HARBOUR PORPOISES

INVESTIGATING TWO DECADES OF CRITICAL RAW MATERIALS CONTAMINATION IN THE NORTH SEA

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ABSTRACT

The North Sea, a semi-enclosed basin with densely populated coastlines, faces substantial anthropogenic pressures due to high urbanization, offshore hydrocarbon extraction, wind farms, navigation, and fisheries. The increasing demand for Critical Raw Materials (CRMs), including Rare Earth Elements (REEs), driven by new technologies and the global energy transition, raises concerns about their environmental impact. Harbour porpoises, with their long lifespan and role as apex predators, serve as effective bioindicators for trace element contamination in the marine food web. However, there is a significant knowledge gap regarding the temporal trends of CRM contamination in marine mammals within the North Sea.

This study aims to address this gap by identifying which tissues accumulate CRMs most significantly, examining whether these elements show an adult accumulation trend, and comparing CRM levels in harbour porpoises from two periods: 1999-2001 and 2019-2024. We quantified concentrations of 33 CRMs and 10 other chemical elements in the liver and muscle tissues of 41 harbour porpoises collected from Belgium and Germany using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Results indicate that the liver accumulates higher CRM levels than the muscle, with Bi, Co, Sc, Sm, Ce, La, Nd, and V showing higher concentrations in adults. Temporal analysis revealed significant increases in liver concentrations of Al, Nb, and Sb by 9%, 9%, and 100%, respectively, while no temporal trends were observed for REE, suggesting they do not bioaccumulate in the marine food web. Thus, marine mammals, alongside other species like mollusks, could serve as effective bioindicators for Light Rare Earth Elements (LREE) in the North Sea, but not for Heavy rare Earth Elements (HREE). Although REE concentrations are low, potential toxicity, especially in combination with other contaminants like mercury and organic pollutants, warrants further investigation.

RÉSUMÉ

La mer du Nord, un bassin semi-fermé avec des côtes densément peuplées, fait face à d'importantes pressions anthropiques en raison de la forte urbanisation, de l'extraction d'hydrocarbures en mer, des parcs éoliens, de la navigation et de la pêche. La demande croissante de Matières Premières Critiques (CRMs), y compris les Éléments de Terres Rares (REE), alimentée par les nouvelles technologies et la transition énergétique mondiale, soulève des préoccupations quant à leur impact environnemental. Les marsouins communs, avec leur longue durée de vie et leur rôle de prédateurs au sommet de la chaîne alimentaire, servent d'indicateurs biologiques efficaces pour la contamination en éléments traces dans le réseau trophique marin. Cependant, il existe une lacune significative dans les connaissances concernant les tendances temporelles de la contamination par les MPC chez les mammifères marins de la mer du Nord.

Cette étude vise à combler ces lacunes en identifiant les tissus qui accumulent le plus les CRMs, en examinant si ces éléments montrent une tendance à l'accumulation chez les adultes, et en comparant les niveaux de CRMs chez les marsouins communs entre deux périodes : 1999-2001 et 2019-2024. Nous avons quantifié les concentrations de 33 CRMs et de 10 autres éléments chimiques dans les tissus hépatiques et musculaires de 41 marsouins communs collectés en Belgique et en Allemagne, en utilisant la spectrométrie de masse à plasma à couplage inductif (ICP-MS).

Les résultats indiquent que le foie accumule des niveaux de CRMs plus élevés que le muscle, avec des concentrations plus élevées de Bi, Co, Sc, Sm, Ce, La, Nd et V chez les adultes. L'analyse temporelle a révélé des augmentations significatives des concentrations hépatiques d'Al, Nb et Sb de 9 %, 9 % et 100 %, respectivement, tandis qu'aucune tendance temporelle n'a été observée pour les REE, suggérant qu'ils ne s'accumulent pas dans le réseau trophique marin. Ainsi, les mammifères marins, aux côtés d'autres espèces comme les mollusques, pourraient servir d'indicateurs biologiques efficaces pour les Éléments de Terres Rares Légers (LREE) dans la mer du Nord, mais pas pour les Éléments de Terres Rares Lourds (HREE). Bien que les concentrations en REE soient faibles, leur toxicité potentielle, en particulier en combinaison avec d'autres contaminants tels que le mercure et les polluants organiques, nécessite une investigation plus approfondie.

ABREVIATIONS

Al: Aluminum

As: Arsenic

ASCOBANS: Agreement on the Conservation of Small Cetaceans of the Baltic, Northeast Atlantic, Irish, and North Seas

Ba: Barium

Be: Beryllium

Bi: Bismuth

Cd: Cadmium

Ce: Cerium

Co: Cobalt

CRMs: Critical raw materials

Cr: Chromium

Cu: Copper

dw: Dry weight

Dy: Dysprosium

Er: Erbium

Eu: Europium

EU: European Union

Fe: Iron

Gd: Gadolinium

Ge: Germanium

GESAMP: Group of Experts on the Scientific Aspects of Marine Environment

HREE: Heavy Rare Earth Elements

Ho: Holmium

ICES: International Council for the Exploration of the Sea

ICP-MS: Inductively Coupled Plasma Mass Spectrometry

In: Indium

La: Lanthanum

LREE: Light Rare Earth Elements

LoD: Limit of Detection

LoQ: Limit of Quantification

Lu: Lutetium

Mn: Manganese

Mo: Molybdenum

Nb: Niobium

Nd: Neodymium

Ni: Nickel

Pb: Lead

PP: primary production

Pr: Praseodymium

Pt: Platinum

REE: Rare Earth Elements

Sb: Antimony

Sc: Scandium

SD: Standard Deviation

Se: Selenium

Sm: Samarium

Sn: Tin

Sr: Strontium

Ta: Tantalum

Tb: Terbium

TE: Trace Elements

Ti: Titanium

Tl: Thallium

U: Uranium

V: Vanadium

ww: Wet weight

Y: Yttrium

Yb: Ytterbium

Zn: Zinc

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INTRODUCTION

1. THE NORTH SEA

1.1 OCEANOGRAPHIC CHARACTERISTICS

The North Sea is a semi-enclosed sea delimited by the English Channel, the Skagerrak and Kattegat straits and the area south of 62°N. Covering an area of 750,000 km² with an average depth of 90 m, it is considered a shallow sea (Ducrotoy et al., 2000). Depth increases from south to north (Fig. 1), with depths of less than 40 meters along the Belgian, German, and Dutch coasts, extending through the Dogger Bank up to a latitude of 54°N. The depth reaches 200 meters at the shelf edge and a maximum of 700 meters in the Norwegian Trench (Howarth, 2001). The North Sea basin is characterized by significant geomorphological diversity, with rocky and mountainous coastlines, cliffs, and fjords in the north and west, and sandy beaches along the eastern shores. The basin is heavily sedimented, particularly in the southern regions, due to the transport of sediments by currents and tides (Ducrotoy et al., 2000).

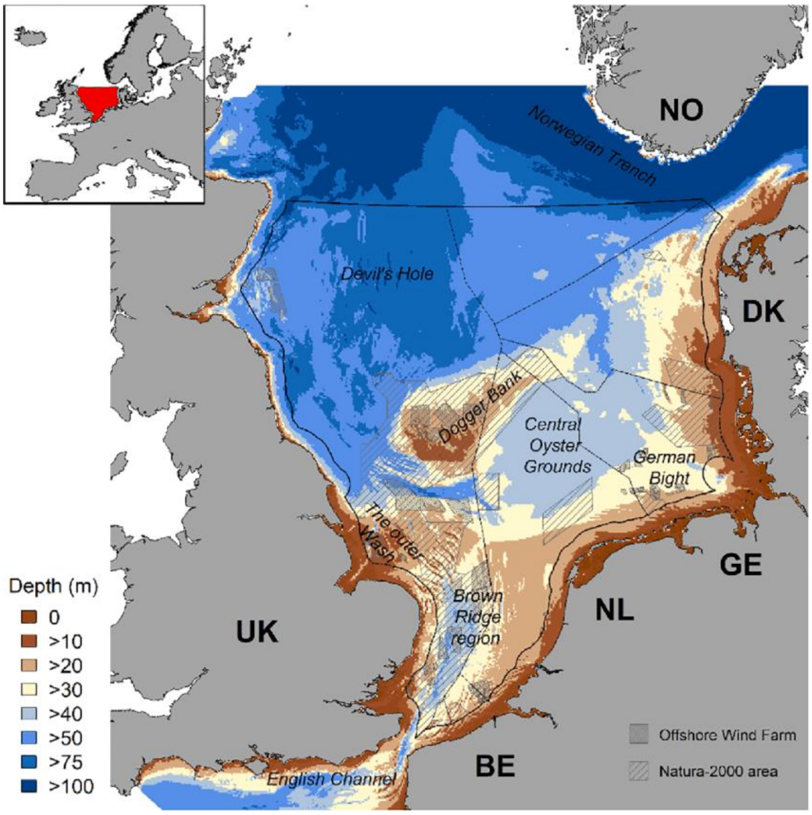


Figure 1: Bathymetry of the North Sea, including names of important subareas. The Southern North Sea is delineated with a black solid line. Grey hatched areas depict Natura-2000 areas and offshore wind farms, and two-letter codes reflect surrounding countries. Black dotted lines represent Exclusive Economic Zones (EEZ) (Van Der Reijden et al., 2021)

The main drivers of the North Sea circulation are tidal currents, wind-generated currents, and density gradients. Tides are responsible for most currents in the North Sea, particularly on the western side, where they account for 50% of water transport. Tidal currents enter the North Sea from the Atlantic Ocean and circulate in an anticlockwise direction. In contrast, along the Norwegian coast, wind forces primarily drive the currents. These winds are seasonal and more pronounced in winter due to storms. Wind-induced waves also play a crucial role in suspending sediments, which are then redistributed by tidal currents (Ducrotoy et al., 2000; Howarth, 2001).

The North Sea receives between 300 and 350 km^3 yr^{-1} of freshwater from numerous rivers, with the Rhine and the Elbe being the main ones (Ducrotoy & Elliott, 2008). Additionally, the Baltic Sea adds approximately 475 km^3 yr^{-1} of brackish water. These inputs of low-salinity water significantly influence the regional density distribution. Together, these three forces, tides, wind, and freshwater inputs, create a long-term circulation pattern in the North Sea (Howarth, 2001).

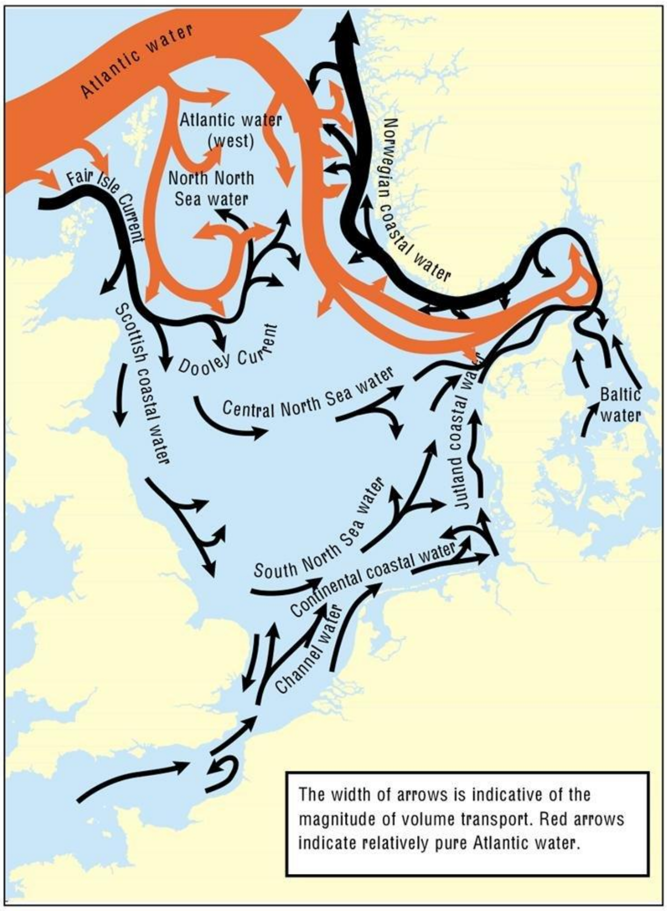


Fig 2: Schematic diagram of the general circulation in the North Sea. The width of the arrows is indicative of the magnitude of volume transport (OSPAR, 2000)

This circulation is broadly cyclonic and weaker in the center (Fig. 2). The main coastal current flows southward along the coasts of Scotland and England into the Southern Bight, then turns northward along Denmark in the Jutland current to join the Norwegian Coastal Current. Salty water enters through the Dover Strait, while major rivers provide freshwater. Large inflows of Atlantic water enter from the north, but most do not penetrate deeply into the North Sea. Instead, most of the water exits through the Skagerrak, with a major outflow along the eastern side of the Norwegian Trench (Howarth, 2001). This anticlockwise circulation, combined with tidal cycles, is primarily responsible for sediment distribution, leading to significant deposition in the south and the formation of bedforms. These processes also contributed to the creation of the Dogger Bank. These circulation patterns not only shape sediment deposition but also drive the accumulation of pollutants within these sediments, which has significant implications for marine pollution in the North Sea. (Ducrotoy et al., 2000; Wang et al., 2020).

1.2 Marine POLLUTION

1.2.1 DEFINITION

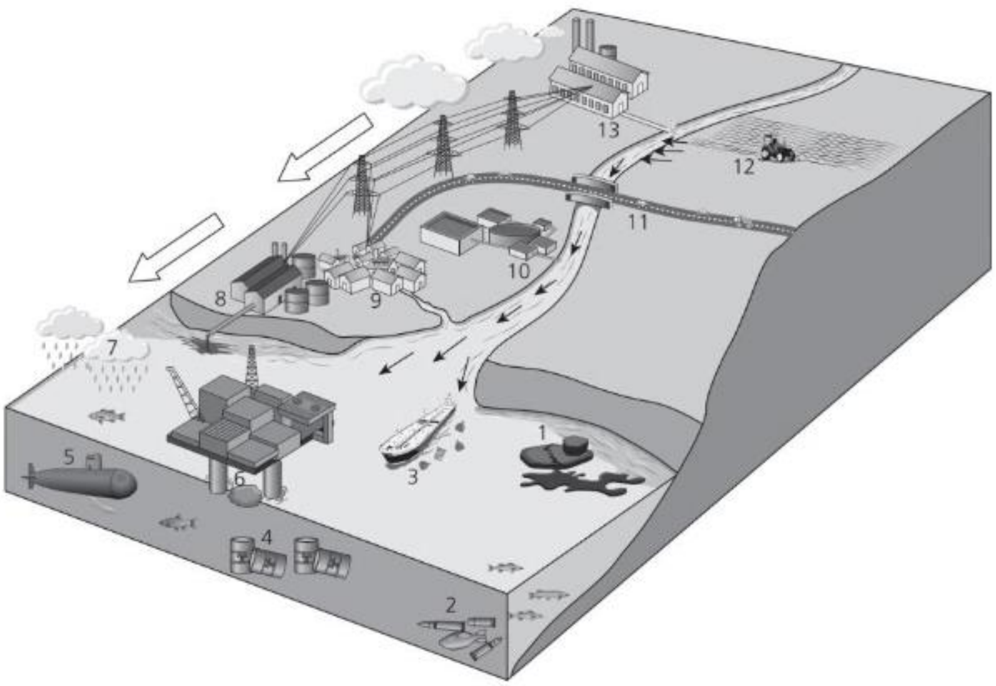


Figure 3: Pathways and sources of contaminants in the marine environment. 1) Oil spills, 2) lost or dumped munitions, 3) waste from ships, 4) dumped nuclear and industrial waste, 5) lost or dumped vessels, 6) contaminated drill cuttings, 7) washout of atmospheric pollutants, 8) industrial waste discharges, 9) urban wastewater, 10) sewage effluent, 11) vehicle exhausts, 12) agricultural fertilizers and pesticides, 13) cooling water (Frid & Caswell, 2017)

According to the Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), marine pollution is “the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water, and reduction of amenities." Hence, pollutants can be nutrients, sediments, pathogens, alien species, persistent toxins/chemicals, oil, plastics, radioactive substances, and even noise and light according to new definitions (Chahouri et al., 2022; Frid & Caswell, 2017).

In the North Sea, pollutants enter the marine environment through several pathways (Fig. 3).

1.2.2 Anthropogenic pressure

In 2005, the North Sea region was one of Europe's most densely populated areas, with a population density of 250 inhabitants per square kilometer, a status that persists today. ("Interreg North Sea Programme 2021-2027," 2021; Eurostat, 2009).

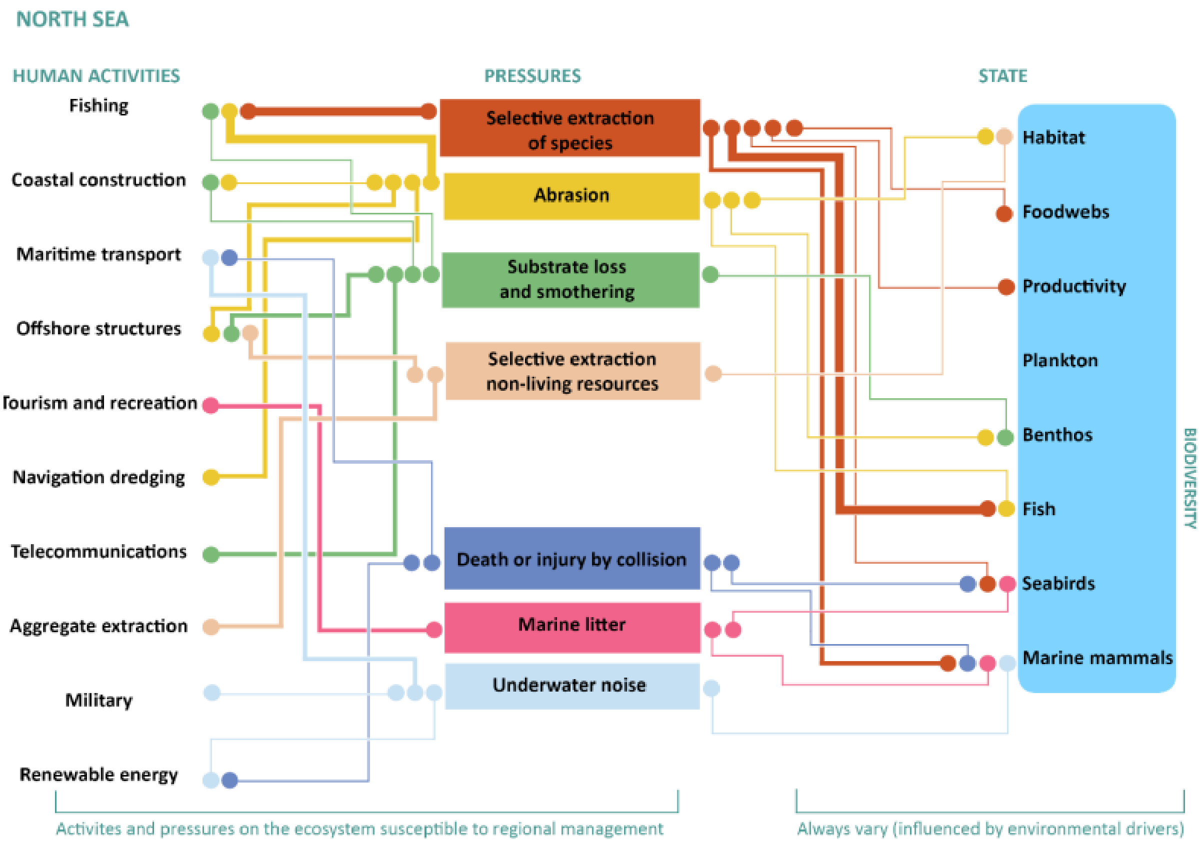


Figure 4: Major regional pressures, human activities, and state of the ecosystem in the North Sea. The width of lines indicates the relative importance of individual links. (ICES 2022).

Coastal seas are particularly vulnerable to anthropogenic pressures due to their proximity to land. In the North Sea, the most significant pressures include the selective extraction of species and non-living resources, abrasion, substrate loss, the death of organisms by collision, marine litter, and underwater noise (Fig. 4). These pressures arise from human activities such as fishing, navigation, tourism, and coastal construction, all of which can have detrimental effects on biodiversity (ICES 2022).

Over the past two decades, some of these pressures have notably increased or shifted, potentially leading to major changes in the North Sea ecosystem. A prime example is the development of wind farms. While relatively undeveloped in the early 2000s (Ducrotoy et al., 2000), there are now more than 41 wind farms in the North Sea, including the largest in the world. This rapid expansion could have significant ecological implications (Chirosca et al., 2022).

