald Eagle, and Eurasian Sparrowhawk) (Chapter 2), two of which only occur in the northern hemisphere (Bald Eagle, and Eurasian Sparrowhawk). This contrasts with the need for monitoring in areas where there is continued use of DDT (Gevao et al., 2010; Leslie et al., 2013), particularly in parts of the Global South and in areas that represent biodiversity hotspots.

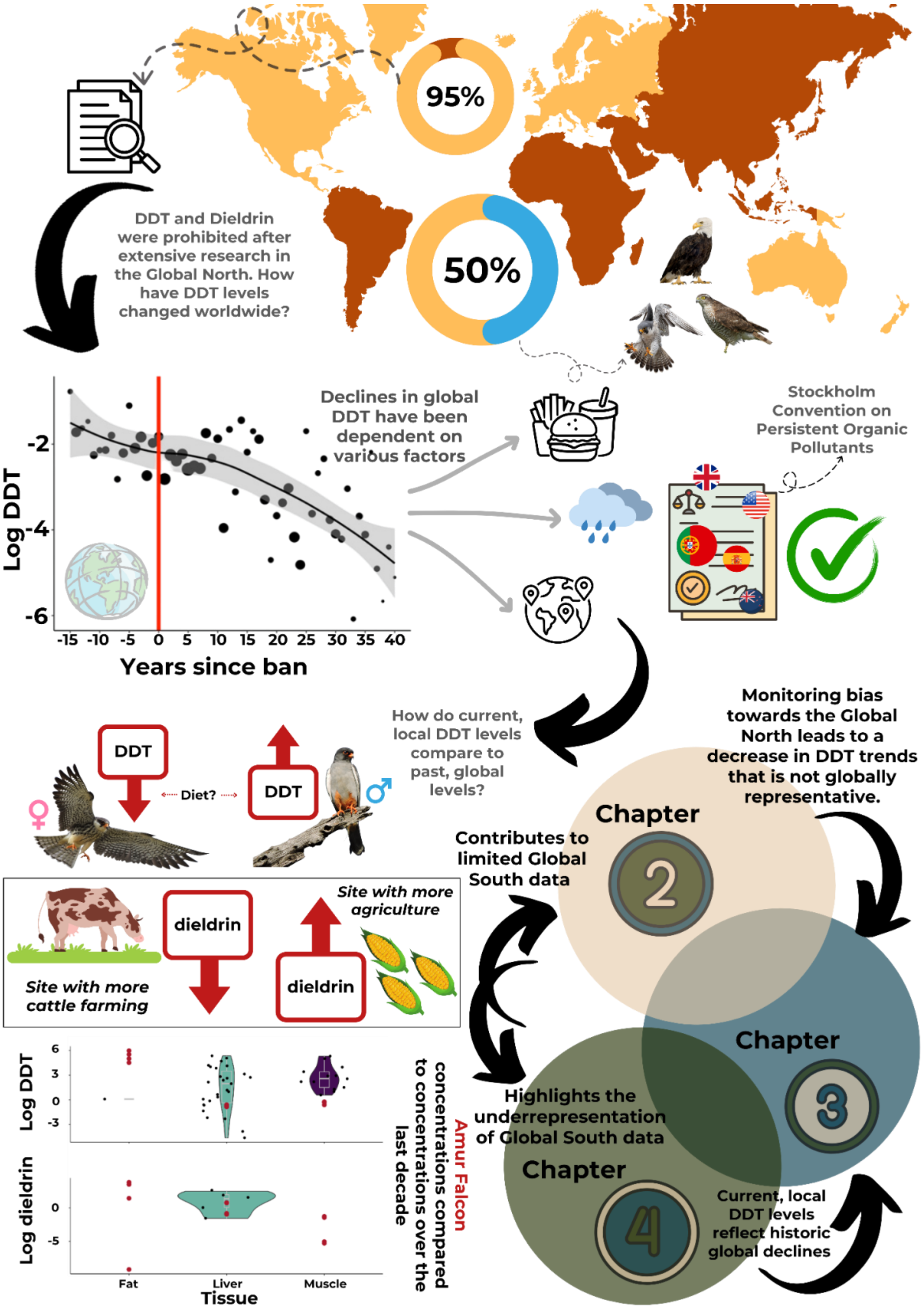

Figure 1: Infographic summarizing the investigation in DDT and dieldrin concentrations and monitoring effort in global raptor populations, showing key findings from each chapter and how they inform one another.

Using concentrations of DDT that were extracted from the consolidated literature sourced in Chapter 2, I analysed the trend in DDT in raptors across the globe to examine how this pesticide has changed since it was banned or restricted, in each respective country where samples were taken. I found that DDT in raptors has declined significantly throughout the Global North. However, this decline could not conclusively be confirmed in regions of the Global South, allowing restricted use of DDT after its reintroduction in 2006, as there were insufficient samples available for the analysis. Furthermore, while declines were consistent across all continents, certain variables such as raptor diet and level of precipitation had a significant influence on DDT.

