

**Analysis and Tracking Chlorinated Hydrocarbons:
PCB, DDT and HCB in Baltic Sea Sediments**

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Distribution, Temporal Trends, and Ecological Risks

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Zusammenfassung

Die Ostsee zeigt nachweisbare Mengen persistenter Schadstoffe in Wasser, Schwebstoffen und Sedimenten aufgrund vergangener industrieller Aktivitäten und weit verbreiteter Verwendung chlorierter Pestizide. Diese Studie konzentriert sich auf chlorierte Kohlenwasserstoffschadstoffe (PCBs, DDT und HCB) in Sedimentproben der Ostsee und untersucht deren Konzentrationen, die räumlich-zeitliche Verteilung, Vorkommensformen sowie ökologische und gesundheitliche Risiken.

Räumliche Variationen in den PCB153-Konzentrationen, die mit verstärkten menschlichen Aktivitäten in zentralen und südlichen Regionen verbunden sind, deuten auf industrielle und hafenbezogene Einträge hin. DDD und DDE zeigen konsistente Verteilungsmuster über Jahrzehnte hinweg, die historische Schadstoffeinträge widerspiegeln.

Langzeitüberwachung an sechs Arkona-Becken-Stationen zeigt vielfältige PCB-Trends, beeinflusst durch Ereignisse des Hauptbaltischen Zuflusses und Schiffsunfälle. Der beobachtete Abwärtstrend steht im Zusammenhang mit regulatorischen Maßnahmen, einschließlich Verbote, internationaler Regeln und Aktionen der Helsinki-Kommission (HELCOM), was die Wirksamkeit von Umweltschutzmaßnahmen betont.

Der Oberflächensedimentbestand für insgesamt 6PCBs in der Ostsee ist deutlich höher als die PCB-Werte in der Wassersäule, was die Sedimente als wichtige Senken für organische Schadstoffe hervorhebt. Die Analyse von acht Sedimentkernproben zeigt ein konsistentes vertikales Muster der Schadstoffverteilung. PCB-Konzentrationen zeigen einen Aufwärtstrend in den oberen Schichten, erreichen in der Mitte des Kerns ihren Höhepunkt und nehmen mit der Tiefe ab, was die Wirksamkeit der Sedimentprofile bei der Darstellung zeitlicher Veränderungen zeigt.

Die Verteilungsmuster von PCB-Kommerzprodukten in Sedimentkernen variieren zwischen Offshore- und Inshore-Kernen, betonen den Einfluss der Küstennähe und Topografie.

Ökologische Risikobewertungen zeigen kein signifikantes ökologisches Risiko in den Oberflächensedimenten der Ostsee, obwohl die PEHI-Methode Risiken während der 2000er Jahre andeutet. Die Hazard Quotient-Berechnungen bestätigen keine Gesundheitsrisiken für Menschen. Diese Ergebnisse liefern umfassende Einblicke in die räumlichen und zeitlichen Dynamiken der Schadstoffverteilung in der Ostsee und betont die Rolle von Sedimenten als Schlüsselreservoirs für organische Schadstoffe.

Abstract

The Baltic Sea, functioning as a discharge area, continues to show detectable levels of persistent pollutants in its seawater, suspended matter, and sediments. This is attributed to the synthesis and industrial use of PCB commercial products, along with the widespread use and discharge of certain chlorinated pesticides into the natural environment during the last century.

This research examines chlorinated hydrocarbon pollutants (PCBs, DDT, and HCB) in Baltic Sea sediment samples, focusing on their concentrations, spatial and temporal distribution, forms of occurrence, and associated ecological and human health risks.

Spatial variations in PCB153 concentrations, linked to heightened human activities in central and southern regions, indicate industrialization and port-related inputs. DDD and DDE exhibit consistent distribution patterns across decades, reflecting historical pollutant inputs. Long-term monitoring at six Arkona Basin stations reveals diverse PCB trends influenced by Major Baltic Inflow events and shipping accidents. The declining trend is associated with regulatory measures, including bans, international rules, and actions by the Helsinki Commission (HELCOM), underscoring the efficacy of environmental protection efforts.

Surface sediment inventory for total 6PCBs in the Baltic is markedly higher than PCB levels in the water column, highlighting sediments as crucial sinks for organic pollutants.

Analysis of eight sediment core samples reveals a consistent vertical pattern of pollution dispersion. PCB concentrations exhibit an upward trend in the upper layers, peak at mid-core depth, and gradually decline with depth, showcasing the sediment profiles' efficacy in depicting temporal changes. The distribution patterns of PCB commercial products in sediment cores vary between offshore and inshore cores, emphasizing the impact of coastal proximity and topography.

Ecological risk assessments reveal no significant ecological risk in Baltic Sea surface sediments, although the PEHI method suggests risks during the 2000s. Hazard Quotient calculations confirm no health risks for humans.

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List of Abbreviations

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1 Introduction

1.1 Pollution background global

Extreme global demand for chemical production has spurred rapid industrialization and technological development since 19th (Wittcoff et al., 2012). The varieties and amounts of harmful compounds, in particular persistent organic pollutants (POPs), have been steadily rising within this variety of substances. These substances not only improve human welfare but also put the world's environment and public health in serious danger, possibly harming them in the long run (Jones and Voogt, 1999).

Organic substances that display traits including long-term persistence, bioaccumulation, semi-volatility, and high toxicity are referred to as persistent organic pollutants (POPs). They pose serious risks to both human health and the environment because they can spread over great distances through a variety of environmental media, including air, water, and living things. Through atmospheric transport, ocean currents, and other mechanisms, these contaminants can spread globally, posing a serious environmental problem (Birnbaum, 1994; Hansen, 1998; Herrman, 1993).

The frightening effects of pesticide usage, notably Dichloro-Diphenyl-Trichloroethane (DDT), became clear in the late 1960s when it resulted in widespread avian deaths. Concerns were expressed regarding the secure application of organic compounds. Pesticides and other contaminants have impacted fish, birds, and animals in North America's Great Lakes area (Béland et al., 1993; Gilbertson et al., 1991). High quantities of pesticide residues were found in species even in remote locations, such as Arctic and Antarctic regions, where pesticides have never been employed (Bylund et al., 1974; Wania and Mackay, 1993).

Organochlorine pesticides, including DDT and its metabolite Dichlorodiphenyldichloroethane (DDD) and Dichlorodiphenyldichloroethylene (DDE), have been linked to reproductive problems in birds and marine animals, according to research done in North America and Europe (Bergman and Olsson, 1985; Pearce et al., 1979; Ratcliffe, 1967; Reijnders et al., 1997). In the upper predators in the food chain, these pollutants caused reproductive problems and population declines. Along with behavioral problems, immune system diseases, gender disruption, and greater susceptibility to tumors and malignancies, they also produced anomalies in hormone

and functional systems.

POP-related environmental contamination episodes shook the entire globe. For instance, the polychlorinated biphenyls (PCBs) in the oil that caused the dioxin spill in Seveso, Italy, in July 1976 and the "rice bran oil" poisoning episodes in Japan in 1968 and the Taiwan region of China in 1979 heightened awareness about the dangers of POPs world wide (Xu et al., 2022).

The effects of persistent organic pollutants, particularly chemicals like dioxins, PCBs, and organochlorine insecticides, on ecosystems and human health became a rising concern in the early 1990s. These compounds were discovered to be capable of causing endocrine system disruption and reproductive problems. POPs have been found to travel great distances and arrive in far-off places like the Tibetan Plateau, the Arctic, and the Antarctic, where they have never been made or used (Wang et al., 2019).

In response to these concerns, the international community established a convention that attempts to restrict and ultimately end the use of such substances. At the Global Diplomatic Conference on May 23, 2001, in Stockholm, Sweden, the Stockholm Convention on Persistent Organic Pollutants was approved. The Convention identified 12 POPs as substances that needed to be regulated and eradicated by all member countries ("Stockholm Convention on Persistent Organic Pollutants," 2008). These compounds are divided into three major groups including insecticides and fungicides (DDT and Hexachlorobenzene (HCB)), Polychlorinated Biphenyls (PCBs) and Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDFs).

1.2 Selected compounds

Due to the superior thermal resistance, flame retardancy, low vapor pressure, and high dielectric constant, polychlorinated biphenyls (PCBs) were initially used as additives in capacitor insulating oils and paints. PCBs are chlorinated aromatic compounds that are produced by chlorinating biphenyls at high temperatures under the influence of a catalyst. PCBs began to be created on a commercial scale in 1929, but as their biotoxicity was gradually identified, production of PCBs came to an end (Erickson and Kaley, 2011). Despite the fact that PCB production and use have been outlawed for a long time, PCBs that have been released into the environment are difficult to degrade and will continue to be a threat to people and ecosystems for a very long time (Jensen, 1972). Therefore, studying the variations and peculiarities of PCB residue distribution

in the environment is crucial.

The first of the current synthetic pesticides, DDT (dichloro-diphenyl-trichloroethane), was created in the 1940s. Malaria, typhus, and other human illnesses spread by insects were the first to be successfully treated with it in both military and civilian populations. Additionally, it worked well to control insects in houses, institutions, gardens, dwellings, and crop and livestock production. Due to DDT's widespread usage and early effectiveness as a pesticide in the US and other nations, many insect pest species have developed resistance to it (Stemmler and Lammel, 2009).

Organochlorine hexachlorobenzene has the chemical formula C_6Cl_6 . Historically, this fungicide has been used to guard seeds against the *Phytophthora infestans* fungus, particularly wheat seeds. The Stockholm Convention bans the use of this fungicide internationally on 22 May 2001 in Stockholm and effective from 17 May 2004 (Barber et al., 2005).

1.2.1 General Information

Physical and chemical properties

Figure 1-1 illustrates the structural formulas of the polychlorinated biphenyls (PCBs), a group of chlorinated aromatic hydrocarbons that are produced synthetically from persistent organic pollutants (POPs) known as biphenyls. There are theoretically 209 isomers of PCBs, and their chemical formula can be written as $C_{12}H_{(10-n)}Cl_n$ ($n=1-10$) depending on how many chlorine atoms are substituted on the benzene ring (Figure 1-1).

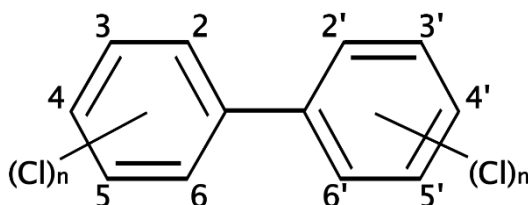


Figure 1-1 Chemical structural formula of PCBs (Grabowska, 2010).

While the melting and boiling points and the alcohol-water partition coefficients of PCBs are positively correlated with the number of substitutions of the chlorine atoms, the solubility in water, vapor pressure, and evaporation rate at room temperature are negatively correlated with the number of substitutions of the chlorine atoms. The half-

life of PCBs in human bodies or other animals is typically 7.7 years, and higher octanol-water partition coefficients of PCBs suggest that their solubility in the organic phase is larger and their bioaccumulation is more intensive. PCBs are rapidly adsorbed to particulate organic matter in aquatic systems and subsequently deposited in sediments as a result of their low water solubility and high K_{ow} (n-octanol-water partition coefficient) (Dueri et al., 2008).

PCB is a good flame retardant because it is semi-volatile or non-volatile at ambient temperature, has a very low vapor pressure (<1 Pa), and has a high boiling point (285–456°C). In contrast to octanol, which has a high water partition coefficient ($\log K_{ow} > 10^4$) and only a very limited solubility in water, PCBs are soluble in non-polar organic solvents as well as biological oils and fats (Beyer and Biziuk, 2009). In conclusion, PCBs have a high insulation and dielectric constant, low volatility, superior thermal insulation, and wettability, as well as other physico-chemical properties. In the printing, plastics processing, and electric power industries, PCBs have been widely used.

DDT, also known as Dichlorodiphenyltrichloroethane, is an organochlorine insecticide with the chemical formula $C_{14}H_9Cl_5$. The compound appears as a white crystalline solid or a yellowish powder and is tasteless and odorless. It has a melting point of 108.1 to 109.0 °C and a boiling point of 260 °C. DDT has a density of 1.55 g/cm³ at 25 °C and a vapor pressure of 2.53×10^{-8} kPa at 20 °C. It has limited solubility in water and high solubility in organic solvents such as benzene, cyclohexanone, and chloroform (Li and Wania, 2005).

DDT is chemically stable under normal conditions and does not decompose easily. It remains stable in acidic environments but promotes decomposition in strong bases or iron-containing solutions. At temperatures above its melting point, especially in the presence of a catalyst or light, p,p'-DDT undergoes dehydrochlorination to form Dichlorodiphenyl-Dichloroethylene (DDE) (Guenzi and Beard, 1976). Because of its properties, DDT has been used as an agricultural pesticide and as an intermediate in the production of trichloromethane and dicofol. However, it has become notorious for its environmental and health effects. DDT is highly insoluble in water and therefore difficult to degrade naturally. Its persistence in the environment has led to widespread contamination with serious consequences for ecosystems and human health. For Instance, studies have shown the majority of Canadian mothers' milk and blood contains polychlorinated biphenyls (PCBs) and other organochlorines (Davies and Mes, 1987; Mes et al., 1984). Therefore, there has been a strong effort to control and reduce

the use of DDT and other POPs to mitigate their adverse impacts on the environment and humans.

Hexachlorobenzene (HCB), also known as hexachlorobenzene, is a chlorinated aromatic compound with the molecular formula C_6Cl_6 and a molecular weight of 284.79. HCB exists as a pure, colorless, needle-like crystalline substance with a melting point of 227 °C and a boiling point range of 309 °C–310 °C at 725 mm Hg. In its industrial form, HCB appears as pale red crystals (Kumar et al., 2013). HCB has a very low solubility, approximately 6×10^{-8} , making it virtually insoluble in water. It is slightly soluble in ethanol but easily dissolves in organic solvents such as benzene, toluene, ether, and chloroform (Reed et al., 2007). Regarding its chemical properties, HCB is stable and resistant to acids. However, at high temperatures, it can undergo alkaline hydrolysis, leading to the formation of sodium pentachlorophenate. HCB is widely used as a selective fungicide and finds applications in seed dressing and soil treatment. It is particularly effective in preventing wheat bunt disease. Given its stability and selective properties, HCB serves as an efficient tool in agricultural practices.

Commercial products of PCBs

German scientists H. Schmidt and G. Schultz succeeded in creating polychlorinated biphenyls (PCBs) artificially in 1881. In the United States, PCB industrial production started in 1929. Commercial PCBs are combinations of several congeners, and from 1929 until 1977, the Monsanto Chemical Company in the United States was the leading PCB producer world wide. Aroclor 1221, 1232, 1242, 1254, and 1260 were some of their most popular commercial PCBs products. The number "12" stands for the 12 carbon atoms in the biphenyl ring, while the next two digits indicate the weight percentage of chlorine. Aroclor 1242, for instance, implies that the average chlorine content of the commercial PCBs product is 42% (with the exception of Aroclor 1016, which is a distilled version of Aroclor 1242 and has an average chlorine content of 41%) (Hutzinger, 1974). Other nations may refer to commercial PCB combinations by different names, such as Kanechlor (KC) in Japan, Clophen in Germany, Phenoehlor in France, Sovols in the Soviet Union etc. The chlorine level in industrial PCB products ranges from 20% to 70%, and there are 130 congeners with concentrations larger than 0.05% (Giesy and Kannan, 1998; Schulz et al., 1989). PCB production is an easy and economical procedure. In the industrial setting, it entails the hot-temperature

chlorination of benzene with metal catalysts. PCB manufacture has steadily risen throughout history, peaking in the middle of the 1960s with an annual output of over 100,000 tons. The amount of PCBs produced world wide is reportedly approximately 1.3×10^6 tons (Breivik et al., 2002). A large number of PCBs were also created in Germany, the United Kingdom, Japan, Spain, and Italy in addition to the 570,000 tons produced by the United States and 202,000 tons by France. PCB production in China began in 1965 and continued until 1974 with a production history of ten years and a cumulative output of nearly ten thousand tons (Xing et al., 2005).

Source

PCBs have a wide range of applications and are primarily used as insulating oils for transformers and capacitors, as heat transfer fluids and lubricants in various instruments and equipment. They are also used as additives in many industrial products such as resins, plastics, rubber, paints, binders, coatings, carbonless copy paper, enamels, fire retardants, pesticide extenders, dye dispersants, etc. They are utilized as heat transfer media in thermal conduction systems and as plasticizers in plastics. PCB production ceased around 1977 due to environmental pollution concerns, but the PCBs that were already produced have been extensively used in industries such as transformer and power capacitor manufacturing (Breivik et al., 2002).

As a result, there are many different environmental sources of PCB contamination. Currently, leaks from batteries and transformers being disassembled and emissions from industrial sites that discharge garbage containing PCBs are the primary causes of PCB contamination. About 50% of PCBs are used in capacitors, and about 25% are used in transformers. About 6% of PCBs are used in capacitor and lubrication fluids, less than 4% in carbonless copy paper, and about 9% of PCBs are used in plasticizers (Erickson and Kaley, 2011). An important factor in PCB contamination is improper management of PCB-containing goods, tools, disposal sites, and storage facilities. Leachate from landfills, industrial incineration of waste, municipal waste incineration, and atmospheric dry and wet deposition are further significant sources of PCB contamination (van Bavel et al., 1996).

DDT was extensively employed as an insecticide and acaricide in agricultural practices, leading to its wide distribution within soil and aquatic ecosystems through extensive spraying activities. Additionally, DDT found significant application in indoor

settings, where it was utilized in sprays and mosquito nets to combat malaria and other mosquito-borne diseases, contributing to environmental contamination. Furthermore, DDT was employed in the treatment of leather and preservation of wood, potentially resulting in the release of DDT into the environment during these industrial processes (Kumar et al., 2013). The following are HCB sources that need to be considered when creating an emission inventory: burning wastes and sewage sludge; smelting base metals (copper, lead, nickel, and zinc); smelting secondary lead and aluminum; sintering process; electric arc furnaces used in the steel industry; production of magnesium; cement; and chlorinated organic solvents or chlorinated monomers; and burning fossil fuels (Jacoff et al., 1986; Tobin, 1986).

1.2.2 Occurrence, Transport and degradation of PCBs

After commercial synthesis and unintentional emissions, PCBs are transported over long distances through the atmosphere and water bodies, leading to their widespread presence in the global environment. PCBs can even be detected in remote regions such as the Arctic and Antarctic. Various environmental media play important roles in the transport process of PCBs (Fu and Wu, 2006; Malanichev et al., 2004). The cyclical process of PCBs can be summarized as shown in the diagram see Figure 1-2.

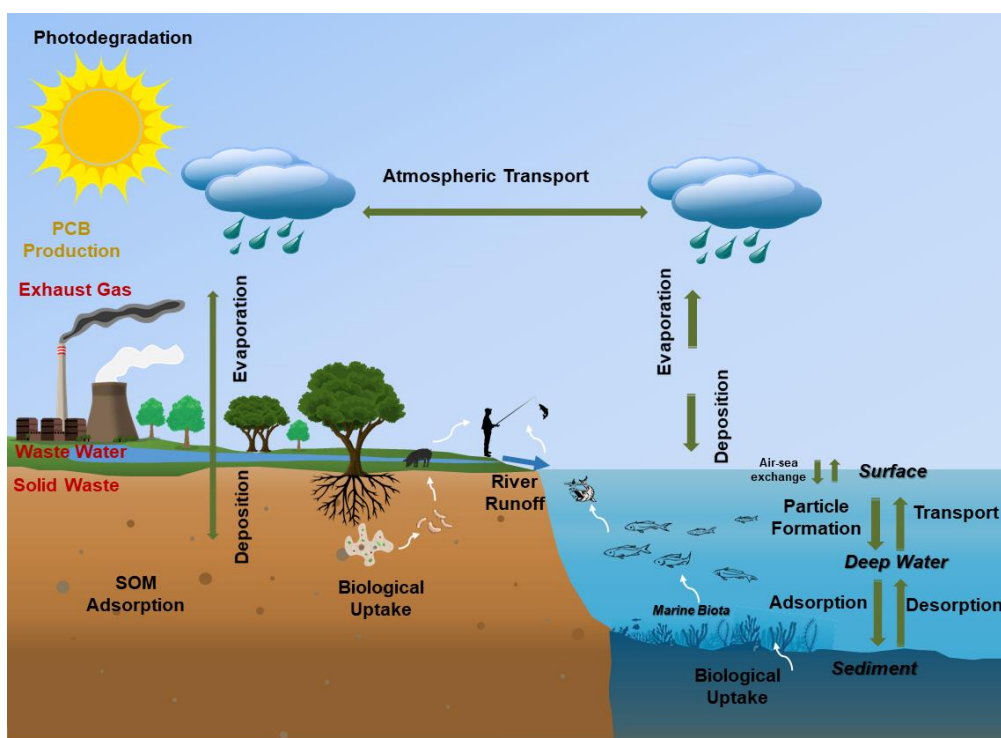


Figure 1-2 Cycling of PCBs in the environment. (data from reference Connolly et al., 2000; Guan et al., 2009; King et al., 2004; Konat, 2001; Montone et al., 2003).

PCBs produced by human activity are released into the environment through a variety of sources, including wastewater, solid waste, and exhaust fumes (Ikonomou et al., 2002; McKay, 2002; Nollet et al., 2003). They are subsequently dispersed globally by air transport and surface runoff. Within different systems, such as the atmosphere, terrestrial environments, water bodies, the biosphere, and sediments (Connolly et al., 2000; Guan et al., 2009; King et al., 2004; Konat, 2001; Montone et al., 2003). PCBs undergo alternations and follow different cycles. However, their ultimate fate is often the seabed sediment, where PCBs exhibit greater stability (Froescheis et al., 2000; Jönsson et al., 2003). Under the extreme conditions of the seabed, PCBs become more stable and are slowly degraded by microorganisms after being buried with particulate matter.

PCBs in Atmosphere

The atmosphere plays a significant role in the transport of PCBs. PCBs enter the atmosphere through waste gases and evaporation and become adsorbed onto particles such as dust, participating in atmospheric circulation. Through processes such as evaporation, deposition, and natural diffusion, PCBs are transported away from their source areas, and they can now be detected even in the Antarctic region (Harner et al., 1995; Kumar et al., 2001). While serving as a transport medium, the atmosphere also contributes to the elimination of PCBs (Anderson and Hites, 1996; Wania and Daly, 2002). Most of the low-chlorinated PCB congeners adsorbed on particles are eliminated through reactions with atmospheric hydroxyl radicals, while the highly chlorinated congeners mainly settle into water bodies along with the particles. The degradation rate of congeners in the atmosphere directly influences their dispersion distance. Although low-chlorinated congeners have higher vapor pressures and are more easily transported through the atmosphere, they are prone to degradation. In the same time frame, highly chlorinated congeners experience shorter distances from source areas to settling regions (Gouin and Wania, 2007).

In the global cycling process, due to differences in vapor pressure, highly chlorinated congeners preferentially deposit due to decreasing temperatures with increasing latitude (Beyer and Biziuk, 2009; Meijer et al., 2003). Most highly chlorinated PCBs accumulate in ice and snow layers or enter the oceans through particle deposition. Only a fraction of low-chlorinated congeners with higher vapor pressures can reach the Polar

Regions. Earlier studies suggested that PCBs released from adsorbed matrices like soil maintain PCB concentrations in the atmosphere (Swackhamer and Armstrong, 1986). However, recent research indicates that PCBs in the atmosphere primarily originate from anthropogenic pollution sources (Gioia et al., 2006; Robson and Harrad, 2004), and in some regions like North America, the atmospheric PCB concentrations show a correlation with local population density (Hafner and Hites, 2003).

PCBs in Terrestrial Environments

Land serves as an important storage medium for PCBs, and the majority of released PCBs become adsorbed onto soil organic matter (SOM) (Ockenden et al., 2003). They can migrate to deeper layers through rainfall erosion or be transported long distances through surface runoff (Ayris and Harrad, 1999). Factors such as temperature, humidity, and congener properties influence the behavior of PCBs in soil, and SOM plays a role in delaying the global cycling of PCBs to some extent. As early as 50 years ago, it was reported that PCBs in soil could evaporate into the air at room temperature, and evaporation is the main pathway for PCB loss in soil (Haque et al., 1974). Migration from the subsurface to the surface is a major factor affecting the rate of PCB evaporation in soil (Meijer et al., 2003).