1.2.3 Biodiversity changes between 2000 and 2020

The North Sea is a rich ecosystem, home to approximately 230 species of fish, showcasing its high biodiversity (Ducrotoy et al., 2000). However, the North Sea ecosystem is currently considered in a perturbed state by the International Council for the Exploration of the Sea (ICES)

Primary production (PP) varies across the North Sea, being highest in freshwater-influenced and transitional regions, and lowest in permanently mixed regions. A declining trend in PP was observed from 1988 to 2013, correlated with a decrease in riverine dissolved nutrient concentrations, especially phosphorus, likely due to fertilizer and detergent policy changes. This decline in PP has significantly impacted biodiversity. There has been a decrease in the average annual abundance of small copepods, essential components of the marine food web. Additionally, there is a correlation between primary production and the standardized index of fish stock recruitment, which includes species such as sandeel, sprat, herring, Norway pout, cod, haddock, and whiting. This index has shown a significant decline despite substantial interannual variability (Capuzzo et al., 2017).

The North Sea, historically a crucial fishing zone in Europe, is among the most intensively exploited marine regions worldwide. Fish stocks have experienced substantial changes, with significant declines in the 1980s and 1990s. Recent recovery of several stocks has occurred due to improved fisheries management since 2000, although recruitment levels remain low. In fact, many fish stocks remain depleted despite international stock recovery strategies, such as cod, (*Gadus morhua*), sardine (*Sardina pilchardus*), sandeel (*Ammodytes spp*), and horse mackerel (*Trachurus trachurus*) (López et al., 2022).

2. TRACE ELEMENTS

2.1 DEFINITION

Numerous definitions have been established over the years to define trace elements. The International Union of Pure and Applied Chemistry considers trace elements to be those with concentrations less than 100 µg g^{-1}, but this definition is incomplete, as an element may be a trace in one phase but a major component in another (Richir & Gobert, 2016). Overall, trace elements are defined as minerals that occur in small quantities in living tissues or in the environment.

Some of these elements are essential for the proper growth and functioning of organisms. The main essential elements are Mn, Fe, Co, Ni, Cu, Zn, Mo, Se, Cr, I and F. There are additional elements that might also be essential, though their roles are not yet clearly understood or fully evidenced. These include V, B, Si, Sn, As, and Br (Chitturi et al., 2015; Newman, 2014; Richir & Gobert, 2016). Whether essential or not, trace elements can become toxic to organisms when their concentrations exceed certain thresholds.

2.2 CRITICAL RAW MATERIALS

2.2.1 DEFINITION

Since 2011, the European Union (EU) has published five lists of materials based on their economic importance and supply risk. These critical raw materials (CRMs) are crucial to the industry at every stage of the supply chain and are essential to produce new technologies, such as smartphones, solar panels, and electric vehicles (Fig. 5). Because of their high impact on technological innovation and industrial processes, CRMs are of strategic importance, making their reliable supply crucial for economic stability and progress.

The list published in 2023 features 51 materials, including rare earth elements (REE), platinum group metals, biomaterials, and other trace elements such as aluminum, cobalt, and strontium. A significant portion of these materials are processed or extracted in China and South Africa (Fig. 6). Consequently, China is the primary supplier of CRMs to the EU, although the EU sources various materials from other countries, such as Belgium for Arsenic, Finland for Nickel, and Poland for Copper (Fig. 7).

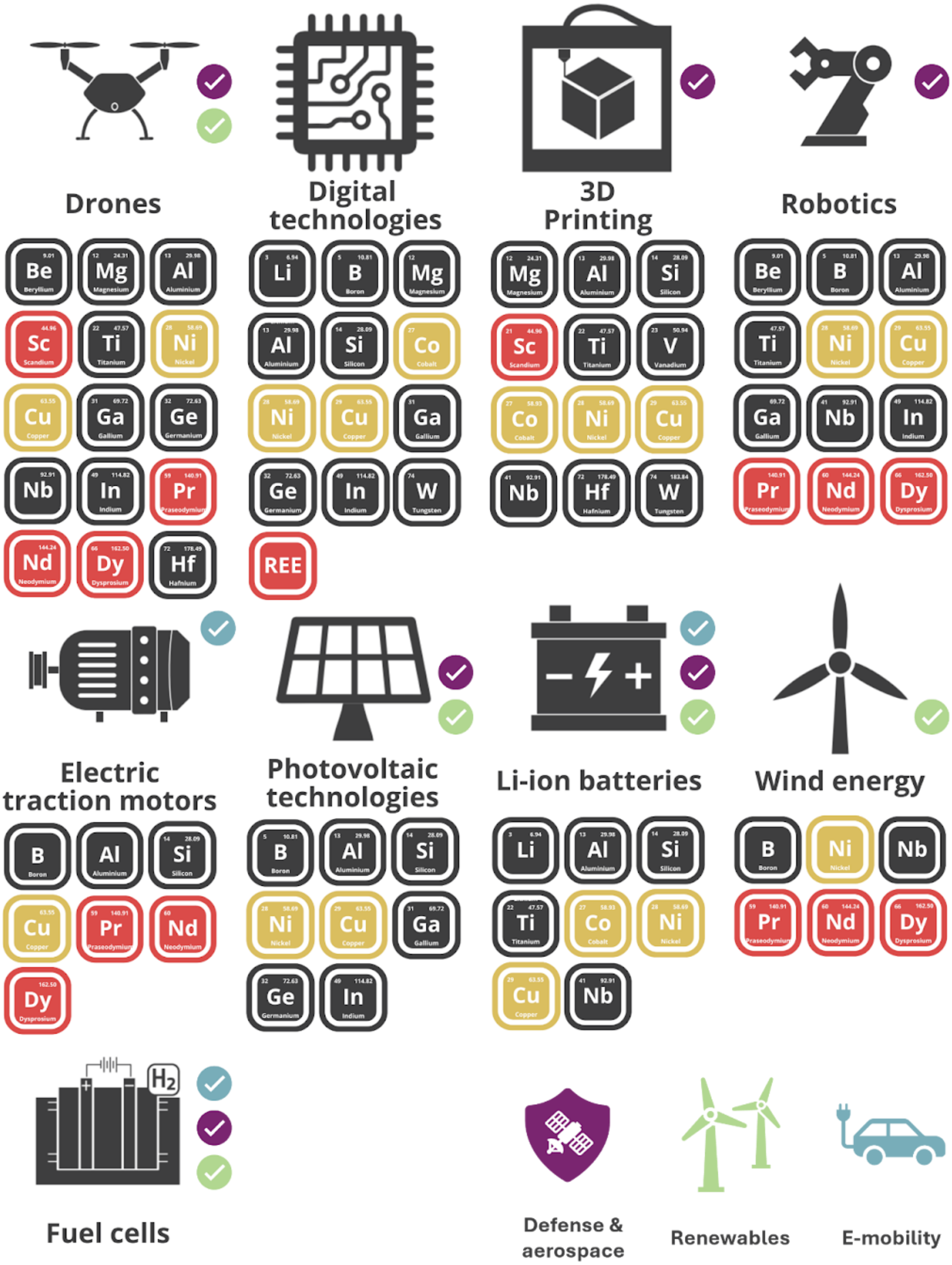


Figure 5: Uses of Critical Raw Materials in the 9 new technologies used in the three strategic sectors: renewable energy, e-mobility, defense and aerospace. Red: rare earth elements, Yellow: essential trace elements. Adapted from Critical Raw Materials for Strategic Technologies and Sectors in the EU- A Foresight Study

Critical Raw Materials (CRMs) are increasingly recognized as emerging contaminants due to their widespread use and potential environmental impact. As these materials are extensively used in high-tech and industrial applications, their release into the environment, whether through mining, processing, or disposal, can lead to contamination of soil and water, posing a threat to wildlife and human health (Kanianska et al., 2023)

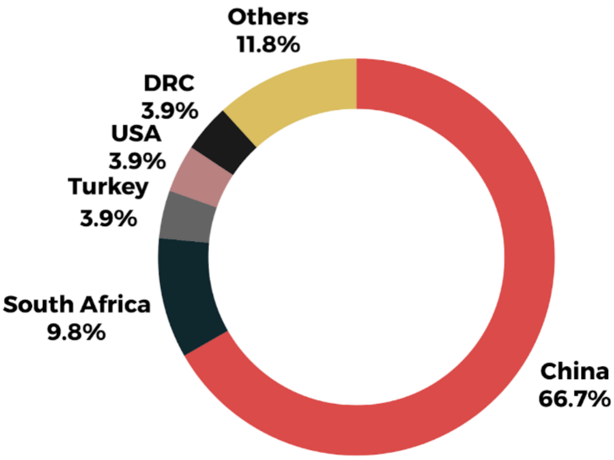


Figure 6: Major global supplier countries of the 2023 Critical Raw Materials (CRMs). The percentages represent the frequency with which a country is the primary supplier of a CRM. The category labeled "Others" includes Chile, France, Brazil, Russia, Iran, and Australia. Adapted from the Study on the Critical Raw Materials for the EU 2023 - Final Report.

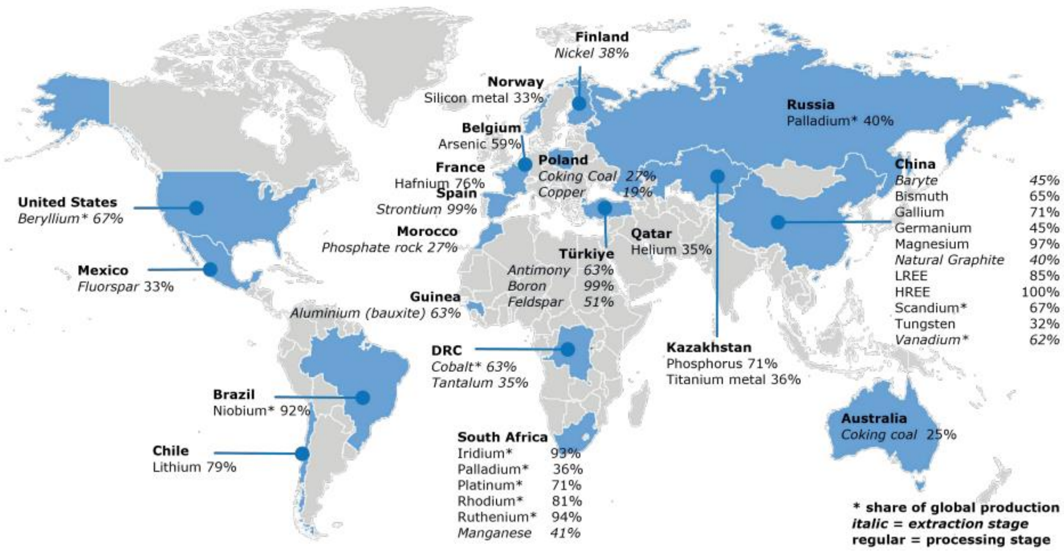


Figure 7: Main EU suppliers of individual CRMs. (Study on the Critical Raw Materials for the EU 2023 - Final Report, 2023)

2.3 Rare earth elements

2.3.1 Definition and classification

Among the Critical Raw Materials, Rare Earth Elements (REE) have attracted particular interest in recent years due to their unique properties and increasing demand (Balaram, 2019). The International Union of Pure and Applied Chemistry (IUPAC) defines REEs as the 15 lanthanides (Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), plus Sc and Y

(Nomenclature of Inorganic Chemistry, 2005). Despite their name, REEs are not particularly rare; for example, cerium (Ce) is more abundant in the Earth's crust than copper (Cu).

REEs are typically divided into two groups based on their atomic weights: Light Rare Earth Elements (LREEs) and Heavy Rare Earth Elements (HREEs). However, there is no universal consensus on the specific elements that belong to each category. For the sake of consistency, this work follows the classification used in the Critical Raw Materials for the EU 2023 - Final Report. According to this classification, LREEs, which are generally the most abundant REEs, include La, Ce, Pr, Nd, Sm, and Sc. HREEs include Y, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu. LREEs are predominantly used in sectors such as catalysts, metallurgy, glass/polishing, and magnets. In contrast, HREEs are primarily employed in applications that exploit their optical properties (Fig. 7).

2.3.2 Sources and distribution in the marine environment

Originally, rare earth elements were primarily extracted in the United States and Australia. However, since the 1980s, China has emerged as the world's leading producer of rare earth elements. Since then, production has continually increased, with China producing 210,000 tons of REEs in 2022, accounting for 70% of the global output. This is followed by the United States, Australia, and Myanmar (Canada, 2024). Furthermore, most rare earth reserves are also located in China (Fig. 8).

REE are commonly found in sediments and soils, particularly in deposits such as iron-REE, carbonatite, or lateritic formations (Castor & Hedrick, 2006). While the concentration of REEs in water is typically low (0.004-0.024 µg L^{-1}), the increased extraction and utilization of REEs in modern technologies can elevate their concentrations in aquatic environments. For instance, in Poland's Wiśniówka mining area, exceptionally high REE concentrations have been detected in ponds and drainage ditches, attributed to arsenic-rich pyrite mineralization. Furthermore, the growing use of REEs, such as gadolinium (Gd) in medical applications, has significantly increased their levels in wastewater and streams, sometimes by up to two orders of magnitude above natural levels (Patel et al., 2023).

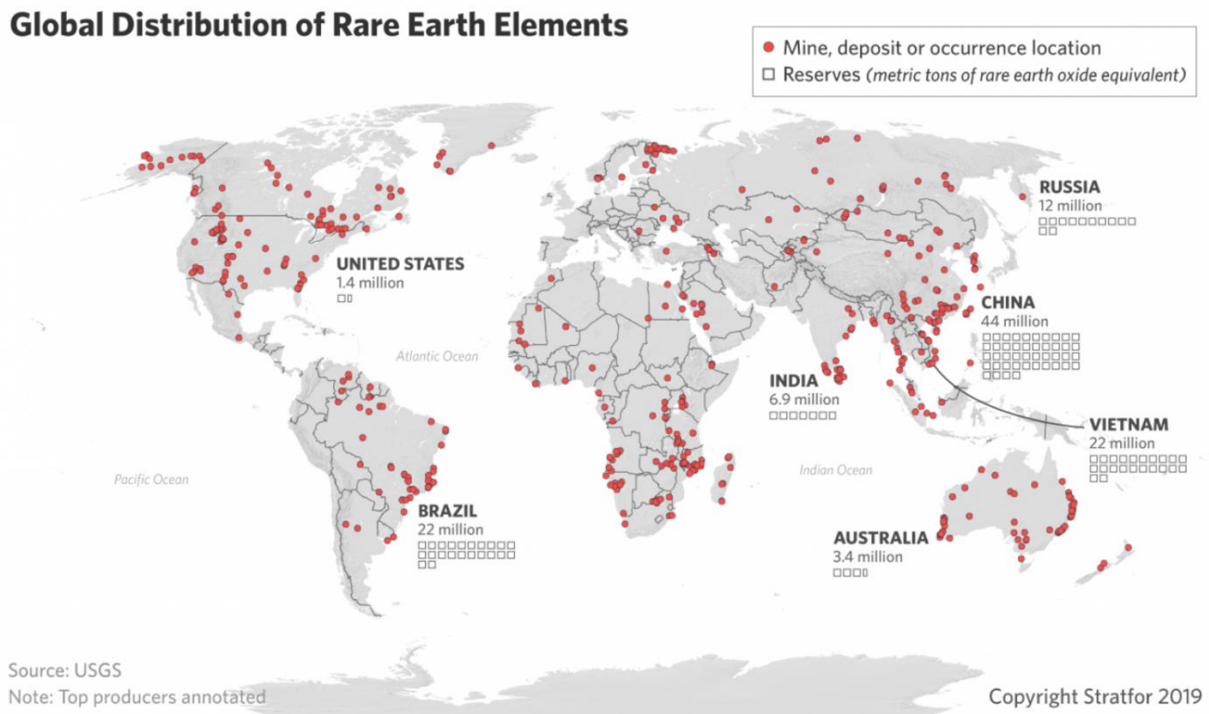


Figure 8: Global distribution of Rare Earth Elements (https://worldview.stratfor.com/article/geopolitics-rare-earth-elements)

3. THE HARBOUR PORPOISE

3.1 General

Figure 9: Harbour Porpoise (*Phocoena phocoena*) https://www.natureplprints.com/2019-april-highlights/harbour-porpoise-phocoena-phocoena-18937249.html

The harbour porpoise *(Phocoena phocoena)* is a marine mammal species that belongs to the order of cetaceans, specifically to the suborder of Odontocetes, commonly known as toothed whales. It is rather small compared to other cetaceans, weighing around 70 kg and measuring 150 cm on average (Fig. 9). This species usually lives up to 10 years and individuals are sexually mature at around 4 years (Bjørge & Tolley, 2018).

Phocoena phocoena is an emblematic species in the North Sea, symbolizing the region's marine biodiversity and the importance of international cooperation in marine conservation efforts. Its protection is crucial not only for maintaining ecological balance but also for fulfilling international conservation commitments.

Although *Phocoena phocoena* are found throughout most coastal areas of the northern hemisphere, they are particularly abundant in the North Sea. With an estimated population of 338,918 individuals in 2022, they are the most prevalent marine mammal species in the North Sea (SCANS-IV, 2023). This estimation has been consistent over the last decades, even though there have been changes in population densities in some areas. Indeed, at the beginning of the 20th century, *Phocoena phocoena* was commonly found in the southern North Sea, including areas such as the Netherlands and Belgium. However, since the 1940s, there has been a significant decline of the southern North Sea population. As a result, between the 1970s and 1990s, sightings of *P. phocoena* were less frequent in the southern North Sea compared to more northern regions. Comparative analysis of data from the 1994 SCANS survey and the 2005 SCANS II survey indicates a population shift, with *P. phocoena* moving back from the northern areas of the North Sea to the southern regions (German Federal Agency for Nature Conservation (BfN), 2009)

Phocoena phocoena tend to prefer shallow coastal areas with depths of less than 200 meters (Stalder et al., 2020; Van Beest et al., 2018). Occasionally, they venture into estuaries, and some individuals have been observed in rivers (Wenger & Koschinski, 2012). In the North Sea, the distribution and density of *P. phocoena* exhibit seasonal variations. During spring, the highest densities, or hotspots, of *P. phocoena* are typically found in the southern and southeastern parts of the North Sea, particularly near the Belgian and Dutch coasts, as well as in the Sylt Outer Reef and in the Dogger Bank. In contrast, during the summer, these hotspots migrate to the German and Danish west coasts, reaching up to the Dogger Bank (Fig. 10). By autumn, the density of *P. phocoena* decreases in the southern North Sea, suggesting a possible movement of the population offshore (Gilles et al., 2016). These migrations are likely driven by prey availability (Hammond et al., 2013).

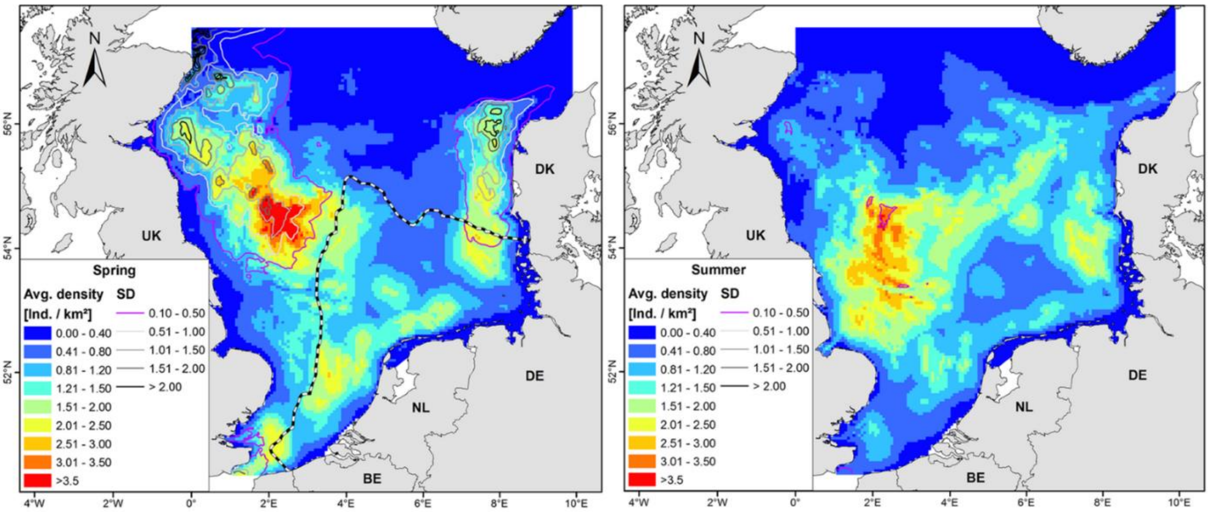


Fig 10: Harbour porpoise (*Phocoena phocoena*) density in spring and summer (Gilles et al., 2016)

In the North Sea, *P. phocoena* exhibit a diverse diet, primarily consisting of various fish species. Stomach content analysis and stable isotope analysis of carbon ($\delta^{13}C$ values) and nitrogen ($\delta^{15}N$ values) have identified their primary prey items. These include gobies (*Pomatoschistus microps* and *Pomatoschistus minutus*), sprat (*Sprattus sprattus*), herring (*Clupea harengus*), cod (*Trisopterus minutus*) and lesser sandeel (*Ammodytes tobianys*). Their diets seem to vary with age. Indeed, juveniles predominantly consume small prey species in the shallow coastal waters, whereas adults tend to feed more often on larger pelagic species (Jansens, 2012).