To supplement the Global North declines and lack of data from regions allowing restricted use discussed in Chapter 3, I analysed DDT and dieldrin concentrations in the Amur Falcon, which migrate from central Asia to South Africa during the austral summer (Schäfer, 2003; Symes and Woodborne, 2010). This was the first detailed description of DDT and dieldrin concentrations in this species, also contributing to the limited pesticide monitoring for the Global South described in Chapter 2. Although ΣDDT and dieldrin were not found at lethal concentrations, we did find differences in concentrations between the sexes, which varied between the two sites. Male falcons from Mooi River had higher ΣDDT concentrations than females. One explanation for this result is a potential dietary difference between sexes in Amur Falcons on their non-breeding grounds. This hypothesis does, however, require further testing as while diet studies on Amur Falcons from their non-breeding grounds report no sex-related differences in prey biomass (Pietersen and Symes, 2010), they do not mention any difference in prey species selection between sexes. An additional consideration for future investigations on how diet of these falcons could influence OC and other POP contamination could include stable nitrogen and carbon isotope analysis to understand dietary factors influencing contaminant signals (Braune and Elliott, 2021). The higher *p,p’*-DDE than *p.p’*-DDT concentrations in these falcons indicates historical contamination (Yohannes et al., 2017; Naso et al., 2003). The lower proportions of *p.p’*-DDT compared to *p,p’*-DDE in the Amur Falcon samples (Chapter 4, Table 3), suggests that even though DDT is still used in parts of Kwa-Zulu Natal, South Africa, for malaria control (Bornman et al., 2022), this restricted use has not contributed to contemporary contamination in these falcons (Yohannes et al., 2017; Naso et al., 2003).

In contrast to ΣDDT, there was a significant site and age difference detected for dieldrin, with juvenile falcons from the Mooi River roost exhibiting higher dieldrin concentrations than those collected at the Newcastle roost. This specific finding was particularly concerning. It was expected that ΣDDT would be present in these falcons since it is still used in South Africa (including within the province that these samples were collected), although, in areas well outside current application regions and only for house spraying to control malaria mosquitoes and not as an agricultural application (Bornman et al., 2022). However, dieldrin has been completely banned in South Africa since 1983 (Naidoo and Buckley, 2003), thus suggesting that these concentrations, while low, may indicate recent, illegal use or exposure to incorrectly stored or disposed of dieldrin stocks. Irrespective of how these falcons were exposed, the significant difference in concentration between the two sites, linked particularly to juveniles, is a strong indicator of local contamination in this part of South Africa, as there is only weak migratory connectivity in this species (Symes and Woodborne, 2010).

The substantial geographical bias in DDT and dieldrin monitoring I have demonstrated in this thesis, underscores the need for a more balanced and comprehensive approach to pesticide monitoring. This thesis forms a suitable benchmark from which to amend and guide future pesticide policymaking to ensure more equitable distribution of monitoring efforts to address regional and local disparities. Local environmental aspects and legislative implementation have an influence on DDT and dieldrin concentrations in raptors. While international policies have been successful in ensuring declining trends in these pesticides in the Global North, the notable lack of monitoring in the Global South means we cannot conclusively affirm these declines as globally representative. These findings therefore demonstrate the value of consistent monitoring. Without the extensive monitoring and research of these pesticides conducted since the mid 1900s in the Global North, there would not have been sufficient information to influence the widespread action responsible for curtailing the use of DDT and dieldrin globally. In this case, the ‘trickle-down science’ concept described by Reidpath and Allotey (2019) can provide benefits for the Global South if implemented efficiently. While most of the research has been conducted in the north, the findings have been used to inform international policy. Although, as a result of limited monitoring, we cannot determine whether they have positively influenced the Global South. Policy has dictated how these OCPs should be used in the Global South to meet human needs while minimising environmental contamination. However, this has been done without implementing the necessary monitoring to evaluate policy efficacy. Further evidence of this influence was demonstrated by the concentrations of ΣDDT and dieldrin in

contemporary Amur Falcon samples. While concentrations were low enough to have no lethal impact on these birds, there were small-scale, local disparities, with fat from two individuals containing the highest ΣDDT concentrations recorded in the only fat sample available for comparison over the last decade. This supports our argument that declines detected in the Global North may not represent declines in South Africa. However, only fat (tissue most susceptible to long-term exposure and storage of OCPs) showed elevated concentrations, while liver and muscle concentrations remained low. This implies that the high concentrations may result from DDT deposition in breeding grounds or along migratory routes. This contemporary research on ΣDDT and dieldrin in Amur Falcons in South Africa is an important contribution to research on OCPs in Global South raptors. It forms part of a growing interest in understanding the trends in OCP (and other pesticide compounds) concentrations in wildlife of the Global South, contributing to the historically low levels of pesticide research in this region and therefore, narrowing the knowledge gap between the developed and developing world.