PCBs in Water

PCBs transported through surface runoff and atmospheric deposition enter water bodies, and therefore, PCBs in the surface waters of the oceans primarily originate from environmental cycling (Moret et al., 2005; Schulz et al., 1988). Water is a determining factor for biological survival, so the toxicity of PCBs is most pronounced in aquatic environments. There exists a dynamic equilibrium of PCBs between the surface ocean and the lower atmosphere, facilitated by particle settling and natural evaporation (Wania et al., 1998). This equilibrium follows Henry's law according to research, but the temperature dependence of Henry's law limits its application in practical environments (Phillips et al., 2008). Most of the PCBs entering water bodies become adsorbed onto particulate organic carbon (POC) (Schulz-Bull et al., 1995; Smith and McLachlan, 2006; Teil et al., 1998), and the higher the Kow value of the congeners, the tighter the adsorption. PCBs in water rapidly settle with the particles to the sediment-water interface, leading to their rapid elimination from the water, with only a small

amount remaining in dissolved form. PCBs adsorbed onto POC can be absorbed by organisms through predation, while dissolved PCBs are not bioavailable and mainly accumulate in organisms through respiration and skin absorption (Baker et al., 1991; Beyer and Biziuk, 2009). PCBs that enter organisms accumulate in their fatty tissues and can be further transferred through the food chain, resulting in higher PCB concentrations in organisms at the top of the food chain compared to their environmental background levels (Bernard et al., 2002; Maervoet et al., 2004).

PCBs in the Biosphere

PCBs are influenced by biological processes throughout the entire cycling process and can be stored in living organisms. Organisms at the bottom of the food chain absorb PCBs from the environment, and through the food chain, PCBs can ultimately accumulate in the adipose tissues of humans (liver, kidneys, etc.) (Takesumi and Yoshimura, 2003; Willman et al., 1997). Biological degradation of PCBs is limited, and a portion of PCBs entering organisms is excreted through feces, while the majority re-enters the environment upon the death of the organism. Due to the PCBs could travel to the seafloor, the levels of PCBs in deep-sea organisms are much higher than those in surface-dwelling organisms (Froescheis et al., 2000; Storelli et al., 2004).

Under certain conditions, microorganisms can degrade PCBs to obtain energy, and the degradation rate is influenced by factors such as congener properties, number and position of chlorine substitutions, nutrient content, and the natural environment (Wiegel and Wu, 2000). Highly chlorinated congeners in sediments can be transformed into lower chlorinated congeners through anaerobic degradation, and then further converted into CO₂, Cl₂ and water through a series of reactions during aerobic degradation (Boyle et al., 1992). PCBs have very low water solubility, and the low temperature and low concentrations of PCBs in sediments are not conducive to the growth of PCB-degrading bacteria, resulting in very slow natural degradation of PCBs in the environment (Field and Sierra-Alvarez, 2008).

Anaerobic degradation of PCBs was first discovered in 1987, and subsequent experiments confirmed the presence of anaerobic degradation (Brown et al., 1987; Quensen et al., 1988). In natural environments, certain anaerobic bacteria can utilize PCBs as electron acceptors replacing chlorine with hydrogen (Morris et al., 1992; Nies and Vogel, 1990).

Different bacterial strains produce different enzymes that can selectively degrade chlorine at different substitution positions, leading to different degradation pathways and rates (Chen et al., 1999). In general, higher degrees of chlorination result in slower degradation rates. In natural environments, para- and meta-chlorines are more easily eliminated, while only a small portion of anaerobic bacteria can eliminate orthochlorines. The anaerobic degradation of PCBs is favored at pH 6.0-7.5 and temperatures of 18-30°C (Nies and Vogel, 1990; Quensen et al., 1988; Wiegel and Wu, 2000). Low-chlorinated PCB congeners can be eliminated through aerobic degradation, which generally involves two steps (Pieper et al., 2005) Only a few bacteria are capable of producing biphenyl 3,4-dioxygenases to degrade PCB congeners with adjacent chlorine substitutions (Bopp, 1986).

PCBs in Sediment

Adsorbed PCBs in water bodies can travel to the bottom layers in the form of marine snow, with the majority being buried in sediment. Sediment serves as the ultimate sink for PCBs (Froescheis et al., 2000; Jönsson et al., 2003). It is estimated that low-chlorinated congeners account for approximately 10% of the PCBs released into the environment stored in continental shelf sediments, while high-chlorinated congeners account for 80% of the PCBs, representing about 10-70% of the total PCB production. PCBs in sediment primarily adsorb onto organic carbon and minerals(Chen et al., 1999). Due to low temperatures, lack of oxygen, and other unique environmental conditions in sediments, PCBs are difficult to degrade, resulting in long half-lives (Sinkkonen and Paasivirta, 2000). A significant portion of PCBs slowly undergoes elimination by migrating into deep-sea sediments. Human or natural disturbances can oxygenate sediments, accelerate the oxidation of sulfur, and change the pH and reduction environment of sediments, leading to intensified microbial activity and accelerated degradation or release of PCBs (Eggleton and Thomas, 2004).

Environmental Persistence and Long-term Residue

As typical persistent organic pollutants (POPs), PCBs exhibit high chemical stability in their structure and properties, making them highly resistant to natural degradation, photolysis, and chemical decomposition under normal environmental conditions. The degradation and persistence of PCBs in the environment vary with their degree of

chlorination, with lower chlorinated PCBs being more susceptible to microbial degradation, while higher chlorinated PCBs degrade more slowly. Highly chlorinated PCBs have extremely low water solubility and tend to adsorb onto suspended particles and sediments, making them resistant to biodegradation (Wania and Mackay, 1996). PCBs also exhibit high heat resistance, requiring temperatures of 1000-1400°C for complete decomposition. Incineration at temperatures above 1200°C with sufficient oxygen for a residence time of 2 seconds can effectively degrade PCBs (Johnston, 1985). Although the use of PCBs has been banned for many years, their long half-life and resistance to degradation allow them to persist in the environment for extended periods.

Bioaccumulation

PCBs are characterized by low water solubility and high lipid solubility, allowing them to accumulate in fatty tissues. They exhibit strong bioaccumulation, reaching toxic concentrations through biomagnification in the food chain. The concentration of PCBs in fish muscle tissue can be over 7,000 times higher than in the surrounding water, while in water birds, the concentration can be 50-100 million times higher than in the water (Safe and Stephen, 1993). As humans occupy the highest trophic level in the food chain, the biomagnification of PCBs along the food chain can lead to human exposure to the highest concentrations of PCBs and subsequent toxicity (McFarland and Clarke, 1989).

Semi-volatility

PCBs possess semi-volatility, allowing them to evaporate from pollution sources into the atmosphere and adsorb onto atmospheric particles. They can undergo long-range transport through air currents and eventually deposit onto the Earth's surface. This cycle repeats continuously. This characteristic of PCBs leads to their widespread presence and detection of PCB residues in various regions globally, including terrestrial areas, deserts, oceans, and the Arctic and Antarctic regions. Residual PCB concentrations of up to 112,900 µg/g (wet weight) have been detected in the tissues of Arctic mammals (Scippo et al., 2008).

1.2.3 Occurrence, Transport and degradation of DDT and HCB

DDT and HCB generally have a high n-octanol-water partition coefficient (K_{ow}) and are therefore mostly partitioned into sediment organic matter. The high organic carbon (or organic matter) adsorption coefficients of chlorinated organic compounds indicate that these compounds are highly susceptible to sediment adsorption. Even though their concentration in water is low, their concentration in sediments is high. Therefore, it can be assumed that most of the chlorinated organic pollutants enter the water body, are adsorbed by the particulate matter of the water body, sink to the bottom of the water body, and become an important constituent of the organic pollutants in the adsorbed state of the sediments (Barber et al., 2005; Berrojalbiz et al., 2014). Organochlorine pesticides mainly enter the marine environment through soil erosion, land runoff, pollution emissions, atmospheric deposition, and other pathways. Organochlorine pesticides adsorbed on suspended particles are finally deposited in sediments, which are therefore considered to be the main fate of organochlorine pesticides in the marine environment (Zacharia, 2019).

1.2.4 Global occurrence of PCBs, DDT&HCB in marine sediment

Numerous studies have indicated that the presence of polychlorinated biphenyls (PCBs) in coastal or nearshore marine sediments primarily originates from both point sources and/or non-point sources on land. Research conducted under the United States National Biomonitoring Specimen Bank (NBSP) program revealed that coastal sediments in highly populated areas, such as San Francisco Bay, Santa Monica Bay, San Pedro Bay, San Diego Bay, and Elliott Bay, exhibited the highest PCB concentrations. Conversely, PCB concentrations in moderately populated regions, like Monterey Bay, San Pablo Bay, and Commencement Bay, were comparatively lower (Brown et al., 1987). In the vicinity of Alexandria Port, Egypt, significantly elevated PCB levels (1210 ng/g) were observed in sediments within the port compared to the outer areas (0.9-2.8 ng/g) (Barakat et al., 2002). The levels of PCBs in Canadian Saglek Bay sediments ranged from 0.24 ng/g to 62,000 ng/g, and their concentrations exhibited an exponential decline with increasing distance from PCB-contaminated beaches (Kuzyk et al., 2005). Furthermore, investigations in coastal sediments of South Korea and Singapore revealed PCB concentrations ranging from 0.088 to 199 ng/g and 1.4 to 329.6 ng/g,

respectively, with sediments near ports and industrial areas displaying higher levels than other regions (Hong et al., 1995). Currently, regions with elevated PCB levels in coastal sediments in China include Jiaozhou Bay, Qingdao adjacent waters (0.65-32.9 ng/g) (Yang et al., 2003), Daya Bay (0.85-27.4 ng/g) (Zhou et al., 2001), and the Pearl River Delta (6.0-290 ng/g) (Fung et al., 2005), all exceeding the sediment quality standard of 22.7 ng/g from the Effects Range Low (ERL) value published by Long et al. (1995).

The distribution and migration of PCBs in sediment are influenced by multiple factors, such as organic carbon content, particle size, sedimentary environment, and interstitial water. Among these, the organic carbon content and particle size in sediments have the most substantial impact on PCB adsorption. Organic compounds with hydrophobic properties, including PCBs, are generally adsorbed by organic substances on the external or internal surfaces of particles (Pignatello, 1998; Xing, 1997), and smaller particle size with larger surface area favors adsorption. Significant correlations between PCBs and organic carbon in marine sediments have been reported in some studies (Lee et al., 2001; Pierard et al., 1996). However, researchers investigating sediments in Saglek Bay found weak or even negative correlations between PCBs and organic carbon, suggesting that various complex factors, such as input mechanisms of PCBs (Kuzyk et al., 2005). Similarly, the relationship between PCBs, organic carbon, and particle size in Yangtze River estuary tidal flats did not exhibit a clear correlation, possibly due to the complexity of pollution sources in the study area (Yang, 2000). The use of PCBs was banned in the mid-'80s, resulting in a decreasing trend, followed by a steady state in the 90's (Sobek et al., 2015). Vanavermaete's study shows a decreasing trend or steady state for most PCBs (CB28, CB52, CB101, CB118, CB180) from 2007 to 2021, but not for CB138 and CB153 (Vanavermaete et al., 2023).

Ecological risk assessment suggested that sediment samples in Bushehr Province's Marine protected areas can be categorized as medium risk. The mean concentration of $\Sigma 18\text{PCB}$ was 0.345-0.419 ng/g d.w., and the main components correspond to PCB77, PCB105, PCB81, PCB101, and PCB114 (Ghaemi et al., 2023). Thus, the correlation between PCB concentrations and sediment physicochemical parameters in marine sediments exhibits intricate regional variations.

Research on organochlorine pesticides in various coastal regions indicates that DDT concentrations in Mediterranean coastal sediments range from 1 to 657 ng/g (Tolosa et

al., 1995). In the Black Sea, DDT levels were reported in sediments varying from 0.01 to 13.4 ng/g (de Mora et al., 2004). An investigation on the pollution status and spatial distribution of DDTs was conducted in the sediments of the East China Sea. Residual DDTs ranged from <0.06 to 6.04 ng/g and were the main pollutant of organochlorine pesticides (Yang et al., 2005). Furthermore, there was a positive correlation between DDT concentrations and the total organic carbon (TOC) content in the sediments. The vertical distribution of residues including organochlorines indicated a possible connection to past consumption trends (Kaiser et al., 2018). In this study, $\Sigma 4$ DDT; 0 - 0.82 ng/g and $\Sigma 24$ PCB; 0 - 0.12 ng/g are below established sediment quality guidelines and suggesting no environmental risk

1.3 Study area

1.3.1 General information

The Baltic Sea, located between Northern and Eastern Europe, is one of the world's largest marginal seas. It is surrounded by nine countries and connected to the North Sea through the Danish Straits, serving as an important maritime gateway. The Baltic Sea covers an area of approximately 410,000 square kilometers, with an average depth of about 55 meters and a maximum depth of approximately 459 meters. The average salinity of the Baltic Sea ranges from 2-25, which is relatively low compared to open ocean waters (Kautsky and Kautsky, 2000; <https://www.io-warnemuende.de/bio-ag-molbio-microbes-in-the-salinity-gradient-en.html>).

The unique environment of the Baltic Sea arises from its semi-enclosed nature, limited water exchange with the open ocean due to its encirclement by land, and the mixing of freshwater from rivers and saltwater from the North Sea. The inflow of freshwater from surrounding rivers results in lower salinity in surface waters. Conversely, the North Sea water, which is saline, enters the Baltic Sea through the Danish Straits, leading to a mixing of fresh and saltwater. Consequently, the salinity varies across different regions and depths, forming vertical and horizontal salinity gradients (Björck, 1995; Reusch et al., 2018).

The Baltic Sea experiences significant environmental challenges, including water pollution and eutrophication. Human activities, such as industrial and agricultural discharges, contribute to the influx of organic pollutants and excess nutrients, leading

to eutrophication. Excessive nutrients fuel algal blooms, deplete oxygen levels, and disrupt the marine ecosystem's balance, resulting in dead zones and negatively impacting marine life (Ojaveer et al., 2010; Wulff et al., 1990). Furthermore, the Baltic Sea's importance as a major international shipping route exposes it to environmental issues associated with maritime traffic, such as oil pollution and ecological hazards resulting from ship collisions (Lavrova et al., 2014; Rheinheimer, 1998).

Given its ecological significance and the threats it faces, continuous research and conservation efforts are imperative to safeguard the Baltic Sea's marine ecosystem, preserve biodiversity, ensure sustainable resource utilization, and protect human well-being.

1.3.2 Previous studies of PCBs, DDT & HCB

Sum of 28 individual PCBs were investigated in 9 sediment cores from the southern Baltic Sea. 2 samples were collected from Arkona Basin, 1 from Bornholm Basin and the others inland waters, including Oderhaff, Achterwasser and Greifswalder Bodden. Vertical profiles of CBs with ^{210}Pb -dating indicated target compound first occurring between 22 and 94.9 yr ago (Blanz et al., 1999). Sediment cores sampled in 1987 in the Bornholm Deep illustrated the increase in PCB concentration towards the top despite the ban on the use of PCB (Nylund et al., 1992). This may be explained by the fact that the disappearance of benthic macrofauna from the deeper sedimentary bottoms during the 1960s and 1970s caused the area of stratified sediments in the Baltic Sea sediments to more than triple (Jonsson et al., 1990). This change in the environment also affected the sediments' ability to sequester contaminants. The results from another study indicated a homogeneous composition of the investigated laminated sediment with respect to the parameters describing the basic sediment characteristics, i.e. density, carbon-, nitrogen- and lipid contents. When associated with ^{210}Pb activity for sediment dating, PCB in laminated sediment which were sampled from north Baltic Sea peaks corresponded roughly to 15 to 30 years (Broman et al., 1994). In the sediment cores in 1993-1994 from western Baltic Sea, PCBs showed homogeneous distribution down to a depth of about 20 cm (Dannenberger and Lerz, 1996). A large-scale investigation of PCB in sediment cores dating with ^{210}Pb and ^{137}Cs and X-ray from the whole Baltic Sea in summer in 1993 had been documented by Jonsson (2000). The result shows that known dating methods are effective in laminated sediments. The dating method has

shown good results in Gdansk Bay, Gotland Basin, Baltic Proper, Gulf of Finland, Bothnian Sea and Bothnian Bay (Jonsson 2000). The investigations by Jonsson (2000) and Olsson et al. (2000), which demonstrated the burial rates of sum PCBs up until the 1990s and the significance of sediment resuspension as well as the unsuitability of using carbon normalized data for the interpretation of temporal patterns, were conducted based on the same sediment core data. Total 33 PCBs concentration in Arkona Basin decreased from 5.7 ng/g d.w. (0-5 cm) to 0.90 ng/g d.w. (40-52.5 cm) (Ricking et al., 2005). Age model and inventories were studied using the sediment cores samples obtained between 2009 and 2013 in main and south Baltic Area ((Moros et al., 2017)). Consistent patterns of pollution are revealed by dating and analyzing sediment cores from several Baltic Sea basins for PCB congeners and organochlorine herbicides. Anthropogenic contaminants reached their peak in the 1960s and 1970s, and the last 30 years have shown falling patterns, a sign of successful regulation. Sediment cores were collected from depositional areas on the sea floor within seven coastal areas in the northern part of the Baltic Sea (Gulf of Bothnia) and five in offshore areas from the shore. Temporal trends of PCBs and environmental half-life for PCBs were discussed. The half-lives of PCBs in offshore sediments in the Baltic Sea are typically longer compared to coastal areas. It was suggested that the effects of emission reductions in urbanized coastal areas occur in the open sea over a period of about ten years (Sobek et al., 2015).

DDT is a kind of water-insoluble but fat-soluble chemical which had been used as pesticides since 1939. In the 1950s-60s, DDT caused environment problem and was present in the sediment. DDT would decompose in marine environment into DDD and DDE. Therefore to study DDT pollution in marine environment, DDT and its metabolites should be detected (Dannenberger, 1996). In Baltic area, DDT and its metabolites were always studied with other organic compounds including PCBs. In the autumn of 1991, DDXs were detected in surface sediment from northern Baltic Sea. The ranges of individual DDTs were 0-0.78 ng/g d.w. and 0-2.3 ng/g d.w. in Bothnian Bay and Bothnian Sea, respectively. Total concentrations were respectively 1.9 ng/g d.w. (Bothnian Bay) and 6.9 ng/g d.w. (Bothnian Sea) (Strandberg et al., 2000). In Gulf of Gdansk, 15 ng/g d.w. DDTs were measured in 1992 (Falandysz and Strandberg, 2004) and 0-4.39 ng/g d.w. during 1996-2005 (Sapota, 2006). The DDTs concentration was 0-0.98 ng/g d.w. in Bornholm Basin in the same study in 1996-2005. 2.6-11.36 ng/g d.w. and 9.6 ng/g d.w. DDTs occurred in Arkona Basin during 1993 and 1995-1997

(Dannenberger, 1996; Ricking et al., 2005). An investigation covering the area from Gulf of Finland to Kattegat was conducted in 2001-2002. The result showed that DDTs concentration decrease from north to south in the Baltic area (Pikkarainen, 2007). The result was verified by Swedish report for the period from 2003 to 2014 (Apler and Josefsson, 2016). The report also revealed a slight temporal trend with increasing concentrations between 2003 and 2008 and decreasing concentration after 2008.

1.4 Motivation and Aims

The Baltic Sea is a unique and fragile ecosystem, renowned for its paramount ecological significance. This region boasts an abundant and diverse marine life, serving as a crucial source of livelihood for the surrounding communities (Kautsky and Kautsky, 2000). However, this delicate ecosystem faces an imminent threat that has garnered increasing attention in recent years – the presence of stable organic pollutants (Moros et al., 2017). Notably, persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs) and organochlorine pesticides such as DDT and their environmental metabolites, pose a substantial risk to the delicate balance of the Baltic Sea, potentially leading to long-term ecological damage (Olsson et al., 2000). Now, more than ever, there is an urgent need to comprehend and alleviate this risk.

PCBs, widely used in various industrial applications, and DDT, a highly effective pesticide, were banned from use decades ago (Nylund et al., 1992). Nevertheless, these toxic and harmful organic pollutants continue to haunt the Baltic Sea (Jonsson et al., 2000). They persist in the environment for extended periods, presenting potential risks to aquatic life and human health.

The motivation behind my research is driven by environmental concerns, scientific curiosity, and the imperative to formulate informed policies. In pursuit of revealing the distribution, transformation, and potential threats of stable organic pollutants in the Baltic Sea sediments, I have formulated three hypotheses for my research:

Hypothesis 1: Sediments serve as primary sinks for stable organic pollutants in the Baltic Sea. The sediments act as repositories for a multitude of contaminants, including PCBs, which accumulate over time, significantly impacting the environmental equilibrium. This hypothesis will be investigated by analyzing PCB concentrations in sediments, estimating the total load, and comparing them with PCB

levels in other Baltic Sea water column and suspended particulate matter.

Hypothesis 2: Temporal changes in pollutant quantities, particularly PCBs, can be demonstrated through sediment profiles from the Baltic Sea. Comprehensive analyses of multiple sediment core samples will reveal concentration variations with depth, indicating a distinct trend over time. These findings underscore the significance of sediment profiles as temporal witnesses of changes in pollutant concentration. This is invaluable for tracing the historical and ongoing effects of stable organic pollutants in the Baltic Sea.

Hypothesis 3: Regional differences in PCB levels within surface sediments are indicative of localized areas with elevated contaminant loading. Diverse environmental and anthropogenic factors contribute to unique regional patterns of PCB contamination. The examination of surface sediment concentrations across the entire Baltic Sea will highlight regional clusters of PCB contamination. Understanding these regional variations enables the identification of areas where contaminant loading is most concentrated, facilitating targeted mitigation strategies.

The results of my investigations regarding Hypothesis 1 to Hypothesis 3 will help to estimate the environmental risk posed by stable organic pollutants, specifically PCBs, in the Baltic Sea. Equipped with a comprehensive understanding of PCB distribution, temporal changes, and regional variations, the aspiration is to assess the overall risk to this precious ecosystem. This estimation will serve as a foundation for developing informed policies and actions to safeguard the Baltic Sea's environmental integrity.

In summary, the overall objective is to gain a comprehensive understanding of the complex interactions between stable organic pollutants and Baltic Sea sediments. The aim is to elucidate the key role of sediments as primary sinks for these pollutants, to track temporal trends, to identify regional hotspots of contamination and ultimately to assess the environmental risk. Through this research, I aim contributing to the conservation and sustainable management of the Baltic Sea to ensure its continued vitality and ecological well-being for generations to come.

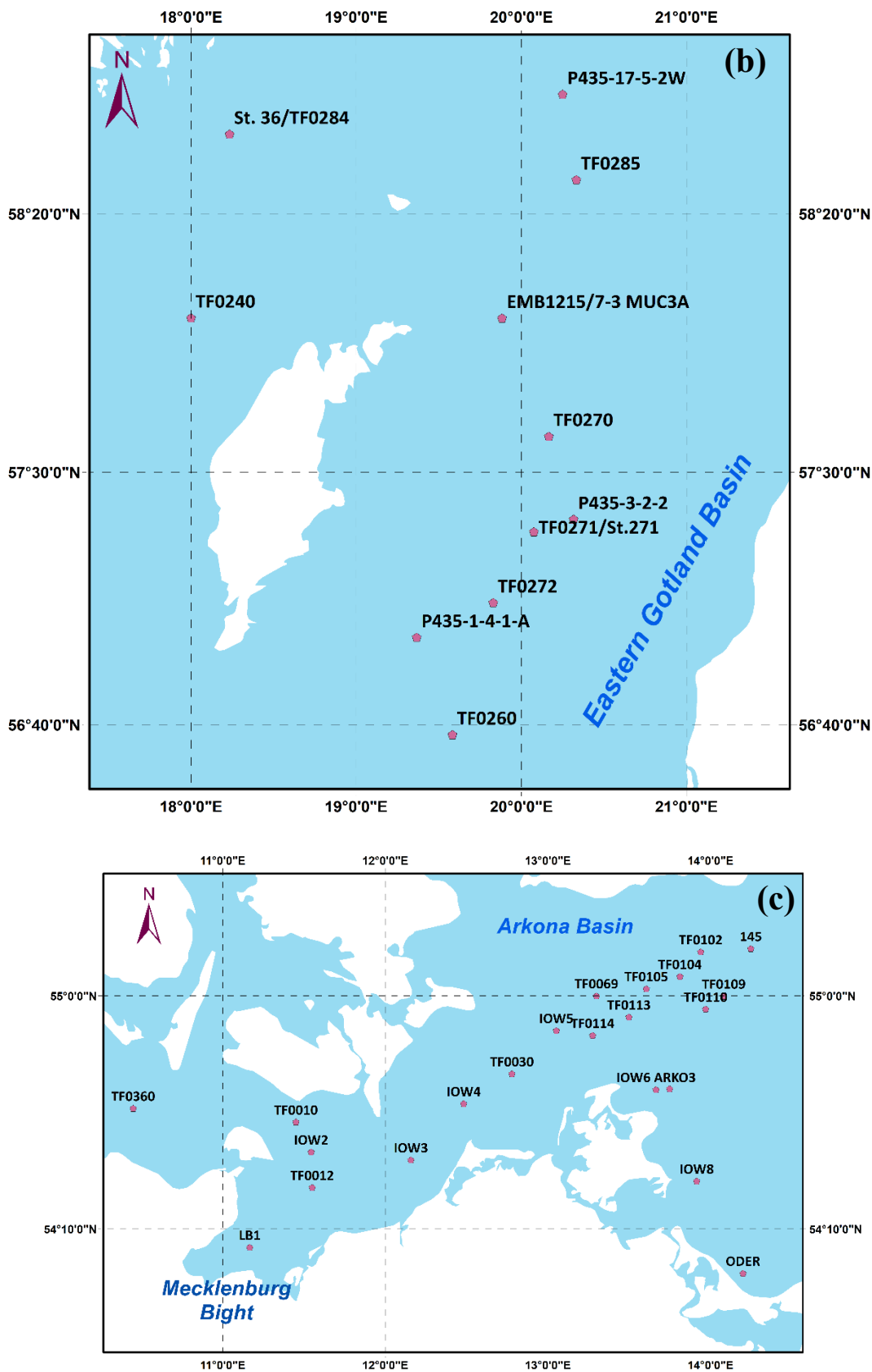


Figure 2-1 Surface sediment sampling stations: (a) whole Baltic, (b) Gotland Basin, (c) Arkona Basin and Mecklenburg Bight.