3.2 Threats

Anthropogenic activities pose a significant threat to *P. phocoena*. These threats include incidental catch in gillnets (bycatch), ship strikes, pollution, and underwater noise (Scheidat et al., 2018). The International Council for the Exploration of the Sea (ICES) estimated that 5,974 *P. phocoena* were bycaught in the North Sea in 2020. This surpasses the 1.7% anthropogenic removal threshold set by the Agreement on the Conservation of Small Cetaceans of the Baltic, Northeast Atlantic, Irish, and North Seas (ASCOBANS), highlighting bycatch a major threat to small cetaceans (Taylor et al., 2022). Acoustic disturbance threatens *P. phocoena* by increasing physiological stress and causing behavioral alterations. This disturbance can reduce available habitat and force them to abandon crucial breeding and feeding areas. Additionally, exposure to loud noises can lead to hearing damage, which is a major issue as *P. phocoena* relies on echolocation for communication (Clausen et al., 2011; German Federal Agency for Nature Conservation (BfN), 2009).

To protect P. phocoena, various conservation strategies have been implemented. *P. phocoena* is listed as a protected species in the Annexes of the European Habitats Directive (Natura 2000). Additionally, in the North Sea *P. phocoena* falls under the framework of the ASCOBANS, which aims to maintain and restore North Sea P. phocoena at a favorable conservation status. This includes reducing bycatch, protecting habitats, developing methods to mitigate threats such as new pingers or gear modifications, monitoring populations, encouraging research, and fostering international cooperation (German Federal Agency for Nature Conservation (BfN), 2009; Reijnders et al., 2009). Overall, *P. phocoena* has been listed as "Least Concern" in the IUCN Red List of Threatened Species in 2020 (Braulik et al., 2023).

3.3 Using the the harbour porpoise, *Phocoena phocoena* as a bioindicator

3.3.1 Definition of a bioindicator

A bioindicator is defined as a species, or a community that is used to evaluate environmental quality and monitor changes over time. Not all species can be bioindicators. One key requirement is that a bioindicator species must have a moderate tolerance to environmental variability. If it is too rare, it may be overly sensitive to changes. Conversely, if it is too widespread, it may not show significant responses to environmental disturbances. By using bioindicators, it is possible to evaluate the cumulative impacts of chemical pollutants and habitat changes over time, integrating past, present, and future environmental conditions through the lifespan of the species (Holt & Miller, 2011).

3.3.2 Why Phocoena phocoena ?

The characteristics that define a good bioindicator are outlined in table 1. In aquatic and coastal environments, marine mammals are considered among the best sentinel organisms, providing critical insights into ecosystem health and the impacts of environmental stressors (Bossart 2010). Marine mammals, including *P. phocoena*, have long lifespans, which cause pollutants to bioaccumulate in their bodies over time. Bioaccumulation results from both bioconcentration and biomagnification. Bioconcentration occurs when a marine organism absorbs pollutants from the water, leading to higher pollutant concentrations within the organism than in the surrounding environment. Biomagnification is the process by which the concentration of pollutants increases as they move up the food chain, resulting in higher levels of pollutants in predators compared to their prey (Szynkowska et al., 2018). *P. phocoena* are predators. Hence, this trophic position makes them particularly susceptible to biomagnification, resulting in significant bioaccumulation of pollutants. Trace elements can enter and accumulate in cetacean bodies through multiple pathways. The primary route is ingestion of contaminated food. Additionally, trace elements can be transferred from mother to offspring via the placenta or during lactation. Direct absorption from the environment can also occur through the skin or via respiration (Aguilar et al., 1999).

Table 1: Characteristics of a valuable bioindicator. The symbol ✓ indicates that *P. phocoena* possesses this characteristic, while the symbol ✕ indicates that it does not. Adapted from Holt & Miller, 2011.

	Characteristics	*Phocoena phocoena*
Good indicator ability	Provide measurable response (sensitive to the disturbance or stress but does not experience mortality or accumulate pollutants directly from their environment	✓
	Response reflects the whole population/community/ecosystem response	✓
	Respond in proportion to the degree of contamination or degradation	✓
Abundant and common	Adequate local population density (rare species are not optimal)	✓
	Common, including distribution within area of question	✓
	Relatively stable despite moderate climatic and environmental variability	✓
Well studied	Ecology and life history well understood	✓
	Taxonomically well documented and stable	✓
	Easy and cheap to survey	✕
Economically/ commercially important	Species already being harvested for other purposes	✕
	Public interest in or awareness of the species	✓

As a coastal species, *P. phocoena* serves as a bioindicator for a limited geographic area, aiding in the understanding of environmental variability within local ecosystems, unlike oceanic species (Lemos et al., 2013). Species living in coastal areas are also more likely to bioaccumulate pollutants, since they are usually heavily contaminated by pollutants coming from anthropic activities, like industries or agriculture (Delgado-Suarez et al., 2023).

Finally, *P. phocoena* have already been used as bioindicators in numerous studies before. These include the monitoring of chlorinated pollutants (Covaci et al., 2002; Das et al., 2006; Das, Holsbeek, et al., 2004; Das, Siebert, et al., 2004; Weijs et al., 2007) and trace elements (Fernández et al., 2022; Mahfouz et al., 2014).

4. OBJECTIVES

The objectives of the present work are to investigate the concentrations of critical raw materials in the liver and the muscle of harbour porpoises (*Phocoena phocoena*) and evaluate the influence of factors such as tissue type and age class on these concentrations. A significant focus of this study is the analysis of critical raw materials levels over a 20-year period, which will provide insights into temporal variations.

Given the recent emergence of interest in rare earth elements, no study has assessed their presence in marine mammals from 2000. Hence, this research aims to establish a historical baseline by examining past concentrations of rare earth elements in porpoises and comparing them to current levels. This comparison will help identify trends and assess changes in contamination over time.

Finally, the potential of *P. phocoena* as a reliable bioindicator for rare earth elements contamination in the North Sea will be evaluated.

MATERIAL AND METHOD

1. SAMPLE COLLECTION

The 72 liver and muscle samples of 26 male and 15 female harbour porpoises (*Phocoena phocoena*) used in this research originated from diverse locations within the North Sea, spanning timeframes from 1999 to 2001 and from 2020 to 2024 (Table 2). Porpoises were necropsied at the Institute of Terrestrial and Aquatic Wildlife Research (ITAW, Prof. U. Siebert and team), Germany and at the veterinary faculty of the University of Liège (Prof. T. Jauniaux and team). Necropsies were performed following international protocols (Kuiken, 1996; IJsseldijk et al., 2019). Age was not measured directly. Individuals were classified as juveniles or adults based on length criteria. Individuals measuring less than 135 cm were considered juveniles, whereas individuals measuring more than 135 cm were considered adults. All samples were stored at –20 °C until further analyses. Detailed information on the sampling can found Annex 1.

Additionally, chemical elements analysed in liver (n=38) and muscle (n=40) samples from two seal species from the North Sea (the grey seal *Halichoerus grypus*, and the harbour seal *Phoca vitulina*), as documented in Laurine Marchand's master's thesis (2023), were integrated in this study for inter-species comparison. Detailed information on these samples is provided in Table 2.

Table 2: Number of samples by tissue type and origin (n=72), adapted from Marchand, 2023

	France, Germany & Belgium 2010-2023		**Germany 2023-2024**	**Belgium 2019-2023**	**Belgium 1999-2001**
	H. grypus	*P. vitulina*	*P. phocoena*	*P. phocoena*	*P. phocoena*
Liver (n=149)	22	16	8	9	22
Muscle (n=136)	21	19	9	1	23

2. SAMPLE PROCESSING

The trace element analysis protocol was adapted from established methodologies in the literature (Damseaux et al., 2021; Fernández et al., 2022; Gosnell et al., 2024). Samples weighing between 3 and 14 g, were cut into smaller pieces using a stainless-steel knife and transferred into polyethylene tubes that had previously been weighed with an analytical balance (AB135-S/FACT, Mettler Toledo®). The cutting board and knife were cleaned between each sample to prevent cross-contamination with ultrapure water. This water is obtained by using a milli-Q water purification system and has a resistivity of 18.2 $M\Omega.cm^{-1}$, which is the ability of a material to resist the flow of electrical current. The purpose of cutting the samples into smaller pieces was to facilitate subsequent lyophilization. Each tube was then reweighed (AB135-S/FACT, Mettler Toledo®) to determine the wet weight (ww) of the sample before being stored in a freezer at -80°C for a minimum of 12 hours to freeze the tissue water. The next step includes lyophilization. During that process, the organic matter is desiccated through sublimation. The samples were placed in a lyophilizer (ALPHA 1-4 LD plus, CHRiST®, Italy) set to -55°C for 48 hours, where a pump created a near vacuum, resulting in a pressure in the system of 0.04 mbar.

Once they were dried, the samples were weighed again (AB135-S/FACT, Mettler Toledo®) to determine their dry weight (dw). To confirm the lyophilization process was successful, the sample needed to lose 70% of its weight. However, since some of the samples had been stored in freezers for 20 years, a weight loss of 50% was also accepted. The samples were then powdered using an agate mortar to prevent potential aluminium contamination from ceramic mortar use.

3. ICP-MS ANALYSIS

The following elements were analyzed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS): lithium (^{7}Li), beryllium (^{9}Be), aluminium (^{27}Al), titanium (^{47}Ti), vanadium (^{51}V), chromium (^{52}Cr), manganese (^{55}Mn), cobalt (^{59}Co), nickel (^{60}Ni), copper (^{63}Cu), zinc (^{66}Zn), germanium (^{72}Ge), arsenic (^{75}As), selenium (^{78}Se), strontium (^{88}Sr), niobium (^{93}Nb), molybdenum (^{95}Mo), cadmium (^{111}Cd), indium (^{115}In), tin (^{118}Sn), antimony (^{121}Sb), barium (^{137}Ba), tantalum (^{181}Ta), platinum (^{195}Pt), thallium (^{205}Tl), lead (^{208}Pb), bismuth (^{209}Bi), uranium (^{238}U), and the rare earth elements scandium (^{45}Sc), yttrium (^{89}Y), lanthanum (^{139}La), cerium (^{140}Ce), praseodymium (^{141}Pr), neodymium (^{146}Nd), samarium (^{147}Sm), europium (^{153}Eu), gadolinium (^{157}Gd), terbium (^{159}Tb), dysprosium (^{163}Dy), holmium (^{165}Ho), erbium (^{166}Er), ytterbium (^{174}Yb), lutetium (^{175}Lu). These elements were chosen for their status as key/emerging pollutants in the North Sea ecosystem and their frequent detection in marine mammals and their prey in this area, as evidenced by the literature (Study on the Critical Raw

Materials for the EU 2023 - Final Report, 2023, Klein et al., 2022). ICP-MS has been used in many studies to analyze trace elements contamination in marine mammals (Celis et al., 2022; Fernández et al., 2022; Ferreira et al., 2016; Reindl et al., 2021; Wilschefski & Baxter, 2019).

Details on the functioning of ICP-MS can be found in Annex 2. Prior to ICP-MS analysis, the samples must undergo a digestion process called mineralization. 80 to 115 mg of each sample were weighed with an analytical balance (AB135-S/FACT, Mettler Toledo®) before being transferred into Teflon vessels cleaned with milli-Q water (18,2 $M\Omega.cm^{-1}$). To achieve a final volume of 8 ml, the following volumes of solvents were added into the Teflon vessels: 4 ml of milli-Q water (18,2 $M\Omega.cm^{-1}$), 2 ml of nitric acid (HNO_3, 65%, Suprapur®, VWR), 1 ml of hydrochloric acid (HCl, 30%), and 1 ml of hydrogen peroxide (H_2O_2, 30%, Suprapur®, VWR). The vessels were then sealed with a force of 20 N and placed into a microwave for 35 minutes, following the cycle described in table 3. This helps accelerate the mineralisation process. The samples were then transferred to a cold chamber at 4°C for a maximum duration of 45 minutes to prevent excessive condensation. Finally, the Teflon vessels were emptied into Falcon tubes and rinsed three times with milli-Q water (18.2 $M\Omega.cm^{-1}$) to ensure complete sample recovery. Milli-Q water (18.2 $M\Omega.cm^{-1}$) was then added to the Falcon tubes to achieve a final volume of 50 ml.

Table 3: Parameters of the 5 steps of the mineralization program

Step	**Time (min)**	**Power (W)**	**Temperature (°C)**
1	5	300	120
2	5	500	160
3	5	600	200
4	15	450	200
Ventilation	5	ROTOR OFF	TWIST OFF

In addition to the 72 samples, certified reference materials were also mineralized and analysed with ICP-MS. Certified reference materials are used to detect potential biases in a method or to calibrate measuring instruments, ensuring traceability and enhancing measurement precision (*XXIRMM - JRC Science Hub - European Commission*). Four duplicates of each CRM underwent the previously described protocol. These included DOLT-5, made from dogfish liver; DORM-4, composed of fish proteins; BCR-668, made from mussel tissues; and GBW. Additionally, 10 blanks also followed the same protocol.

After completing the analysis, the sensitivity was calculated based on measurements from the blanks. This involved determining the limit of detection (LoD) and the limit of quantification (LoQ). The LoD is the smallest concentration of an analyte that can be reliably distinguished from the highest concentration likely observed in multiple replicates of a blank sample. On the other hand, the LoQ refers to the minimum concentration at which an analyte is not only detectable but also achieves predefined standards for bias and precision (Armbruster & Pry, 2008).

The LoD is calculated with the standard deviation (SD) of the blanks.

$$LoD_{element} = 3 \times SD_{blank}$$

Finally, the LoD for each sample is calculated by using the LoD of each element.

$$LoD_{sample} = \frac{LoD_{element} \times dilution\ \ factor}{DW_{sample}}$$

4. Trace elements categories

The 44 elements analyzed in the present work (Li, Be, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Sr, Nb, Mo, Cd, In, Sn, Sb, Ba, Ta, Pt, Tl, Pb, Bi, U, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu) were classified into five categories.

1) Elements designated as Critical Raw materials in the Critical Raw Materials for the EU 2023 - Final Report, excluding the rare earth elements (REE): Li, Be, Al, Ti, V, Ge, As, Sr, Nb, Sb, Ta, Bi, Pt, In, Mn, Co, Ni, Cu.
2) Light rare earth elements (LREE) as listed in Marginson et al., 2023: La, Ce, Pr, Nd, Sm, Eu, Gd.
3) Heavy rare earth elements (HREE) as listed in Marginson et al., 2023 plus Sc: Y, Tb, Dy, Ho, Er, Yb, Lu, Sc.
4) The fourth category consists of essential trace elements: Zn, Se, Mo, Mn, Co, Ni, Cu.
5) The final category includes elements analyzed in this study that do not fall into the previous categories: Cr, Cd, Sn, Ba, Tl, Pb, U.

5. STATISTICAL ANALYSIS

Statistical analyses were performed using R studio version 4.1.3 (R Core Team, 2011) with the following packages: ggplot2 (3.5.1), dplyr (1.1.4), FSA (0.9.5). For all tests, results were judged significant when $p<0.05$. To assess the normality of the data, Shapiro-Wilk tests were conducted. Despite attempting a log1p transformation to achieve normality, most elements did not follow a normal distribution. Consequently, no transformation was applied, and non-parametric tests were used for all elements to ensure consistency in the results. Wilcoxon-Mann-Whitney tests were employed to compare groups, specifically to evaluate the effects of age, sex, and tissue type on trace element concentrations, as well as to compare data from 2000 and 2020 within each tissue type. Additionally, a Kruskal-Wallis test was performed to compare rare earth element (REE) concentrations in porpoises with those reported in a separate study on seals, followed by a Dunn post-hoc test for detailed pairwise comparisons.

Concentrations below the limit of detection (LoD) or limit of quantification (LoQ) were replaced with LoD/2 or LoQ/2. However, elements for which all concentrations were below the LoQ in all samples were excluded from the statistical analysis.

RESULTS

1. CERTIFIED VERSUS MEASURED CRM?

The certified reference materials (CRMs) displayed a close agreement between the certified and measured element concentrations as determined by ICP-MS, confirming the accuracy and reliability of the analytical method (Table X).

2. TRACE ELEMENT CONCENTRATIONS IN HARBOUR PORPOISES SAMPLED BETWEEN 1999 AND 2001

Trace element concentrations measured in the liver decreased in the following order: Zn > Se > Cu > Mn > Al > Sn > Mo > Sr > As > Sb > Cd > Ba > V > Pb > Ti > Cr > Bi > Co > Nb > Ce > La > Nd > Tl > Sm > Y > Pr > Gd > U > Sc (Table 4). The concentrations of Li, Be, Ni, Ge, Nb, In, Ta, Pt, Eu, Tb, Dy, Ho, Er, Yb and Lu were always below the detection or quantification limits in all samples. Concentration of Al, Cr, Sb, Tl, U, Sc, Y, Pr, Sm and Gd were below the detection or quantification limits in more than 75% of the samples. Trace element concentrations measured in the muscle decreased in the following order: Zn > Se > Cu > Mn > Al > Sb > Mo > Sr > As > Ba > Cr > Sn > V > Cd > Pb > Ti > Ni > Co > Ce > La > Y > Nd > Gd > Sm > Pr > Dy > Ta > Er > Yb > U > Sc > Tb. The concentrations of Li, Be, Ge, Nb, In, Ta, Pt, Tl, Bi, Eu, Ho and Lu were always below the detection or quantification limits in all samples, and Al, Cr, Ni, Mo, U, Sc, Y, La, Pr, Sm, Gd, Tb, Dy, Er and Yb were below the detection or quantification limits in more than 75% of the samples.

3. TRACE ELEMENT CONCENTRATIONS IN HARBOUR PORPOISES COLLECTED BETWEEN 2019 AND 2024

Trace element concentrations in the liver decreased in the following order: Zn > Cu > Se > Mn > Al > Mo > Sb > Cr > As > Ba > Sr > V > Cd > Pb > Ti > Sn > Ni > Bi > Nb > Co > Ce > La > Nd > Tl > Sm > Pr > Sc. The concentrations of Li, Be, Ge, In, Ta, Pt, U, Y, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu were always below the detection or quantification limits in all samples. Concentrations of Cr, Ni, Tl, Sc, Pr and Sm were below the detection or below quantification limits in more than 75% of the samples. In muscle samples, the trace element concentrations decreased in the following order: Zn > Cu > Al > Se > Mn > Sb > Ba > As > V > Sr > Pb > Ti

> Cr > Ni > Nb > Sn > Cd > Ce > Co > Tl > La > Nd > Sc. The concentrations of Li, Be, Ge, Mo, In, Ta, Pt, Bi, U, Y, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu were below the detection or quantification limits in all samples, and Ti, Cr, Co, Ni, Cd, Sb, Tl, Sc, La and Nd were below the detection or quantification limits in more than 75% of the samples.

The concentrations of Li, Be, Ge, In, Ta, Pt, Eu, Ho, Lu were all below the LoQ or LoD, and therefore, these elements were excluded from further data analysis.