FUTURE RESEARCH

For decades there has been a notable contrast in knowledge production and representation between the Global North and Global South, with Global South knowledge often being underrepresented and underappreciated (Okune et al., 2016; Reidpath and Allotey, 2019). This stems primarily from the fact that frameworks used to evaluate and legitimise knowledge are owned and controlled by Global North entities (Okune et al., 2016). The consequence of this being that most global scientific output remains Euro-American in language, excluding non-English knowledge (Marginson and Xu 2023). I experienced this specific concept when compiling this thesis, particularly when conducting the global review on monitoring effort afforded to DDT and dieldrin in raptors. Using only the Web of Science platform, a database owned and controlled by Clarivate®, which is a British-American company, excluded certain publications, particularly non-English publications. Additionally, the use of “Raptor” alone as a search term for identifying literature assessing DDT and dieldrin in birds of prey may have limited the number of studies detected in this thesis. Furthermore, most environmental monitoring programmes dedicated to monitoring pesticides in raptors, from which the data in this thesis originates from, exist only in the Global North (Espín et al., 2016). Most data in this thesis representing the Global South originates from individual studies. Therefore, the establishment of long-term pesticide monitoring schemes based in the Global South would be beneficial to future monitoring of OCPs as well as other emerging agricultural and industrial chemicals. This thesis can be used as a framework and foundation for the development of such

monitoring programs to contribute to the lack of knowledge from this socio-geographic region in the future. I originally intended to have the Amur Falcon samples analysed for ΣDDT and dieldrin within South Africa, however, after an comprehensive investigation it became clear that this was not logistically nor economically feasible. Thus, via a collaboration these samples were eventually analysed in Spain. This demonstrates the current resource and logistical constraints experienced within the Global South that prevent widespread testing of pesticides in wildlife, which is less prevalent in the Global North.

The detailed analysis of ΣDDT and dieldrin concentrations in Amur Falcons presented in this thesis was the first of its kind, providing a substantial knowledge contribution to this species in general. However, this data is relevant specifically to this falcon on their non-breeding grounds. Therefore, collecting samples from tracked individuals on their breeding grounds and comparing them with the data in this thesis would provide a holistic understanding of not only ΣDDT and dieldrin contamination but potentially other emerging agricultural and industrial chemicals. This is viewed as particularly important given the indication of high ΣDDT concentrations in the fat of these birds, but low concentrations in the liver and muscle, which suggested that exposure may be higher in their breeding or migratory grounds. This could be further enhanced by including the analysis of eggs from nest sites on their breeding grounds to identify potential contamination sources. In addition, it is important to try and establish some of the likely mechanisms that may explain some of the patterns of ΣDDT and dieldrin concentrations seen in the Amur Falcons. For example, a comprehensive gut analysis and detailed diet investigation may further assist in identifying potential ΣDDT and dieldrin contamination sources, aid in understanding the difference in concentrations between roost sites, as well as provide a reason behind the sex-related difference in ΣDDT contamination in falcons collected from Mooi River. This should still be possible, because many of the dead birds from the hailstorm remain in freezer storage. Furthermore, these samples were collected from migratory, insectivorous raptors, making it difficult to identify contamination sources with any certainty and specificity (Tanabe et al., 1998). Future studies should include resident raptors, which utilise a variety of trophic levels, to enhance our understanding of contamination by agricultural and industrial chemicals in the broader environment. This will also provide us with the ability to compare concentrations between resident species and migratory species, further improving our ability to identify potential South African contamination sources or whether the sources are likely to be elsewhere. This will also enable us to expand on the

research by Garcia-Heras et al. (2018), and determine the risk posed to species of concern by OCPs like DDT and dieldrin.

CONCLUSION

I have managed to demonstrate that geographic bias in scientific knowledge extends to the monitoring of pesticides in raptors of the Global South. However, I have also demonstrated that this bias may not limit local and international measures in reducing DDT and dieldrin in raptors but does influence our ability to evaluate their success. These pesticides have declined in the Global North despite their characteristic persistence in the environment. However, the lack of consistent monitoring of these pesticides in the Global South and the continued use of, particularly, DDT in this region, necessitates a greater monitoring effort to determine whether declines observed in the Global North have been realised in the Global South. This thesis can contribute to future effectiveness evaluations by the Stockholm Convention, demonstrating the continued decline in OCPs such as DDT and dieldrin. Findings from this thesis suggest that challenges remain in securing sufficient data to evaluate the effectiveness of global agreements like the Stockholm Convention in certain regions. However, mitigation methods, including local legislation and global agreements, have been effective in reducing and controlling environmental contamination by these OCPs in the Global North. This suggests a potential that similar declines can be achieved in the Global South.