2.1.2 Sediment cores

Sediment samples were collected between 2012 and 2020 from several regions of the Baltic Sea. Detailed sample information is presented in Table 2-1 and Figure 2-2. Sediment cores were collected with a short gravity coring device (MUC – Multi Corer). Cores were divided into slices (usually in 1 cm or 0.5 cm) from top to the bottom. PCB contents and organic/inorganic carbon contents were analysed in each sample (Blanz et al., 1999).

Table 2-1 Information of sediment core sampling stations.

Station	ID	Position	Cruise No	Year	Area	Core Length (cm)
TF0271	GD Gotland Deep	57°18.3'N, 20°4.6'E	Annox 2017	Nov. 2017	Eastern Gotland Basin	0-10
P435-3-2-2	GB-1 Gotland Basin-1	57°20.751'N, 20°19.203'E	Geokern 2012-13	Jun. 2012	Eastern Gotland Basin	0-27
P435-1-4-1-A	GB-2 Gotland Basin-2	56°57.397'N, 19°22.244'E	Geokern 2012-13	Jun. 2012	Eastern Gotland Basin	0-19
P435-17-5-2W	NCB Northern Central Basin	58°42.745'N, 20°14.667'E	Geokern 2012-13	Jun. 2012	Northern Gotland Basin	1-36
EMB046/2 0-2	SK Skagerrak	58°31.6'N, 9°29'E	OP-2016- 02 NAR	May. 2013	Kattegat	0-31
SP15	SP Gulf of Gdansk	54° 49.09'N, 19° 17.13'E	EMB242	Jul. 2020	Gulf of Gdansk	0-34
EMB05816	AB Arkona Basin	54°47.52'N, 13°15.13'E	SECOS 2015	2013	Arkona Basin	0-30
EMB262_1 2-2	GF Gulf of Finland	59°34.44' N, 23°36.46' E	EMB262	Jul.20 22	Gulf of Finland	0-31

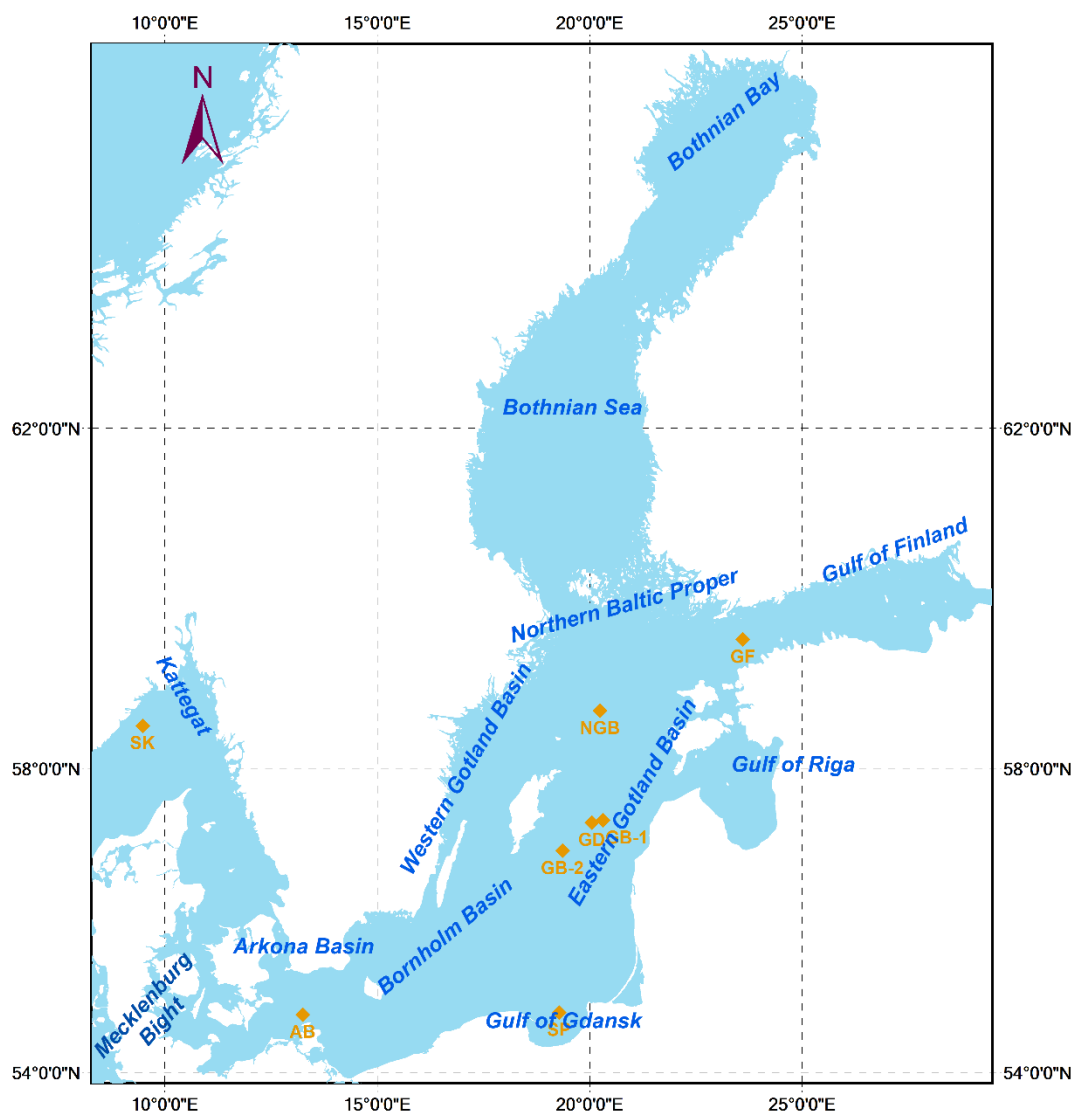


Figure 2-2 Sediment core sampling stations.

2.2 Sampling processing

Sediment samples were taken using a Multi Corer (MUC) respectively Frahm Corer (FC). For surface sediment samples the upper two centimeters of the core were taken. Sediment cores were cut into different layers using a punch and rings of particular height. For sediment surface samples a box corer was used, too. Therefore the protruding water was removed and the upper two centimeters were taken. The sediment samples were stored in clean aluminium foil or glass containers and kept at -20°C until further analysis at the IOW laboratory.

2.3 Pretreatment

Sediment samples were frozen dried and grounded. 1-10 g sediment samples with 225 μ L internal standard were added into the extraction cell and extracted with ASE350. For desulphurization, 2 prepared copper spirals were added to the ASE (Accelerated Solvent Extraction) extracts in the vials. The vials were shaken for two hours, if necessary copper spirals were replaced after one hour in case of black discoloration. The sample extracts were filtered by a glass column with Teflon frit in BÜCHI. ASE vials and copper spirals were rinsed twice with 2 mL hexane. Using a BÜCHI SYNCORE, sample extracts were concentrated to around 0.5 mL, and then transferred to a centrifuge tube and using a rotary evaporator concentrated to 500 μ L for next step. Two 6 mL glass columns with Teflon frit were connected by a Teflon adapter and stainlesssteel taps into a Teflon frame. The upper column was filled with 3 g deactivated aluminium oxide. 3 g deactivated silica gel was added into the lower column. The filled columns were cleaned and conditioned with 10 mL Dichloromethane (DCM) and 10 mL Hexane. Hereby, dry running should be avoided. The eluate was concentrated to 200 μ L with a rotary evaporator. The eluate was purified by HPLC L2130, concentrated to less than 50 μ L by rotary evaporator. The concentrated eluate was made up to final volume with hexane and stored in the freezer at -20°C until measurement on GC-MS/MS. Blanks were processed the same way as the samples in order to monitor any contamination problems. All glassware was cleaned in Edisonit, rinsed with distilled water and dried at 250°C .

2.4 Analysis

To analyse Polychlorinated Biphenyl concentrations an aliquot of 2 μ L of a sample extract was injected in a GC-MS/MS (Gas Chromatography–Mass Spectrometry/ Mass Spectrometry) system (7890B GC/TQ7010 equipped with a liquid autosampler 7650 A, Fa. Agilent, Waldbronn, Germany). The MultiMode Inlet (MMI) was programmed by an increasing temperature from 65°C to 250°C . For chromatography a DB-5 fused silica gel column (325°C : 60 m x 250 μ m x 0.25 μ m, Agilent) and helium (1.5 mL/min) were used. The GC oven temperature for PCB analysis was programmed as follows: initial temperature of 60°C with initial time of 1 min, first ramp with $40^{\circ}\text{C}/\text{min}$ to 120°C , second ramp with $4^{\circ}\text{C}/\text{min}$ to 300°C and held for 10 min. The transfer line temperature

was set to 280°C. A triple quad MS (mass selective detector, TQ7010) was used for the quantification of all compounds by mass spectrometry. For a higher sensitivity the triple quad MS operated in the MRM (Multiple-Reaction-Monitoring) acquisition mode, three ion masses (precursor and 2 product ions) for each compound were monitored. To quantify the concentrations the precursor mass was used, while the mass of qualifier 1 and 2 (product ion masses) and the retention time were used for quality purposes.

To control quality and sensitivity of the GC-MS/MS system a calibration over multiple calibration points were performed periodically. For PCBs following calibration levels were used: 0; 0.25; 0.5; 1; 5; 10; 15; 20; 25; 30; 35 and 40 pg/μL. Reference material IAEA-459 (IAEA, Austria) and standard recoveries using the external standard PCB-Mix 3/Pesticide-Mixture 14 added to a blank extraction procedure were calculated for all target compounds for quality control and assurance of the extraction method. Quality was also controlled by continuous participation in QUASIMEME inter-laboratory tests. All work was carried out under accredited conditions.

2.5 Typical PCB and PCB product indicator selection

The detected congeners of Polychlorinated Biphenyls are listed in Table 2-2. The categorization method for identifying PCB markers is based on the result from Schulz et al. (1989). In that study, weight percentage contributions of Clophens A30, A40, A50 and A60 were described. According to the result, A30 and A40 mainly consisted of low chlorinated PCB congeners. Therefore A30 and A40 were considered together in this study.

Table 2-2 information of Target Compounds.

(The marker compounds for technical mixture are given on the last column.)

	Mass	Log k_{ow}	Cl amount	Clophen
PCB 28/31	257.543	5.67	3	A30/A40
PCB 52	291.988	5.84	4	A30/A40
PCB49	291.988	5.85	4	A30/A40
PCB44	291.988	5.75	4	A30/A40
PCB95	326.433	6.13	5	

PCB 101	326.433	6.38	5	
PCB 99	326.433	6.39	5	A50
PCB 110	326.433	6.48	5	A50
PCB 77	291.988	6.36	4	
PCB 151	360.878	6.64	6	
PCB 149	360.878	6.67	6	A60
PCB 118	326.433	6.74	5	A50
PCB 146	360.878	6.89	6	
PCB 153	360.878	6.92	6	A60
PCB 132	360.878	6.58	6	A60
PCB 105	326.433	6.65	5	
PCB 138	360.878	6.83	6	A60
PCB 187	395.323	7.17	7	A60
PCB 183	395.323	7.2	7	
PCB 128	360.878	6.74	6	
PCB 177	395.323	7.08	7	
PCB 180	395.323	7.36	7	A60
PCB 170	395.323	7.27	7	A60
p,p'-DDE	318.03	6.51		
p,p'-DDD	320.04	6.02		
HCB	290.83	3.78		

2.6 Inventory calculation for surface sediment

Inventory of PCBs in the Baltic Sea surface sediment was calculated by the equation below (Blanz et al., 1999),

$$M = A \times C \times DBD \times D \quad (2-1)$$

Where A is the size of the area (km²), C is the concentration of PCBs (pg/g), D is layer width (cm), and DBD is the dry bulk density (g/m³).

DBD value is calculated using the study of Leipe et al. (2011) and the area sizes are

taken from Myrberg (2006) and Naumann (pers. communication, IOW), see Table 2-3,

Table 2-3 Surface area of the Baltic Sea basins based on personal communication of Naumann (IOW) (criteria: water depth) and Myrberg et al. (2006).

Basin	Area (km ²)	Water Depth (m)
Mecklenburg Bight	2540	15
Arkona Basin	6174	30
Bornholm Basin	10253	60
Eastern Gotland Basin	21785	80
Slupsk Channel	2450	60
Gulf of Gdansk	8440	80
Northern Gotland Basin	18794	80
Western Gotland Basin	13606	80

2.7 Risk assessment

2.7.1 Ecological risk assessment

Conducting different levels of ecological risk assessment can help to provide a comprehensive understanding of the ecological risks of PCBs in the Baltic. Various research methods have been developed for ecological risk assessment of PCBs in sediments, among which the widely used ones are the sediment quality guidelines (ERL/ERM) method, Potential Ecological Hazard Index (PEHI) method and the toxicity equivalent factor (TEF) method.

Sediment quality guidelines (ERL/ERM) method

The marine sediments were screened and classified into different levels of caution based on the probability of toxic effects occurring in the organisms, based on a large number of measurements (Long et al., 1995). The major effective application ranges are the low impact range, (Effects Range Low ERL) and the moderate impact range (Effects Range Moderate ERM). Where the concentration of contaminants in the sediment is below the ERL, the probability of ecological risk is considered to be less than 10% and the adverse effects on organisms exposed to this concentration are negligible. With concentrations above the ERM, the probability of ecological risk is

considered to be greater than 75% and exposure to this concentration will have a significant adverse effect on organisms. Contaminants may adversely affect organisms at concentrations between ERL and ERM (Table 2-4).

Table 2-4 ERL and ERM guideline values for PCB and DDT (ng/g, d.w.).(Long et al., 1995)

Chemical	Guideline	
	ERL	ERM
Total PCBs	22.7	180
p,p'-DDD	2	20
p,p'-DDE	2.2	27
p,p'-DDT	1	46
Total DDT	1.58	46.1

Potential Ecological Hazard Index (PEHI) method

PEHI method proposed by a Swedish scientist Hakanson (Hakanson, 1980), is employed for assessing the potential risks of PCBs to ecosystems. The calculation formula and parameter explanations are as follows:

$$Er^i = Tr^i \times \frac{C_s^i}{C_n^i} \quad (2-2)$$

Er^i represents the potential risk coefficient for an individual pollutant.

Tr^i is the toxicity response coefficient for an individual pollutant.

C_s^i is the measured concentration of the pollutant in sediment.

C_n^i is the pre-industrial global sediment pollutant content.

The risk levels corresponding to the index of individual risk factors are classified into five categories: low potential ecological risk ($Er^i < 40$), moderate potential ecological risk ($40 \leq Er^i < 80$), considerable potential ecological risk ($80 \leq Er^i < 160$), high potential ecological risk ($160 \leq Er^i < 320$) and very high ecological risk ($Er^i \geq 320$).

Toxicity Equivalency Factor (TEF) method

The ecological risk of dioxin-like polychlorinated biphenyls (dl-PCBs), which are potentially carcinogenic in the environment, has been an issue of concern. An assessment has been carried out to comprehensively assess the ecological risk of dichlorobiphenyls in the environment (Lang et al., 2014). 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) has been used as a reference substance for assessing the toxicity of PCBs, with the toxicity of different substances expressed as a toxicity equivalence factor (TEF) relative to 2,3,7,8-TCDD. The product of the concentration of a particular substance in a sample and its corresponding TEF represents the toxicity of that substance. The sum of the toxic equivalents (TEQ) of the different substances represents the overall toxicity of the sample (Lang et al., 2014). Currently, TEF is widely used in the toxicological assessment of dioxin-like contaminants and is gradually becoming the standard for the control of dioxin-like contaminants in various countries and organizations.

The following equation is used to calculate the TEQ for a given contaminant,

$$TEQ = C_i \times TEF_i \quad (2-3)$$

where C is the pollutant concentration and TEF is the toxicity equivalent factor of the pollutant relative to the 2,3,7,8- TCDD (Table 2-5).

Table 2-5 TEF values for dl-PCB (Van Den Berg et al., 2006).

Compounds	WHO 1998 TEF	WHO 2005 TEF
Non- ortho –substituted PCBs		
PCB 77	0.0001	0.0001
PCB 81	0.0001	0.0003
PCB 126	0.1	0.1
PCB 169	0.01	0.03
Mono- ortho –substituted PCBs		
PCB 105	0.0001	0.00003
PCB 114	0.0005	0.00003
PCB 118	0.0001	0.00003
PCB 123	0.0001	0.00003

PCB 156	0.0005	0.00003
PCB 157	0.0005	0.00003
PCB 167	0.00001	0.00003
PCB 189	0.0001	0.00003

2.7.2 Health risk assessment

Yang has calculated the health risk via the dietary exposure pathway by converting the PCBs content in sediment to concentrations in fish based on the biota-sediment accumulation factors (BSAF) based on the evaluation of sediment measurements in Jiaozhou Bay wetlands (Yang et al., 2014). This method establishes a relationship between sediment and contaminant concentrations in fish. This method was employed in this study to calculate health risks for the Baltic Sea sediments, which is the health risk derived from the intake of food (fish, shellfish, etc.), see Equation (2-4):

$$CDI = C_{fish} \times IR_{fish} \times CF \times ED \times EF \div (BW \times AT) \quad (2-4)$$

Where CDI is chronic daily intake, which means PCBs ingested as food (mg/kg/d), C_{fish} is concentration of PCBs in fish (mg/kg), IR_{fish} is fish intake (g/d), the value from U.S. Environmental Protection Agency (USEPA) is 14.1g/d (U.S. EPA., 1997), CF is concentration conversion factor (10^{-6} kg/mg), ED is exposure duration (a), EF is exposure frequency (d/a), BW is body weight (kg), AT is averaging time (d).

There may be differences in the physical characteristics and exposure conditions of different populations. Therefore, in my study, health risks were evaluated separately for adult men and women aged over 20 years in Europe, with weight parameters from the Exposure Factors Sourcebook for European Populations (ECETOC, 2001). The average weight for male and female was assumed 76.46 kg and 66.57 kg, respectively.

USEPA specifies the ratio of contaminant levels in organisms to sediment contaminants as the bio-sediment accumulation factor (BSAF).

$$C_{fish} = C_{sediment} \times BSAF \div TOC_{sediment} \quad (2-5)$$

where $C_{sediment}$ is concentration of PCBs in sediment, $TOC_{sediment}$ is total organic carbon in sediment, BSAF is bio-sediment accumulation factor, the value is 1.03 (Tracey et al., 1996). Hazard Quotient (HQ) is employed to evaluate human health

risks:

$$HQ = CDI/TDI \quad (2-6)$$

Where TDI is Tolerable Daily Intake.

When $HQ > 1$, the pollutant has a potential impact on human health (Zhao et al., 2011).

3 Results and discussion

3.1 Surface sediment

3.1.1 Spatial distribution of PCB153

Spatially, as it shown in Figure 3-1 (c1) and (c2), during the 2010s, PCB153 concentrations were notably high in the Eastern Gotland Basin with the value 0.74-2.39 ng/g d.w., while lower and moderate concentrations were found in the Arkona Basin (0.03-1.24 ng/g effectic). Similarly, the Kattegat region had lower concentrations with 0.37 and 0.38 ng/g d.w. Within the Arkona Basin, the northeastern areas had higher concentrations (1.18-1.64 ng/g d.w.), while the southwestern areas near the coast and straits had lower concentrations (0.03-1.24 ng/g d.w.).

In the 2000s, overall PCB153 concentrations were higher compared to the other two decades, see Figure 3-1 (b1) and (b2). In the entire Baltic Sea region, the northern parts had moderate to low concentrations, which 0.67-1.24 ng/g d.w. detected in Bothnian Bay and 0.47-0.62 ng/g d.w. in Bothnian Sea. In the central Baltic regions, Baltic Proper (0.72-2.12 ng/g d.w.) and Gotland Basin (0.94-2.83 ng/g d.w.) still had moderate to high concentration levels. PCB153 concentrations in the Bornholm Basin were at a moderate level with 1.39 ng/g d.w. In the densely sampled Arkona Basin, sampling sites closer to the coast (0.14-1.66 ng/g d.w.) generally had lower concentrations than offshore sampling sites (0.52-2.07 ng/g d.w.), although sampling site LB1 consistently had the highest concentrations with 3.74 ng/g d.w., similar to the results in the 2010s. This occurrence could be attributed to the geographical characteristics of the region, where the sea is enclosed by land on three sides. This configuration reduces the likelihood of pollutant migration, leading to the accumulation of pollutants in the area.

In the 1990s, there were fewer sampling sites, primarily concentrated in the Arkona Basin, see Figure 3-1 (a). Near the coast of the Mecklenburg Bight, concentrations were higher than in the offshore areas, while concentrations were lowest along the coast close to the Oder. On one hand, this suggests that PCB emissions in the Bay of Mecklenburg might be higher than in the Oder region. This similarities to Witt and Siegel's study in 2000. Following the Oder Flood in 1997, the concentrations of polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants similar to PCBs, significantly

increased in the Mecklenburg Bight region.

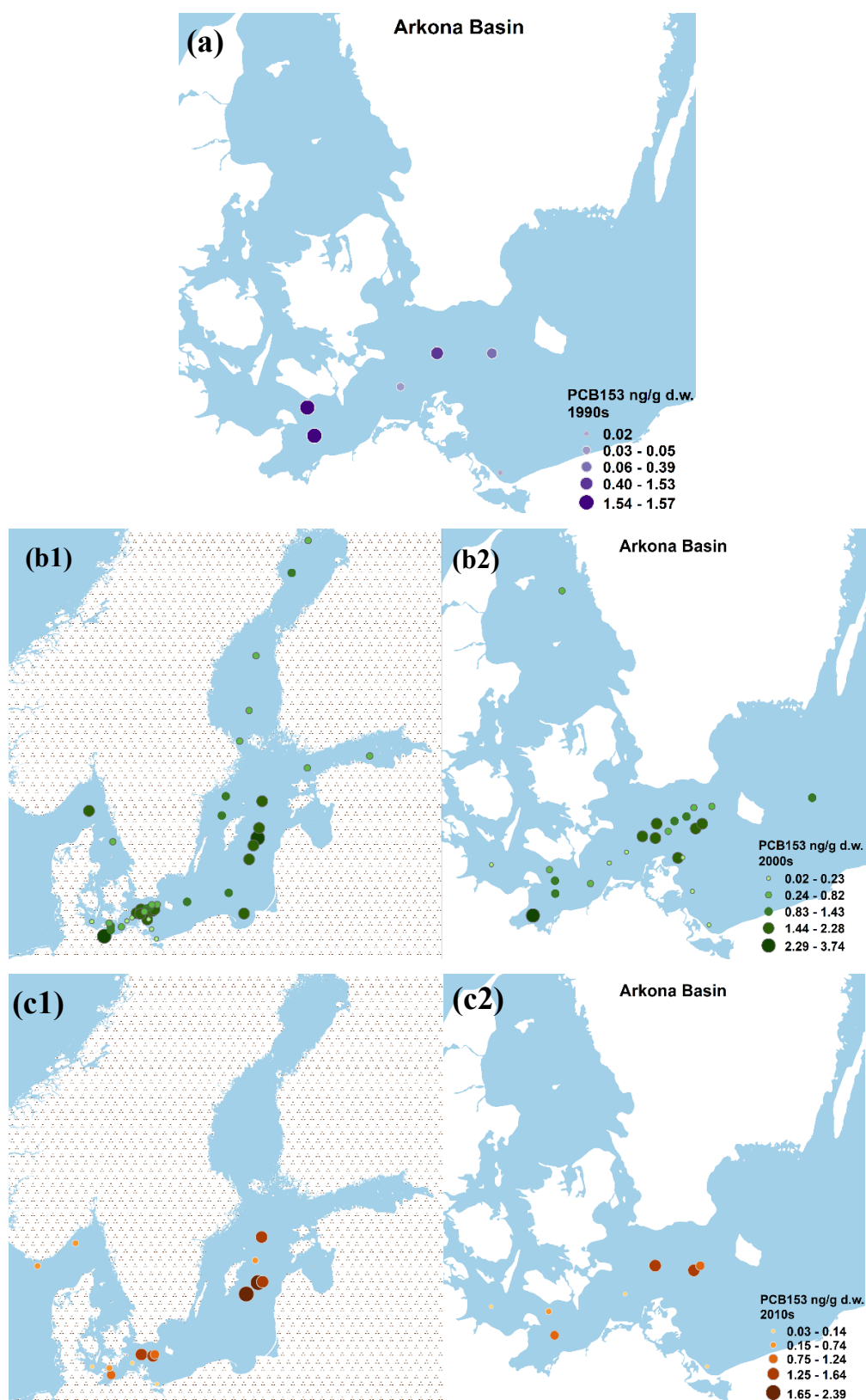


Figure 3-1 PCB153 (ng/g d.w.) in surface sediments across different time periods: (a) 1990s in Arkona Basin; (b1) 2000s in the whole Baltic Sea; (b2) 2000s in Arkona

Basin; (c1) 2010s in the whole Baltic Sea; (c2) 2010s in Arkona Basin.