Table 4: Concentrations of Light Rare Earth Elements (LREE) and Sc (ng g^{-1} dw) in the liver and muscle of the harbour porpoise *Phocoena phocoena* in the North Sea. Values are expressed as mean (median) ± standard deviation, with the range of concentrations (minimum-maximum). n indicates the number of samples analyzed. #<value# denotes values below the limit of quantification (LoQ), and *#<value#* denotes values below the limit of detection (LoD)

		1999-2001		**2019-2024**	
		n	mean (median) ± SD (min-max)	n	mean (median) ± SD (min-max)
La	Liver	22	6.5 (3.2) ± 6.8 (2.3-32)	17	5.6 (3.3) ± 3.6 (2.3-12)
	Muscle	23	5.2 (3.1) ± 5.9 (2.3-24)	10	3.4 (3.2) ± 1.2 (2.3-6.6)
Ce	Liver	22	13 (8.7) ± 11 (4.8-56)	17	12 (10) ± 5.6 (7.1-28)
	Muscle	23	12 (6.7) ± 15 (2.1-59)	10	8.5 (8.4) ± 2.5 (5.5-14)
Pr	Liver	22	1.3 (0.9) ± 1.4 (0.2-2.7)	17	1 (0.9) ± 0.6 (0.2-3.3)
	Muscle	23	1.3 (0.8) ± 2 (0.2-8.4)	10	<1.7
Nd	Liver	22	4.4 (2.7) ± 5.6 (1.3-26)	17	3.8 (2.6) ± 3.1 (1.3-12)
	Muscle	23	5.1 (1.5) ± 8.6 (0.5-32)	10	1.8 (1.5) ± 1.1 (1.1-5)
Sm	Liver	22	2.2 (0.6) ± 3.6 (0.4-16)	17	1.7 (0.6) ± 1.8 (0.5-6.6)
	Muscle	23	1.3 (0.6) ± 1.7 (0.4-6.5)	10	<3.8
Eu	Liver	22	<1.7	17	*<0.53*
	Muscle	23	<1.7	10	*<0.52*
Gd	Liver	22	1.2 (1.5) ± 0.8 (0.4-3.7)	17	<3.3
	Muscle	23	1.7 (0.5) ± 2.6 (0.4-9.7)	10	<3.2
∑LREE	**Liver**	**22**	**28 (18) ± 29 (9.5-153)**	**17**	**24 (18) ± 15 (11-62)**
	Muscle	**23**	**27 (13) ± 38 (5.9-150)**	**10**	**14 (13) ± 4.8 (8.9-26)**

Table 5: Concentrations of Heavy Rare Earth Elements (HREE) (ng g^{-1} dw) in the liver and muscle of the harbour porpoise *Phocoena phocoena*. Values are expressed as mean (median) ± standard deviation, with the range of concentrations (minimum-maximum). n indicates the number of samples. #<value# denotes values below the limit of quantification (LoQ), and *#<value#* denotes values below the limit of detection (LoD)

		2000		2020	
		n	mean (median) ± SD (min-max)	n	mean (median) ± SD (min-max)
Y	Liver	22	1.7 (0.8) ± 2.8 (0.6-14)	17	<5.1
	Muscle	23	5.1 (0.8) ± 10.8 (0.6-45)	10	<4.9
Tb	Liver	22	<0.9	17	*<0.3*
	Muscle	23	0.3 (0.2) ± 0.3 (0.1-1.3)	10	*<0.3*
Dy	Liver	22	<2.4	17	<2.5
	Muscle	23	1.2 (0.4) ± 2.1 (0.3-8.2)	10	*<0.75*
Ho	Liver	22	*<0.41*	17	*<0.42*
	Muscle	23	<1.3	10	*<0.42*
Er	Liver	22	<2.1	17	<2.2
	Muscle	23	0.7 (0.3) ± 1.1 (0.3-4.8)	10	<2.2
Yb	Liver	22	<2.3	17	*<0.7*
	Muscle	23	0.6 (4.8) ± 0.6 (0.3-2.5)	10	*<0.7*
Lu	Liver	22	<1.5	17	*<0.46*
	Muscle	23	<1.5	10	*<0.45*
Sc	Liver	22	0.06 (0,00) ± 0.2 (0,00-0.8)	17	0.4 (0.00) ± 1.4 (0.00-5.7)
	Muscle	23	0.4 (0.00) ± 1.8 (0.00-8.4)	10	0.5 (0.00) ± 1.1 (0.00-3.4)
∑HREE	Liver	22	1.7 (0.7) ± 2.8 (0.6-14)	17	<LoQ
	Muscle	23	7.8 (6.5) ± 15 (1.5-62)	10	<LoQ
∑REE	Liver	22	30 (18) ± 32 (10-167)	17	24 (18) ± 15 (11-62)
	Muscle	23	34 (20) ± 53 (7.4-211)	10	14 (13) ± 4.8 (8.9-26)

Table 6: Concentrations of Critical Raw Materials (CRM) (μg g^{-1} dw) in the liver and muscle of the harbour porpoise *Phocoena phocoena*. Values are expressed as mean (median) ± standard deviation, with the range of concentrations (minimum-maximum). n indicates the number of samples. #<value# denotes values below the limit of quantification (LoQ), and *#<value#* denotes values below the limit of detection (LoD)

		2000		2020	
		n	mean (median) ± SD (min-max)	n	mean (median) ± SD (min-max)
Li	Liver	22	<2.5	17	<2.7
	Muscle	23	<2.5	10	<2.6
Be	Liver	22	<0.2	17	<0.2
	Muscle	23	<0.2	10	<0.2
Al	Liver	22	6.3 (5.7) ± 3.6 (4.3-22)	17	8.1 (6.2) ± 3.9 (4.4-17)
	Muscle	23	7.6 (5.8) ± 4.8 (4.3-23)	10	8.2 (6.2) ± 3.5 (4.3-13)
Ti	Liver	22	0.3 (0.2) ± 0.2 (0.1-0.7)	17	0.4 (0.2) ± 0.3 (0.1-1.5)
	Muscle	23	0.3 (0.2) ± 0.2 (0.1-0.6)	10	0.3 (0.2) ± 0.2 (0.1-0.7)
V	Liver	22	0.6 (0.6) ± 0.2 (0.4-1.8)	17	0.6 (0.6) ± 0.1 (0.4-0.8)
	Muscle	23	0.6 (0.6) ±0.1 (0.5-0.8)	10	0.5 (0.5) ± 0.06 (0.4-0.5)
Mn	Liver	22	19 (20) ± 5 (9.9-26)	17	18 (17) ± 6.9 (5-28)
	Muscle	23	15 (16) ±10 (0.8-28)	10	1.3 (1.3) ± 0.4 (0.7-1.9)
Co	Liver	22	0.02 (0.02) ± 0.009 (0.004-0.05)	17	0.02 (0.02) ± 0.01 (0.001-0.05)
	Muscle	23	0.02 (0.02) ±0.01 (0.002-0.05)	10	0.01 (0.01) ± 0.006 (0.001-0.02)
Ni	Liver	22	<0.2	17	0.10 (0.08) ± 0.07 (0.06-0.37)
	Muscle	23	0.09 (0.08) ±0.07 (0.02-0.4)	10	0.08 (0.08) ± 0.06 (0.02-0.25)
Cu	Liver	22	(35 (27) ± 25 (13-128)	17	56 (34) ± 49 (20-206)
	Muscle	23	42 (28) ± 47 (5-206)	10	8.3 (8.5) ± 2.2 (5-12)
Ge	Liver	22	<0.2	17	<0.2
	Muscle	23	<0.2	10	<0.2
As	Liver	22	1.4 (1.2) ± 0.7 (0.5-3.3)	17	1.3 (1) ± 0.8 (0.5-1.9)
	Muscle	23	1.2 (0.9) ± 0.6 (0.5-2.2)	10	0.8 (0.8) ± 0.4 (0.3-1.6)
Sr	Liver	22	1.5 (0.7) ± 2.4 (0.3-11)	17	0.7 (0.6) ± 0.4 (0.4-2.2)
	Muscle	23	1.2(0.6) ± 2.3 (0.3-11)	10	0.5 (0.5) ± 0.1 (0.3-0.7)
Nb	Liver	22	0.02 (0.02) ± 0.005 (0.01-0.04)	17	0.04 (0.04) ± 0.02 (0.01-0.08)
	Muscle	23	<0.03	10	0.04 (0.04) ±0.02 (0.02-0.07)
In	Liver	22	*<0.03*	17	*<0.03*

	Muscle	23	*<0.03*	10	*<0.03*
Sb	Liver	22	1.3 (1.1) ± 0.5 (0.8-2.5)	17	1.6 (1.2) ± 0.7 (0.9-2.7)
	Muscle	23	1.5 (1.2) ± 0.7 (0.8-2.8)	10	1.2 (1.1) ± 0.4 (0.8-2.3)
Ta	Liver	22	*<0.002*	17	<0.005
	Muscle	23	0.001 (0.001) ± 0.001 (0.001-0.003)	10	<0.005
Pt	Liver	22	*<0.02*	17	*<0.02*
	Muscle	23	*<0.02*	10	*<0.02*
Bi	Liver	22	0.08 (0.03) ±0.1 (0.007-0.5)	17	0.08 (0.07) ± 0.06 (0.01-0.2)
	Muscle	23	*<0.02*	10	*<0.02*

Table 7: Concentrations of Essential Trace Elements (µg g^{-1} dw) in the liver and muscle of the harbour porpoise *Phocoena phocoena*. Values are expressed as mean (median) ± standard deviation, with the range of concentrations (minimum-maximum). n indicates the number of samples. #<value# denotes values below the limit of quantification (LoQ), and *#<value#* denotes values below the limit of detection (LoD)

		1999-2001		**2019-2024**	
		n	mean (median) ± SD (min-max)	n	mean (median) ± SD (min-max)
Mn	Liver	22	19 (20) ± 5 (9.9-26)	17	18 (17) ± 6.9 (5-28)
	Muscle	23	15 (16) ±10 (0.8-28)	10	1.3 (1.3) ± 0.4 (0.7-1.9)
Co	Liver	22	0.02 (0.02) ± 0.009 (0.004-0.05)	17	0.02 (0.02) ± 0.01 (0.001-0.05)
	Muscle	23	0.02 (0.02) ±0.01 (0.002-0.05)	10	0.01 (0.01) ± 0.006 (0.001-0.02)
Ni	Liver	22	<0.2	17	0.1 (0.08) ± 0.07 (0.06-0.4)
	Muscle	23	0.09 (0.08) ±0.07 (0.02-0.4)	10	0.08 (0.08) ± 0.06 (0.02-0.3)
Cu	Liver	22	35 (27.3) ± 25 (13-128)	17	56 (34) ± 49 (20-206)
	Muscle	23	42 (28) ± 47 (5-206)	10	8.3 (8.5) ± 2.2 (5-12)
Zn	Liver	22	245 (166) ± 171 (92-788)	17	213(139) ± 187 (53-861)
	Muscle	23	217 (145) ± 211 (53-861)	10	80 (74) ± 24 (45-122)
Se	Liver	22	79 (20) ± 199 (2-947)	17	41 (11) ± 61 (1-192)
	Muscle	23	76 (6.3) ± 200 (0.9-947)	10	1.4 (1.03) ± 1 (0.7-4.1)
Mo	Liver	22	1.9 (1.9) ± 0.7 (0.7-3.2)	17	1.8 (2.1) ± 0.9 (0.2-3)
	Muscle	23	1.3 (1.2) ± 1.1 (0.02-3)	10	<0.1

Table 8: Concentrations of Other Trace Elements (µg g^{-1} dw) in the liver and muscle of the harbour porpoise *Phocoena phocoena*. Values are expressed as mean (median) ± standard deviation, with the range of concentrations (minimum-maximum). n indicates the number of samples. #<value# denotes values below the limit of quantification (LoQ), and *#<value#* denotes values below the limit of detection (LoD)

		1999-2001		2019-2024	
		n	mean (median) ± SD (min-max)	n	mean (median) ± SD (min-max)
Cr	Liver	22	0.1 (0.1) ± 0.03 (0.08-0.2)	17	1.3 (0.12) ± 4.4 (0.09-18)
	Muscle	23	0.9 (0.1) ± 3.8 (0.1-18)	10	0.1 (0.1) ± 0.1 (0.08-0.4)
Cd	Liver	22	0.9 (0.8) ± 0.7 (0.01-2.2)	17	0.4 (0.1) ± 0.5 (0.004-1.5)
	Muscle	23	0.4 (0.04) ± 0.6 (0.003-1.7)	10	0.01 (0.01) ± 0.01 (0.003-0.03)
Sn	Liver	22	2.1 (1.9) ± 1.4 (0.5-6.4)	17	0.2 (0.13) ± 0.2 (0.01-0.7)
	Muscle	23	0.7 (0.1) ± 1.3 (0.01-5.1)	10	0.03 (0.02) ± 0.02 (0.002-0.08)
Ba	Liver	22	0.9 (0.8) ± 0.2 (0.3-1.5)	17	1.1 (1.2) ± 0.2 (0.8-1.3)
	Muscle	23	0.9 (0.8) ± 0.3 (0.4-1.5)	10	1.1 (1.2) ± 0.2 (0.9-1.4)
Tl	Liver	22	0.003 (0.002) ± 0.003 (0.001-0.02)	17	0.004 (0.002) ± 0.004 (0.002-0.02)
	Muscle	23	<0.01	10	0.004 (0.003) ± 0.003 (0.002-0.01)
Pb	Liver	22	0.4 (0.3) ± 0.2 (0.2-1)	17	0.4 (0.4) ± 0.07 (0.3-0.6)
	Muscle	23	0.2 (0.2) ± 0.17 (0.1-0.4)	10	0.3 (0.3) ± 0.04 (0.3-0.4)
U	Liver	22	0.0005 (0.0002) ± 0.0008 (0.0002-0.004)	17	<0.001
	Muscle	23	(0.0005 (0.0002) ± 0.0008 (.0002-0.039)	10	<0.001

Shapiro-Wilk tests were conducted to evaluate the normality of the distribution in each group (Liver 2000, Muscle 2000, Liver 2020, Muscle 2020). Most elements did not follow a normal distribution across the groups. Among the groups, Muscle 2020 had the highest number of elements following a normal distribution, including Mn, Fe, Cu, Zn, As, Sr, Nb, Ba, Pb, Bi, Ce, Pr, Dy, and Yb. Conversely, Liver 2000 had the fewest elements with a normal distribution, which were Mn, Fe, Co, Mo, and Cd.

4. LIVER AND MUSCLE COMPARISON

Concentration were higher in the liver compared to muscle for the following chemical elements: As, Bi, Cd, Ce, Co, Cu, Fe, Mn, Mo, Nd, Pb, Se, Sn, Sr, V, Zn (Wilcoxon-Mann-Whitney, α=0.05; As: W=346, p-value<0.01; Bi: W=135.5, p-value<0.01; Cd: W=118, p-value<0.01; Ce: W=377, p-value<0.01; Co: W=215.5, p-value<0.01; Cu: W=0, p-value<0.01; Fe: W=393, p-value<0.01; Mn: W=0, p-value<0.01; Mo: 0, p-value<0.01; Nd: W=455.5, p-value<0.05; Pb: W=297, p-value<0.01; Se: W=80, p-value<0.01; Sn: W=274, p-value<0.01; Sr: W=409, p-value<0.01; V: W=344, p-value<0.01; Zn: W=50, p-value<0.01). Bi was not detected in muscle but was present in liver (Fig 12).

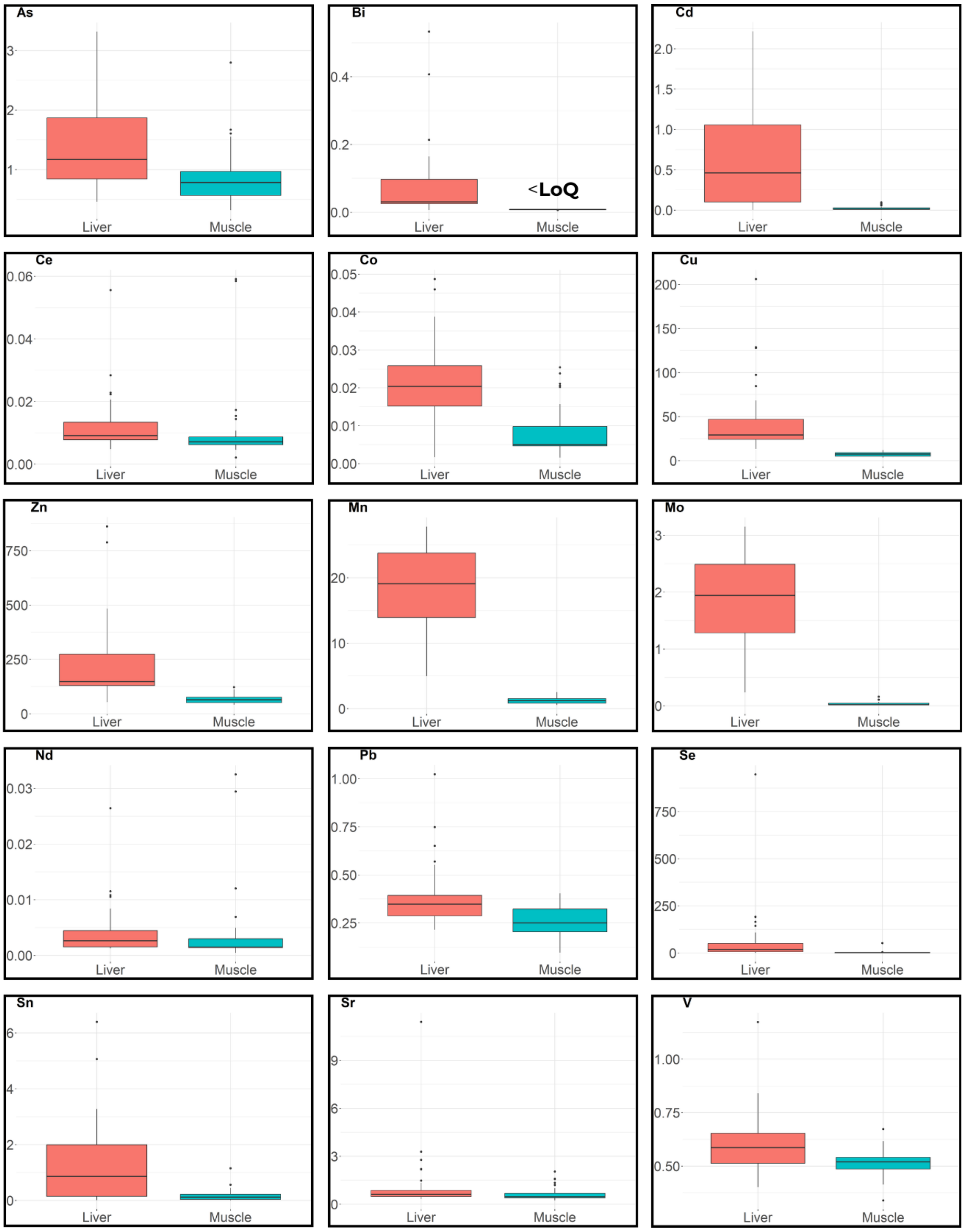


Figure 12: Trace elements concentration in liver and muscle samples (μg g^{-1}) of harbour porpoises from the North Sea (Belgium and Germany)

5. AGE CLASS

Ce and Sr concentrations were higher in muscle of juveniles compared to adults collected between 1999-2001, whereas Sn concentrations were higher in muscles of adults (Wilcoxon-Mann-Whitney, α=0.05; Ce: W=33.5, p-value<0.05; Sr: W=31, p-value<0.05; Sn: W=104, p-value<0.05) (Fig 13).

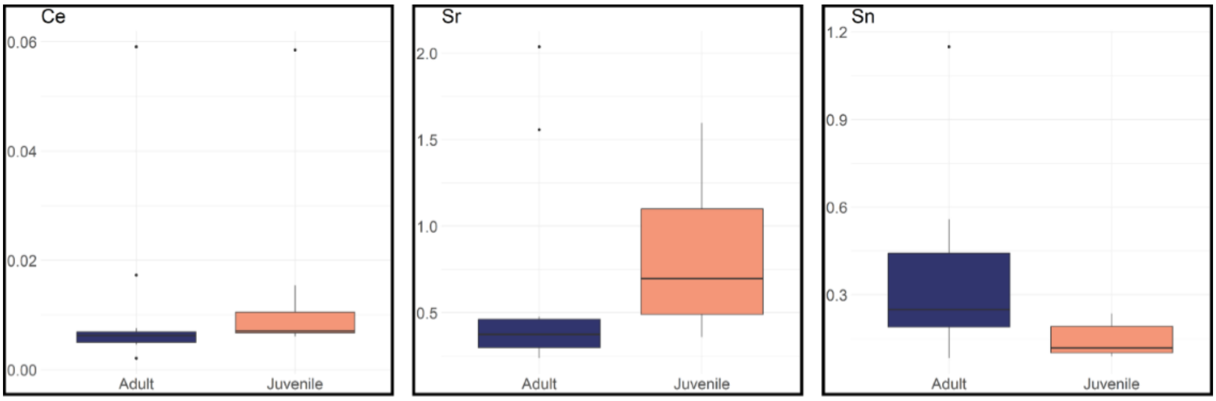


Figure 13: Ce, Sr and Sn concentrations in muscle of juvenile and adult harbour porpoises (*Phocoena phocoena*) collected between 1999 and 2001.

No significant differences in terms of trace element concentrations were observed in muscle samples from 2019-2024.

Trace element concentrations in liver differed significantly between adults and juveniles sampled between 1999-2001 for the following elements: Cd, Mo, Pb, Se, V, Ce, La, Nd (Wilcoxon-Mann-Whitney, α=0.05; Cd: W=106, p-value<0.01; Mo: W=101, p-value<0.01; Pb: W=99, p-value<0.01; Se: W=116, p-value<0.01; V: W=98, p-value<0.05; Ce: W=101.5, p-value<0.01; La: W=105.5, p-value<0.01; Nd: W=90.5, p-value<0.05). Overall, all elements were more concentrated in adults than in juveniles (Fig 14).

Significant differences in trace element concentrations were observed between adult and juvenile liver samples from 2019-2024 for the following elements: Bi, Cd, Se, V, Co, Sc, Ce, La, Nd, Sm (Wilcoxon-Mann-Whitney, α=0.05; Bi: W=49, p-value<0.05; Cd: W=60, p-value<0.01; Se: W=60, p-value<0.01; V: W=60, p-value<0.01; Co: W=51, p-value<0.05; Sc: W=42, p-value<0.05; Ce: W=59, p-value<0.01; La: W=60, p-value<0.01; Nd: W=56, p-value<0.01; Sm: W=50.5, p-value<0.05). However, as only one sample exceeded the limit of detection (LoD) for Sc, this element was excluded from the final analysis (Fig. 15).