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APPENDICES

Chapter 3 Table S1: DDT and dieldrin status in Global North and Global South Countries gathered from National Implementation Plans, when available and published literature.

Country	DDT Status		Dieldrin Status	Information source
Australia	Complete Ban	(Stockholm Convention On Persistent Organic Pollutants Australia's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Australia's National Implementation Plan
Belgium	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Belgium's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Belgium's National Implementation Plan
Canada	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Canada's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Canada's National Implementation Plan
China	Restricted Use	Stockholm Convention on Persistent Organic Pollutants China's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants China's National Implementation Plan

Czech Republic	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Czech Republic's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Czech Republic's National Implementation Plan
Denmark	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Denmark's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Denmark's National Implementation Plan
Finland	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Finland's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Finland's National Implementation Plan
France	Complete Ban	Stockholm Convention on Persistent Organic Pollutants France's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants France's National Implementation Plan
Germany	Complete Ban	Stockholm Convention on Persistent Organic Pollutants	Complete Ban	Stockholm Convention on Persistent Organic Pollutants

		Germany’s National Implementation Plan		Germany’s National Implementation Plan
Greece	Complete Ban	Tsatsakis et al., 2008	Complete Ban	Katsoyiannis and Samara, 2004
Iceland	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Iceland’s National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Iceland’s National Implementation Plan
India	Restricted Use	Stockholm Convention on Persistent Organic Pollutants India’s National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants India’s National Implementation Plan
Indonesia	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Indonesia’s National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Indonesia’s National Implementation Plan
Iraq	Complete Ban	Douabul and Al-Timari, 2014	Complete Ban	Douabul and Al-Timari, 2014
Ireland	Complete Ban	Stockholm Convention on Persistent Organic Pollutants	Complete Ban	Stockholm Convention on Persistent Organic Pollutants

		Ireland's National Implementation Plan		Ireland's National Implementation Plan
Italy	Complete Ban	Bettinetti et al., 2011	Complete Ban	Qu et al., 2018
Japan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Japan's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Japan's National Implementation Plan
Korea	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Republic of Korea's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Republic of Korea's National Implementation Plan
Mexico	Restricted use	Stockholm Convention on Persistent Organic Pollutants Mexico's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Mexico's National Implementation Plan
Morocco	Complete	Stockholm Convention on Persistent Organic Pollutants Morocco's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Morocco's National Implementation Plan

Namibia	Restricted Use	Stockholm Convention on Persistent Organic Pollutants Namibia’s National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Namibia’s National Implementation Plan
Netherlands	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Netherland’s National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Netherland’s National Implementation Plan
Norway	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Norway’s National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Norway’s National Implementation Plan
Poland	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Poland’s National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Poland’s National Implementation Plan
Romania	Complete Ban	Stockholm Convention on Persistent Organic Pollutants	Complete Ban	Stockholm Convention on Persistent Organic Pollutants

		Romania's National Implementation Plan		Romania's National Implementation Plan
Russia	Complete Ban	AMAP Assessment Report	No Information	AMAP Assessment Report
South Africa	Restricted Use	Stockholm Convention on Persistent Organic Pollutants South Africa's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants South Africa's National Implementation Plan
Spain	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Spain's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Spain's National Implementation Plan
Sweden	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Sweden's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Sweden's National Implementation Plan
Switzerland	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Switzerland's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Switzerland's National Implementation Plan

Uganda	Restricted Use	Stockholm Convention on Persistent Organic Pollutants Uganda's National Implementation Plan	Restricted Use	Stockholm Convention on Persistent Organic Pollutants Uganda's National Implementation Plan
United Kingdom	Complete Ban	Stockholm Convention on Persistent Organic Pollutants United Kingdom's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants United Kingdom's National Implementation Plan
United States of America	Complete Ban	Edwards, 2004	Complete Ban	Stern, 2014
Zimbabwe	Restricted Use	Stockholm Convention on Persistent Organic Pollutants Zimbabwe's National Implementation Plan	Complete Ban	Stockholm Convention on Persistent Organic Pollutants Zimbabwe's National Implementation Plan

Chapter 3 Table S2: Estimated Marginal Means table (emmeans) exhibiting significant decline in DDT concentrations in raptors from 15 years before the global DDT bans and restrictions to 40 years after global DDT bans and restrictions.