On the other hand, from a geographical perspective, the region around Oder is located close to the coast as well, but in rather wide embayment, making the PCB migration easier.

In summary, concentrations were generally higher in the central and southern regions compared to the north. This is because the northern regions had lower emissions, while the central and southern regions had higher population density, more industrial activities, numerous ports, river inflows, and, consequently, higher pollutant discharges, resulting in more severe pollution. Additionally, during the 2000s and 2010s, offshore regions generally had higher concentrations, except for the Bay of Mecklenburg, where pollutant concentrations were higher near the coast.

3.1.2 Spatial distribution of DDT metabolics

The spatial distribution of DDD and DDE was similar to PCB153 in the three different decades. In the 1990s, as it shown in Figure 3-2 (a) and Figure 3-3 (a), surface sediment samples were collected only in the Arkona Basin, with DDD concentrations (ranging from 0.01 to 3.61 ng/g d.w.) showing a wider range than DDE (ranging from 0.04 to 2.49 ng/g d.w.). Similar to PCB153, sampling sites in the Mecklenburg Bight region (TF0012) exhibited higher concentrations of both DDD (3.61 ng/g d.w.) and DDE (2.38 mg/g d.w.). However, at sampling site TF0069, DDD concentrations were at the lowest level as 0.01 ng/g d.w., while DDE concentrations were the highest as 2.49 ng/g d.w. This might be because at this site, the majority of DDT had degraded into DDE, with only a small portion remaining as DDD. Conversely, in the Oder region, DDD concentration was at moderate level of 0.05 ng/g d.w. and DDE concentrations were low with 0.04 ng/g d.w.

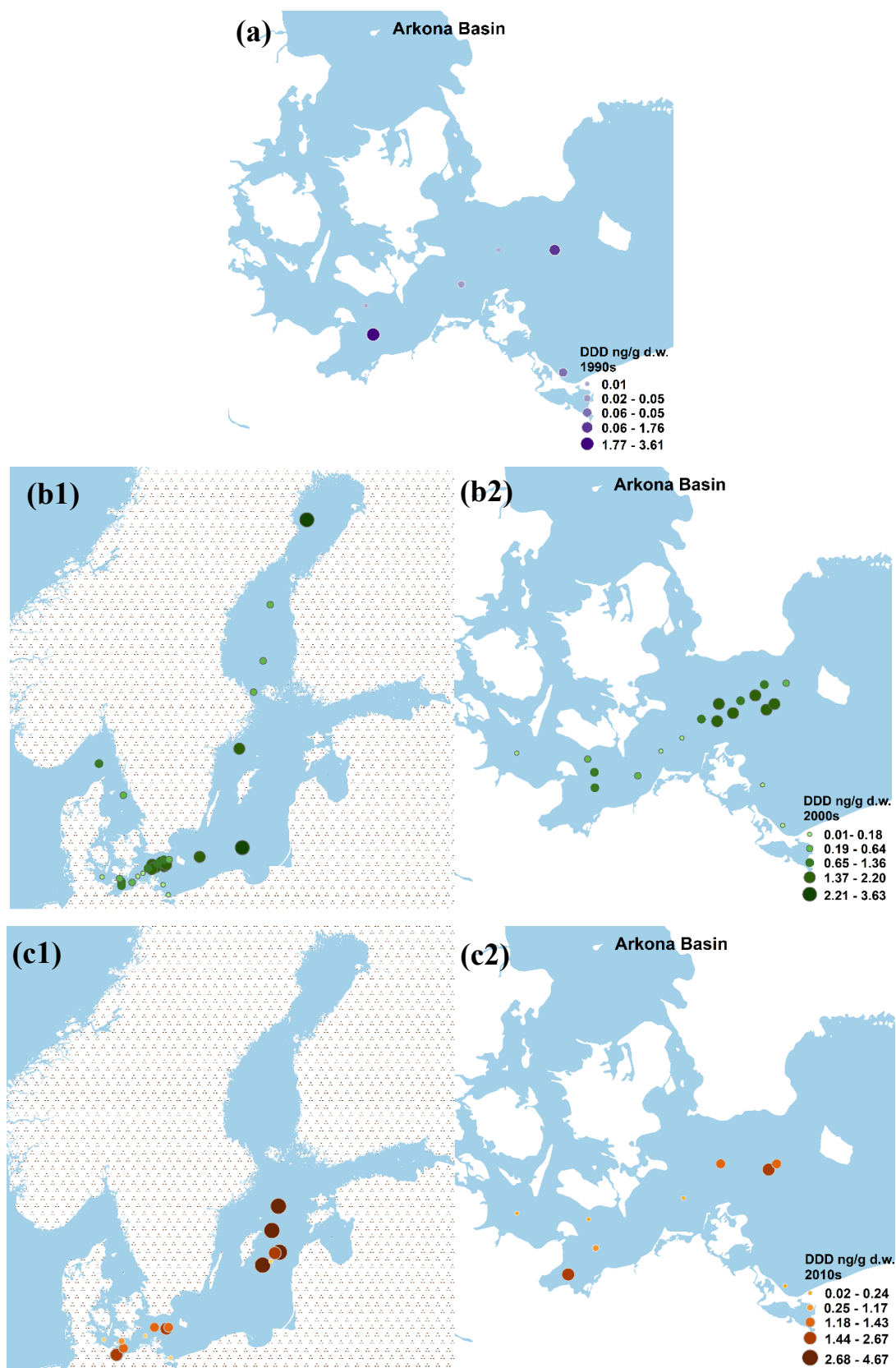


Figure 3-2 DDD (ng/g d.w.) in surface sediments across different time periods (a): 1990s in Arkona Basin; (b1): 2000s in the whole Baltic Sea; (b2): 2000s in Arkona Basin; (c1): 2010s in the whole Baltic Sea; (c2): 2010s in Arkona Basin.

In the 2000s (Figure 3-2 (b1), (b2) and Figure 3-3 (b1), (b2)), sampling sites with the highest DDE concentrations were found in the Gotland Basin (8.47 ng/g d.w.). However, since data for DDD in this region were lacking, DDE concentrations appeared higher. At the sampling sites at which both were detected, their concentrations did not differ significantly. Across the entire Baltic Sea, the northern regions, specifically Bothnian Bay, exhibited high concentrations (DDD: 2.68 ng/g d.w., DDE: 3.19 ng/g d.w.), while Bothnian Sea sampling sites had concentrations at a moderate to low level (DDD: 0.26-0.52 ng/g d.w., DDE: 0.59-0.93 ng/g d.w.). The northern Baltic Sea regions had fewer pollution sources, resulting in lower concentrations further away from the coast. In the central regions, only one sampling site in the Western Gotland Basin had DDD with 2.08 ng/g d.w., showing moderately high concentrations. The same area exhibited similar high concentrations for DDE with 2.21-3.62 ng/g d.w. In the Bornholm Basin, DDE concentrations (2.60 ng/g d.w.) were significantly higher than DDD concentrations (1.70 ng/g d.w.). DDD was considered a high-concentration area in this region, while DDE showed moderate concentrations. Both DDD (0.06-2.20 ng/g d.w.) and DDE (0.02-0.40 ng/g d.w.) concentrations in the Arkona Basin were quite similar, with slightly higher DDD concentrations. Offshore regions generally had higher concentrations (DDD: 0.65-2.20 ng/g d.w., DDE: 1.20-2.60 ng/g d.w.), while concentrations near the coast were slightly lower (DDD: 0.01-1.36 ng/g d.w., DDE: 0.02-1.19 ng/g d.w.). The coastal areas near the Mecklenburg Bight showed higher concentrations (DDD: 1.09 ng/g d.w., DDE: 1.17 ng/g d.w.), consistent with previous results (Dannenberger and Lerz, 1996).

As shown in Figure 3-2 (c1, c2) and Figure 3-3 (c1, c2), in the 2010s, the sampling sites for DDD and DDE largely overlapped, with consistent spatial distribution patterns. The main Baltic Sea region, Gotland Basin and Northern Baltic Proper, was characterized by high concentrations of DDD as 1.27-7.89 ng/g d.w. and DDE as 0.12-4.67 ng/g d.w., while the Arkona Basin had lower concentrations (DDD: 0.02-2.06 ng/g d.w., DDE: 0.05-2.17 ng/g d.w.). The sites offshore and the coastal areas near the Mecklenburg Bight generally had high concentrations with 0.25-2.67 ng/g d.w. for DDD and 0.42-2.58 ng/g d.w. for DDE, whereas the concentrations near the coast and closer to land were lower. These results were consistent with those from the 2000s. The lowest concentration (DDD: 0.02 ng/g d.w., DDE: 0.05 ng/g d.w.) at the site TF0030 was likely due to its location near a sill formation.

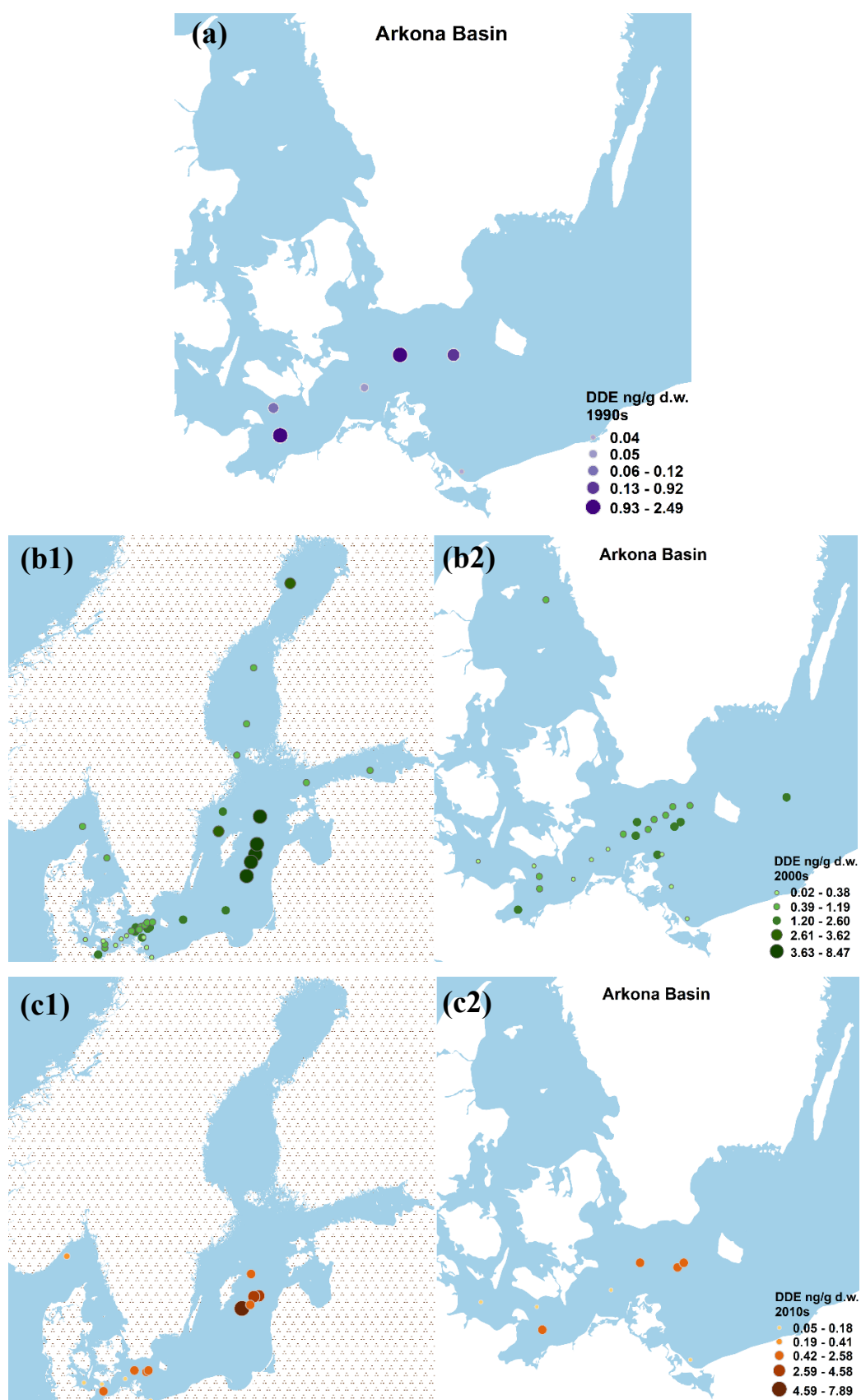


Figure 3-3 DDE (ng/g d.w.) in surface sediments across different time periods: (a) 1990s in Arkona Basin; (b1) 2000s in the whole Baltic Sea; (b2) 2000s in Arkona Basin; (c1) 2010s in the whole Baltic Sea; (c2) 2010s in Arkona Basin.

3.1.3 Time development of PCB concentrations

The results of long-term surface sediment sampling at six monitoring stations (Oder, TF0012, TF0010, TF0030, TF0069, and TF0110) in the Arkona Basin, covering the years 1993 and 2003–2022, indicate that the concentrations of several parameters, including TOC, PCB 153, and total concentration of 6 PCB congeners (sum 6 PCBs: 28/31, 52, 101, 138, 153, 180) (Duinker et al., 1988), show significant changes over the time (Figure 3-4).

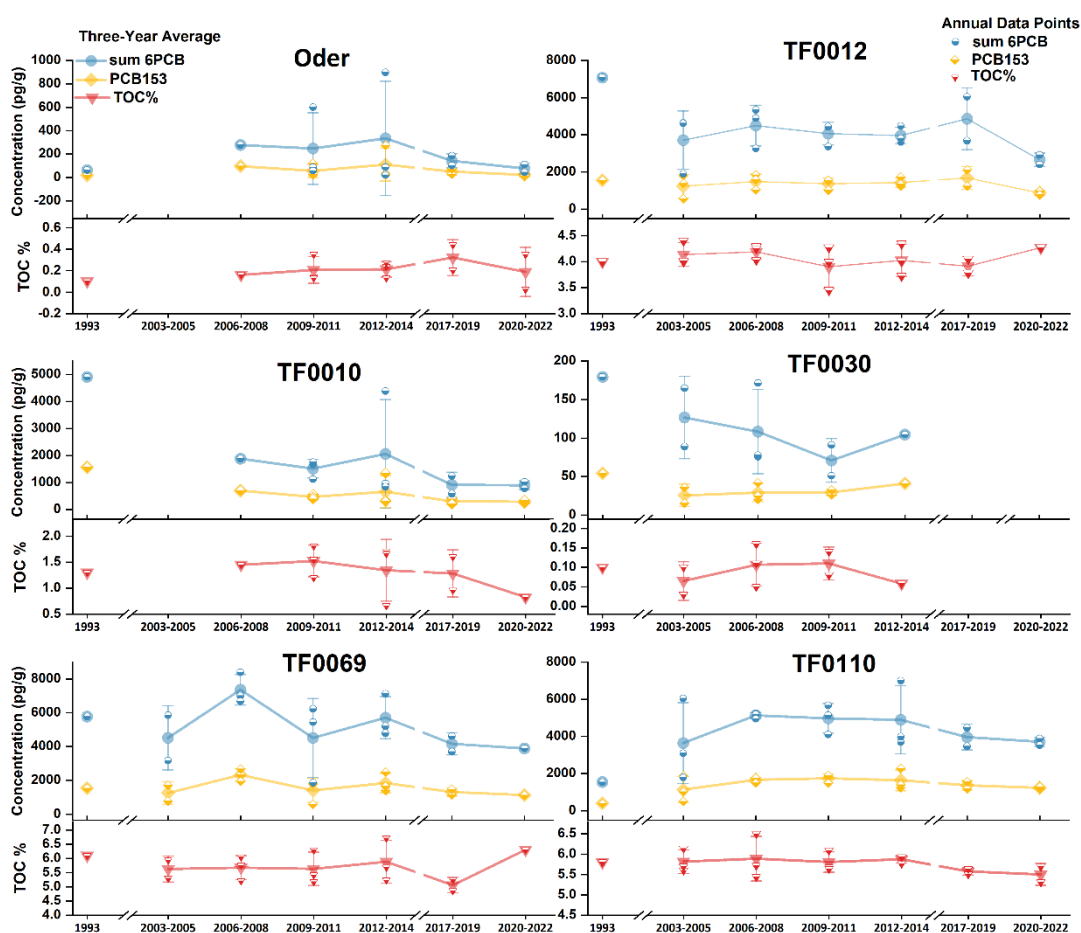


Figure 3-4 The sum 6 PCB (pg/g d.w), PCB153 (pg/g d.w.) concentration and TOC (%) at 6 monitoring stations during 1993-2022.

Oder

During the analyzed period, there was a rising trend in the sum 6 PCB concentration and PCB 153 levels at the Oder sampling location, followed by a decline. Despite gaps in the data between 1993 and 2006, there is a consistent rise in the PCB levels. The maximum was reached in 2012 (sum 6 PCB: 897.3 pg/g, PCB 153: 273.6 pg/g), and a

sharp decline occurred in 2013. With PCB 153 ranging from 12.19 pg/g (2022) to 72.43 pg/g (2018) and the sum 6 PCB ranging from 44.5 pg/g (2022) to 186 pg/g (2018), pollutant concentrations were relatively low after 2018. Following a gradual rise that reached its maximum in 2017–2019 (averaging $0.32 \pm 0.12\%$), the TOC levels decreased, matching the reduced TOC values in 2020–2022, see Figure 3-4.

TF0012

At the sampling site TF0012, there was an overall increase followed by a reduction in both, the levels of PCB153 and the total concentration of six PCBs. There were two maxima, from 1993 (sum 6 PCBs: 7081.4 pg/g, PCB153: 1555.9 pg/g) to 2020–2022, (sum 6 PCB: 2659.10 ± 96.16 pg/g, PCB 153: 874.63 ± 96.16 pg/g). There was a decline after the first maximum between 2006 and 2008 (6 PCB: 4499.22 ± 896.29 pg/g, PCB 153: 1486.00 ± 334.27 pg/g). In the years 2017–2019, the second maximum was recorded (6 PCB: 4866.17 ± 1177.92 pg/g, PCB 153: 1679.09 ± 434.18 pg/g). Nonetheless, in 2020–2022, concentrations were comparatively low, averaging just sum 6 PCB: 2659.1 ± 262.38 , PCB 153: 874.6269 ± 96.16 pg/g.

The TOC levels at this station varied a little, from 4.4% (2004) to 3.5% (2010). The TOC values showed some increase at the start of the 2020s (4.3%) compared to the late 2010s ($3.9 \pm 0.13\%$), albeit remaining generally steady.

TF0010

The concentration of PCBs at sampling site TF0010 showed a declining trend; the largest peak was seen in 1993, when the PCB 153 concentration was 1565.9 pg/g and the total concentration of the six PCBs reached 4908.9 pg/g. While still less than the 1993 peak, the overall concentration of the six PCBs (4379.8 pg/g) and PCB 153 (1344.2 pg/g) in 2012 was at its greatest level since the turn of the twenty-first century.

The TOC values for 2013 and 2010 varied from 0.7% to 1.8%. In general, the PCB trend and the TOC trend lined up. At sampling site TF0010, there was a discernible rise in TOC and PCB measurements in 2012, suggesting the likelihood of new pollution inputs during that time.

TF0030

The concentrations of the six PCBs at sampling point TF0030 showed a continuous decrease from 1993 (179.4 pg/g) to 2011 (three-year average: 71.0 ± 19.93 pg/g). However, in 2012, there was a sudden increase to 104.4 pg/g, a phenomenon similar to that observed at TF0010. PCB153 concentration was notably high in 1993 at 54.2 pg/g. Subsequently, from 2003 to 2011, there were slight fluctuations, with the highest concentration recorded in 2006 (42.24 pg/g). In 2012, the concentration reached another peak at 41.0 pg/g.

TOC levels were 0.1% in both 1993 and 2003, but there was a sharp decline to 0.03% in 2004. A subsequent increase was observed in 2006–2007 ($0.11 \pm 0.04\%$), followed by a decrease in 2012 to 0.06%. The fluctuation in TOC levels mirrored the changes in PCB concentrations at TF0030, see Figure 3-4.

TF0069

At sampling point TF0069, pollutant concentrations exhibited significant fluctuations, both within individual three-year intervals and in-between. The maximum in the PCB concentration occurred in the 2006–2008 period, with a total of the six PCBs reaching 7356.54 ± 742.65 pg/g. However, when considering the entire time series from 1993 (5764.4 pg/g) to 2020 (3881.78 pg/g), there was an overall decrease in pollutant concentrations. The trend in the PCB 153 mirrored that of the sum of the six PCBs, reaching its highest value in 2006–2008 at 2319.13 ± 300.83 pg/g and decreasing from 1993 (1529.1 pg/g) to 2020 (1123.33 pg/g).

In the early 21st century, the three-year average of TOC of $5.6 \pm 0.33\%$ (2003–2005), $5.7 \pm 0.35\%$ (2006–2008), and $5.6 \pm 0.48\%$ (2009–2011) was almost stable. Nonetheless, a little decline in TOC ($5.1 \pm 0.20\%$) was noted during the years 2017–2019. TOC had maximum at 6.3% in 2020, the highest value for the whole period.

TF0110

The total concentration of the six PCBs and PCB 153 was reported at 1538.1 pg/g and 394.1 pg/g, respectively, marking the lowest PCB values at the sampling station TF0110 since the 1990s. The levels of the PCBs had maximum in 2003 (sum 6 PCB: 6038.12 pg/g, PCB153: 1884.22 pg/g), but in 2004 they began to decline. Consequently,

PCB concentrations were lower than in 2003–2005 and in the following years. There PCB concentrations between 2006 and 2014 were relatively stable. Following 2017, there was a decline: by 2020–2022, PCB 153 declined to 1227.79 ± 51.35 pg/g and sum 6 PCB declined to 3706.21 ± 182.40 pg/g. Nevertheless, the pollutant concentrations were still much higher than in 1993, though.

The 30-year period witnessed a rather constant range of TOC values, from 6.5% in 2007 to 5.3% in 2020. The TOC values decreased to $5.5 \pm 0.19\%$ in the years 2020–2022.

Table 3-1 Shipping accident during 2003-2019 (HELCOM). Empty spaces indicate either the absence of shipping accidents or incidences without pollution, while marks with an 'x' indicate shipping accidents related to pollution. Cases where there have been shipping accidents but no information regarding pollution is available are given by 'n'.

Year	Oder	TF0010	TF0012	TF0030	TF0069	TF0110
2003			x		x	x
2004						
2005				x		
2006						
2007		x	x			
2008						
2009	x					
2010						x
2011						
2012		n	n			
2013		n	n			
2014						
2015	x					
2016					x	
2017					x	x
2018						
2019						

A number of environmental factors could be responsible for the observed decline in

PCB contents at these six monitoring stations in the 2020s in comparison to earlier years. Notably, the variations in the PCB concentrations were probably influenced by the Major Baltic Inflow (MBI) occurrences in the Baltic Sea, which were recorded in the years 2003 and 2014 (Dellwig et al., 2021; Meier et al., 2018).

Variations in the PCB concentrations may have resulted from the transport and dispersion of contaminants being impacted by MBI, which have the potential to dilute or redistribute PCBs in the water column and sediments.

Moreover, another possible cause of the PCB contamination in the maritime environment are the shipping accidents. Table 3-1 gives a historical summary of shipping incidents near each monitoring station, with reference to the “Annual Report on Shipping Incidents in the Baltic Sea” released by Baltic Marine Environment Protection Commission (HELCOM, 2003-2009).

Knowing how these environmental elements interact with MBI events and maritime accidents is essential to understanding the dynamics of the PCB concentration in the Baltic Sea, particularly in the years after 2003 and 2014. In addition, the decreasing trend may be also the result of the ban of the production and usage, international rules and the action of HELCOM.