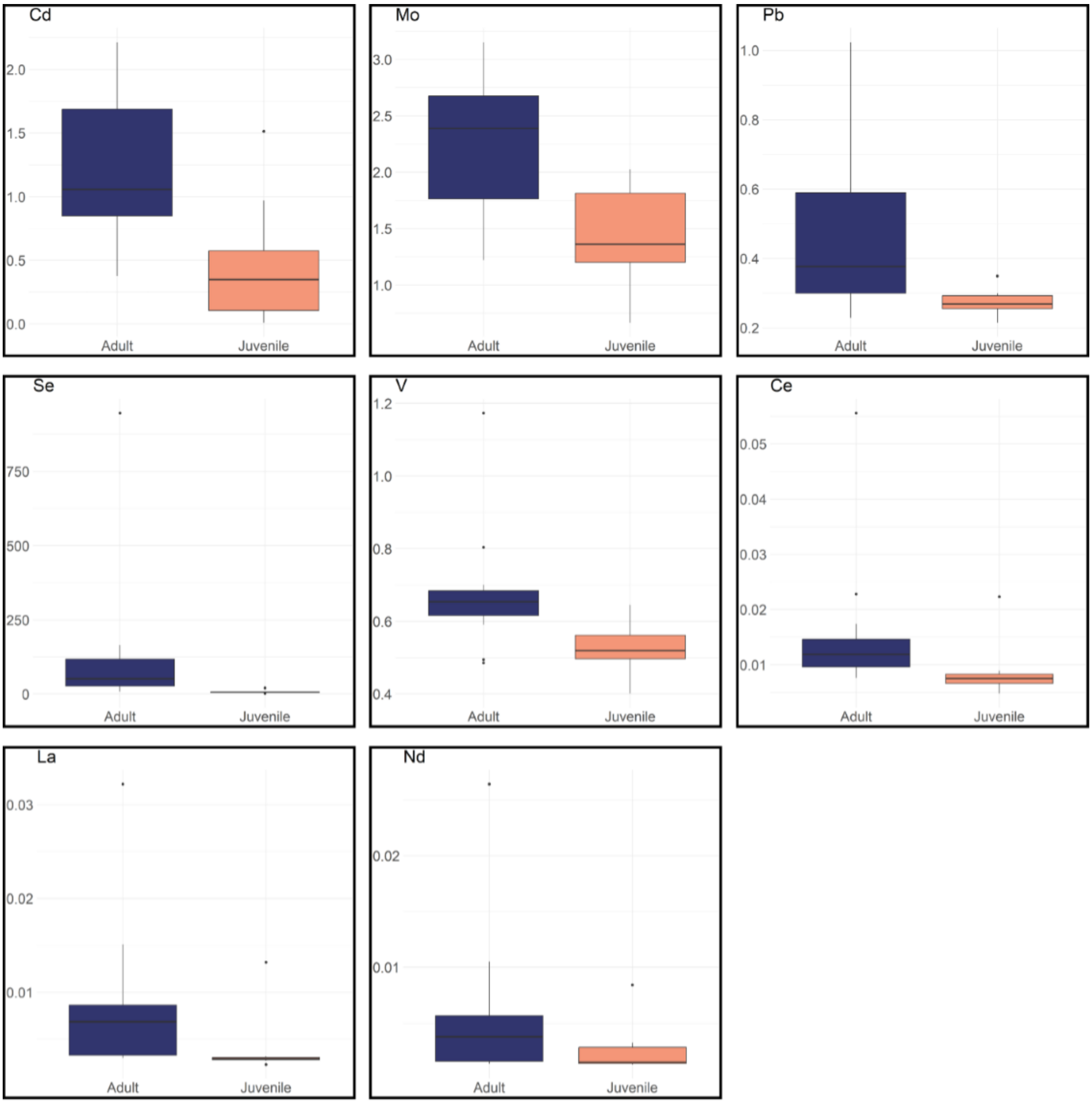


Figure 14: Hepatic trace element concentrations in relation to the age of P. phocoena from 1999-2001

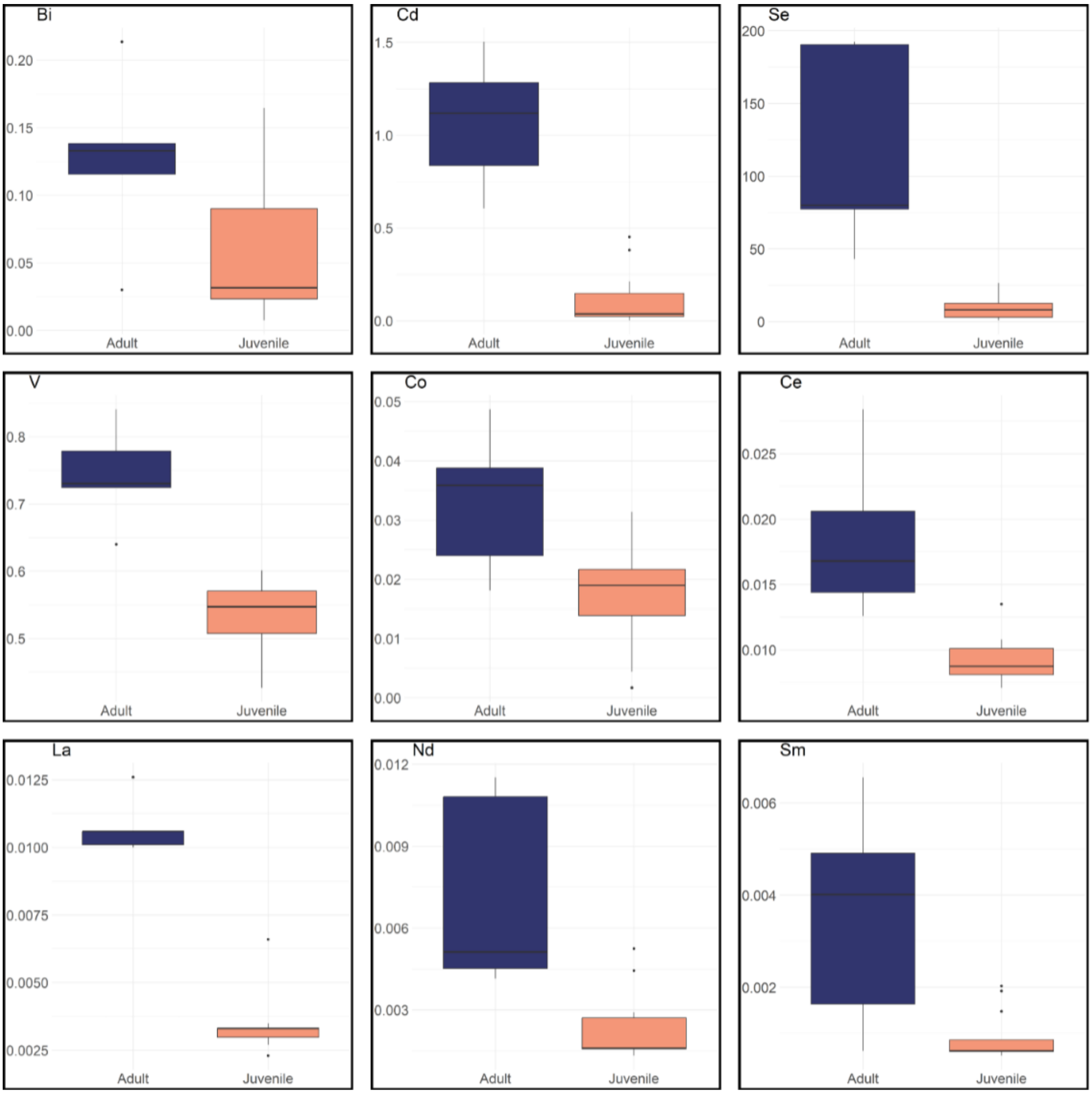


Figure 15: Trace element concentrations in the liver of adult and juvenile harbour porpoises (*Phocoena phocoena*) sampled between 2019 and 2024.

There were no differences between males and females across all tissues.

6. Comparison of element concentrations in harbour porpoises: 1999-2001 vs. 2019-2024

The analysis revealed significant differences in trace element concentrations in liver samples collected between 1999 and 2001 (referred as "2000" and between 2019 and 2024 (hereafter referred as "2020": Al, Fe, Ni, Nb, Cd, Sn, Sb, Ba (Wilcoxon-Mann-Whitney, α=0.05; Al: W=110, p-value<0.05; Fe: W=259, p-value<0.05; Ni: W=109, p-value<0.05; Nb: W=46, p-value<0.01; Cd: W=276, p-value<0.05; Sn: W=373, p-value<0.01; Sb: W=114.5, p-value<0.05; Ba: W=47, p-value<0.05). Al, Sb, Ni and Ba concentrations were significantly higher in liver samples collected between 2019 and 2024 compared to older samples. Sn, Cd and concentrations have decreased during the same time gap. Additionally, Nb was not quantifiable in 2000 but was measurable in 2020 (Fig. 16).

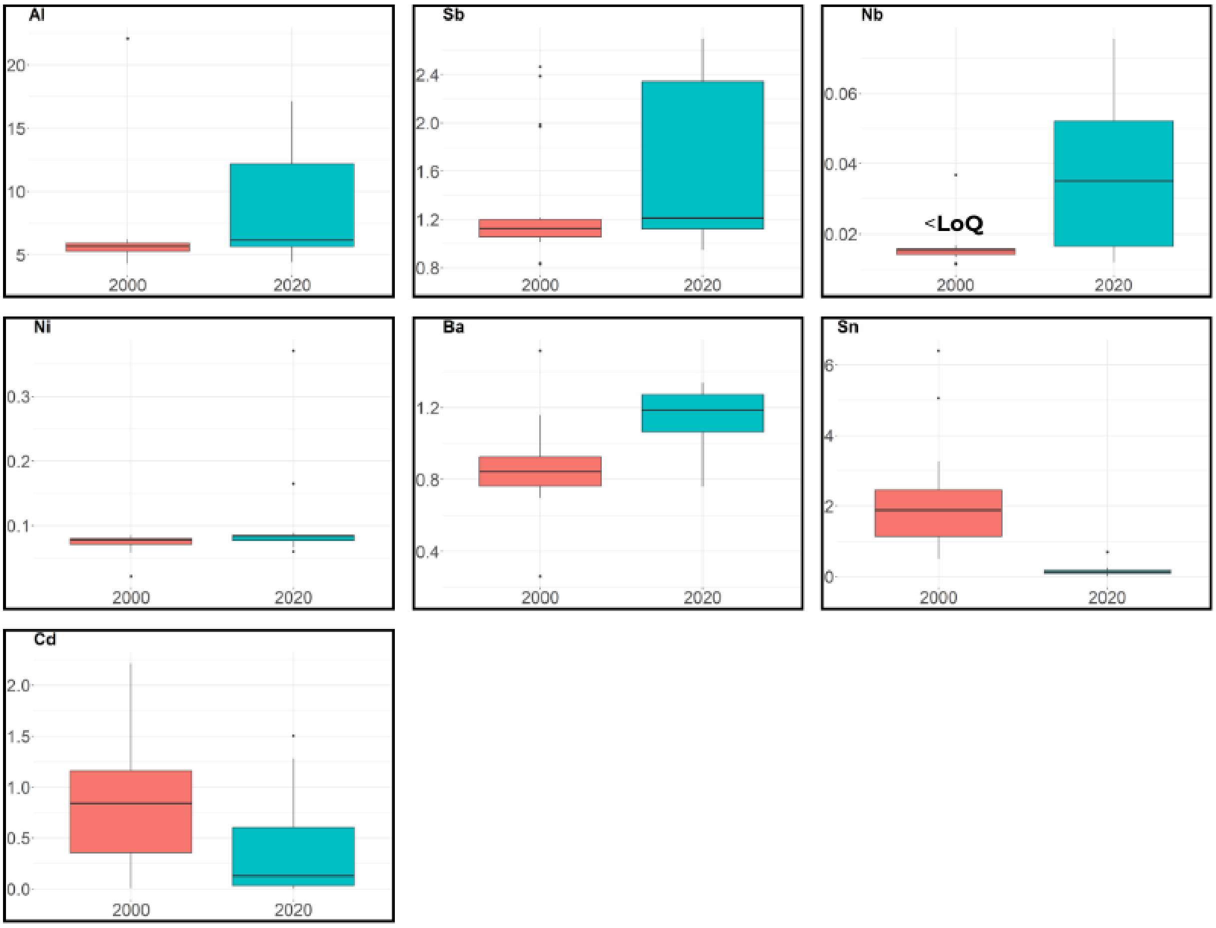


Figure 16: Concentrations (µg g^{-1}) of Al, Sb, Nb, Ni, Ba, Sn and Cd in liver samples from harbour porpoises, *Phocoena phocoena* sampled between 1999-2001 (referred as "*2000*") and between 2019-2024 (referred as "*2020*")

In Muscles, significant differences in trace element concentrations between 2000 and 2020 were observed for the following elements: V, Se, Nb, Sn, Ba, Tl, Pb (Wilcoxon-Mann-Whitney, α=0.05; V: W=168, p-value<0.05; p-value<0.01; Se: W=188, p-value<0.01; Nb: W=7, p-value<0.01; Sn: W=230, p-value<0.01; Ba: W=51, p-value<0.05; Tl: W=49, p-value<0.01; Pb: W=37, p-value<0.01). Ba and Pb concentrations have increased in 2020, whereas Se, V and Sn concentrations have decreased. Additionally, Nb and Tl were unquantifiable in 2000 but present in 2020 (Fig. 17).

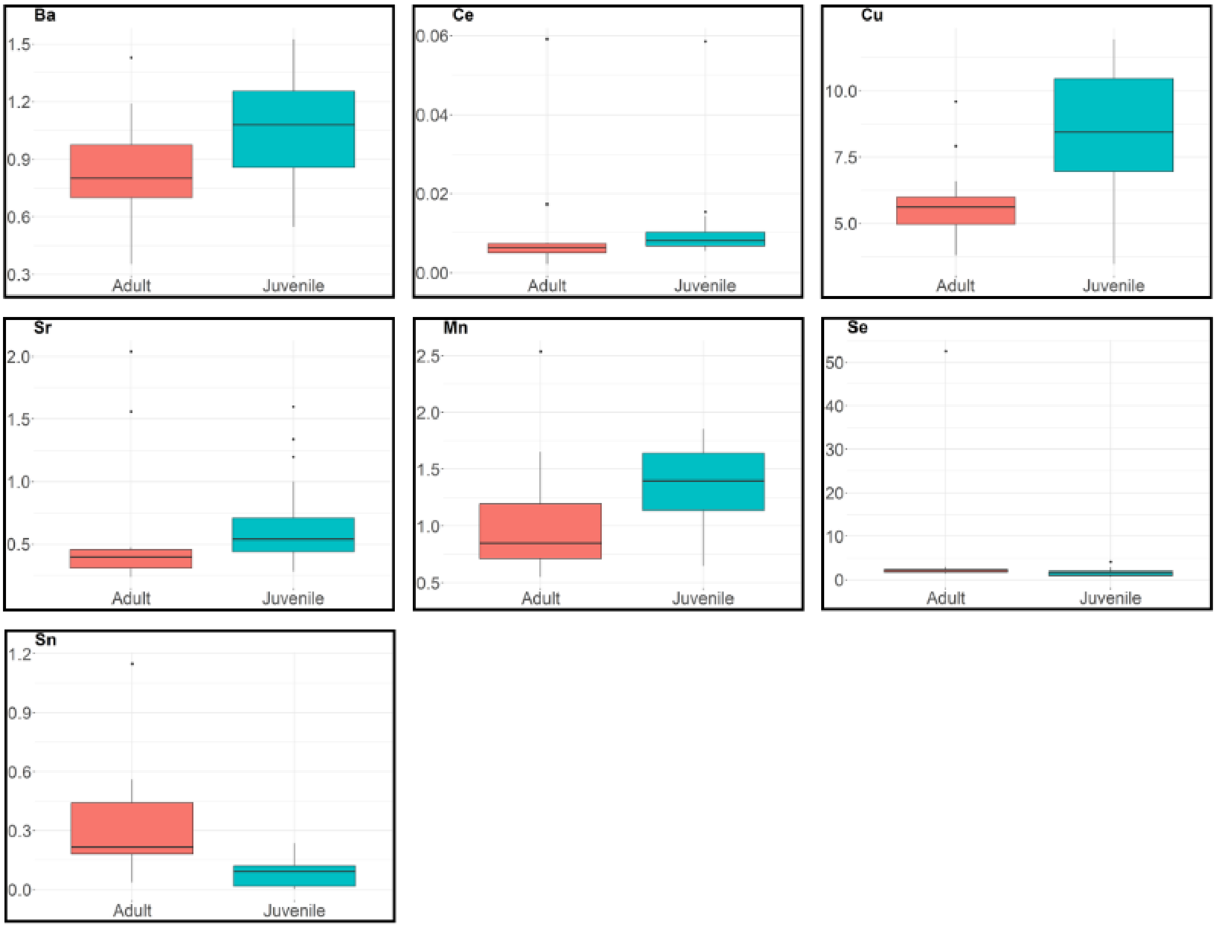


Figure 17: Concentrations (µg g^{-1}) of Ba, Nb, Tl, Pb, Fe, Sc, V and Sn in muscle samples from *Phocoena phocoena* in 1999-2001 (referred as ”*2000*”) and 2019-2024 (referred as ”*2000*”)

The analysis of trace elements in liver and muscle samples of harbour porpoises from the North Sea in 2000 and 2020, with measurements below the limit of quantification (LoQ) reveals distinct patterns in the occurrence of non-quantifiable values.

7. Rare earth elements variations

For all tissues and regardless of the year, the REE present in the highest quantities in the analyzed *P. phocoena* samples were always the LREE, particularly Ce, La, and Nd (Fig 18). Most HREE had concentrations below the limits of detection or quantification in all tissues, except for the muscles from 2000. However, the frequency of concentrations above the LoQ among the HREE was always less than 15% (Annex 3). Thus, LREE/HREE ratios indicate an enrichment of LREE in both the liver and muscle from 2000 (Liver: LREE/HREE = 16.35; Muscle: LREE/HREE = 3.41). These ratios were not calculated for the 2020 samples, as no HREE was above the LoQ.

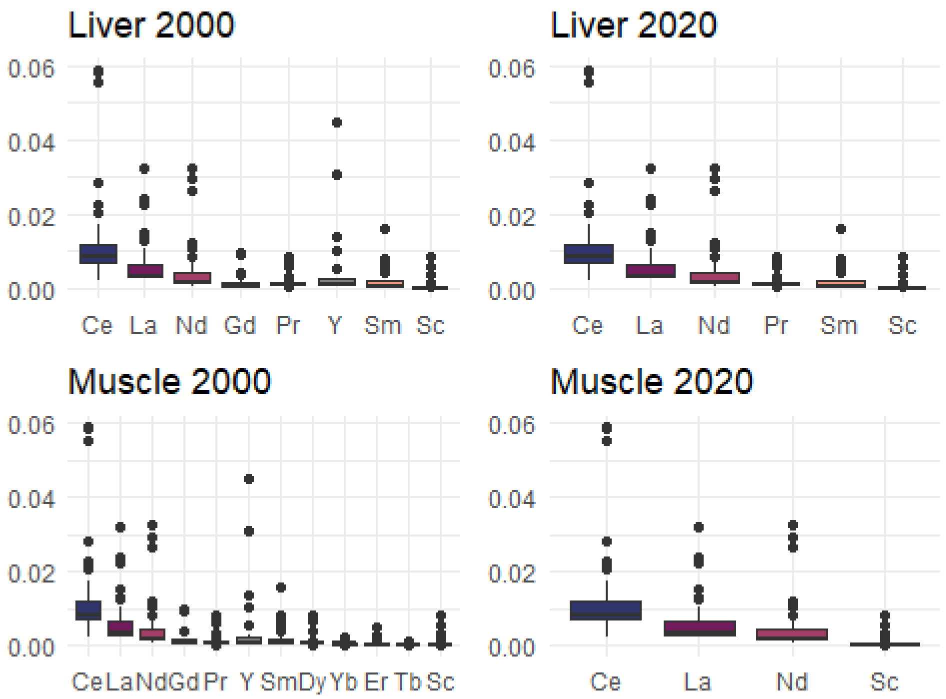


Figure 18: Concentrations of Rare Earth Elements (REE) in Liver and Muscle Tissues of harbour Porpoises (*Phocoena phocoena)* sampled between 1999-2001 (referred as ”*2000*”) and between 2019-2024 (referred as ”*2020*”)

DISCUSSION

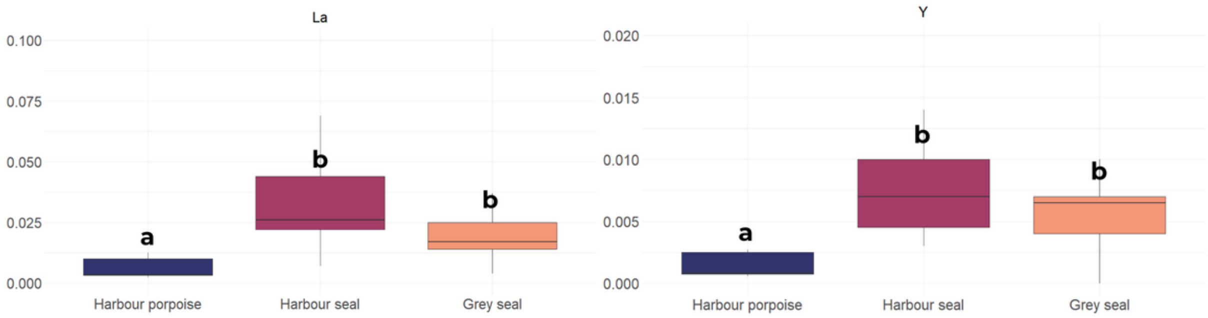
The North Sea, surrounded by industrialized coastlines and offshore industries like oil, gas, and wind farms, is further impacted by pollutants carried by major rivers such as the Elbe and the Rhine (Ducrotoy et al., 2000). Between 1999 and 2024, the North Sea has faced numerous anthropogenic pressures, including significant chemical pollution (Brumovský et al., 2016; Ducrotoy et al., 2008). The harbour porpoise, *Phocoena phocoena*, a key marine mammal in this region due to its predator status, has been used as a bioindicator for chemical element contamination in the Northeast Atlantic. Most studies have focused on heavy metals and other trace elements such as Cd and Hg (Das et al., 2006; Das et al., 2004a; Das et al., 2004b; Fernández et al., 2022; Ferreira et al., 2016), leaving a gap in understanding emerging trace elements and their temporal trends. However, data on the concentrations of chemical elements classified in Critical Raw Materials (Study on the Critical Raw Materials for the EU 2023 – Final Report) in harbour porpoises *(Phocoena phocoena)* remain limited. Critical Raw Materials (CRMs) are essential materials that are crucial for the economy and important to produce various high-tech products, renewable energy technologies, and other industries (Study on the Critical Raw Materials for the EU 2023 – Final Report).