Time since ddt ban	**emmean**	**SE**	**df**	**lower.CL**	**upper.CL**
-15	-0.77	2.25	9	-17.59	16.04
-14	-1.72	2.10	7	-21.34	17.90
-13	-1.63	2.11	7	-20.91	17.65
-12	-1.47	2.15	8	-19.92	16.98
-11	-2.26	2.13	7	-21.24	16.73
-10	-2.14	2.14	8	-20.85	16.56
-9	-2.14	2.11	7	-21.51	17.24
-8	-1.80	2.11	7	-21.16	17.56
-7	-2.82	2.13	8	-21.67	16.03
-6	-2.21	2.10	7	-21.74	17.32
-5	-1.10	2.16	8	-19.39	17.19
-4	-2.10	2.11	7	-21.57	17.38

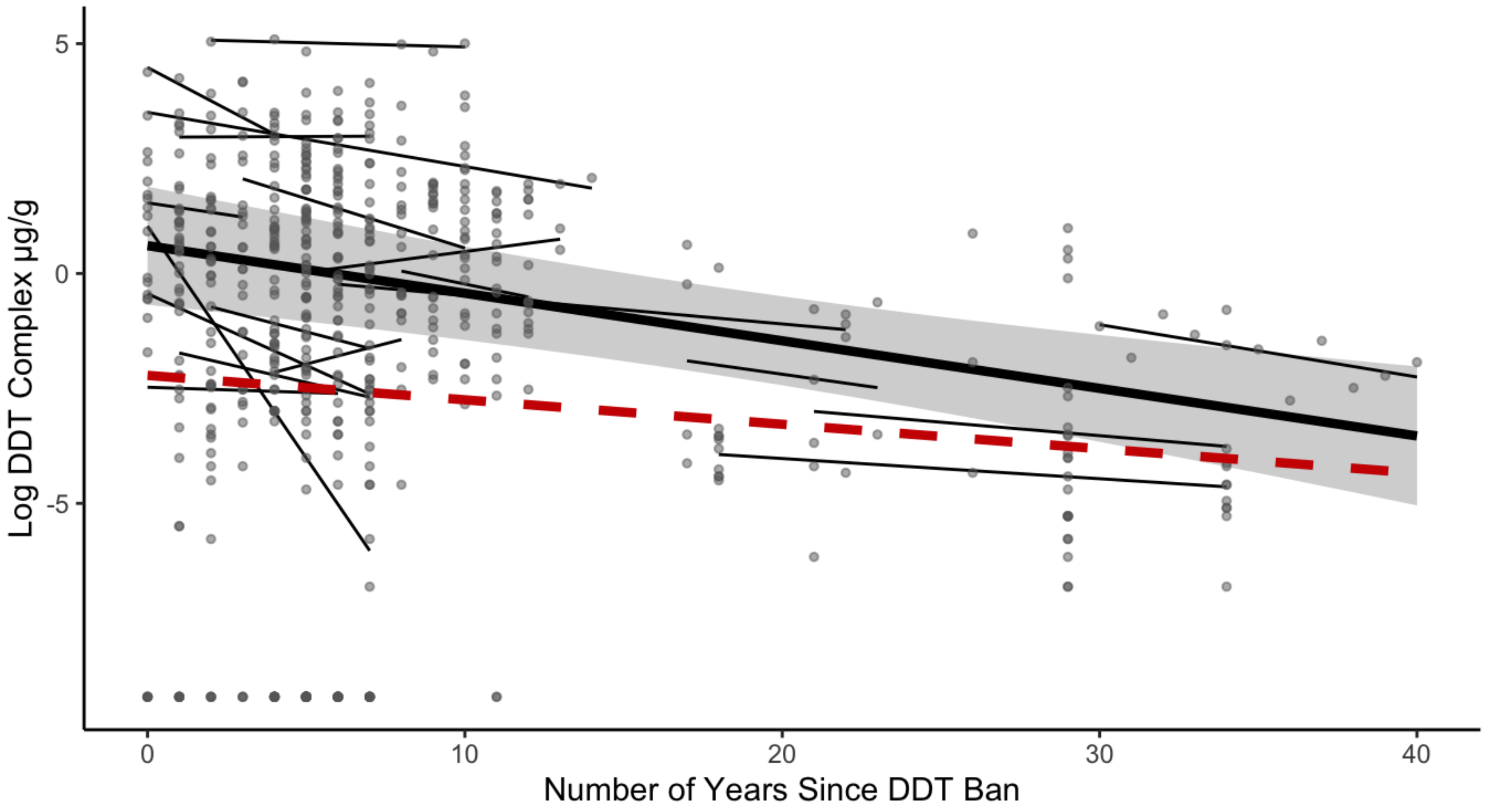
-3	-1.84	2.10	7	-21.48	17.81
-2	-2.74	2.10	7	-22.40	16.93
-1	-1.97	2.11	7	-21.47	17.52
0	-1.82	2.11	7	-21.31	17.66
1	-2.82	2.10	7	-22.55	16.92
2	-2.25	2.10	7	-21.98	17.47
3	-2.40	2.10	7	-22.09	17.30
4	-2.23	2.10	7	-21.85	17.38
5	-2.59	2.09	7	-22.33	17.16
6	-2.52	2.09	7	-22.24	17.21
7	-2.57	2.10	7	-22.26	17.13
8	-1.74	2.10	7	-21.34	17.85
9	-2.33	2.11	7	-21.64	16.98
10	-1.87	2.11	7	-21.15	17.40
11	-3.96	2.11	7	-23.35	15.44