3.1.4 Inventory calculation

According to Equation (2-1), inventories of total six PCBs, DDTs and HCB in the Baltic Sea is calculated (see Table 3-2, Table 3-3 and Table 3-4). For the whole Baltic, sum 6 PCBs in the surface 1 cm depth sediment amounts to 1.69 ± 0.69 tons. The amounts of DDTs and HCB are 1.05 ± 0.34 tons and 0.19 ± 0.06 tons, respectively.

Table 3-2 Mass balance for the sum 6 PCBs for the different regions of the Baltic Sea. (SD-standard deviation.)

Region	Area (km²)	Amount of sum 6PCBs (t)	Amount SD (t)
Mecklenburg Bight	2540.00	0.13	0.11
Arkona Basin	6174.00	0.05	0.02
Bothnian Bay	36260.00	0.35	0.22
Bothnian sea	64886.00	0.48	0.09
Gulf of Finland	29498.00	0.03	0.01

Region (Table 3-2 continue)	Area (km²)	Amount of sum 6PCBs (t)	Amount SD (t)
Northern Gotland Basin	18794.00	0.06	0.03
Western Gotland Basin	13606.00	0.06	0.00
Eastern Gotland Basin	21785.00	0.10	0.10
Gulf of Gdansk	8440.00	0.05	0.01
Bornholm Basin	10253.00	0.08	0.00
Kattegat	22287.00	0.31	0.09
Total		1.69	0.69

Table 3-3 Mass balance for the sum DDTs in different regions of the Baltic Sea. (SD-standard deviation.)

Region	Area (km²)	Amount of sum DDT (t)	Amount SD (t)
Mecklenburg Bight	2540.00	0.02	0.01
Arkona Basin	6174.00	0.03	0.01
Bothnian Bay	36260.00	0.19	0
Bothnian sea	64886.00	0.25	0.05
Gulf of Finland	29498.00	0.03	0.02
Northern Gotland Basin	18794.00	0.06	0.02
Western Gotland Basin	13606.00	0.04	0
Eastern Gotland Basin	21785.00	0.16	0.20
Gulf of Gdansk	8440.00	0.11	0.00
Bornholm Basin	10253.00	0.08	0
Kattegat	22287.00	0.11	0.03
Total		1.05	0.34

Table 3-4 Mass balance for the sum HCB in different regions of the Baltic Sea. (SD-standard deviation.)

Region	Area (km²)	Amount of sum HCB (t)	Amount SD (t)
Mecklenburg Bight	2540.00	0.00	0.00
Arkona Basin	6174.00	0.00	0.00

Region (Table 3-4 continue)	Area (km²)	Amount of sum HCB (t)	Amount SD (t)
Bothnian Bay	36260.00	0.01	0
Bothnian sea	64886.00	0.10	0.02
Gulf of Finland	29498.00	0.01	0.00
Northern Gotland Basin	18794.00	0.01	0.00
Western Gotland Basin	13606.00	nd	nd
Eastern Gotland Basin	21785.00	0.01	0.02
Gulf of Gdansk	8440.00	0.01	0.00
Bornholm Basin	10253.00	0.01	0.00
Kattegat	22287.00	0.04	0.01
Total		0.19	0.06

The amount of sum 6 PCBs in the Arkona Basin initially increases and then decline (Figure 3-5). The amount rose from 95.95 ± 52.98 kg in the 1990s to 163.78 ± 62.78 kg in the 2000s, but in the 2010s, it decreased to 106.93 ± 1.88 kg. In the Mecklenburg Bight, there is a continuous and pronounced decreasing trend, from 126.07 ± 75.35 kg (1990s) to 1.85 ± 0.28 kg (2010s).

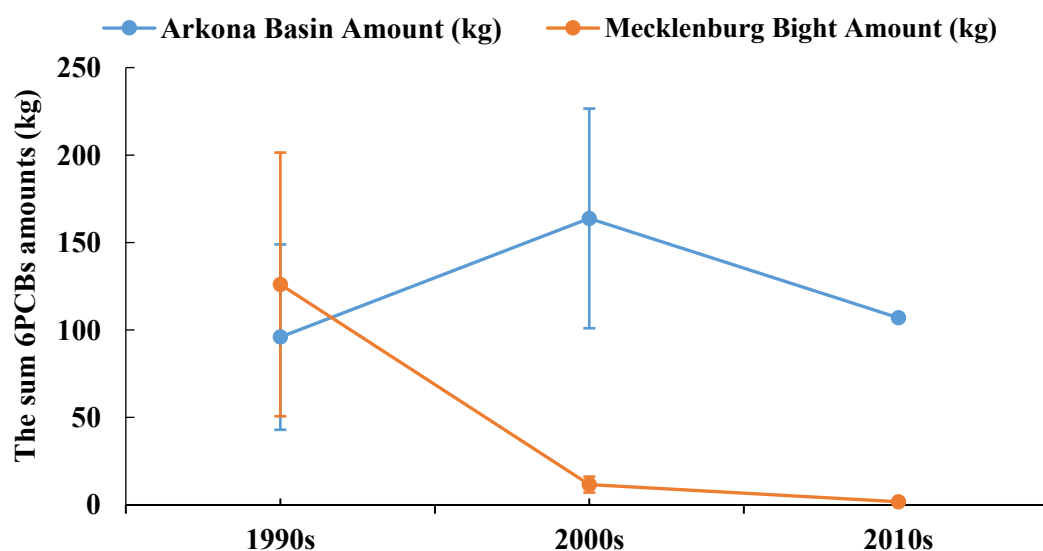


Figure 3-5 The sum 6PCBs amounts over three decades in Arkona Basin and Mecklenburg Bight.

The amount of DDT metabolites in the Arkona Basin inventory varies relatively little,

but it shows a steady growth over time, going from 22.49 ± 1.67 kg in the 1990s to 35.65 ± 5.24 kg in the 2010s (Figure 3-6). The DDT metabolic inventory in Mecklenburg Bight declined from 22.15 ± 78.57 kg in the 1990s to 17.17 ± 0.18 kg.

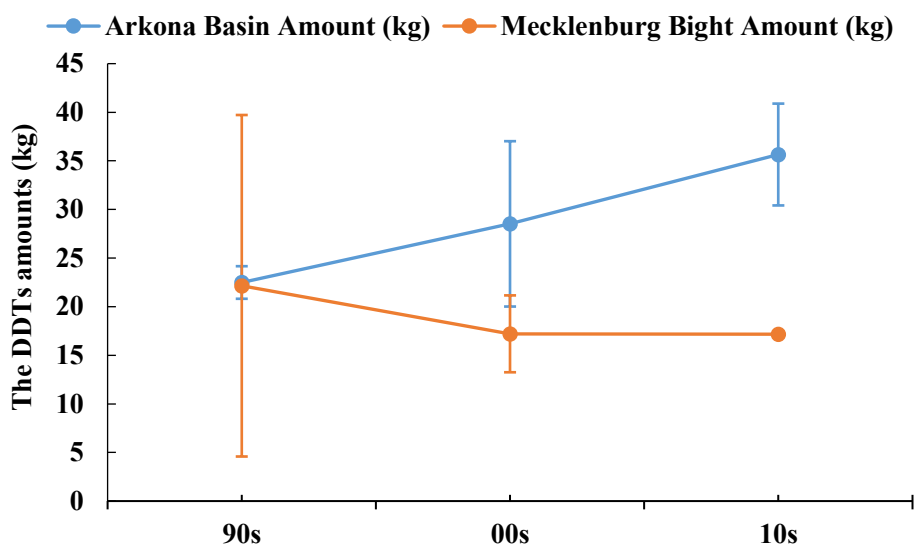


Figure 3-6 The DDTs amounts over three decades in the Arkona Basin and the Mecklenburg Bight.

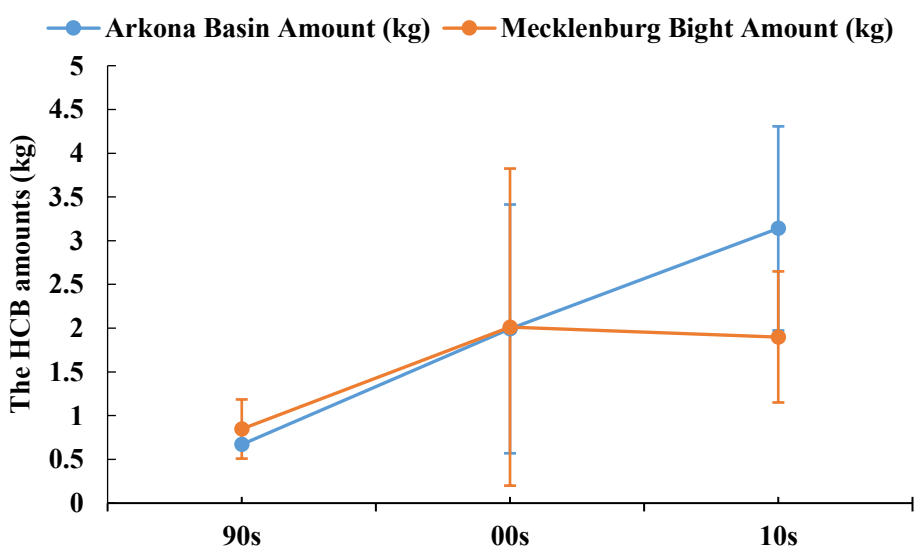


Figure 3-7 The HCB amounts over three decades in the Arkona Basin and the Mecklenburg Bight.

The overall difference in the HCB inventory between the Arkona Basin and the Mecklenburg Bight regions is moderate; however, the standard deviation reveals a significant fluctuation in the content across sampling positions within each region. Furthermore, the two regions' historical tendencies diverge, see Figure 3-7.

The HCB accumulation in the Arkona Basin has been increasing continuously, from 0.67 kg in the 1990s to 1.99 ± 0.42 kg in the 2000s and then to 3.14 ± 1.17 kg in the 2010s.

The amount of HCB showed an upward trend in the Mecklenburg Bight region between the years 1990 (0.85 ± 0.34 kg) and 2000 (2.01 ± 1.81 kg), and decline in the 2010s (1.90 ± 0.75 kg).

3.2 Sediment cores

3.2.1 PCB

PCB composition

In this study, a total of 23 polychlorinated biphenyl (PCB) congeners were identified and assessed. Figure 3-8 presents the percentage distribution of these congeners across multiple sediment cores, offering a visual representation of their composition. The compositional profiles of these 23 PCB congeners were systematically compared and analyzed. Notably, for each sediment core sample, the highest concentration profile of PCBs was selected for detailed analysis. This profile was chosen as it represents the most prominent accumulation of PCB congeners within the respective core. Subsequently, the percentage distribution of these prominent congeners was examined. In all sediment cores, six selected representative PCB congeners (PCB28/30, PCB52, PCB101, PCB153, PCB138, PCB180), each characterized by distinct concentration levels, were consistently detected.

Furthermore, it is noteworthy that among these core samples, several congeners of dioxin-like PCBs (PCDD/F PCBs) were also detected. Specifically, PCB118 was detected at each sampling point and accounted for a significant proportion with 5.9%-9.0%. Additionally, PCB105 was identified in several samples, including Arkona Basin (AB), Skagerrak (SK), Gulf of Finland (GF), and Gotland Deep (GD). Of particular interest is the relatively high proportion as 5.6% of PCB77 in the core sample from Arkona Basin (AB), while trace amounts of PCB77 were also detected in the core samples from Gulf of Gdansk (SP), Gulf of Finland (GF) and Gotland Deep (GD). For further analysis, six indicator PCB congeners (28/31, 52, 101, 138, 153, 180) were selected based on their consistently high proportions within the 23 PCB congener

dataset, as depicted in Figure 3-8. Individual concentration profiles for these six indicator PCB congeners are provided in the Appendix. Spatial variability in PCB concentrations was observed across the Baltic Sea area. Total concentrations of the six indicator PCBs exceeded 20,000 pg/g dry weight in the offshore areas (NCB, GB-1, GB-2, and GD), while they remained below 10,000 pg/g (d.w.) in the Arkona Basin (AB), Skagerrak (SK), and the Gulf of Gdansk (SP). The Gulf of Finland (GF) exhibited intermediate concentrations, surpassing 10,000 pg/g (d.w.) only at its greatest depth. This spatial distribution indicates the accumulation of PCBs in offshore regions, likely due to the continuous discharge of fresh PCBs from rivers and estuaries into the Baltic Sea. This influx leads to the adsorption of PCBs in the sediment as they transport away from the coastline, a phenomenon suggestive of the absence of recent anthropogenic inputs in the Baltic Sea region. With the cessation of PCB production and usage, the natural attenuation of PCBs in fresh sediments along the coast is evident.

Consistent distribution patterns were observed for the six indicator PCB congeners within the same sediment core, with peaks occurring at similar depths. Furthermore, distribution trends across various regions exhibited striking similarities. As it shown in Figure 3-9, PCB concentrations generally increased with depth in the upper part of the core, peaking at a specific stratum within the mid-core. In the deeper layers, PCB concentrations gradually decreased, approaching negligible levels.

Upon detailed examination of each sediment profile, PCB153 emerged as the predominant PCB congener, displaying a distribution pattern akin to that of the sum 6 PCBs. In offshore areas, peaks in the PCB concentration profiles consistently occurred within the mid-core section. The peak depths for the sum of all PCB congeners and PCB153 coincided in the same sediment core. In the Gulf of Gdansk (SP), the primary distribution trend closely resembled that of other cores, albeit with minor undulations around the maximum. Notably, in the Arkona Basin, two distinct peaks were observed for both the sum of all PCBs and PCB153, attributed to the 1997 Order Flood event, which transported contaminants into the Arkona Basin. The remarkable consistency between PCB153 and the total of the six indicator PCB congeners across all sediment cores underscores their shared behavior and fate under uniform environmental conditions, even after over half a century of environmental transformation.

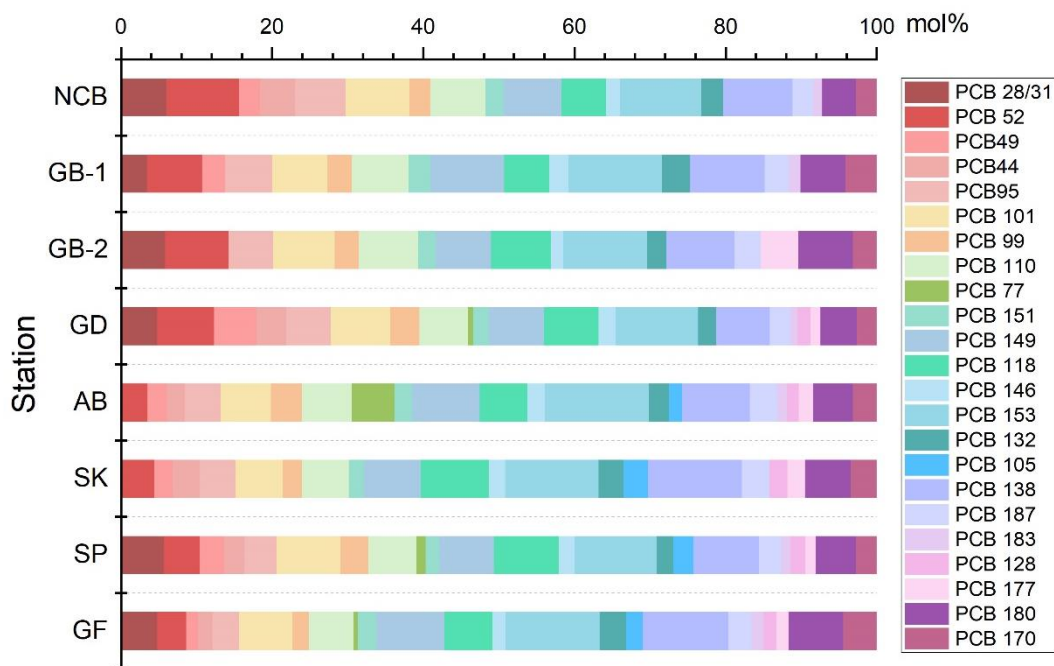


Figure 3-8 Percentage distribution of total 23 PCB content (mol%) in selected cores.

PCB and TOC in vertical profile

The cumulative concentrations of the six selected representative PCB congeners are depicted in Figure 3-10, revealing distinct patterns across the sediment cores. Notably, each sediment core exhibited a concentration maximum within the mid-section of the core. In the NCB (Northern Gotland Basin), GB-1 (Gotland Basin), and GB-2 (Gotland Basin) cores, the distribution of PCBs during earlier time periods demonstrated a correlation with Total Organic Carbon (TOC) values over time, with a notable maximum in the mid-depth section. However, as PCB concentrations diminished over time, TOC levels sustained high values, even increasing in surface slices. It's noteworthy that when PCBs were initially detected in the Baltic sediment in the 1960s, their concentrations were not notably high. Subsequently, with the widespread utilization of PCB commercial products, PCB concentrations rapidly increased with shallower depths, culminating in a maximum around the 1980s (Stockholm Convention, 2008). Following the enforcement of bans, PCB concentrations displayed a gradual decline, as evidenced by the decreasing trend observed in the uppermost sediment layers.

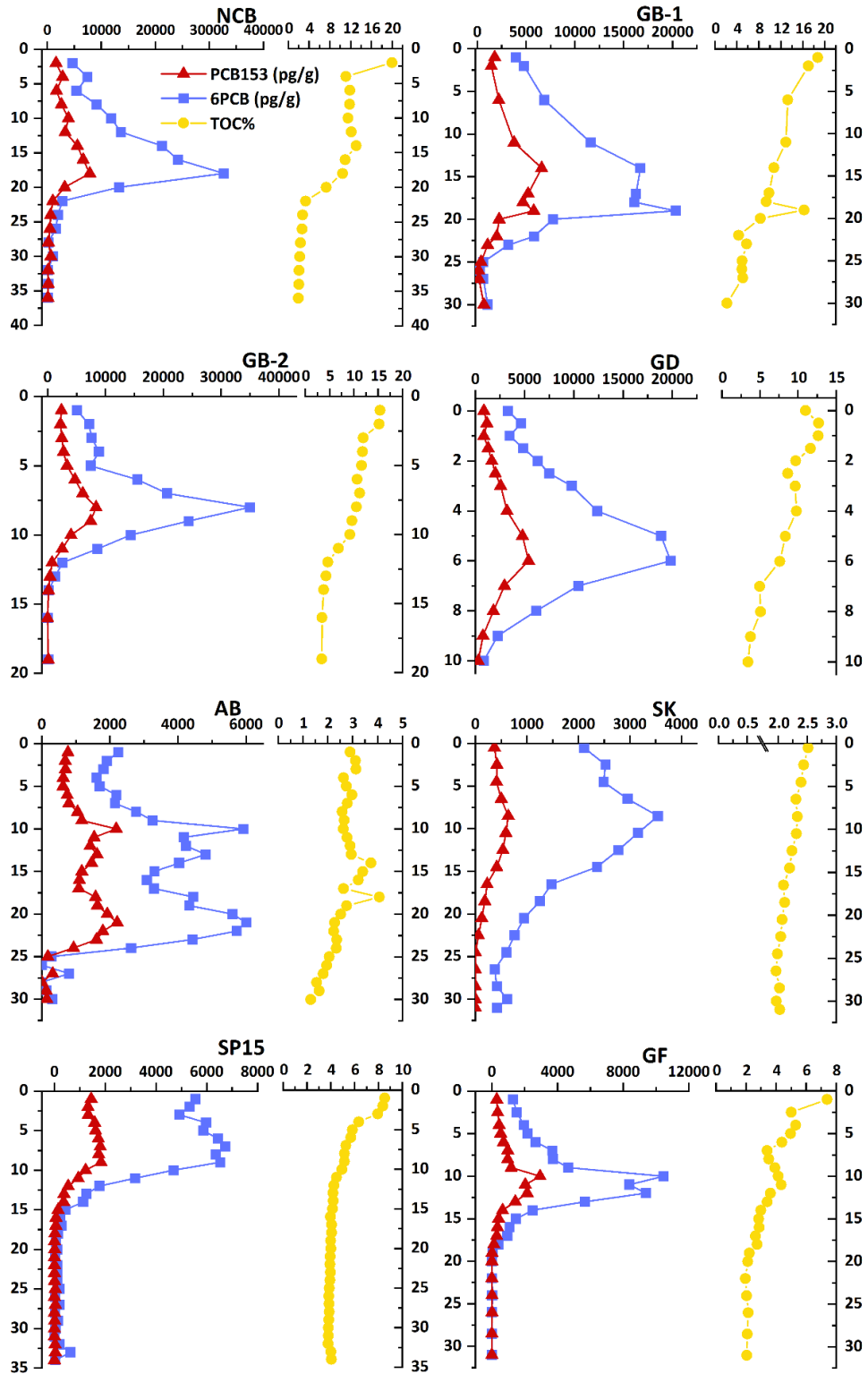


Figure 3-9 The profiles of the PCB153 and the total six PCBs concentration (d.w.) and TOC (% , yellow). GD (Gotland Deep), GB-1 (Gotland Basin-1), GB-2 (Gotland Basin-1), NCB (Northern Gotland Basin), SK (Skagerrak), SP (Gulf of Gdansk), AB (Arkona Basin) and GF (Gulf of Finland). The red line represents concentration of PCB153 (ng/g d.w.), the blue line the total six PCBs (ng/g d.w.).

Over the course of several decades, PCB concentrations exhibited an initial increase, culminating in a maximum, followed by a subsequent decline in recent years. Conversely, TOC values demonstrated a decrease over time, with noteworthy variations in the depth at which the maxima of PCB and TOC occurred. This discrepancy may be attributed to disturbances within the sediment layers. In Arkona Basin, the profiles of the six PCBs exhibited two concentration maxima, mirroring the distribution of TOC. However, the depth positions at which these maxima occurred were not entirely congruent between PCB and TOC (Figure 3-9).

Vertical TOC distributions exhibited similarities in cores NCB, GB-1, and GB-2, characterized by values below 20% in Northern Gotland Basin and Gotland Basin. Deeper sections of these cores exhibited a trend toward diminishing TOC values, indicating a paucity of organic compounds in earlier time periods, which gradually increased over subsequent decades. Gotland Deep (GD) displayed slightly lower TOC values (<15%) compared to the aforementioned cores, while Arkona Basin (AB) showcased TOC values fluctuating with higher values in deeper sediment layers. Of particular interest was the Skagerrak (SK) core, where TOC values remained relatively stable throughout the core length, with a slight increase observed from deeper sections towards the surface.

Analysis of TOC pattern indicated that surface TOC values were significantly higher than the adjacent sections below at some sampling sites (NCB, GB-1, GB-2, and SP). In contrast, sediment cores (AB and GD) from Arkona Basin and Gotland Deep displayed an opposing pattern, attributed to the seasonal timing of sampling. Samples collected during the summer months (NCB, GB-1, GB-2, and SP from Gotland Basin and Gulf of Gdansk) corresponded to intensive phytoplankton activity, leading to increased organic matter production.

Normalization of pollutant concentrations by TOC content offers valuable insights into the extent of environmental contamination. Across all sampling sites, the concentration ranges normalized to TOC were within the hundreds of ng/TOC. The Baltic Sea's main region and Arkona Basin exhibited values exceeding 300 ng/TOC, indicative of more severe PCB contamination. In contrast, Skagerrak and the Gulf of Gdansk displayed values less than 150 ng/TOC, signifying a comparatively lower PCB contamination level. The TOC-normalized sum of the six selected PCB congeners is illustrated in Figure 3-10.