This study addresses this gap by analysing liver and muscle samples from 41 harbour porpoises collected in the Southern North Sea during two periods: 1) 1999-2001 and 2) 2019-2024, with a focus on Critical Raw Materials.

The concentrations of selected elements classified as Critical Raw Materials (Al, As, Bi, Co, Cu, Mn, Nb, Ni, Sb, Sr, V) including Rare Earth Elements (Ce, La, Nd, Sc, Sm) and other chemical elements (Ba, Cd, Mo, Pb, Sn, Tl and Zn) varied depending on tissue type (liver *vs*. muscle), age class (adult *vs*. juvenile), and time of sampling.

The concentrations of As, Bi, Cd, Cr, Cu, In, Li, Mn, Mo, Ni, Se, Sn, Sr, V and Zn observed in the liver of harbour porpoises closely align with previously published data for marine mammals (Annex 5, 6, 7). To the best of our knowledge, concentrations of Nb and Ge have never been detected in marine mammals before, and there is a lack of data exhibiting their contamination in marine vertebrates in the North Sea.

The present study represents the first assessment of Rare Earth Elements (La, Ce, Pr, Nd, Sm, Sc, Y, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu) in harbour porpoises (*Phocoena phocoena*) from the North Sea. A comparison with seal species, specifically the grey seal (*Halichoerus grypus*) and the common seal (*Phoca vitulina*), as reported in Laurine Marchand's master's thesis (2023), indicated that the REE concentrations in the liver of harbour porpoises fall within a similar range, although concentrations in harbour porpoise livers were lower compared to the seal species (Fig. 19).



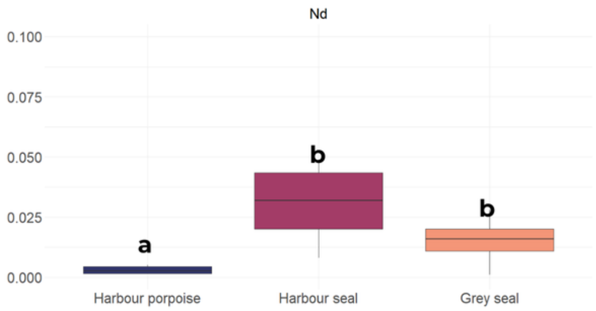


Figure 19: Concentrations of Rare Earth Elements (REE) in the liver of the harbour porpoises *Phocoena phocoena* collected between 2019 and 2024 (this work) and in the liver of grey seals (Halichoerus grypus) and harbour seals (P*hoca vitulina*) collected between 2010 and 2023 (Marchand ,2023). Samples not sharing any letter are significantly different by Dunn post-hoc test at 5% significance level.

The consistently higher concentrations of La, Nd, and Y in seals compared to porpoises may be linked to differences in trophic positions or dietary habits. According to Das et al. (2003), H. *grypus and P.vitulina* occupy similar trophic positions at the top of the food web, while *P. phocoena* is positioned lower, likely due to its consumption of lower trophic level prey. Although harbor seals, gray seals, and harbor porpoises share overlapping foraging zones and may consume similar prey species, seals are opportunistic feeders, adapting their diet based on prey availability (Kavanagh et al., 2010). In contrast, porpoises consume a wide variety of prey, such as gobies, sprat, herring, cod, and lesser sandeel, sourced from different locations depending on the individual's sex and age. Juveniles and their mothers tend to forage closer to the coast, with juveniles consuming smaller prey, while males forage offshore (Jansen, 2013)

1. ACCUMULATION OF CHEMICAL ELEMENTS IN LIVER AND MUSCLE

The liver is crucial for metabolizing biological substances or detoxifying harmful compounds (Kalra et al., 2023). Consequently, the liver is a key organ for studying chemical elements contamination. Historically, in marine mammals such as harbour porpoises, many chemical elements have been found to accumulate more significantly in the liver than in muscle tissue, particularly essential elements like Cu, and Zn, as well as pollutants such as Cd and Pb (Saeki et al., 1999; Szefer et al., 2002). Thus, the question arises whether Critical Raw Materials (CRMs) also accumulate more in the liver than in the muscle.

In this study, none of the analysed elements were more concentrated in the muscle compared to the liver. The essential elements Cu, Co, Mn, Mo, Se and Zn were all found in higher concentrations in the liver, reflecting the liver's role in metabolisation and in storing essential trace elements like Cu (Kalra et al., 2023). The trace elements Co, Cu, Mn, Mo, Se, and Zn play essential roles in animal health and biological processes (Mackey et al., 1995) such as enzymatic activity, or the maintenance of immune system integrity.

Cd, As, V, Sr and Pb were also more concentrated in the liver than in the muscle. This aligns with the literature, as Cd, As, V and Pb were found to accumulate more in the liver than in the muscle of harbour porpoises (Szefer et al., 2002), and Sr has exhibited higher concentrations in the liver of harp seals from the southern Labrador (Yeats et al., 1999).

The concentrations of the CRMs Bi, Ce and Nd had never been compared between the liver and the muscle of marine mammals. However, Bi levels were found to be higher in the liver than the muscle of Northen Pike, which aligns with the results. Ce and Nd were the only rare earth elements (REE) showing significantly higher concentrations in the liver compared to the muscle. Other REE concentrations such as Eu, Tb, Dy and Er were often below the limit of quantification in both tissues (Annex 3).

Thus, the liver is a more suitable tissue than muscle for studying the bioaccumulation of chemical elements and CRMs in *P. Phocoena* due to the higher concentrations detected.

There is a lack of data concerning the potential biomagnification or biodilution of several Critical Raw Materials, such as Ge, Nb, Ta, and In (Romero-Freire et al., 2019). REE appear to bioaccumulate in organisms at the bottom of the food chain, with biodilution occurring at higher trophic levels (MacMillan et al., 2017; Marginson et al., 2023; Rétif et al., 2024). In the present study, harbour porpoises were compared to molluscs from Castro et al. (2023) (Fig. 20). The ΣREE levels in the least contaminated *Mytilus spp*. samples were 32 times higher than those in harbour porpoises. Additionally, some mussels collected from a different site exhibited ΣREE levels that were 164 times higher than those in harbour porpoises.

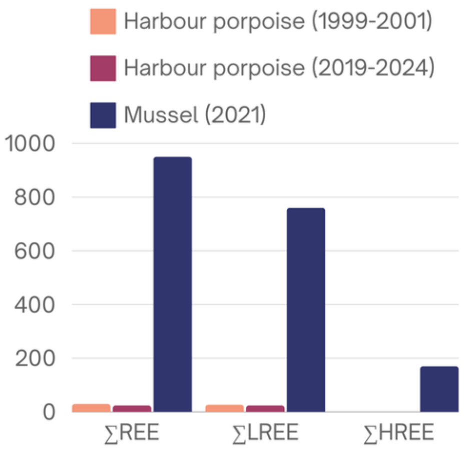


Figure 20: Rare Earth elements sums ΣREE (ng g^{-1}) in the liver of the harbour porpoises *Phocoena phocoena* (this work) and from and in the soft tissues of mussels (*Mytilus spp*.) (Castro et al., 2023). ΣREE included the sum of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y.

2. AGE CLASS

Bioaccumulation is commonly observed in *Phocoena phocoena*, resulting in many trace elements being more concentrated in adults than in juveniles, such as Hg and Cd (Das et al., 2003). Therefore, it is not surprising that, regardless of the time- period and the tissue, several elements were found at higher concentrations in adults compared to juveniles (Fig. 21). To date, there has been no comparison of rare earth element concentrations between age classes in marine mammals. Consequently, direct comparisons cannot be made. However, it seems plausible that elements such as Ce, La, Nd, Sc, and Sm may follow a similar trend to other chemical elements, accumulating in the tissues of *P. phocoena* as the animals age.

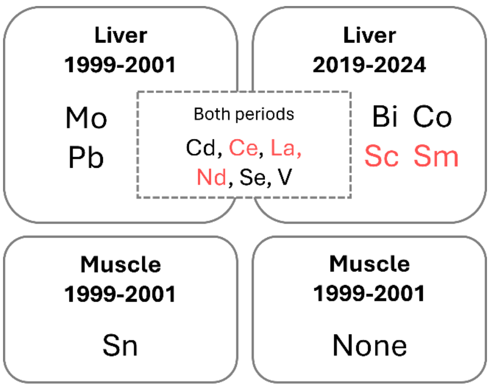


Figure 21: Chemical elements with higher concentrations in adults compared to juveniles in liver and muscles collected during the “1999-2001” and the “2019-2024” periods

In the study of bioaccumulation of elements within marine mammals, it is critical to recognize that not all elements exhibit a linear relationship with age. Specifically, Cu concentrations are notably higher in neonates, likely reflecting the essential role of this element during the early stages of development and ontogeny (Das et al., 2003). This trend suggests a physiological requirement for elevated Cu levels during the neonatal period, potentially related to the rapid growth and metabolic demands characteristic of this life stage.

Ce and Sr levels were higher in juveniles and neonates compared to adults in muscle from porpoises collected during the "1999-2001" period. This trend was not observed in the liver, and Ce levels were higher in adults compared to juveniles and neonates in the liver of porpoises collected during the "1999-2001" and the "2019-2024" periods. To date, there remains no comprehensive explanation for the observed higher concentrations of these elements in neonates and juveniles. The underlying mechanisms driving the elevated levels of cerium, and strontium during these early life stages are not fully understood. This gap in knowledge highlights the need for further investigation on a higher number of samples to elucidate the factors contributing to these age-specific accumulation patterns.

3. TEMPORAL VARIATIONS

Given the rapid advancements in technology and shifts in industrial practices, it is not surprising that trace element contamination patterns in harbour porpoises have also evolved over the past 20 years. Specifically, Al, Ba, Cd, Nb, Ni, Pb, Sb, Se, Sn and V exhibited significant temporal variations in the liver or in the muscle. Detailed information on the elements that showed temporal variations between the 1999-2001 and 2019-2024 periods in the liver and muscle of harbor porpoises is presented in Fig. 22.

Figure 22: Increase and decrease of chemical elements levels in the liver and the muscle of harbour porpoises over the last 20 years. Critical Raw materials are underlined.

3.1 Increase between the two periods 1999-2001 and 2019-2024

There is a clear increase of the Critical Raw Materials Al, Sb and Nb in the liver of porpoises collected during the “2019-2024” compared to 20 years ago. Indeed, the median concentrations of Al, Sb and Nb increased by 9%, 9% and 100%, respectively. This is concomitant with the crucial roles of Al, Sb and Nb in growing strategic technologies such as Digital technologies, robotics, drones, 3D printing, and the technologies linked with Renewable energies and E-mobility (Fig. 7). Additionally, the high concentrations of these Critical Raw Materials are similar to the high levels of Al and Sb found in grey seals and harbour seals from Marchand (2023).

In the North Sea, Aluminium galvanic or sacrificial anodes are commonly employed in to protect steel structures of offshore wind farms from corrosion. Although the release of Al into seawater due to these anodes is minimal at a regional scale due to dilution, localized impacts may occur near the anodes (Bell et al., 2020; Deborde et al., 2015; Reese et al., 2020). In these areas, contamination of surface sediments can affect benthic organisms, particularly filter feeders that interact with the sediment. Furthermore, bioaccumulation of Al could potentially impact higher trophic levels within the marine food web (Bell et al., 2020; Deborde et al., 2015; Reese et al., 2020). Notably, seals and porpoises have been observed foraging around wind farms and other man-made structures (Leemans & Fijn, 2023; Russell et al., 2014). Therefore, further investigation is needed to understand the potential link between the 9% increase in Al levels and the foraging of porpoise in wind farms.

Sb enters the environment through both geogenic and anthropogenic sources. Pollution in water bodies can result from natural weathering of antimony ores and minerals, runoff from contaminated soils (including dust from automobile tires, brake pads, and shooting activities), and discharges from mining and smelting industries (Nishad & Bhaskarapillai, 2021). High Sb levels in seals, as observed by Marchand (2023), further suggest possible Sb contamination in the North Sea, especially given that the EU processes and refines 17% of the global antimony supply in Belgium, France, Germany, and the Netherlands (Study on the Critical Raw Materials for the EU 2023 – Final Report).

Nb is mostly used in the steel industry to produce microalloy and low-alloy steels. These alloys are used in several new technologies sectors, such as wind turbines, robotics, drones, and 3D printing, leading to its classification as a Critical Raw Material. Nb concentrations in *P.*

phocoena were twice higher in the livers collected during the “2019-2024” period compared to 20 years ago. This aligns with the recent contamination of technology-critical elements, including Nb, that may have occurred in German Bight sediments, as indicated by Klein et al., 2022.

Although Ba is not a Critical Raw Material, a 50% increase of Barium concentrations in the liver and the muscle of porpoises collected during the “2019-2024” period compared to the “1999-2001” period has been observed. Ba is predominantly utilized as a weighting agent in oil and gas well drilling mud, with smaller amounts used in the production of alloys, glass, and ceramics (Oskarsson, 2022). A major source of Ba in the North Sea is hydrocarbon extraction, as drilling muds used in oil and gas operations are composed of 60-90% barite (Lepland, 2000). In the Barents and Norwegian Seas, increased Ba levels in sediments have been linked to the expansion of the oil and gas industry (Haanes et al., 2023). Despite a decline in oil and gas production in the North Sea since 2000 (OSPAR, 2010), Ba levels in *P. phocoena* continued to rise, indicating that reduced oil and gas production did not prevent this increase.

3.2 Decrease between 1999-2001 and 2019-2024 in the liver

The concentrations of Sn and Cd in the liver of harbor porpoises have shown a significant decrease between the periods 1999-2001 and 2019-2024. Specifically, the median concentration of Sn decreased by a factor of 14, while that of Cd decreased by a factor of 8.

Sn and Cd are well-known historical contaminants and have been of particular concern due to their high toxicity and tendency to bioaccumulate in marine organisms. Organotin compounds, particularly tributyltin, have been used since the 1970s in antifouling paints to prevent biofouling on ships and marine structures (Gipperth, 2009). Cadmium, on the other hand, was commonly employed in the production of nickel-cadmium (Ni-Cd) batteries, pigments, and coatings. The primary sources of Cd contamination in the environment stem from various industrial activities, including smelting, mining, fossil fuel combustion, and waste incineration (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2012).

To prevent further Cd and Sn pollution in the environment, the European Union to banned organotin compounds in 2003, with a complete ban enacted in 2008 (Goud, 2011), and banned Ni-Cd batteries (European Union, 2006).

The observed reduction in Sn levels in both the liver and muscle tissues of harbour porpoises aligns with the 10% decreases per year noted in southern North Sea sediments (Parmentier et al., 2020). Furthermore, the 8-fold decrease in Cd levels observed in the liver of *Phocoena phocoena*, mirrored the trend reported by Méndez-Fernandez et al. (2022) for *P. phocoena* in the North Sea between 2008 and 2016. Thus, the decreases of Cd and Sn in harbour porpoises from the North Sea is likely attributable to the impact of these regulatory measures (Gipperth, 2009).

3.3 Temporal trends in the muscle

The temporal trends of V and Pb in muscle tissue were unexpected, with V decreasing and Pb increasing between 1999-2001 and 2019-2024, contrary to literature findings. Méndez-Fernandez et al. (2022) reported decreasing Pb levels in *P. phocoena* from the North Sea, Celtic Sea, and Irish Sea, likely due to the EU's ban on leaded gasoline. In contrast, Ścibior et al. (2021) noted high V levels in surface sediments along the Polish coasts of the Baltic Sea. Furthermore, V, a Critical Raw material, is a crucial alloying element used in the metal-based 3D printing industry. Its use in strategic new technologies is likely to inscrease in the future, linked with the development of new vanadium-based materials.

Muscle tissue is not ideal for studying V and Pb, as V typically accumulates in the liver for marine mammals (Ikemoto et al., 2004; Ścibior et al., 2021) and Pb tends to accumulate in bone (Collin et al., 2022). However, no temporal trend of V concentrations was observed in the liver of porpoises collected during the “1999-2001” period and the “2019-2024” period, so it is unlikely that the V decrease during the two periods is due to a decline of V pollution in the North Sea (European Commission, Critical materials for strategic technologies and sectors in the EU - a foresight study, 2020).

3.4 The lack of REE temporal trends

Rare Earth Elements (REE) (La, Ce, Pr, Nd, Sm, Sc, Y, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu) are classified as Critical Raw Materials. Their use is rapidly expanding. Specifically, the demand for Dy, Nd, and Pr in e-mobility and renewable energy is expected to increase by 500%, 200%, and 100% by 2030, and by 1000%, 400%, and 300% by 2050, respectively (Fig. 23) (European Commission, Critical materials for strategic technologies and sectors in the EU - a foresight study, 2020).

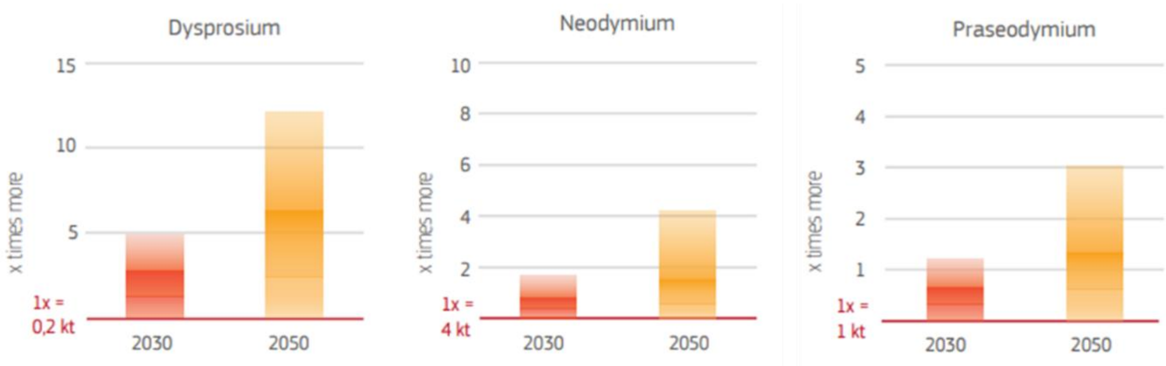


Figure 23: Combined critical raw materials use in different technologies in the EU in 2030 and 2050 (European Commission, Critical materials for strategic technologies and sectors in the EU - a foresight study, 2020)

Despite this rise in REE usage, no corresponding increase was observed in the concentrations of these elements in the liver or muscle tissues of porpoises from the North Sea, as no significant temporal trends were detected between the "1999-2001" and "2019-2024" periods.