12	-1.66	2.15	8	-20.10	16.78
13	-3.11	2.13	8	-21.95	15.72
14	-1.44	2.14	8	-20.22	17.33
15	-2.19	2.13	8	-21.00	16.62
16	-1.70	2.17	8	-19.76	16.36
17	-1.89	2.11	7	-21.37	17.60
18	-3.30	2.10	7	-22.90	16.30
19	-4.70	2.16	8	-22.91	13.51
20	-3.67	2.13	7	-22.61	15.27
21	-3.37	2.11	7	-22.84	16.10
22	-3.03	2.10	7	-22.56	16.50
23	-4.17	2.10	7	-23.68	15.34
24	-4.82	2.10	7	-24.27	14.64
25	-1.70	2.14	8	-20.32	16.92
26	-3.62	2.13	7	-22.51	15.26

27	-2.68	2.16	8	-20.81	15.45
28	-2.34	2.14	8	-21.01	16.32
29	-3.77	2.10	7	-23.34	15.80
30	-4.10	2.10	7	-23.61	15.42
31	-4.22	2.14	8	-22.87	14.44
32	-3.04	2.13	8	-21.86	15.78
33	-6.08	2.26	9	-22.78	10.62
34	-3.68	2.10	7	-23.13	15.76
35	-4.11	2.13	7	-23.02	14.80
36	-2.18	2.33	11	-18.11	13.74
37	-4.91	2.21	9	-22.30	12.48
38	-5.67	2.72	20	-20.20	8.87
39	-4.40	2.13	8	-23.21	14.41
40	-5.11	2.68	19	-19.67	9.45

Chapter 3 Table S3: GLMM model exhibiting how the DDT-complex (all DDT congeners and isomers) has declined over time, using concentrations from a small subset of studies (n=19) from the original dataset (n=208), that are suitable for a time series analysis. This model used “year since DDT was banned” as a fixed effect with the study fitted as a random intercept and slope. Values in **bold** indicate significance.

Predictor	Estimate	CI	P
Intercept	0.60	-0.68 – 1.89	0.356
Time	**-0.10**	**-0.15 – -0.05**	**<0.001**
Random Effects			
Study	5.81		
(Time | Study)	0.008		



Chapter 3 Figure S1: Model prediction for Log DDT-complex which represents modelled concentrations of all DDT isomers and congeners, using 19 studies analysing DDT, spanning a minimum of five years and reporting a minimum of three concentrations for raptors from the same region after DDT was banned. The thick black line represents the modelled slope for all the studies through time while the thinner black lines represent the slopes for the individual studies. The red dashed line is the overall downward trend of the DDT-complex reported in Chapter 3, Figure 6.

Chapter 4 Table S1: Compounds analysed, and ion transitions used for qualification and quantification purposes.

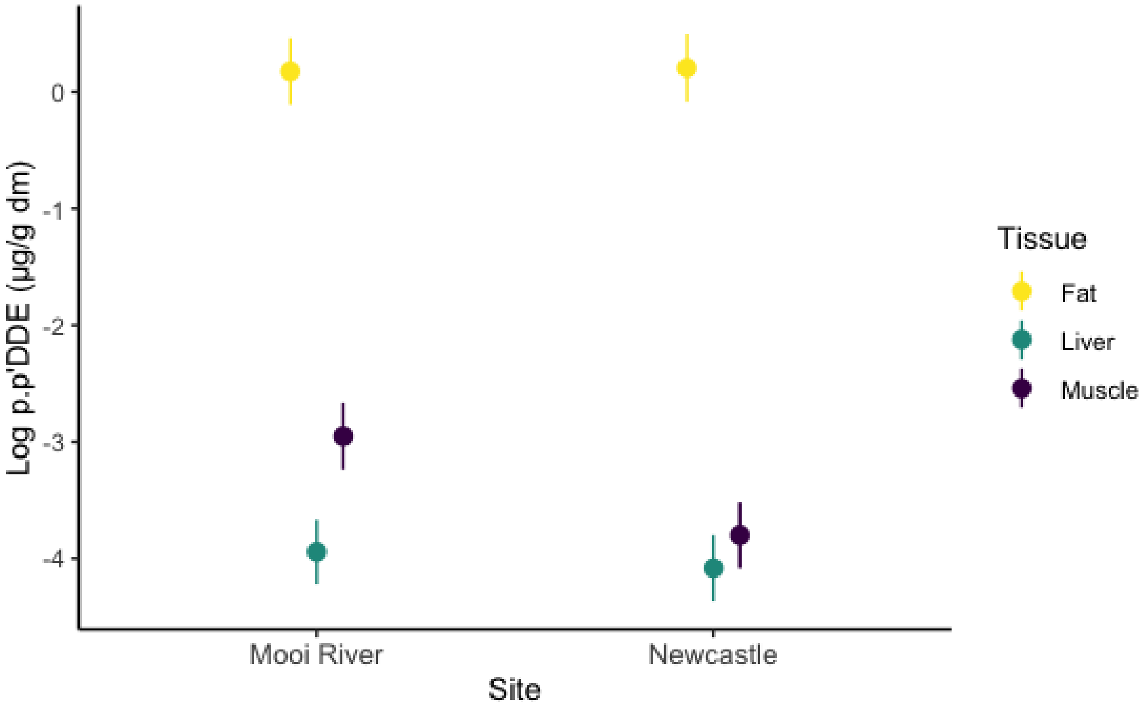
Compounds	Quantifier	Transitions	Qualifier
p,p'-DDD	237.0 → 200.1	237.0 → 165.1	165.1 → 115.0
p,p'-DDE	246.1 → 176.2	315.8 → 246.0	317.8 → 246.0
p,p'-DDT	235.0 → 199.2	235.0 → 165.2	
Dieldrin	262.9 → 193.0	262.9 → 191.0	277.0 → 241.0
PCB 209 (IS)	495.8 → 425.7	497.7 → 427.7	499.8 → 427.7