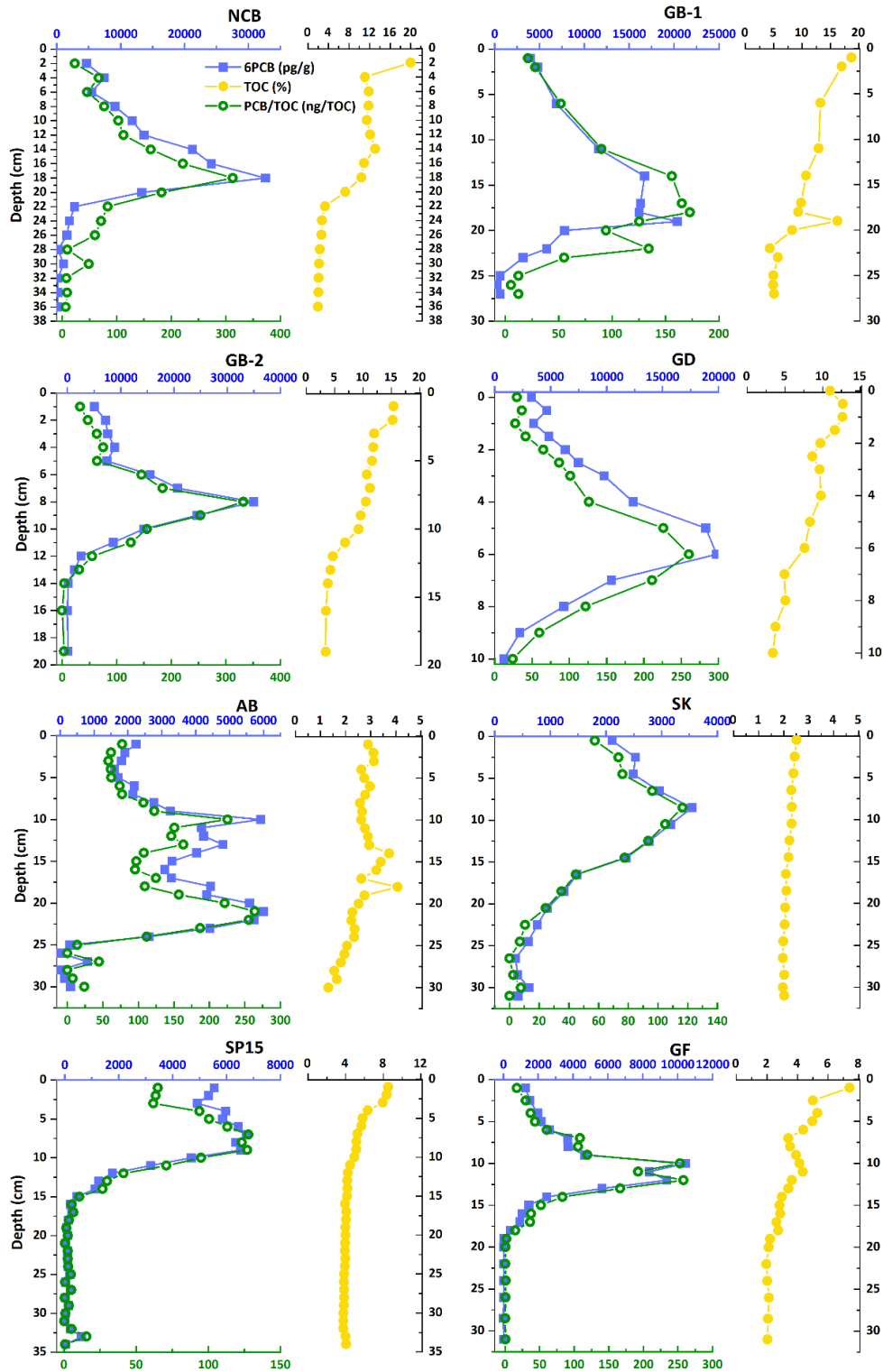


Figure 3-10 The total of the six PCBs normalized by TOC concentrations (yellow, %) in the core profiles. GD (Gotland Deep), GB-1 (Gotland Basin-1), GB-2 (Gotland Basin-1), NCB (Northern Gotland Basin), SK (Skagerrak), SP (Gulf of Gdansk), AB (Arkona Basin) and GF (Gulf of Finland). The blue line represents concentration of total six PCBs (ng/g d.w.), the green line represents concentration of the total six PCBs normalized by total organic carbon (ng/TOC).

The distribution of TOC-normalized values closely resembled the total values of the six PCB congeners, often nearly overlapping at specific depths. Notably, within the GB-1 core (13-18 cm depth range), the PCB/TOC value exhibited no distinct maximum, indicating the highest PCB concentration on a dry weight basis at 19 cm depth, while the 13-18 cm range exhibited a broad range of PCB/TOC values.

3.2.2 Commercial products distribution

Fourteen distinct PCB markers (see Table 2-2) were thoughtfully selected to serve as indicators for different commercial PCB products. Their respective percentages by weight were calculated to facilitate further analysis. As visually represented in pie charts derived from various sediment cores and sections, the fate of these distinct PCB products was strikingly evident (Figure 3-11 to 3-18). These charts not only elucidated the proportion of each PCB marker but also revealed the composition of each specific product. Moreover, it was apparent from the distribution at varying depths how these products initially emerged and the extent of their compositional diversity over time.

Northern Baltic Proper

As it shown in Figure 3-11, in the context of the Northern Baltic Proper core, a systematic division into individual 1 cm slices allowed for detailed insights into the dynamics of PCB products. Within each slice, the predominant product was A60, accounting for more than 40.90% of the composition. A50 preceded the appearance of A30/40 in the core. A30/40, however, exhibited a higher proportion than A50 in the mid-core slices, gradually diminishing in the surface slices. Notably, A30/40 was initially detected at a depth of 19–20 cm. The proportion of low-chlorinated products remained stable at percentages ranging from 20.73% to 30.20% within the middle section of the core (7–20 cm). This percentage decreased to a range of 8.82% to 13.84% in the upper core slices (1-6 cm), see Figure 3-11.

Within the A60 category, PCB153 and PCB149 emerged as the major components, being detected earliest and consistently present throughout the entire core. Additional A60 markers became apparent concurrently with the introduction of A50, which featured only PCB118 and was initially discovered in the 25–26 cm slice. In the 19–20 cm slice, the remaining two A50 markers began to emerge, with PCB118 and PCB110

taking turns as the primary components with the highest percentages in various slices. The low-chlorinated PCB product A30/40 exhibited varied compositional forms across different slices. PCB52 and PCB28/31 were initially identified at a depth of 19–20 cm, and subsequently, all four markers were detected in the 17–18 cm slice. PCB44 was exclusive to this particular layer. PCB52 predominated in the composition of A30/40 throughout the entire core, while PCB28/31 intermittently occurred in shallower depths. PCB49 was present in both mid-core (13–18 cm) and upper-core (5–6 cm) slices, though in smaller proportions.

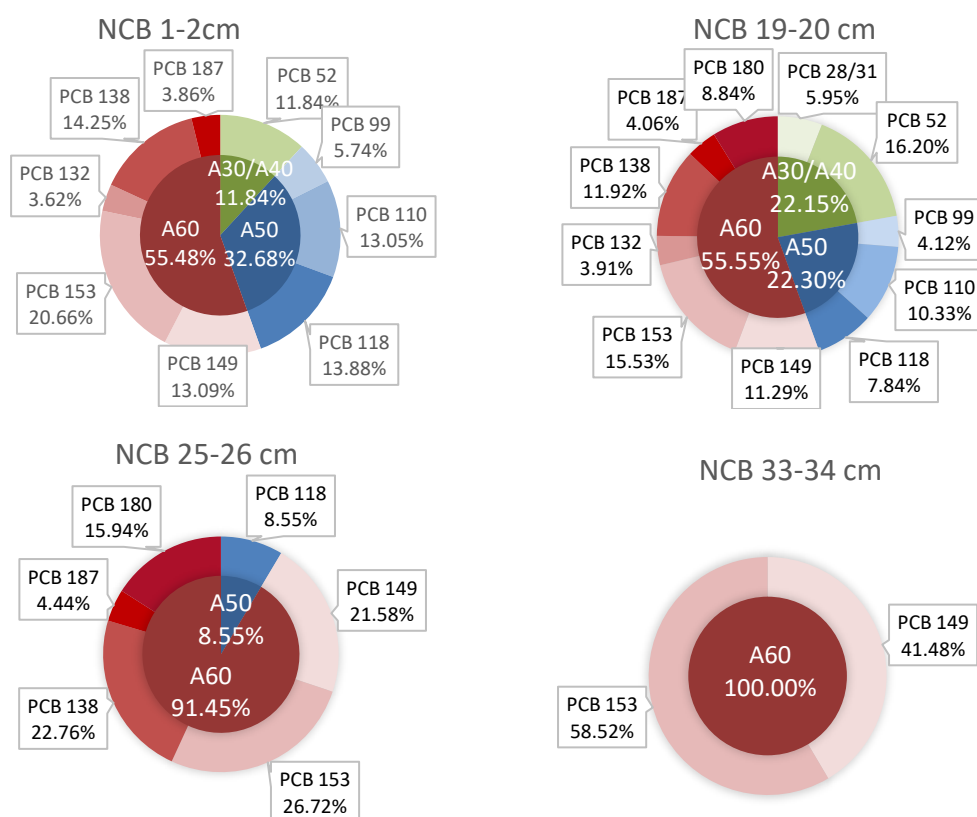


Figure 3-11 The distribution of commercial products from typical slices in the sediment cores of NCB in Northern Gotland basin.

The highly chlorinated PCB product A60 dominated this particular region, with A50 representing a smaller proportion. A30/40 was the most recently detected product within this core. Over time, it is evident that all three PCB products have coexisted to the present day. High percentages in deeper slices, implying that high concentrations of the three products were more prevalent in a specific era (Figure 3-11 NCB 19-20 cm).

Western Gotland Basin

The sediment cores collected from the Western Gotland Basin, including GB-1 (see Figure 3-12), GB-2 (see Figure 3-13), and GD (see Figure 3-14), revealed distinct PCB distribution patterns. In GB-1, PCBs were not uniformly detected at each centimeter interval throughout the entire sediment core. A60 emerged as the dominant product, constituting more than 57.78% of the three distinct PCB commercial products. In the uppermost layer down to 20 cm, A50 exhibited a consistent proportion within the range of 20.36% to 31.38%. A30/40, the low-chlorinated product, had the lowest representation among the three products, with its percentage gradually increasing with depth from 14.34% to 19.01% in the 10–20 cm range.

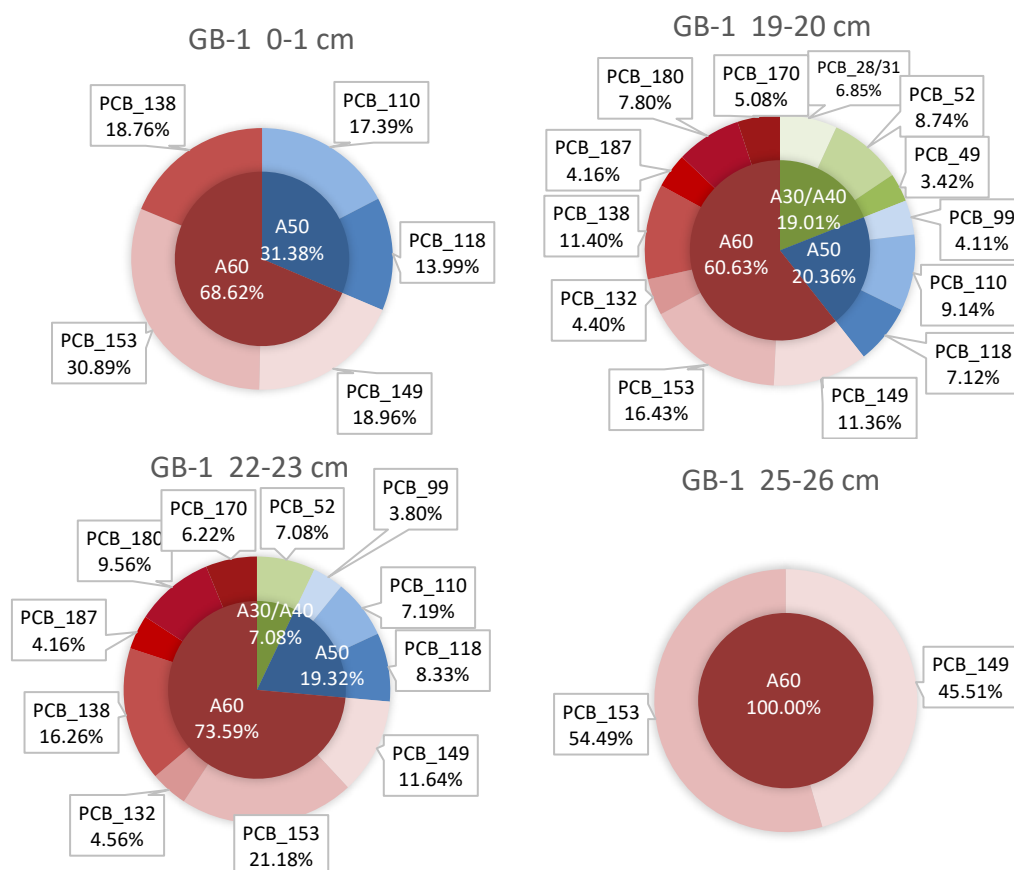


Figure 3-12 The distribution of commercial products from the typical slices in the sediment cores of GB-1 from the Gotland Basin.

These three products exhibited different combinations of PCB congeners in various slices. PCB153 and PCB149 were the major constituents of the A60 indicators. In the surface slice, seven A60 markers were detected, including PCB138, 153, and 149. At a

depth of 1-2 cm, five markers of A60 were present, excluding PCB170 and 132. All seven A60 markers were identified in the 5–6 cm slice. In the middle section of the core (10–20 cm), the combination of PCB types fluctuated, declining and then rebounding to seven. PCB153 contributed the most to the proportion. PCB118 was consistently present in every slice where A50 was detected, and PCB110 exhibited similar dominance as PCB118 as long as it was present. PCB99 was exclusively detected in the uppermost layers. In deeper slices, PCB99 was only present at 22–23 cm. PCB52 was the primary component of the A30/40 markers, see Figure 3-12.

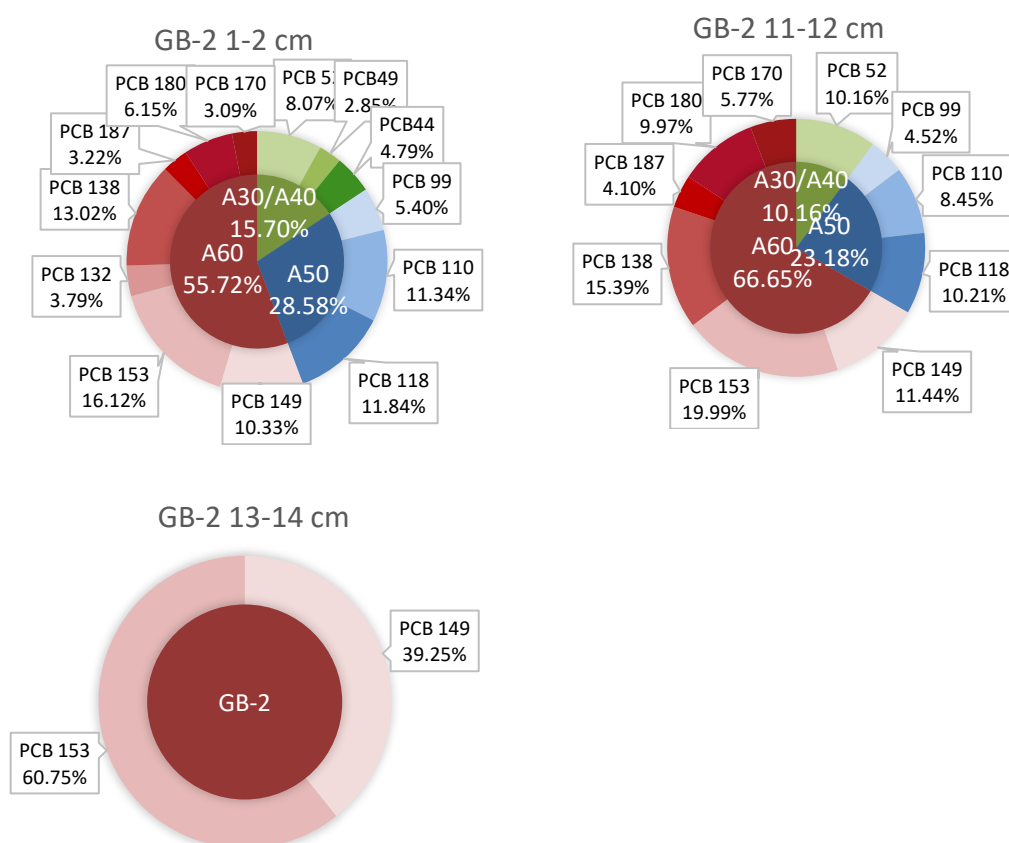


Figure 3-13 The distribution of commercial products from the typical slices in the sediment cores of GB-2 from the Gotland Basin.

In Gotland Basin, A60 was the first to be discovered and constituted the largest proportion among the three products. PCB153 was the dominant congener in the selection of 14 PCBs. A30/40 was also detected in the deepest slice of the core but disappeared in the upper two slices, reappeared in the 22–23 cm depth, disappeared once more, and ultimately persisted for an extended period. A50 was initially detected at a depth of 22–23 cm and continued to exist.

Similar results were observed in GB-2, see Figure 3-13, with the percentage distributions of each of the three products in both the upper and lower layers of the core being nearly identical. This suggests that the three PCB products shared a similar fate within this core. In the GB-2 core, the contents were ranked from highest to lowest as A60 (more than 50%), A50, and A30/40. In the 4-5 cm slice, A50 exhibited a different percentage compared to adjacent slices. In the 13–14 cm slice, only A60 was detected. PCB153 consistently dominated the composition of A60. The three PCB markers of A50 were present in slices ranging from 1 to 12 cm (except for the 4-5 cm slice) and were ranked in content as PCB118 > PCB110 > PCB99. The PCB markers of A30/40 followed a similar distribution pattern in five slices from 1 to 7 cm (except for the 4-5 cm slice) as PCB52 > PCB49 > PCB44. Each product exhibited nearly identical compositional content distribution at various depths throughout the core, indicating their similar fates over the decades.

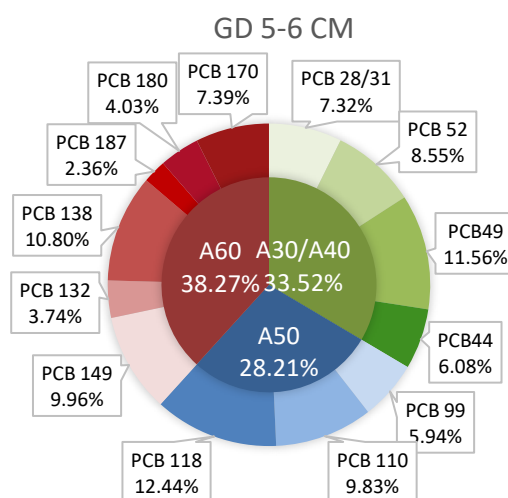


Figure 3-14 The distribution of the commercial products from the typical slices in the sediment cores of GD from the Gotland Basin.

The TF0271 core (Figure 3-14), which covered a shallower depth range (surface-10 cm), exhibited A60 as the predominant product, with A30/40 as the second major constituent throughout the entire core. Both of these products displayed minimal fluctuations in their percentage values (within 3%) from the surface to a depth of 1.5 cm. Deeper than 6 cm, A60's dominance became more pronounced (>40%), while A30/40's percentage gradually decreased with increasing depth. The proportion of A50 remained stable, ranging between 25.85% and 30.15%. All PCB indicators were detected throughout the entire ten-centimeter-depth core, with PCB153 consistently

ranking as the most predominant PCB in the entire core. This core's shallower depth allowed for relatively stable and consistent distribution patterns, aligning with the other cores from the same geographical area.

Arkona Basin

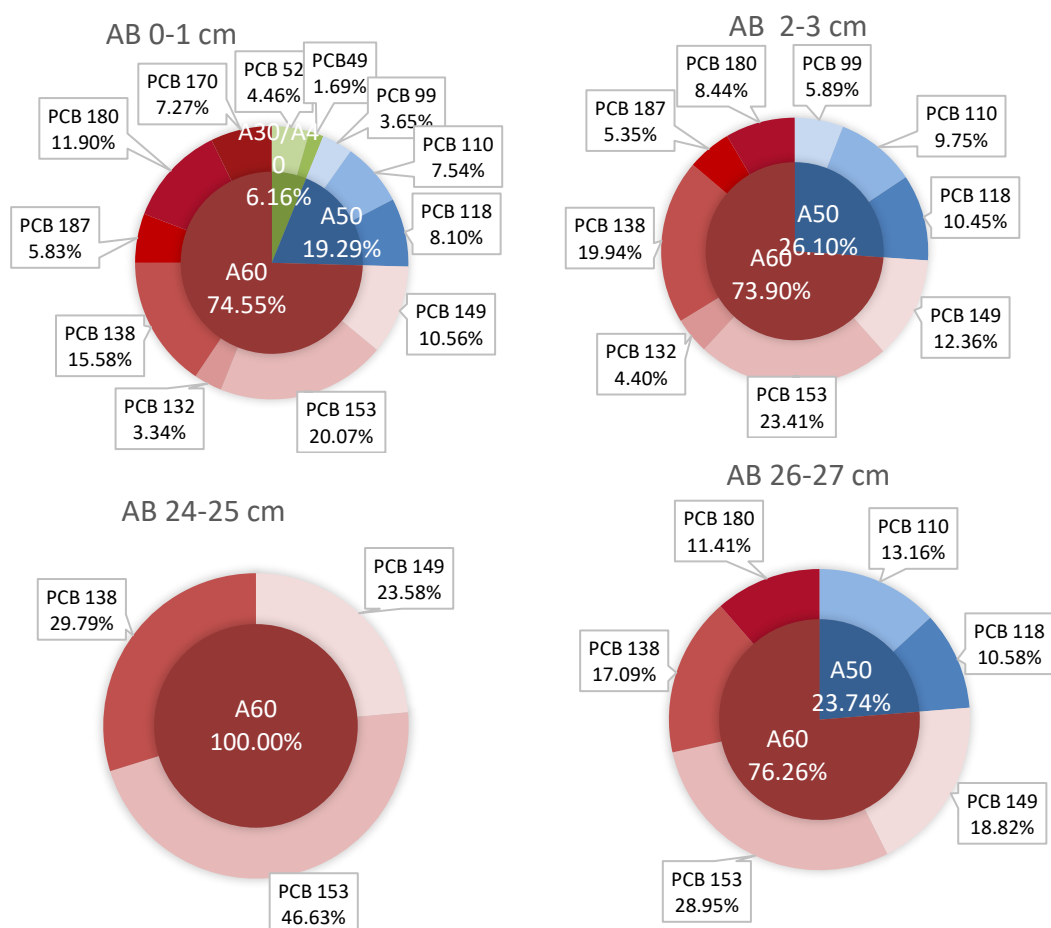


Figure 3-15 The distribution of the commercial products from the typical slices in the sediment cores of AB from the Arkona Basin.

In a sediment core sampled from the Arkona Basin, see Figure 3-15, spanning a depth of thirty centimeters, the distribution of three distinct PCB products exhibited a consistent and stable pattern. A60 emerged as the dominant product, accounting for a minimum of 58.59% throughout the entire core. The percentage of A50 fluctuated within the range of 14.22% to 26.10%. A30/A40 consistently constituted the smallest proportion in every slice. The predominant compound within this core was PCB153. In the uppermost slices (0–24 cm), nearly all seven A60 markers were detected, with the exceptions being the 1-3 cm and 7-8 cm slices, where PCB170 was absent (see

Appendix). The composition of A50 markers displayed stability similar to that of A60 markers. In the upper 24 centimeters, the percentages of PCB110 and PCB118 were comparable and exceeded that of PCB99. The primary component of A30/40 was PCB52, present in most slices except for the 2-4 cm slice. PCB49 ranked as the second-most prevalent A30/40 marker. This core's consistent and stable distribution pattern suggests a uniform fate for these PCB products across various depths, indicative of the core's historical sedimentation and PCB composition over time.

Skagerrak

Figure 3-16 illustrated the distribution of PCB products in this core, which exhibited a stable and regular pattern with respect to depth. Within the range of 0-14.5 cm, there were slight variations in the distribution. A60 dominated from slice 0.5-2.5 cm to slice 10.5-12.5 cm, with a gradual increase in percentage from 41.47% to 49.49%. A50 and A30/A40 accounted for percentages ranging from 33.25% to 39.76% and 20.41% to 17.26%, respectively. In the uppermost slices (surface to 14.5 cm), the distribution displayed small and steady fluctuations. Notably, there were differences of less than 1% among all products at depths of 6.5 cm to 12.5 cm. In slices deeper than 22.5 cm, A30/A40 constituted 100% of the composition, indicating the exclusive presence of A30/A40 in the sediment. This distinction set it apart from other cores. All seven high-chlorinated markers were detected from the surface down to 14.5 cm. PCB153 and PCB138 emerged as the dominant components of A60 in these upper cores, each constituting more than 10% of the total composition. As depth increased, the number of A60 markers decreased. In the upper nine slices (surface to 16.5 cm), three PCBs served as markers for A50, with proportions ranking as PCB118 > PCB110 > PCB99 (Figure 3-16).

Low-chlorinated PCBs, indicative of A30/A40, were found in the top eight slices (surface to 14.5 cm), with proportions arranged as PCB52 > PCB44 > PCB49. In the deeper two slices (14.5 cm-18.5 cm), PCB44 was not detected, and PCB49 did not appear in three slices (18.5 cm-24.5 cm). In this particular area, A30/A40 was the first product to be discovered. Over time, A60 gradually became the dominant component of the PCB commercial products, mirroring the patterns observed in other cores. A60, primarily composed of high-chlorinated PCB congeners, was initially detected in the 20.5-22.5 cm slice, signifying the accumulation of high-chlorinated PCBs during that

particular period in this geographical region (Figure 3-16).