No temporal assessments were conducted on other REE bioindicators from the North Sea, such as *Mytilus* spp. This leaves a gap in our understanding of how REE contamination may be affecting this region over time.

4. *P. PHOCOENA* AS POTENTIAL BIOINDICATORS FOR CRMS CONTAMINATION

Overall, REE concentrations in the liver and muscle of *Phocoena phocoena* were relatively low. Eu, Tb, Dy, Ho, Er, Yb and Lu were not detected in liver from porpoises collected during the "1999-2001" and the "2019-2024" periods. Additionally, Gd and Y were detected in only 4.5% of liver samples collected during the "1999-2001" period and were undetected for liver samples collected during the "2019-2024" period. The LREE La, Ce, Pr, Nd and Sm were detected in liver from porpoises collected during both periods, with Ce being the only REE detected in 100% of porpoises. This aligns with previous studies where vertebrates, including seal species such as *Erignathus barbatus* and *Pusa hispida,* also exhibited undetectable levels of heavy rare earth elements (HREE), except for Y (Marginson et al., 2023). In contrast, mussels (*Mytilus spp.*) from southern Norway exhibited detectable concentrations of all REEs except for Lu and Tm, with 13 and 17 samples, respectively, below the limit of quantification (LoQ) (Castro et al., 2023).

Positive Gd anomalies are typically found in densely populated areas and near hospital effluents, as wastewater treatment does not effectively remove Gd, leading to its release into rivers (Castro et al., 2023). Positive Gd anomaly was observed in mussels (*Mytilus Spp*) from southern Norway, with Gd levels 20 to 80 times higher than those retrieved in the liver of *P. phocoena* collected during the "1999-2001" period (Castro et al., 2023). In the present work, Gd was undetected in 38 out of 39 porpoise livers, contradicting expectations of a Gd anomaly (Annex 3). This suggests either a lack of anthropogenic Gd contamination in the southern North Sea or poor bioaccumulation of Gd in *P. phocoena*. However, significant Gd anomalies were observed in major rivers in western Germany (Elbe, Weser, Ems) (Kulaksız & Bau, 2007). As Gd concentrations were also undetectable in seal species from the North Sea (Annex 7) (Marchand, 2023), marine mammals might not be effective bioindicators of Gd contamination.

Given the lack of HREE detection in most porpoises collected from the North Sea, porpoises might not be suitable bioindicators to monitor the HREE contamination in this region. Instead, filter-feeders such as *Mytilus* spp. may be more appropriate for this purpose. However, marine mammals like harbour porpoises could serve as bioindicators for light rare earth element (LREE) contamination in the North Sea, complementing the use of mussels to provide a more comprehensive understanding of rare earth element (REE) contamination in the North Sea. Nonetheless, ΣREE concentrations in porpoises were found to be lower than those observed in seals from the same region, although they were within a similar range. Therefore, seals might be more effective bioindicators of LREE contamination than porpoises, though using both could offer a more complete understanding of REE contamination in the North Sea.

CONCLUSION

The objectives of the present work were to investigate the concentrations of Critical Raw Materials (CRMs) and other chemical elements in the muscle and the liver of harbour porpoises, evaluate the influence of the tissue type or the age class on these concentrations, and investigate the temporal variation of critical raw materials over the last 20 years in harbour porpoises collected during the “1999-2001” and the “2019-2024” periods. The present work constitutes the first temporal assessment of contamination by critical raw materials, including rare earth elements, in harbour porpoises from the North Sea.

Most CRMs exhibited higher concentrations in the liver and their concentrations in the liver were higher among the adults.

The observed decrease in highly toxic chemical elements, such as Cd and tin Sn, in the liver of porpoise collected during the “2019-2024” period compared to the “1999-2001” period, is likely a result of European regulatory measures and bans, which is an encouraging development.

However, the increase over time of critical raw materials such as antimony Sb, Nb and Al in porpoises collected during the “2019-2024” period highlights the significant changes driven by anthropogenic pressures that the North Sea has been experiencing over the last twenty years, as well as the shift in chemical associated with new technologies and the global energy transition.

No temporal trend was observed in the analysis of Rare Earth Elements (REE). Ce, La, and Nd showed the highest concentrations in the liver and muscle of porpoises during the periods "1999-2001" and "2019-2024." Most Heavy Rare Earth Elements (HREE) were undetected in these tissues, suggesting that marine mammals may be less effective bioindicators for HREE compared to mollusks. However, they may be suitable for monitoring Light Rare Earth Elements (LREE). Therefore, other bioindicator species may be necessary to assess REE contamination in the North Sea. Despite low REE levels, potential toxicity remains a concern, particularly due to co-contamination with mercury and organic pollutants, causing potential cocktail effect, underscoring the need for further studies on the combined effects of multiple contaminants on marine mammals.

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ANNEXES

Annex 1: Details on the sampling of harbour porpoises. n indicates the number of samples

Belgium (1999-2001)					
Liver	n=22	Female	n=8	Adult	n=12
		Male	n=14	Juvenile/Neonate	n=10
Muscle	n=23	Female	n=8	Adult	n=12
		Male	n=15	Juvenile/Neonate	n=11
Belgium (2019-2023)					
Liver	n=9	Female	n=3	Adult	n=4
		Male	n=6	Juvenile/Neonate	n=5
Muscle	n=1	Female	n=0	Adult	n=0
		Male	n=1	Juvenile/Neonate	n=1
Germany (2019-2023)					
Liver	n=8	Female	n=4	Adult	n=1
		Male	n=4	Juvenile/Neonate	n=7
Muscle	n=9	Female	n=4	Adult	n=1
		Male	n=5	Juvenile/Neonate	n=8

Annex 2: Functioning of ICP-MS (Inductively Coupled Plasma Mass Spectrometry)

First, the sample is introduced in the ICP-MS and a pneumatic nebulizer converts it into an aerosol using an argon gas flow. Once the droplets reach the spray chambers, the smallest ones are selected by a peristaltic pump. The plasma, which consists of ionised argon gas, dries the droplets that are injected into the plasma torch. The sample is then decomposed and dissociated into individual atoms that are then ionised. Post-ionization, the ions are extracted from the plasma and transported through multiple cones situated in the vacuum interface. This extraction is followed by the passage of the ions through an electrostatic lens, which not only enhances sensitivity but also aids in the separation of the ions from other particles. The ions finally reach the mass filter which in this case is a quadrupole. Its structure creates a time-varying electric field in its centre, and the ions can pass through it, which separates them based on their mass-to-charge ratio (m/z ratio) (Fig. A1) (*A Beginner's Guide to ICP-MS, Mass Spectrometry Basics | Agilent*; Wilschefski & Baxter, 2019).

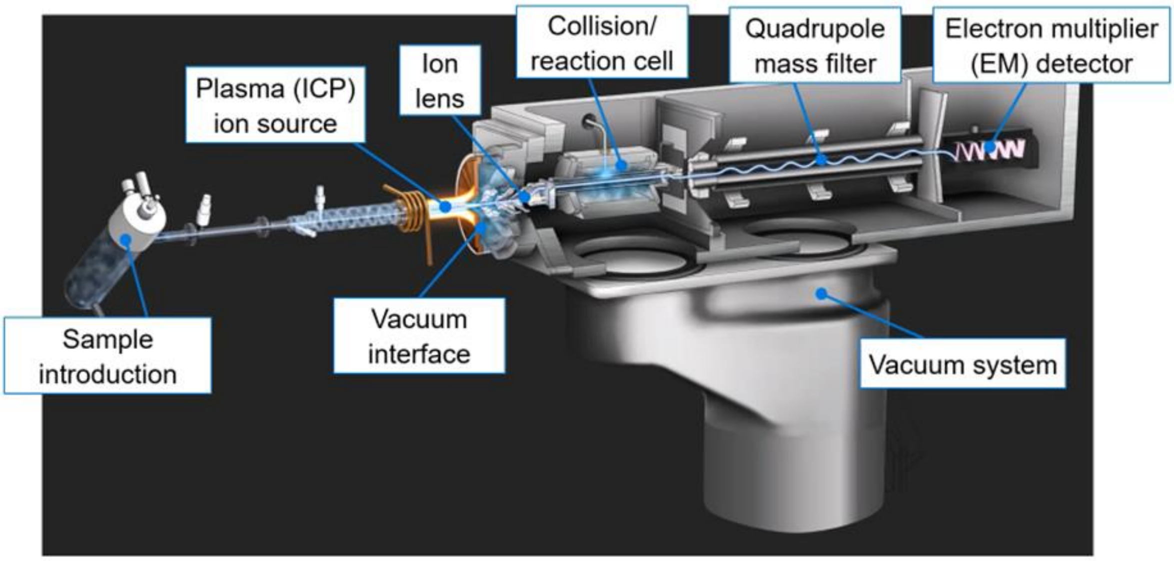

Figure A1: Diagram illustrating the operation of an Inductively Coupled Plasma Mass Spectrometer (*A Beginner's Guide to ICP-MS, Mass Spectrometry Basics | Agilent*)

Annex 3: Frequency of detection/quantification of Rare Earth Elements

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	Y	Sc
Liver 1999-2001	40,9	100	18,2	54,5	13,6	0	4,5	0	0	0	0	0	0	4,5	14
Liver 2019-2024	35,3	100	11,8	52,9	17,6	0	0	0	0	0	0	0	0	0	12
Muscle 1999-2001	21,7	95,7	17,4	34,8	8,7	0	13	8,7	8,7	0	8,7	8,7	0	17	8,7
Muscle 2019-2024	10	100	0	10	0	0	0	0	0	0	0	0	0	0	20
	LREE							HREE							

Annex 4a: Frequency of detection/quantification of chemical elements

	Li	Be	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se
Liver 1999-2001	0	0	4,5	31,8	100	4,5	100	100	100	0	100	100	0	100	100
Liver 2019-2024	0	0	29,4	35,3	100	17,6	100	100	88,2	11,8	100	100	0	100	100
Muscle 1999-2001	0	0	17,4	34,8	100	21,7	100	100	95,7	13	100	100	0	100	100
Muscle 2019-2024	0	0	40	20	100	10	100	100	30	10	100	100	0	100	100

Annex 4b: Frequencty of detection/quantification of chemical elements

	Sr	Nb	Mo	Cd	In	Sn	Sb	Ba	Ta	Pt	Tl	Pb	Bi	U
Liver 1999-2001	100	0	100	95,5	0	100	18,2	95,5	0	0	4,5	100	36,4	9,1
Liver 2019-2024	100	70,6	100	82,4	0	94,1	35,3	100	0	0	5,9	100	52,9	0
Muscle 1999-2001	100	0	8,7	56,5	0	100	34,8	95,7	0	0	0	95,7	0	13
Muscle 2019-2024	100	90	0	10	0	80	10	100	0	0	10	100	0	0

Annex 5: Comparison of Critical Raw Materials concentrations in the liver and muscle of the harbour porpoise *P. phocoena* with literature. Values are expressed as mean ± standard deviation, median, and the range of concentrations minimum-maximum. n indicates the number of samples analyzed. <LoQ means values below the limit of quantification, <LoD means values below the limit of detection (LoD)

Species	Tissue	Sampling site	Year	n	Mean ± SD	Median	Min-Max	References
Al								
P. phocoena	Liver	Southern North Sea	1999-2001	22	5.69 ± 3.57	6.28	4.29-22.08	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	8.10 ± 3.93	6.17	4.41-17.13	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.052	<LoD-0.707	Fahrenholtz et al., 2009
P. phocoena	Muscle	Southern North Sea	1999-2001	23	8.60 ± 4.80	6.14	5.05-22.08	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	8.25 ± 3.52	6.20	4.29-13.10	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD	Fahrenholtz et al., 2009
As								
P. phocoena	Liver	Southern North Sea	1999-2001	22	1.35 ± 0.68	1.18	0.53-3.32	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	1.32 ± 0.76	1.02	0.46-1.89	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.323	0.137-0.899	Fahrenholtz et al., 2009
P. phocoena	Liver	Southern North Sea	2006-2013	105	2.5 ± 0.9	-	<LoQ-6.6	Mahfouz et al., 2014
P. phocoena	Liver	Bay of Biscay	2006-2013	25	3.0 ± 0.9	-	1.4-5.2	Mahfouz et al., 2014
P. phocoena	Liver	Iberian Peninsula	2005-2013	42	0.47 ±0.03	-	0.22-1.00	Ferreira et al., 2016

P. phocoena	Muscle	Southern North Sea	1999-2001	23	1.18 ± 0.56	0.94	0.46-2.21	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	20	0.80 ± 0.43	0.81	0.46-1.89	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	0.190	0.084-0.429	Fahrenholtz et al., 2009
P. phocoena	Muscle	Iberian Peninsula	2005-2013	42	0.29 ± 0.02	-	0.10-0.69	Ferreira et al., 2016
Bi								
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.08	0.03	0.007-0.5	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.08	0.07	0.01-0.2	This study
Enhydra lutris	Liver	California	1992-2002	80	0.01	0.01	<LoD-0.08	Kannan et al., 2006
Co								
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.02 ± 0.009	0.02	0.004-0.05	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.02 ± 0.01	0.02	0.001-0.05	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.006	<LoD-0.011	Fahrenholtz et al., 2009
P. phocoena	Muscle	Southern North Sea	1999-2001	23	0.02 ± 0.01	0.02	0.002-0.05	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	0.01 ± 0.006	0.01	0.001-0.02	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	-	<LoD-0.006	Fahrenholtz et al., 2009
Cu								
P. phocoena	Liver	Southern North Sea	1999-2001	22	35.00 ± 25.06	27.27	13.41-128.11	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	55.58 ± 49.36	34.27	19.91-206.24	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	9.198	5.492-29.75	Fahrenholtz et al., 2009
P. phocoena	Liver	Southern North Sea	2006-2013	105	38 ± 36	-	6-320	Mahfouz et al., 2014
P. phocoena	Liver	Bay of Biscay	2006-2013	25	33 ± 23	-	12-136	Mahfouz et al., 2014
P. phocoena	Liver	Iberian Peninsula	2005-2013	42	16.28 ± 1.94	-	4.60-57.73	Ferreira et al., 2016
P. phocoena	Liver	North Sea (Belgium)	1994-2001	49	39 ± 38	30	9-257	Das et al., 2004
P. phocoena	Muscle	Southern North Sea	1999-2001	23	41.90 ± 46.56	28.45	4.97-206.24	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	8.25 ± 2.21	8.45	4.96-11.85	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	2.160	0.870-4.771	Fahrenholtz et al., 2009
P. phocoena	Muscle	Iberian Peninsula	2005-2013	42	1.94 ± 0.08		0.96-2.99	Ferreira et al., 2016
P. phocoena	Muscle	North Sea (Belgium)	1994-2001	51	7 ± 4	6	2-22	Das et al., 2004
In								

P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoD	<LoD	<LoD	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoD	<LoD	<LoD	This study
Enhydra lutris	Liver	California	1992-2002	80	0.01	0.002	<LoD-0.03	Kannan et al., 2006
Li								
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoQ	<LoQ	<LoQ	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	<LoQ	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.006	<LoD-0.005	Fahrenholtz et al., 2009
P. phocoena	Muscle	Southern North Sea	1999-2001	23	<LoQ	<LoQ	<LoQ	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	<LoQ	<LoQ	<LoQ	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.032	Fahrenholtz et al., 2009
Mn								
P. phocoena	Liver	Southern North Sea	1999-2001	22	18.98 ± 5.01	20.13	9.90-26.30	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	18.44 ± 6.93	16.96	4.98-27.83	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	6.362	2.111-9.722	Fahrenholtz et al., 2009
P. phocoena	Liver	Iberian Peninsula	2005-2013	42	5.10 ± 0.01	-	1.71-10.40	Ferreira et al., 2016
P. phocoena	Muscle	Southern North Sea	1999-2001	23	14.79 ± 10.00	15.98	0.76-27.83	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	1.32 ± 0.38	1.32	0.74-1.86	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	0.328	0.144-0.969	Fahrenholtz et al., 2009
P. phocoena	Muscle	Iberian Peninsula	2005-2013	42	0.35 ± 0.02	-	0.12-0.65	Ferreira et al., 2016
Ni								
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoQ	<LoQ	<LoQ	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.10 ± 0.07	0.08	0.06-0.37	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.044	Fahrenholtz et al., 2009
P. phocoena	Liver	Iberian Peninsula	2005-2013	42	0.18 ± 0.02	-	0.01-0.59	Ferreira et al., 2016
P. phocoena	Muscle	Southern North Sea	1999-2001	23	0.09 ± 0.07	0.08	0.02-0.37	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	0.08 ± 0.06	0.08	0.02-0.25	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.023	Fahrenholtz et al., 2009
P. phocoena	Muscle	Iberian Peninsula	2005-2013	42	0.30 ± 0.03	-	0.02-0.62	Ferreira et al., 2016
Pt								

P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoD	<LoD	<LoD	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoD	<LoD	<LoD	This study
Stenella sp.	Liver	Ghana	2006	3	0.7-0.9	-	-	Essumang, 2008
Sb								
P. phocoena	Liver	Southern North Sea	1999-2001	22	1.3	0.5	0.8-2.5	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	1.6	1.2	0.9-2.7	This study
Enhydra lutris	Liver	California	1992-2002	80	0.01	0.01	<LoD-0.02	Kannan et al., 2006
Sr								
P. phocoena	Liver	Southern North Sea	1999-2001	22	1.5	0.7	0.3-11	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.7	0.6	0.4-2.2	This study
Enhydra lutris	Liver	California	1992-2002	80	1.46	0.6	0.08-23	Kannan et al., 2006
Small cetaceans	Liver	Hawaii	1997-2011	31	0.12	-	0.04-2.77	Hansen et al., 2016
Harp seal	Liver	Labrador	1994	10	3.1	-	-	Yeats et al., 1999
Ti								
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoD	<LoD	<LoD	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoD	<LoD	<LoD	This study
*Steno bredanensi*s	Liver	Brazil	2005-2012	8	16 ± 6.33	-	-	Monteiro et al., 2020
Tl								
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.08	0.03	0.007-0.5	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.08	0.07	0.01-0.2	This study
Enhydra lutris	Liver	California	1992-2002	80	0.003	0.002	<LoD-0.01	Kannan et al., 2006
V								
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.61 ± 0.16	0.59	0.40-1.17	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.60 ± 0.11	0.57	0.43-0.84	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.017	<LoD-0.128	Fahrenholtz et al., 2009
P. phocoena	Liver	Southern North Sea	2006-2013	105	0.6 ± 0.4	-	0.2-2.4	Mahfouz et al., 2014
P. phocoena	Liver	Bay of Biscay	2006-2013	25	0.7 ± 0.4	-	0.4-1.76	Mahfouz et al., 2014

P. phocoena	Muscle	Southern North Sea	1999-2001	23	0.58 ± 0.11	0.55	0.46-0.84	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	0.48 ± 0.06	0.49	0.37-0.54	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.013	Fahrenholtz et al., 2009

Annex 6: Comparison of chemical elements concentrations in the liver and muscle of the harbour porpoise *P. phocoena* with literature. Values are expressed as mean ± standard deviation, median, and the range of concentrations minimum-maximum. n indicates the number of samples analyzed. <LoQ means values below the limit of quantification, <LoD means values below the limit of detection (LoD)

Species	Tissue	Sampling site	Year	n	Mean ± SD	Median	Min-Max	References
				Ba				
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.9	0.8	0.3-1.5	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	1.1	1.2	0.8-1.3	This study
Enhydra lutris	Liver	California	1992-2002	80	0.02	0.02	0.006-0.2	Kannan et al., 2006
				Cd				
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.88 ± 0.65	0.84	0.01-2.21	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.40 ± 0.50	0.13	0.004-1.50	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.051	<LoD-0.503	Fahrenholtz et al., 2009
P. phocoena	Liver	Southern North Sea	2006-2013	105	0.4 ± 0.5	-	<LoQ-3.3	Mahfouz et al., 2014
P. phocoena	Liver	Bay of Biscay	2006-2013	25	0.5 ± 0.5	-	<LoQ-1.5	Mahfouz et al., 2014
P. phocoena	Liver	Iberian Peninsula	2005-2013	42	0.15 ± 0.03	-	0.00-0.63	Ferreira et al., 2016
P. phocoena	Liver	North Sea (Belgium)	1994-2001	49	0.5 ± 0.6	0.2	<LoD-2.5	Das et al., 2004
P. phocoena	Muscle	Southern North Sea	1999-2001	23	0.43 ± 0.63	0.04	0.003-1.72	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	0.01 ± 0.01	0.01	0.003-0.03	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.150	Fahrenholtz et al., 2009
P. phocoena	Muscle	Iberian Peninsula	2005-2013	42	0.01 ± 0.00	-	0.00-0.01	Ferreira et al., 2016
P. phocoena	Muscle	North Sea (Belgium)	1994-2001	51	<LoD	<LoD	<LoQ-0.2	Das et al., 2004
				Cr				
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.11 ± 0.03	0.11	0.08-0.23	This study