Chapter 4 Table S2: Recovery (±RSD) of samples spiked with 100 ng of each compound and limits of detection (LOD) and quantification (LOQ) in ng/g of muscle, liver and fat samples.

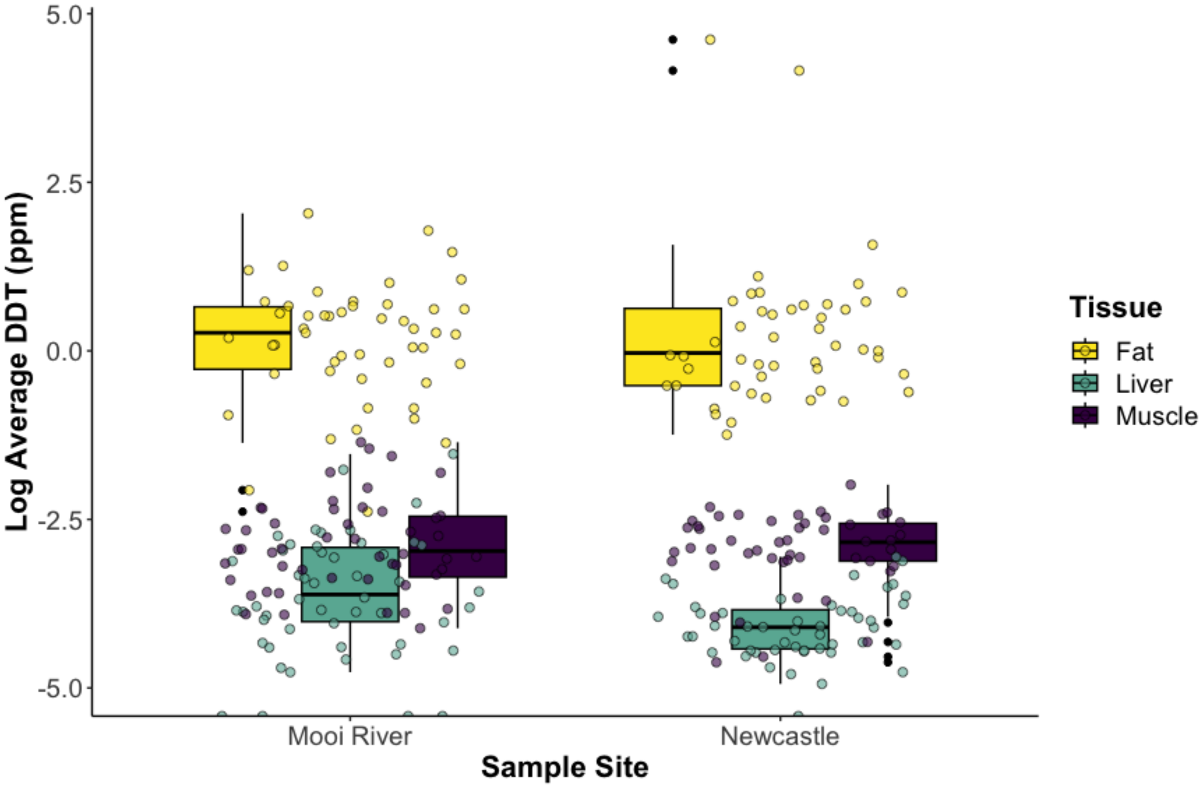
	Muscle					Liver					Fat				
Compounds	Recovery			LOD	LOQ	Recovery			LD	LOQ	Recovery			LOD	LOQ
	N	Mean (%)	RSD			N	Mean (%)	RSD			N	Mean (%)	RSD		
p,p'-DDE	4	114	13	3.3	10.0	4	93	17	2.3	7.0	4	106	26	17.7	53.1
p,p'-DDD	4	113	12	10.0	30.0	4	98	10	2.0	6.0	4	105	22	4.0	12.0
p,p'-DDT	4	101	7	8.7	26.0	4	94	20	2.1	6.3	4	96	20	13.3	40.0
Dieldrin	4	92	7	0.3	1.0	4	87	11	0.3	1.0	4	95	27	12.0	36.0