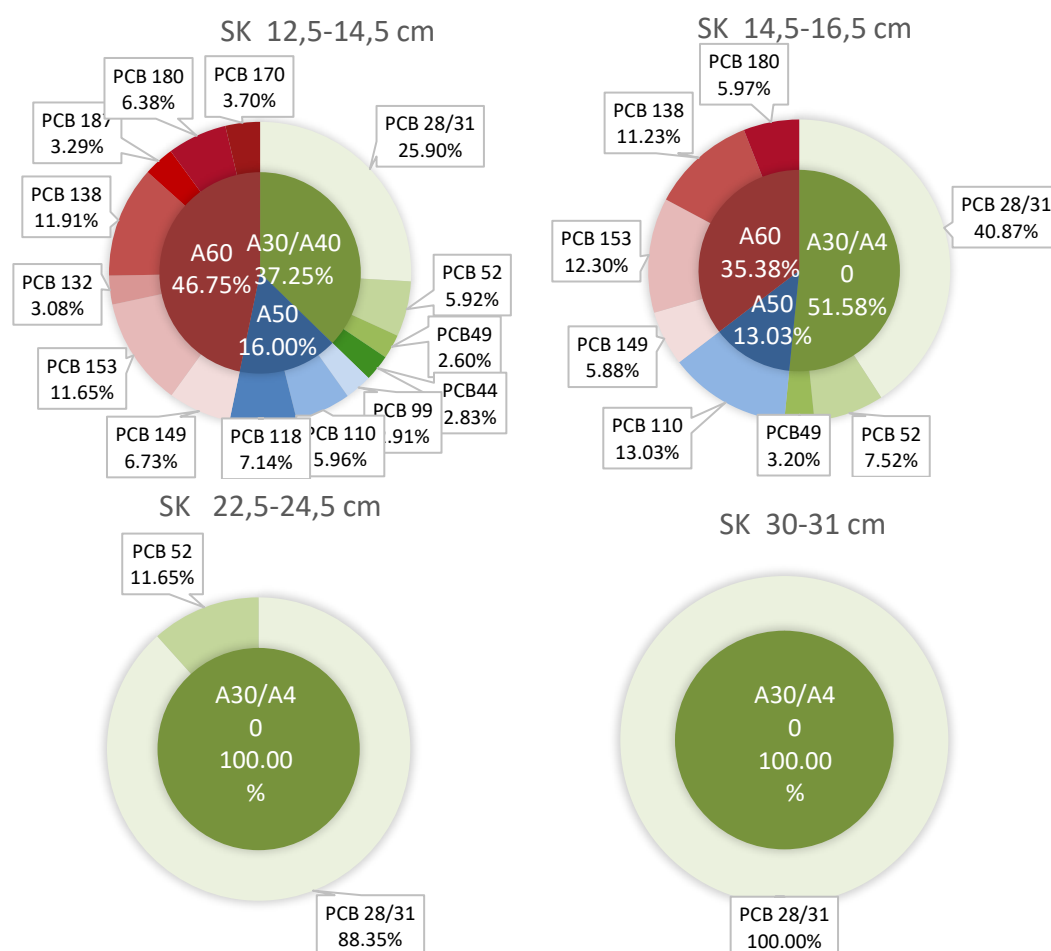


Figure 3-16 The distribution of the commercial products from the typical slices in the sediment cores of SK from the Skagerrak.

Gulf of Gdansk

In Figure 3-17, a lengthy sediment core (SP) collected from the Gulf of Gdansk was divided into 34 slices, each separated by one centimeter. From slice 15–16 cm to the surface, A60 consistently dominated as the primary product. Towards the surface, the proportion of A60 exhibited a declining trend, decreasing from 66.08% to 48.72%. An interesting observation was that A60 alternated between appearing and disappearing in the deeper 14 slices, spanning from 18 cm to 32 cm. A50 maintained a stable proportion between 18.94% and 26.11% from the surface down to 18 cm. However, A50's proportion displayed similar instability in deeper slices, reminiscent of A60. A30/A40 prevailed from 16 cm to 34 cm, indicating that A30/A40 was the predominant product in the early decades, reaching its highest proportion at 96.54% (Figure 3-17).

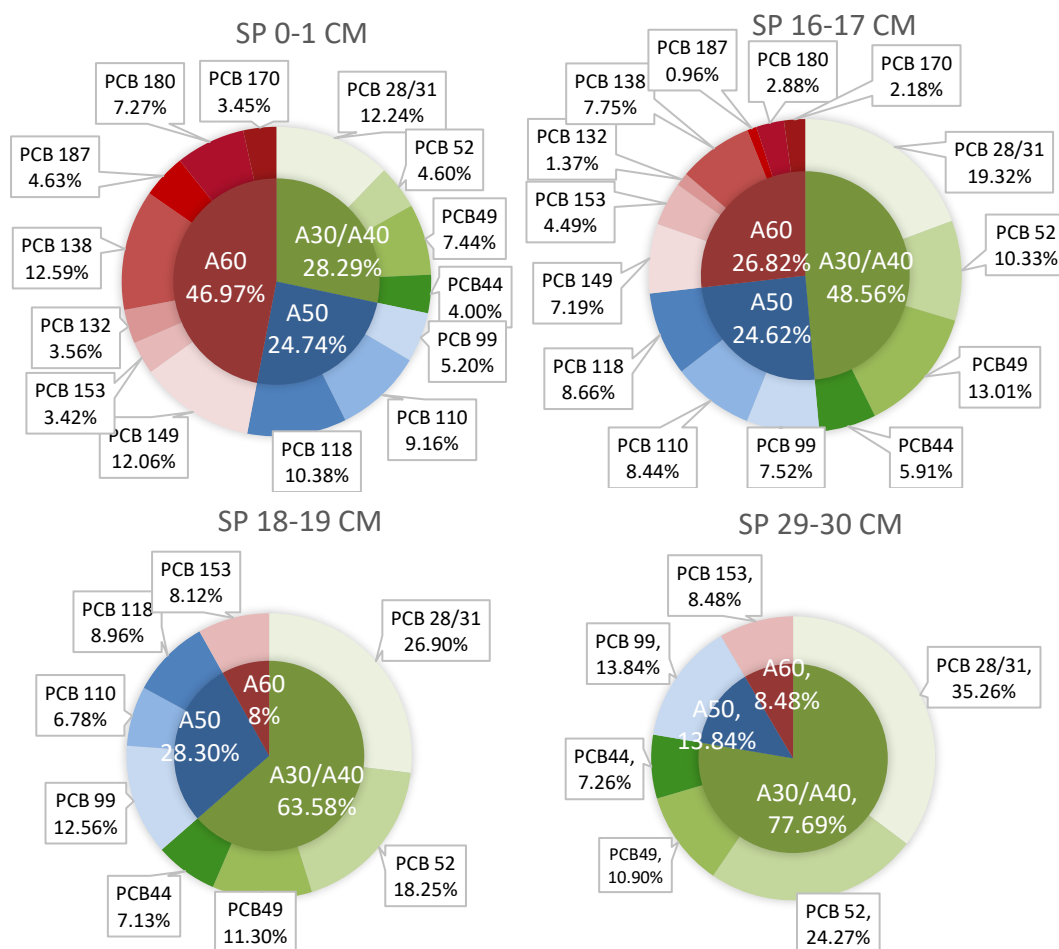


Figure 3-17 The distribution of the commercial products from the typical slices in the sediment cores of SP (Gulf of Gdansk).

The distribution of high-chlorinated PCBs remained stable from the surface slice to 17 cm, with PCB153, PCB138, and PCB149 being the three most prevalent congeners. PCB153 accounted for the largest proportion among the high-chlorinated PCB products and was consistently detected in the presence of A60. PCB149 also emerged as a significant component of A60 in this core. In several deeper and irregular slices, PCB149 constituted the majority of A60. The highest PCB concentration was observed at a depth of 6-7 cm. Consequently, contaminants were less pronounced in deeper slices and did not significantly affect the overall analysis. From the surface to 17 cm, the distribution remained stable, with PCB118, PCB110, and PCB99 serving as indicators of A50 in that order. Throughout the entire core, PCB 28/31 was the most prevalent congener among the A30/A40 indicators, except in the 30-31 cm slice. In that particular slice, the proportion of PCB49 (comprising 93.43% of all indicators) was significantly higher than that of PCB28/31 (constituting 3.11% of all indicators). In this core, A30

and A40 were the earliest products to appear. Over time, A60 gradually became the dominant product, surpassing the other two products (Figure 3-17). This trend was also confirmed by the comparison of concentration and percentage graphs.

Gulf of Finland

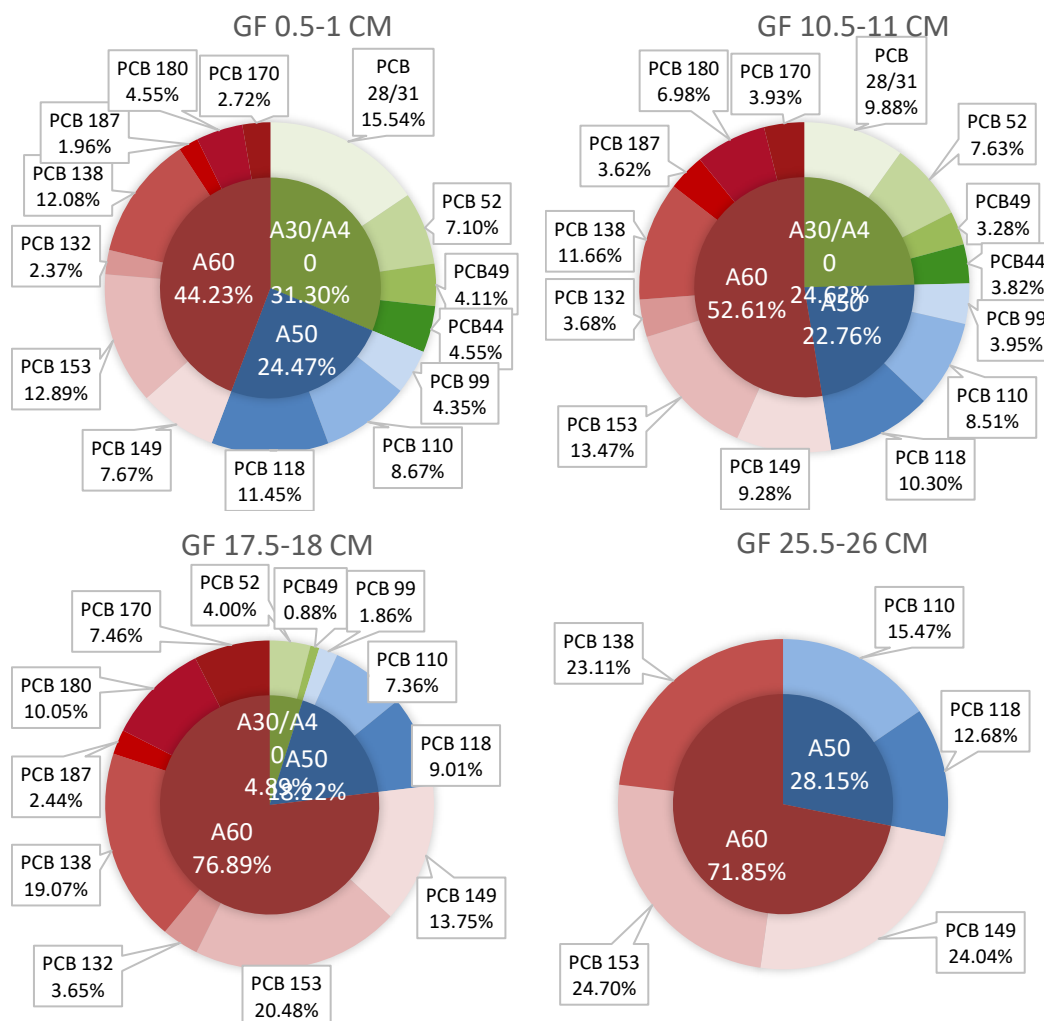


Figure 3-18 The distribution of the commercial products from the typical slices in the sediment cores of SP from Gulf of Finland.

The sediment core obtained from the Gulf of Finland was divided into intervals of 0.5 cm from the surface down to 31 cm, see Figure 3-18. The distribution of commercial products in this core closely resembled that of offshore areas rather than the patterns observed in other near-coastal stations. Three products displayed stable distribution in the upper slices (surface to 17 cm): A60 emerged as the predominant product throughout the entire core, accounting for more than 43.14% of the composition,

followed by A50 as the second most prevalent product (comprising more than 16.57%). A30/A40 consistently represented the least abundant group in the core and was not observed in the earlier years (deeper slices).

The dominance of PCB153 and PCB138 among A60 markers was consistent with findings in other cores. Among A50 markers, PCBs were detected in the following order: PCB118 > PCB110 > PCB99. The prevalence of these typical combinations in other stable cores, coupled with the diverse array of PCB congeners in this area, indicates that the sampling site GF offers valuable insights into PCB distribution in the region. This core may serve as a reference point for various future studies, not only pertaining to PCBs but also other persistent contaminants in the area (Figure 3-18).

Summary

The sediment cores displayed a consistent distribution pattern of the PCB commercial products. In all the offshore cores, the three products, Clophens A30/A40, A50 and A60, exhibited similarities, with typically a single maximum in the middle of the core. Surface slices generally contained a higher concentration of PCB mixtures compared to the deeper slices. However, in the inshore cores, the mixture contents were higher at the surface and decreased with depth. This pattern aligns with the distribution of the total of six PCB congeners in their corresponding cores.

Upon conducting analyses, it was evident that PCB commercial products exhibited a regular distribution with regard to spatial variation. In the Northern Baltic Proper and the group of stations in the Eastern Gotland Basin, A60 consistently dominated throughout the cores and was the sole product to persist in the deeper slices. A different phenomenon was observed in the Gulf of Finland, Gulf of Gdansk and the Skagerrak. A60 dominated in the upper slices, while A40 was the product that settled and remained in the deeper slices. The location of these stations played a crucial role in these findings. The regions where A40 persisted in the parts of the cores were situated near the coast, whereas stations in the Northern Baltic Proper and Eastern Gotland Basin were offshore. This suggests that low-chlorinated PCB products tend to accumulate at the bottom of cores collected in close proximity to coastal areas. Consequently, A30/A40 content was higher in coastal areas, whereas a relatively higher proportion of A60 was observed in the upper cores of offshore areas. This pattern aligns with the observations in the Gulf of Gdansk and Skagerrak, where high-chlorinated PCBs were transported over greater

distances and persist in the bottom layers of the sediment cores.

However, there was an exceptional phenomenon in the Gulf of Finland, likely due to topographic factors. Unlike the other more open regions, the Gulf of Finland is a three-sided enclosed water area, with all substance exchange occurring through a very narrow entrance. The sampling site is located at the entrance of the gulf to the open sea. As a result, PCB products have stabilized in this area compared to the near-coastal regions, and their behavior in terms of both migration and deposition over the years closely resembles that of offshore areas, particularly the Arkona Basin.

3.2.3 DDT metabolites and HCB

The distribution of DDT metabolites, specifically p,p'-DDE and p,p'-DDD, is presented in Figure 3-19. Across all selected sediment cores, it was evident that p,p'-DDD values were significantly higher than p,p'-DDE values. The distribution patterns of these two metabolites within each core exhibited similarities, which aligns with the findings of previous studies in the Baltic Sea (Moros et al., 2017; Müller et al., 1980). This pattern can be attributed to the Baltic Sea's characteristic of being partly an anoxic area. Under anoxic conditions, DDT undergoes reductive dechlorination, leading to the formation of DDD, while under aerobic conditions, it transforms into DDE (Aislabie et al., 1997). Notably, the distribution of DDE and DDD values exhibited an exception in the Arkona Basin. Station EMB058/6 displayed different results, with DDD values lower than DDE in the upper core. Across all offshore cores, a consistent distribution pattern was observed. As depicted, the concentrations of pesticide metabolites were lower in the bottom sections of the cores, increased over time, peaked in the middle of the core, and then decreased.

In most of the collected cores, the shapes of PCB distribution charts closely resembled those of DDE and DDD from the same core. DDT was found to be below the limit of detection. This observation aligns with previous studies indicating that DDT metabolites transform into DDD through reductive dechlorination in anoxic conditions (Huang et al., 2001). These results regarding DDT metabolites suggest that Baltic Sea sediment represents a relatively anoxic environment, and DDT has largely transformed into its metabolites in the Baltic Sea sediment.

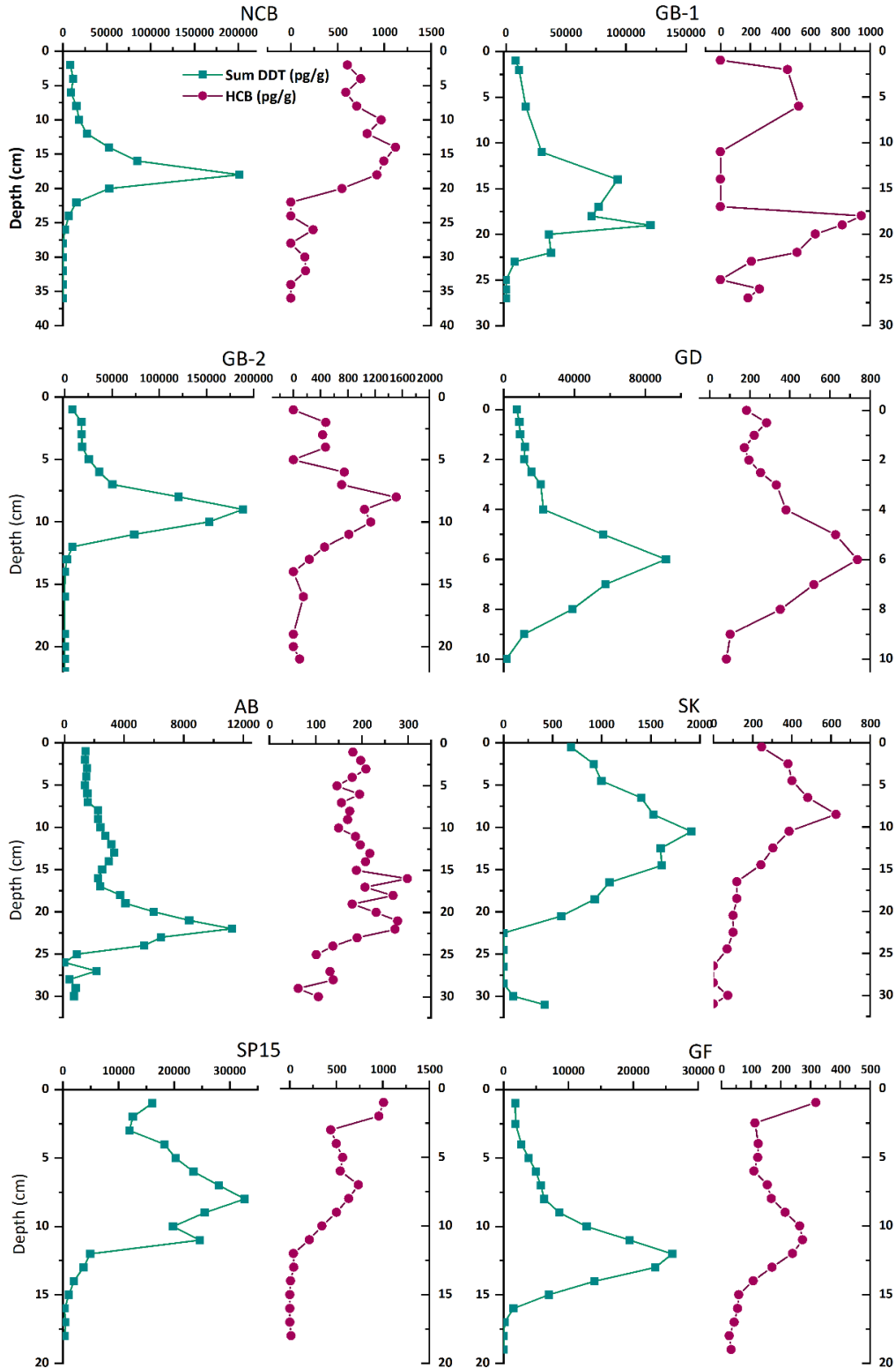


Figure 3-19 The DDT metabolites and the HCB distribution in core profiles from different areas of the Baltic Sea: GD (Gotland Deep), GB-1 (Gotland Basin-1), GB-2 (Gotland Basin-1), NCB (Northern Gotland Basin), SK (Skagerrak), SP (Gulf of Gdansk), AB (Arkona Basin) and GF (Gulf of Finland).

The distribution patterns of DDE and DDD in offshore cores underscore the fate of a chemical that was rapidly used and its subsequent decline as a result of policies and regulations. The sediment cores from the inshore coastal areas exhibited a different pattern, characterized by a secondary increase in the upper slices. Two stations in the gulf area, Gulf of Gdansk and Gulf of Finland, appeared to be influenced by pollution sources from estuaries, as contaminants were transported into the marine environment by river water and sediment.

Hexachlorobenzene (HCB), another pesticide that was rapidly used in the last century and subsequently banned in 1978 across Europe due to its high toxicity, displayed a significantly different vertical profile compared to PCBs and DDTs. HCB exhibited a moderate decrease in the concentration from maximum levels, accompanied by rebounding volatility and even an increasing trend. This phenomenon has been observed in previous studies as well and is attributed to revolatilization from other environmental matrices, such as soil (Sobek et al., 2015).

3.3 Risk assessment

3.3.1 Ecological risk assessment

Sediment quality guidelines (ERL/ERM) method

According to Table 2-4 the ERL and ERM guideline values for PCB and DDT (ng/g, d.w.), the highest concentration of total 23 PCBs in the surface sediment occurred at station P435-1-4-1-A during 2012, with a value of 16,379.26 pg/g d.w., which is below the ERM of Σ PCB, 22,700 pg/g d.w. This means, there is no ecological risk in the whole Baltic Sea based on sampling stations during the period from 1993 to 2022.

Potential Ecological Hazard Index (PEHI) method

The Potential Ecological Hazard Index (PEHI) of total PCBs (23 congeners) for the surface sediments in the Arkona Basin during the 1990s regularly registered values below 40, ranging from 0.25 to 30.58. Based on the calculations derived from Formula 2-2, the risk level associated with it was classified as "low risk".

In 2000s (Figure 3-20), the ecological risk of total PCBs related to the surface sediments was more variable, with Potential Ecological Hazard Index (PEHI) values

recorded the highest value with 58.57 at sampling station 233 in the Gulf of Gdansk, exceeding the threshold of 40 and signifying a "moderate potential ecological risk".

As depicted in Figure 3-20, the ecological risk in the Gotland Basin along the coastal area to the Gulf of Gdansk is classified as presenting a 'moderate potential ecological risk'. This assessment stems from the observation that during the risk evaluation process, the area encompassing TF0271 in the Gotland Basin and the Gulf of Gdansk exhibited a high risk profile. Consequently, it was inferred that a moderate ecological risk is likely to be present in the vicinity of both points. Additionally, two other points identified as having a moderate potential ecological risk are situated in the Mecklenburg Bight and the Kattegat region.