P. phocoena	Liver	Southern North Sea	2019-2024	17	1.34 ± 4.38	0.12	0.09-18.19	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.016	Fahrenholtz et al., 2009
P. phocoena	Liver	Southern North Sea	2006-2013	105	2 ± 1	-	0.6-7	Mahfouz et al., 2014
P. phocoena	Liver	Bay of Biscay	2006-2013	25	1.5 ± 0.2	-	1.4-5.2	Mahfouz et al., 2014
P. phocoena	Muscle	Southern North Sea	1999-2001	23	0.90 ± 3.77	0.11	0.10-18.19	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	0.14 ± 0.10	0.11	0.08-0.42	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.022	Fahrenholtz et al., 2009
Mo								
P. phocoena	Liver	Southern North Sea	1999-2001	22	1.89 ± 0.67	1.88	0.67-3.15	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	1.79 ± 0.92	2.11	0.24-3.03	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.538	0.083-1.100	Fahrenholtz et al., 2009
P. phocoena	Muscle	Southern North Sea	1999-2001	23	1.25 ± 1.08	1.20	0.02-2.96	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	<LoQ	<LoQ	<LoQ	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	0.007	<LoD-0.036	Fahrenholtz et al., 2009
Pb								
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.38 ± 0.20	0.30	0.22-1.02	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.37 ± 0.07	0.37	0.25-0.55	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.003	<LoD-0.212	Fahrenholtz et al., 2009
P. phocoena	Liver	Iberian Peninsula	2005-2013	42	0.07 ± 0.32	-	0.02-0.20	Ferreira et al., 2016
P. phocoena	Liver	Celtic & Irish Sea	2004-2015	31	0.061 ± 0.036	-	-	Méndez-Fernandez et al., 2022
P. phocoena	Liver	North Sea	2004-2015	26	0.060 ± 0.042	-	-	Méndez-Fernandez et al., 2022
P. phocoena	Muscle	Southern North Sea	1999-2001	23	0.41 ± 0.17	0.37	0.25-1.02	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	0.32 ± 0.04	0.33	0.25-0.40	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.003	Fahrenholtz et al., 2009
P. phocoena	Muscle	Iberian Peninsula	2005-2013	42	0.02 ± 0.00	-	0.00-0.12	Ferreira et al., 2016
Se								
P. phocoena	Liver	Southern North Sea	1999-2001	22	79.24 ± 199.2	20.36	2.03-946.91	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	41.28 ± 61.48	10.91	1.04-192.41	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	2.933	0.416-46.54	Fahrenholtz et al., 2009

P. phocoena	Liver	Southern North Sea	2006-2013	105	24 ± 46	-	1.9-311	Mahfouz et al., 2014
P. phocoena	Liver	Bay of Biscay	2006-2013	25	24 ± 31	-	2-106	Mahfouz et al., 2014
P. phocoena	Liver	Iberian Peninsula	2005-2013	42	11.50 ± 2.34	-	0.75-49.46	Ferreira et al., 2016
P. phocoena	Liver	North Sea (Belgium)	1994-2001	37	14 ± 21	7	0.6-99	Das et al., 2004
P. phocoena	Muscle	Southern North Sea	1999-2001	23	76.07 ± 199.9	6.31	0.87-946.91	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	1.43 ± 1.01	1.03	0.70-4.08	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	0.601	0.271-0.989	Fahrenholtz et al., 2009
P. phocoena	Muscle	Iberian Peninsula	2005-2013	42	0.44 ± 0.03	-	0.20-0.99	Ferreira et al., 2016
P. phocoena	Muscle	North Sea (Belgium)	1994-2001	20	3.8 ± 8.5	1.5	0.4-39	Das et al., 2004
Sn								
P. phocoena	Liver	Southern North Sea	1999-2001	22	2.13 ± 1.40	1.88	0.50-6.40	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	0.16 ± 0.15	0.02	0.01-0.69	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	0.17	0.018-0.799	Fahrenholtz et al., 2009
P. phocoena	Muscle	Southern North Sea	1999-2001	23	0.73 ± 1.25	1.88	0.50-6.40	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	0.03 ± 0.02	0.02	0.002-0.08	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	<LoD	<LoD-0.183	Fahrenholtz et al., 2009
Zn								
P. phocoena	Liver	Southern North Sea	1999-2001	22	245 ± 171	166	91.55-787.72	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	213 ± 187	139	53.35-861.21	This study
P. phocoena	Liver	North & Baltic Sea	2004-2006	22	-	37.97	21.89-165.2	Fahrenholtz et al., 2009
P. phocoena	Liver	Southern North Sea	2006-2013	105	193 ± 106	-	67-635	Mahfouz et al., 2014
P. phocoena	Liver	Bay of Biscay	2006-2013	25	152 ± 62	-	77-303	Mahfouz et al., 2014
P. phocoena	Liver	Iberian Peninsula	2005-2013	42	60.48 ± 6.26	-	21.7-192	Ferreira et al., 2016
P. phocoena	Liver	North Sea (Belgium)	1994-2001	49	234 ± 172	163	40-684	Das et al., 2004
P. phocoena	Muscle	Southern North Sea	1999-2001	23	217 ± 211	145	53.35-861.21	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	79.76 ± 24.35	74.21	44.68-122.22	This study
P. phocoena	Muscle	North & Baltic Sea	2004-2006	22	-	18.63	12.46-36.97	Fahrenholtz et al., 2009
P. phocoena	Muscle	Iberian Peninsula	2005-2013	42	19.11 ± 1.02	-	10.66-35.32	Ferreira et al., 2016
P. phocoena	Muscle	North Sea (Belgium)	1994-2001	51	74 ± 33	65	24-193	Das et al., 2004

Annex 7: Comparison of Rare Earth Elements (REE) concentrations in the liver and muscle of the harbour porpoise *P. phocoena* with those reported for seal species from the literature. Values are expressed as mean ± standard deviation, and the range of concentrations minimum-maximum. n indicates the number of samples analyzed. <LoQ refers to values below the limit of quantification, <LoD refers to values below the limit of detection (LoD) . * indicates that some REE were not included in the reference data, which may result in an underestimated sum.

Species	Tissue	Sampling site	Year	n	Mean ± SD	Min-Max	References
∑REE							
P. phocoena	Liver	Southern North Sea	1999-2001	22	29.85 ± 31.69	10.01-166.9	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	23.96 ± 14.79	11.48-62.35	This study
E. barbatus	Liver	Nunavik, Canada	2017-2021	9	500 ± 530	130-880	Marginson et al. (2023)
P. hispida	Liver	Nunavik, Canada	2017-2021	9	150 ± 170	3-490	Marginson et al. (2023)
H. grypus	Liver	North Sea		22	99.12 ± 145.4*	14.49-364	Marchand (2023)
P. vitulina	Liver	North Sea		16	116.6 ± 141.6*	89.69-608.7	Marchand (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	23	34.33 ± 52.58	7.35-211.26	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	13.69 ± 4.80	8.9-25.97	This study
E.barbatus	Muscle	Nunavik, Canada	2017-2021	9	40 ± 30	20-60	Marginson et al. (2023)
P. hispida	Muscle	Nunavik, Canada	2017-2021	9	3 ± 3	0.7-10	Marginson et al. (2023)
H. grypus	Muscle	North Sea		21	44.98 ± 110.7*	2.18-457	Marchand (2023)
P. vitulina	Muscle	North Sea		19	11.37 ± 23.82*	2.09-102	Marchand (2023)
Mytilus spp.	Soft tissue	Southern Norway	2021	49	950-4900 ± 100-2400	-	Castro et al. (2023)
∑LREE							
P. phocoena	Liver	Southern North Sea	1999-2001	22	26.94	-	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	23.96	-	This study

Mytilus spp.	Soft tissue	Southern Norway	2021	49	760-4200 ± 87-2100	-	Castro et al. (2023)
∑HREE							
P. phocoena	Liver	Southern North Sea	1999-2001	22	0.17	-	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	-	This study
Mytilus spp.	Soft tissue	Southern Norway	2021	49	170-660 ± 25-300	-	Castro et al. (2023)
Y							
P. phocoena	Liver	Southern North Sea	1999-2001	22	1.72 ± 2.81	0.56-13.79	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Liver	North Sea		22	12 ± 15	<LoQ-66	Marchand (2023)
P. vitulina	Liver	North Sea		16	10 ± 10	2.8-47	Marchand (2023)
P. groenlandicus	Liver	OSPAR I		16	15 ± 10	3.3-41	Marchand (2023)
C. cristata	Liver	OSPAR I		17	20 ± 12	4.4-55	Marchand (2023)
P. hispida	Liver	OSPAR I		33	10 ± 11	<LoQ-55	Marchand (2023)
E. barbatus	Liver	OSPAR I		6	13 ± 10	4.5-26	Marchand (2023)
Mytilus spp.	Soft tissue	Southern Norway	2021	49	100-420 ± 15-190	-	Castro et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	22	5.08 ± 11	0.57-45	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Muscle	North Sea		21	16 ± 23	<LoD-81	Marchand (2023)
P. vitulina	Muscle	North Sea		19	8.8 ± 15	1.8-69	Marchand (2023)
P. groenlandicus	Muscle	OSPAR I		17	3.2 ± 5.5	<LoD-18	Marchand (2023)
C. cristata	Muscle	OSPAR I		14	1.7 ± 3.4	0.86-14	Marchand (2023)
P. hispida	Muscle	OSPAR I		32	5.8 ± 8.3	<LoD-38	Marchand (2023)
La							

P. phocoena	Liver	Southern North Sea	1999-2001	22	6.50 ± 6.75	2.3-32.2	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	5.57 ± 3.61	2.3-12.6	This study
H. grypus	Liver	North Sea		22	43 ± 81	3.9-390	Marchand (2023)
P. vitulina	Liver	North Sea		16	62 ± 84	7.1-360	Marchand (2023)
P. groenlandicus	Liver	OSPAR I		16	100 ± 63	43-220	Marchand (2023)
C. cristata	Liver	OSPAR I		17	160 ± 62	4.2-270	Marchand (2023)
P. hispida	Liver	OSPAR I		33	71 ± 48	19-200	Marchand (2023)
E. barbatus	Liver	OSPAR I		6	81 ± 74	33-230	Marchand (2023)
Mytilus spp.	Soft tissue	Southern Norway	2021	49	220-1500 ± 26-91	-	Castro et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	22	5.23 ± 5.86	2.3-24	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	3.39 ± 1.17	2.3-6.6	This study
H. grypus	Muscle	North Sea		21	18 ± 45	1.2-200	Marchand (2023)
P. vitulina	Muscle	North Sea		19	5.1 ±10	1.1-44	Marchand (2023)
P. groenlandicus	Muscle	OSPAR I		17	2.3 ± 1.5	<LoD-5	Marchand (2023)
C. cristata	Muscle	OSPAR I		14	2 ± 0.55	0.99-3	Marchand (2023)
P. hispida	Muscle	OSPAR I		32	2.2 ± 1.5	<LoD-10	Marchand (2023)
Ce							
P. phocoena	Liver	Southern North Sea	1999-2001	22	13 ± 8.7	4.8-45	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	12 ± 5.6	7.1-28	This study
Mytilus spp.	Soft tissue	Southern Norway	2021	49	300-1800 ± 32-980	-	Castro et al. (2023)
Nd							
P. phocoena	Liver	Southern North Sea	1999-2001	22	4.39 ± 5.57	1.29-26.42	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	3.75 ± 3.13	1.33-11.53	This study
H. grypus	Liver	North Sea		22	49 ± 53	<LoQ-270	Marchand (2023)

P. vitulina	Liver	North Sea		16	49 ±53	80-230	Marchand (2023)
P. groenlandicus	Liver	OSPAR I		16	83 ± 50	32-180	Marchand (2023)
C. cristata	Liver	OSPAR I		17	140 ± 37	<LoQ-230	Marchand (2023)
P. hispida	Liver	OSPAR I		33	52 ± 37	10-140	Marchand (2023)
E. barbatus	Liver	OSPAR I		6	79 ± 51	37-230	Marchand (2023)
Mytilus spp.	Soft tissue	Southern Norway	2021	49	160-660 ± 18-310	-	Castro et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	22	5.07 ± 8.56	0.47-32.49	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	1.81 ± 1.12	1.1-4.97	This study
H. grypus	Muscle	North Sea		21	19 ± 47	0.56-190	Marchand (2023)
P. vitulina	Muscle	North Sea		19	4.1 ± 8.7	0.57-38	Marchand (2023)
P. groenlandicus	Muscle	OSPAR I		17	1.4 ± 1.5	<LoD-4	Marchand (2023)
C. cristata	Muscle	OSPAR I		14	1.6 ± 0.87	<LoD-3	Marchand (2023)
P. hispida	Muscle	OSPAR I		32	2 ± 4.3	<LoD-25	Marchand (2023)
Sm							
P. phocoena	Muscle	Southern North Sea	1999-2001	22	2.2 ± 3.6	0.4-16	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	1.7 ± 1.8	0.5-6.6	This study
Mytilus spp.	Soft tissue	Southern Norway	2021	49	30-96± 3-45	-	Castro et al. (2023)
Eu							
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoQ	<LoQ	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Liver	North Sea		22	<LoQ	<LoQ	Marchand (2023)
P. vitulina	Liver	North Sea		16	<LoD	<LoD	Marchand (2023)
P. groenlandicus	Liver	OSPAR I		16	<LoQ	<LoQ	Marchand (2023)
C. cristata	Liver	OSPAR I		17	<LoQ	<LoQ	Marchand (2023)

P. hispida	Liver	OSPAR I		33	<LoD	<LoD	Marchand (2023)
E. barbatus	Liver	OSPAR I		6	<LoQ	<LoQ	Marchand (2023)
Mytilus spp.	Soft tissue	Southern Norway	2021	49	5.2-15 ± 0.48-7.3	-	Castro et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	22	<LoQ	<LoQ	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Muscle	North Sea		21	0.65 ± 1.4	<LoD-6	Marchand (2023)
P. vitulina	Muscle	North Sea		19	<LoQ	<LoQ	Marchand (2023)
P. groenlandicus	Muscle	OSPAR I		17	<LoD	<LoD	Marchand (2023)
C. cristata	Muscle	OSPAR I		14	<LoD	<LoD	Marchand (2023)
P. hispida	Muscle	OSPAR I		32	<LoD	<LoD	Marchand (2023)
Gd							
P. phocoena	Liver	Southern North Sea	1999-2001	22	1.19 ± 0.82	0.36-3.66	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Liver	North Sea		22	<LoQ	<LoQ	Marchand (2023)
P. vitulina	Liver	North Sea		16	<LoQ	<LoQ	Marchand (2023)
P. groenlandicus	Liver	OSPAR I		16	10 ± 7.4	<LoQ-30	Marchand (2023)
C. cristata	Liver	OSPAR I		17	17 ± 5.8	<LoQ-28	Marchand (2023)
P. hispida	Liver	OSPAR I		33	5.3 ± 4.7	<LoD-18	Marchand (2023)
E. barbatus	Liver	OSPAR I		6	8 ± 8.3	<LoQ-25	Marchand (2023)
Mytilus spp.	Soft tissue	Southern Norway	2021	49	28-96 ± 4.7-46	-	Castro et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	22	1.72 ± 2.58	0.37-9.67	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Muscle	North Sea		21	3.9 ± 9.8	<LoD-36	Marchand (2023)

P. vitulina	Muscle	North Sea		19	0.77 ± 1.8	<LoD-8	Marchand (2023)
P. groenlandicus	Muscle	OSPAR I		17	0.4 ± 0.34	<LoD-1	Marchand (2023)
C. cristata	Muscle	OSPAR I		14	0.2 ± 0.2	<LoD-0.7	Marchand (2023)
P. hispida	Muscle	OSPAR I		32	0.23 ± 0.49	<LoD-2	Marchand (2023)
Tb							
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoQ	<LoQ	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Liver	North Sea		22	<LoD	<LoD	Marchand (2023)
P. vitulina	Liver	North Sea		16	<LoD	<LoD	Marchand (2023)
P. groenlandicus	Liver	OSPAR I		16	<LoD	<LoD	Marchand (2023)
C. cristata	Liver	OSPAR I		17	<LoD	<LoD	Marchand (2023)
P. hispida	Liver	OSPAR I		33	<LoD	<LoD	Marchand (2023)
E. barbatus	Liver	OSPAR I		6	<LoD	<LoD	Marchand (2023)
Mytilus spp.	Soft tissue	Southern Norway	2021	49	2.8-9.7 ± 0.23-4.7	-	Castro et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	22	0.25 ± 0.32	0.11-1.26	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Muscle	North Sea		21	0.51 ± 1.1	<LoD-4	Marchand (2023)
P. vitulina	Muscle	North Sea		19	0.15 ± 0.21	<LoD-1	Marchand (2023)
P. groenlandicus	Muscle	OSPAR I		17	<LoD	<LoD	Marchand (2023)
C. cristata	Muscle	OSPAR I		14	<LoD	<LoD	Marchand (2023)
P. hispida	Muscle	OSPAR I		32	<LoD	<LoD	Marchand (2023)
Dy							
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoQ	<LoQ	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study

H. grypus	Liver	North Sea		22	<LoQ	<LoQ	Marchand (2023)
P. vitulina	Liver	North Sea		16	<LoQ	<LoQ	Marchand (2023)
P. groenlandicus	Liver	OSPAR I		16	<LoQ	<LoQ	Marchand (2023)
C. cristata	Liver	OSPAR I		17	3.8 ± 1.8	<LoD-7	Marchand (2023)
P. hispida	Liver	OSPAR I		33	<LoQ	<LoQ	Marchand (2023)
E. barbatus	Liver	OSPAR I		6	<LoQ	<LoQ	Marchand (2023)
Mytilus spp.	Soft tissue	Southern Norway	2021	49	19-63 ± 2-30	-	Castro et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	22	1.21 ± 2.12	0.28-8.17	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Muscle	North Sea		21	2.1 ± 4.7	<LoD-15	Marchand (2023)
P. vitulina	Muscle	North Sea		19	0.62 ± 1.3	<LoD-6	Marchand (2023)
P. groenlandicus	Muscle	OSPAR I		17	0.29 ± 0.27	<LoD-1	Marchand (2023)
C. cristata	Muscle	OSPAR I		14	0.31 ± 0.18	0.13-0.7	Marchand (2023)
P. hispida	Muscle	OSPAR I		32	0.13 ± 0.22	<LoD-1	Marchand (2023)
Er							
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoQ	<LoQ	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Liver	North Sea		22	<LoD	<LoD	Marchand (2023)
P. vitulina	Liver	North Sea		16	<LoD	<LoD	Marchand (2023)
P. groenlandicus	Liver	OSPAR I		16	<LoD	<LoD	Marchand (2023)
C. cristata	Liver	OSPAR I		17	<LoD	<LoD	Marchand (2023)
P. hispida	Liver	OSPAR I		33	<LoD	<LoD	Marchand (2023)
E. barbatus	Liver	OSPAR I		6	<LoD	<LoD	Marchand (2023)

Mytilus spp.	Soft tissue	Southern Norway	2021	49	9.1-30 ± 1.2-13	-	Castro et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	22	0.69 ± 1.06	0.25-4.79	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
H. grypus	Muscle	North Sea		21	0.82 ± 1.7	<LoD-6	Marchand (2023)
P. vitulina	Muscle	North Sea		19	0.46 ± 0.81	<LoD-3	Marchand (2023)
P. groenlandicus	Muscle	OSPAR I		17	<LoD	<LoD	Marchand (2023)
C. cristata	Muscle	OSPAR I		14	<LoD	<LoD	Marchand (2023)
P. hispida	Muscle	OSPAR I		32	<LoD	<LoD	Marchand (2023)
Yb							
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoQ	<LoQ	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
Mytilus spp.	Soft tissue	Southern Norway	2021	49	7.3-22 ± 0.72-8.8	-	Castro et al. (2023)
Lu							
P. phocoena	Liver	Southern North Sea	1999-2001	22	<LoQ	<LoQ	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	<LoQ	<LoQ	This study
Mytilus spp.	Soft tissue	Southern Norway	2021	49	1.3-2.9 ± 0.34-1.2	-	Castro et al. (2023)
LREE/HREE							
P. phocoena	Liver	Southern North Sea	1999-2001	22	16.35	-	This study
P. phocoena	Liver	Southern North Sea	2019-2024	17	NA	-	This study
E. barbatus	Liver	Nunavik, Canada	2017-2021	9	37.9	-	Marginson et al. (2023)
P. hispida	Liver	Nunavik, Canada	2017-2021	9	27.9	-	Marginson et al. (2023)
P. phocoena	Muscle	Southern North Sea	1999-2001	23	3.4	-	This study
P. phocoena	Muscle	Southern North Sea	2019-2024	10	NA	-	This study

E. barbatus	Muscle	Nunavik, Canada	2017-2021	9	3.6	-	Marginson et al. (2023)
P. hispida	Muscle	Nunavik, Canada	2017-2021	9	2.6	-	Marginson et al. (2023)