Chapter 4 Table S3: GLMM model exhibiting the important predictors influencing the differences in *p.p'*-DDE concentrations in Amur Flacons sampled in Newcastle and Mooi River, KwaZulu-Natal, South Africa. This model used sample name as a random term. Values in **bold** indicate significance.

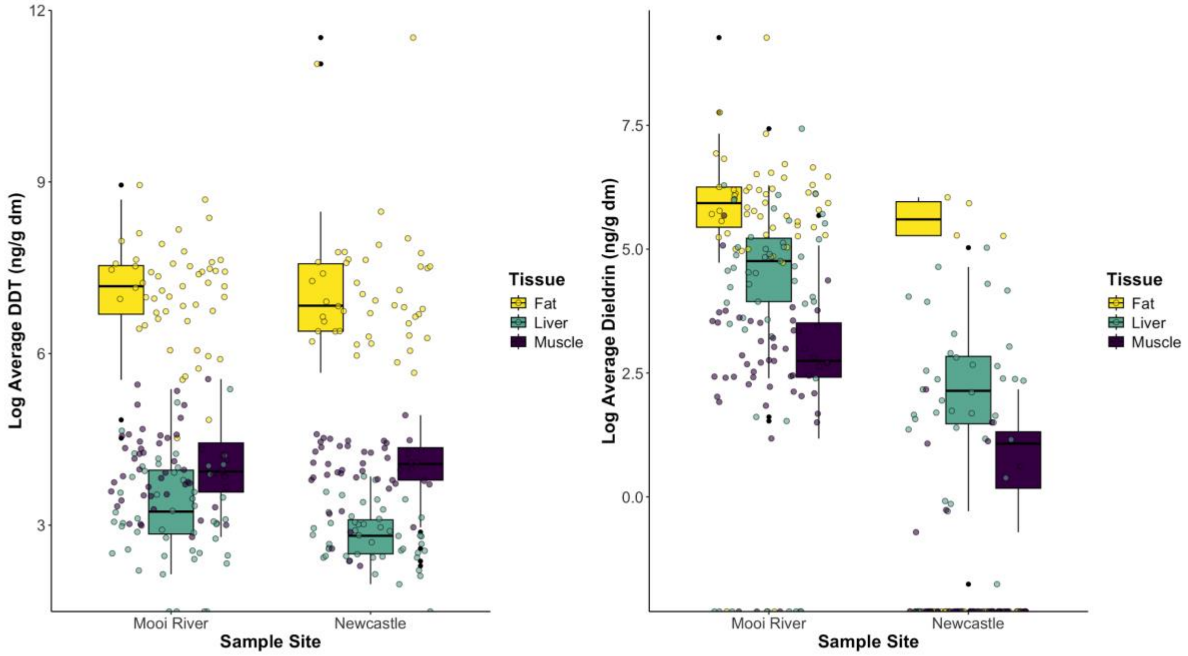
Model	Predictors	Chisq	DF	P
p.p'-DDE	**Site**	**5.01**	**1**	**0.03**
	Age	1.36	1	0.24
	Sex	**8.16**	**1**	**0.00**
	Tissue	**1295.03**	**2**	**0.00**
	Body Condition	0.84	1	0.36
	Lipid Fraction	1.59	1	0.21
	Site*Age	2.71	1	0.10
	Sex*Site	**4.16**	**1**	**0.04**
	Site*Tissue	**16.14**	**2**	**0.00**
	Age*Sex	0.32	1	0.57
	Age*Tissue	0.32	2	0.85
	Sex*Tissue	2.38	2	0.30



Chapter 4 Figure S1: Estimated marginal means of (log) *p.p'*-DDE concentrations µg/g dry mass by sex and tissue showing the strong interaction between sex and tissue. The *p.p'*-DDE concentrations in falcon muscle from Mooi River were significantly higher than those in falcon muscle from Newcastle. Concentrations in fat from both sites are significantly higher than those of liver and muscle.



Chapter 4 Figure S2: Mean naturally logged ΣDDT concentrations in fat, liver, and muscle tissue of Amur Falcons collected in Mooi River and Newcastle, South Africa, plotted against raw data points.



Chapter 4 Figure S3: Mean naturally logged dieldrin concentrations in ng/g dm in fat, liver, and muscle tissue of Amur Falcons collected in Mooi River and Newcastle, South Africa, plotted against raw data points.

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