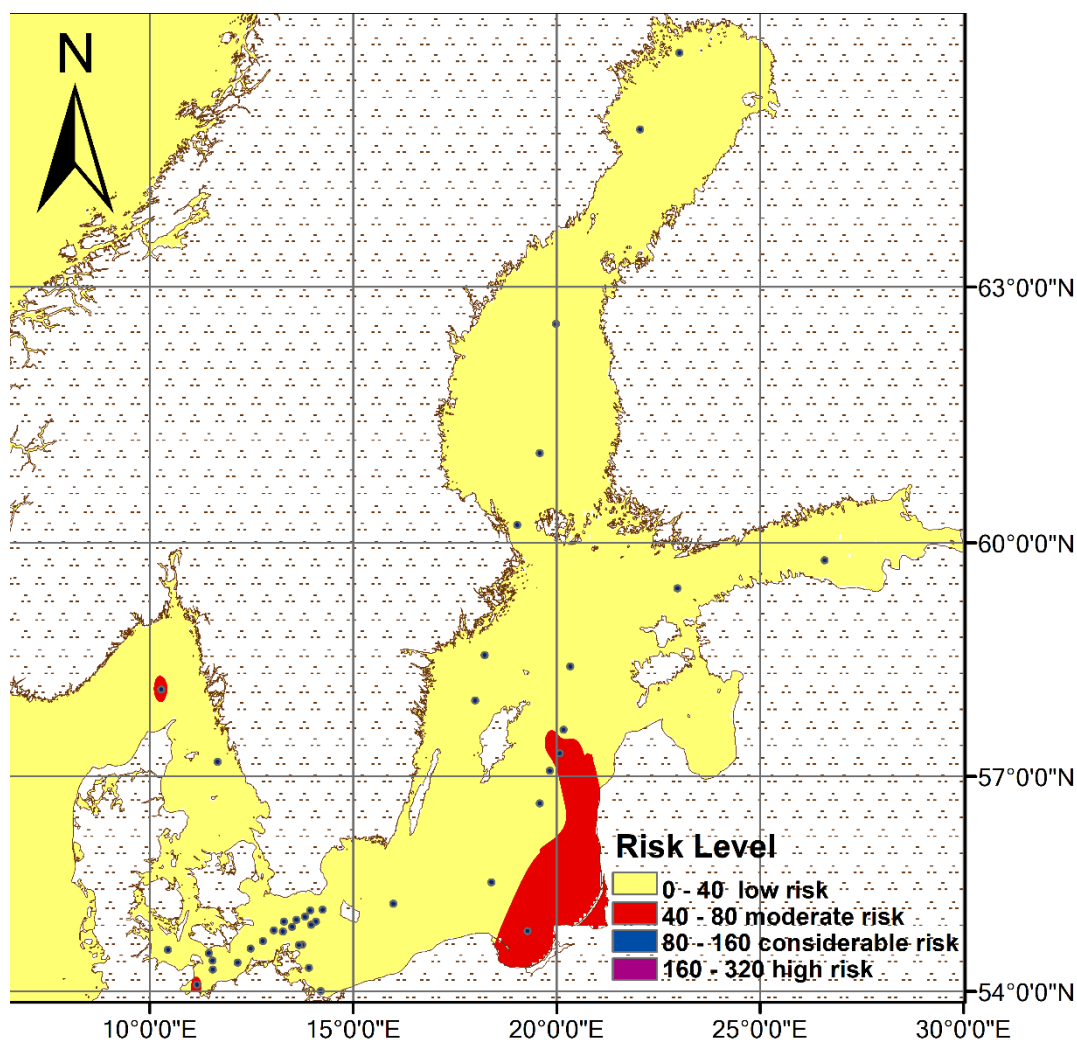


Figure 3-20 The Potential Ecological Risk levels of the total PCBs in 2000s in the Baltic Sea surface sediment.

In the 2010s, the potential ecological risk associated with total PCBs, with PERI values ranging between 0.20 and 48.12, witnessed a decline, with only two sites registering a "moderate potential ecological risk": P435-17-5-2W in the Gotland Basin and TF0069 in the Arkona Basin. The rest of the area was assessed as "low risk".

Toxicity Equivalency Factor (TEF) method

In the surface sediment, only three dl-PCB congeners were detected, PCB77, PCB 105 and PCB 118. After the calculation with WHO 2005 TEF and Equation 2-3, the TEQ maximum values of PCB77, PCB105 and PCB118 in analysed samples were 0.027 pg TEQ/g, 0.047 pg TEQ/g and 0.044 pg TEQ/g, respectively. For dioxin-like chemicals (PCDD/Fs and DL-PCBs), the NEA suggests 0.86 pg TEQ/g as the threshold level for insignificant risk in Level 1 (ecological risk alone) (Canlı et al., 2022). Therefore, there is no significant ecological risk of dl-PCBs in the surface sediment from the Baltic Sea.

3.3.2 Health risk assessment

The health risk of 23 PCBs in the surface sediments of the Baltic Sea was evaluated for both males and females using the Hazard Quotient (HQ) calculation. The highest HQ values of male and female are 1.51×10^{-7} and 1.23×10^{-7} , respectively. The results show that all of the HQ values are less than 1, indicating that there is little risk to the health of both males and females resulting from the surface sediments.

4 Summary and outlook

This study focused on several types of chlorinated hydrocarbon pollutants, including polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), and hexachlorobenzene (HCB), in the sediment samples from the Baltic Sea. Samples were collected from both core sediments and surface sediments. The main objectives of the study were to determine the concentrations of pollutants in the sediments, analyze their spatial and temporal distribution, investigate their forms of occurrence, and assess the associated risks to both, the ecological systems and the human health.

Results indicate that PCB153 concentrations in the surface sediment varied spatially. Overall, higher concentrations were observed in the central and the southern regions compared to the north. This is attributed to lower emissions in the north, while the central and southern regions, with higher population density, increased industrial activities, numerous ports, river inflows, experienced more significant pollutant discharges, leading to heightened pollution. Notably, during the 2000s and 2010s, offshore regions generally exhibited elevated concentrations, except for the Bay of Mecklenburg, where coastal areas had higher pollutant concentrations.

Spatial distribution of DDD and DDE in the Baltic Sea sediments showed consistency across the decades. In the 1990s, higher concentrations were observed in the Bay of Mecklenburg, with TF0069 exhibiting a unique DDD/DDE profile. In the 2000s, northern regions had elevated concentrations, while the Bornholm Basin showed higher DDD levels. In the 2010s, concentrations remained high in the main Baltic Sea, particularly offshore and in the Bay of Mecklenburg coastal areas. TF0030 exhibited lower concentrations, possibly due to its proximity to a sill formation.

In addition, long-term monitoring at six Arkona Basin stations (Oder, TF0012, TF0010, TF0030, TF0069, and TF0110) reveals varying trends in PCB concentrations. Oder saw a rise and fall, peaking in 2012, followed by lower concentrations post-2017. TF0012 exhibited two maxima around 2008 and 2019, with a decline afterward. TF0010 showed a decline since 1993, with a notable maximum in 2012. TF0030 witnessed a continuous decrease until 2011, spiking in 2012. TF0069 showed fluctuations, but an overall decline from 1993 to 2020. TF0110 had maximum in 2003, declining thereafter. TOC trends generally followed PCB patterns. The decline in PCB concentrations post-2017 aligns with MBI events and shipping accidents near the

monitoring stations, emphasizing the need to understand their interactions for a comprehensive assessment of the Baltic Sea pollution dynamics. The overall declining trend is also associated with the ban and internationally introduced rules, monitoring and action by HELCOM, indicating that these measures have played a fundamental role in the environmental protection in the Baltic Sea.

The surface sediment inventory for total 6 PCBs at 1 cm depth in the Baltic region is 1.69 ± 0.69 tons; DDTs and HCBs reach 1.05 ± 0.34 tons and 0.19 ± 0.06 tons, respectively. These results indicate a significantly higher concentration compared to PCB levels in the Baltic Sea water column. The calculations were carried out for the entire water volume of the Baltic Sea (21630 km³).

The concentrations of PCBs, DDTs and HCH in seawater have been measured annually in the IOW's long-term monitoring program since 2001 (Schulz-Bull, pers. comm.). A distinction is made between the dissolved water phase and suspended particles.

Slightly higher concentrations of POPs are found in the western Baltic Sea and in the Oder catchment area than in the central and northern Baltic Sea. However, the differences in the concentrations of the investigated components in the seawater of the Baltic Sea are not very large. PCBs 28/31 and 52 dominate in the dissolved phase, PCBs 138 and 153 in the particulate phase. The proportion of the particulate phase is often higher than the dissolved concentrations in the shallower regions of the Baltic Sea. This was measured particularly in storm situations and intensively mixed water columns. Table in Appendix summarizes the concentrations (pg/dm³) and calculations for the western Baltic Sea (MB - BB) and central Baltic Sea (GB).

The POPs in the water phase are influenced by resuspension and mobilization of the components from the surface sediments. The compositions of the particulate phase correspond to the relative compositions of the sediments.

The organically rich deeper sediments in the Baltic Sea are the dominant sinks for POPs. Their actual contents exceed the quantities in the water phase by 2-3 orders of magnitude.

Thus, sediments play a crucial role as primary sinks for stable organic pollutants in the Baltic Sea.

Eight sediment core samples were analyzed, and the results showed a regular vertical pattern of pollution dispersion. PCB concentrations usually showed an increasing trend in the upper layers of the core, with a maximum at a certain depth in

the mid-core. PCB concentrations steadily declined with depth, eventually reaching insignificant levels in deeper layers. This result emphasizes how well sediment profiles from the Baltic Sea may be used to depict temporal changes in the contaminant levels, particularly PCBs.

Furthermore, the sediment cores consistently revealed the distribution pattern of PCB commercial products, such as Clophens A30/A40, A50, and A60. The offshore cores showed similarities with a single maximum in the middle, while inshore cores exhibited higher surface concentrations. A60 dominated in the Northern Baltic Proper and Eastern Gotland Basin, persisting in deeper slices. In the Gulf of Finland and Kattegat, A60 dominated at the surface, and A40 settled in deeper slices. The coastal areas showed higher A30/A40 content, while offshore areas had a higher proportion of A60. Exceptions occurred in the Gulf of Finland due to topography, resembling offshore behavior. Overall, the PCB products exhibited regular spatial variation, influenced by proximity to the coasts and topographic features like enclosed water areas.

Three methods were employed to assess the ecological risk of PCBs. The ERL and ERM guidelines and the TEF method. They indicated no ecological risk in the Baltic Sea surface sediments. However, the PEHI method revealed ecological risks associated with PCBs, particularly during the 2000s. The Hazard Quotient calculations demonstrated that the Baltic Sea surface sediments pose no risk to human health.

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[https://doi.org/10.1016/S0269-7491\(00\)00180-9](https://doi.org/10.1016/S0269-7491(00)00180-9)

Appendix

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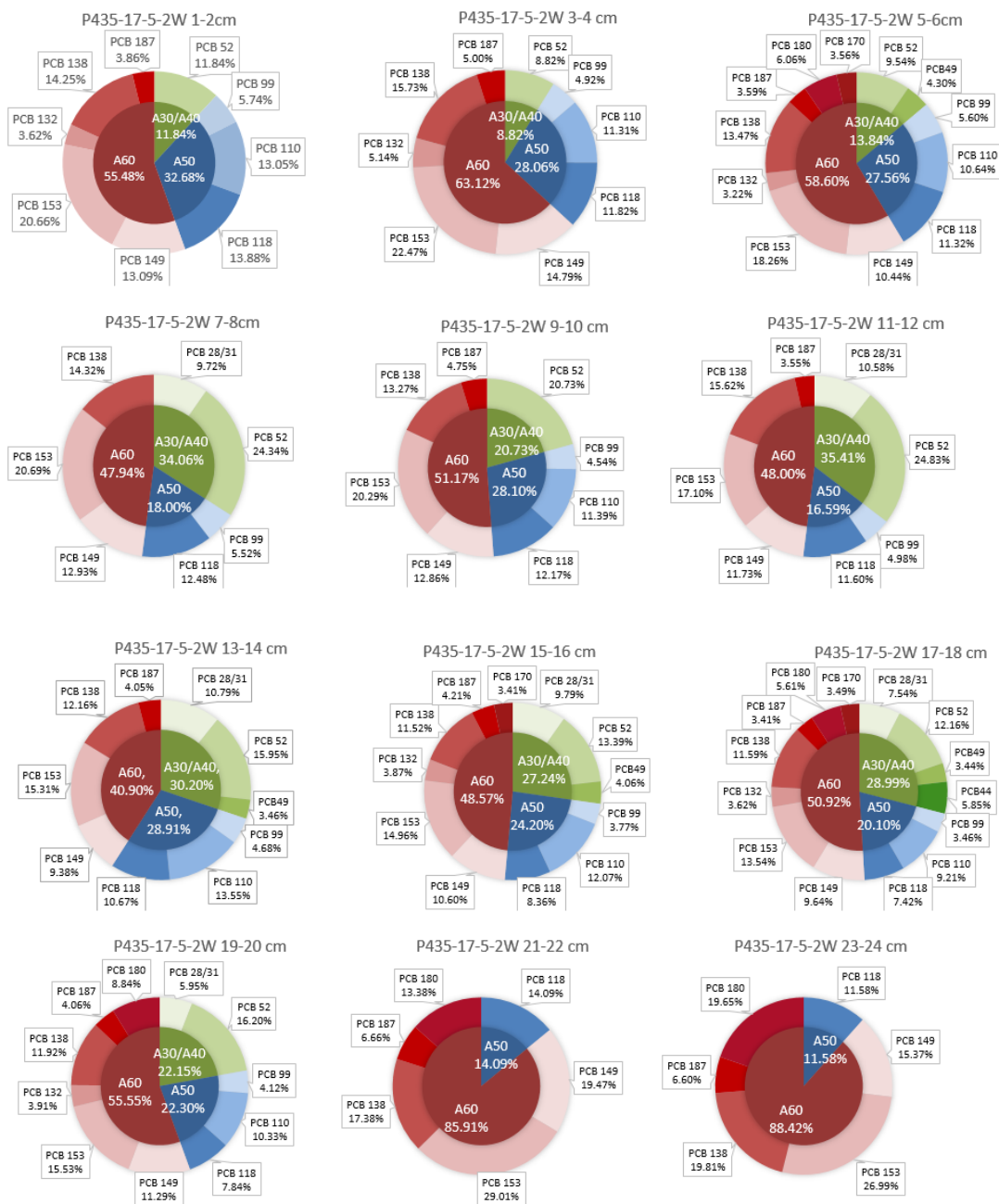


Figure S1. (continued)

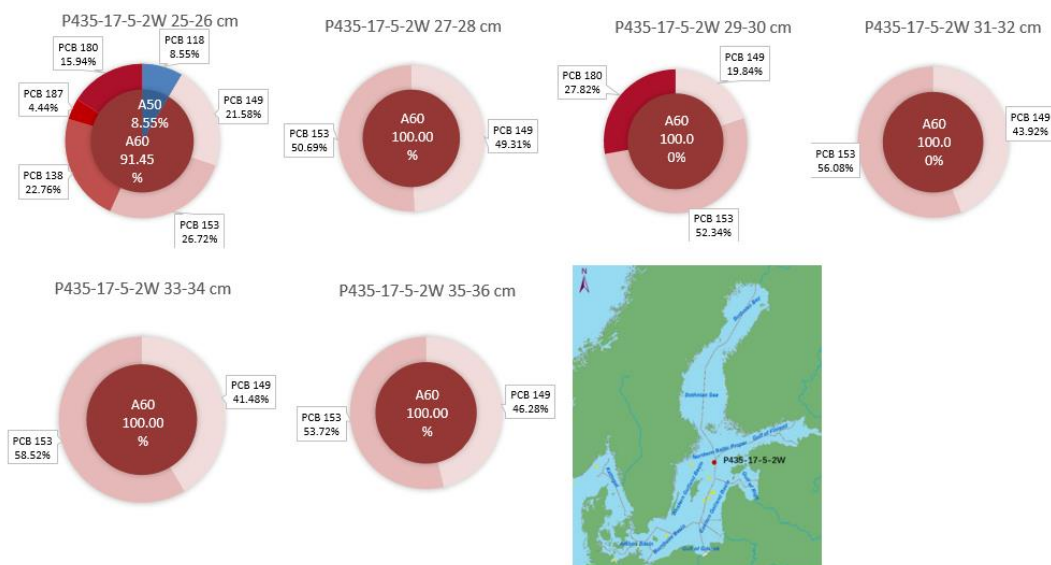


Figure S2. The distribution of the commercial products from all the slices in the sediment cores P435-17-5-2W (NCB).

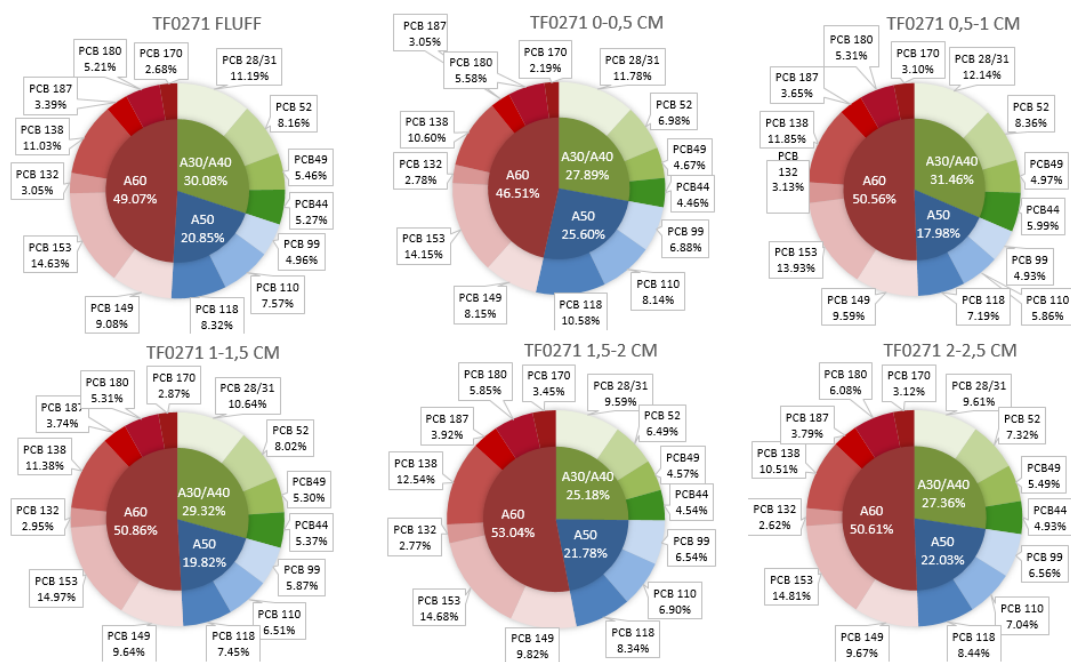


Figure S3. (continued)

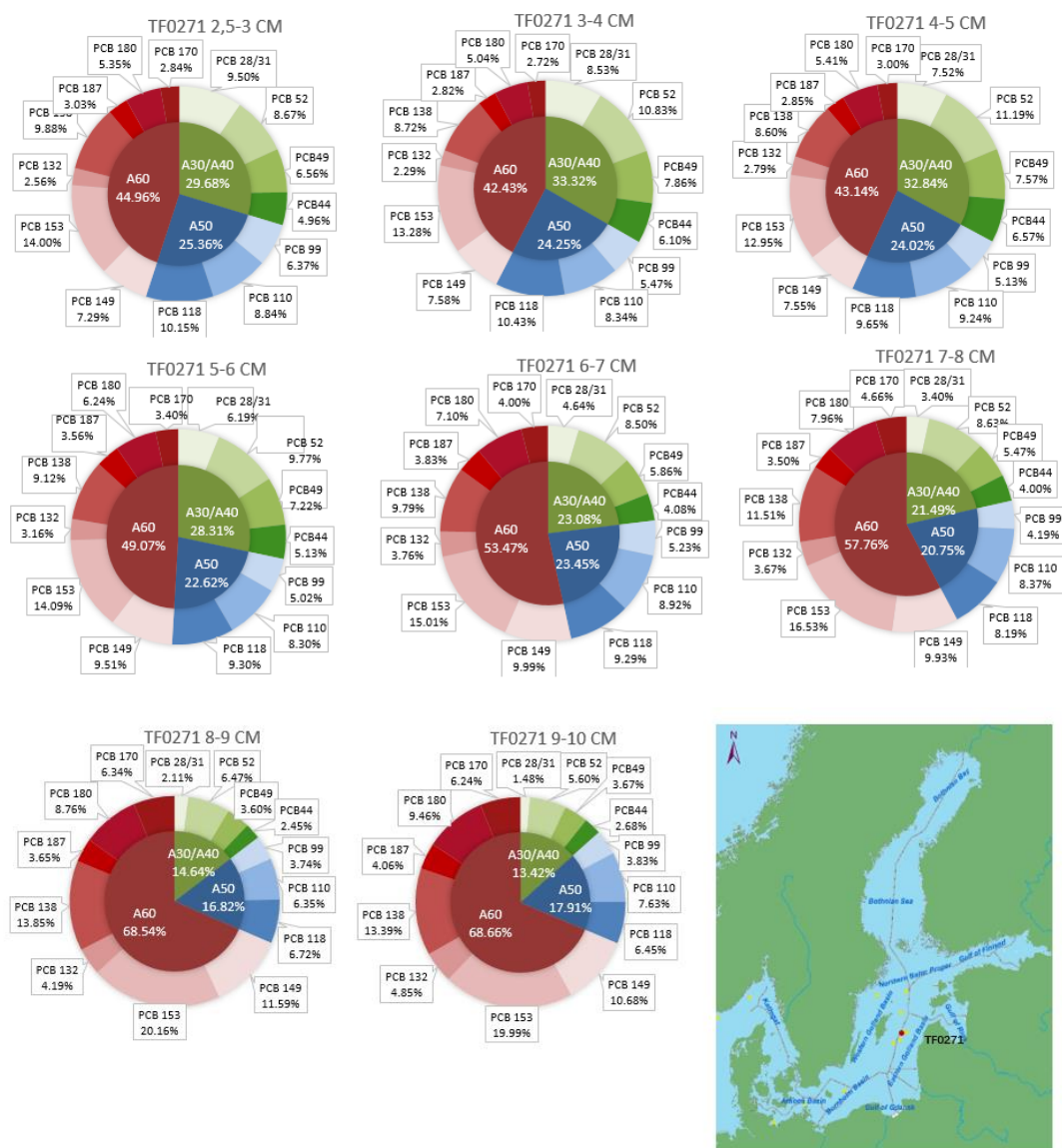


Figure S4. The distribution of the commercial products from all the slices in the sediment cores TF0271 (GD).

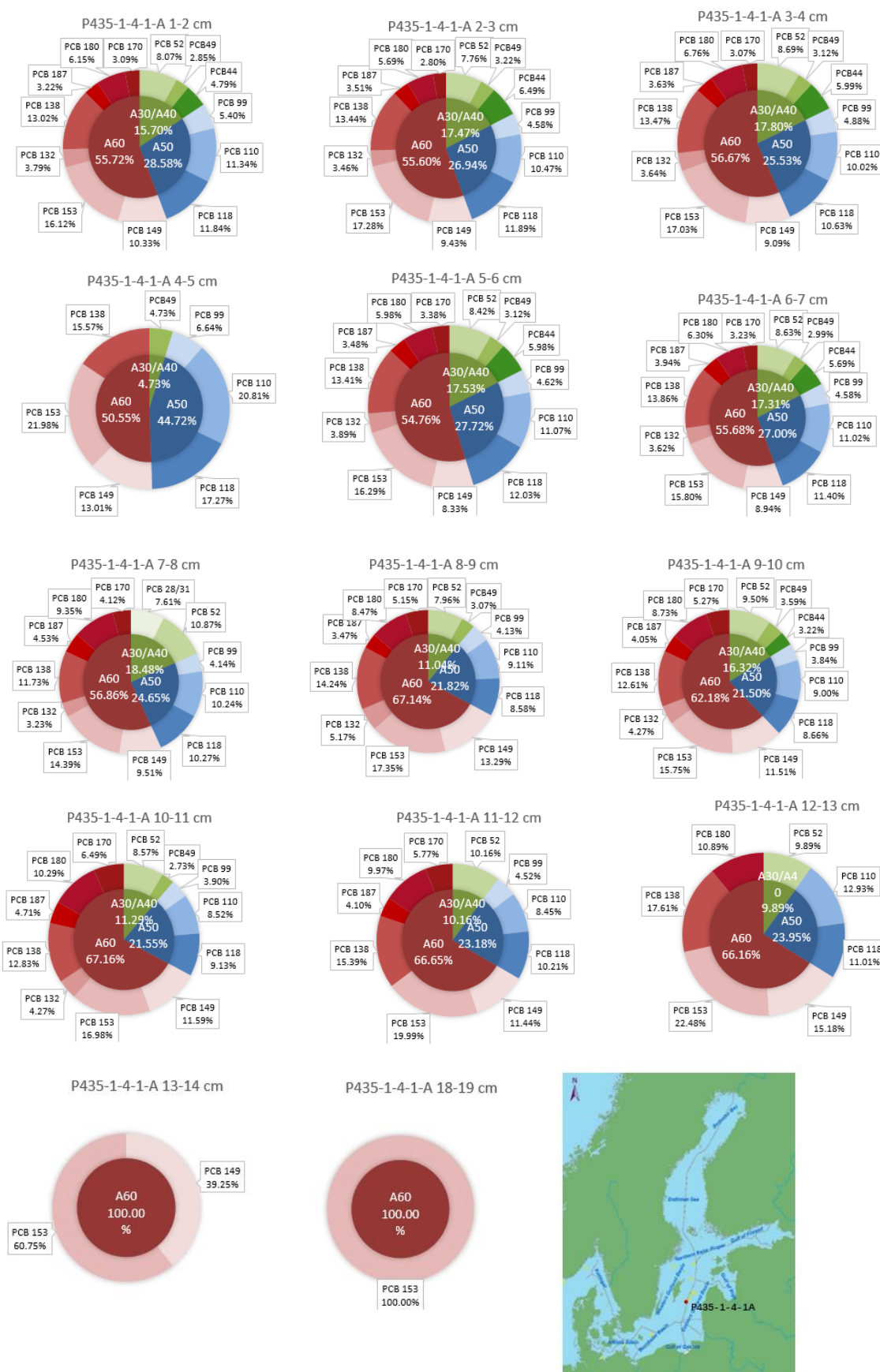


Figure S6. The distribution of the commercial products from all the slices in the sediment cores P435-1-4-1A (GB2).

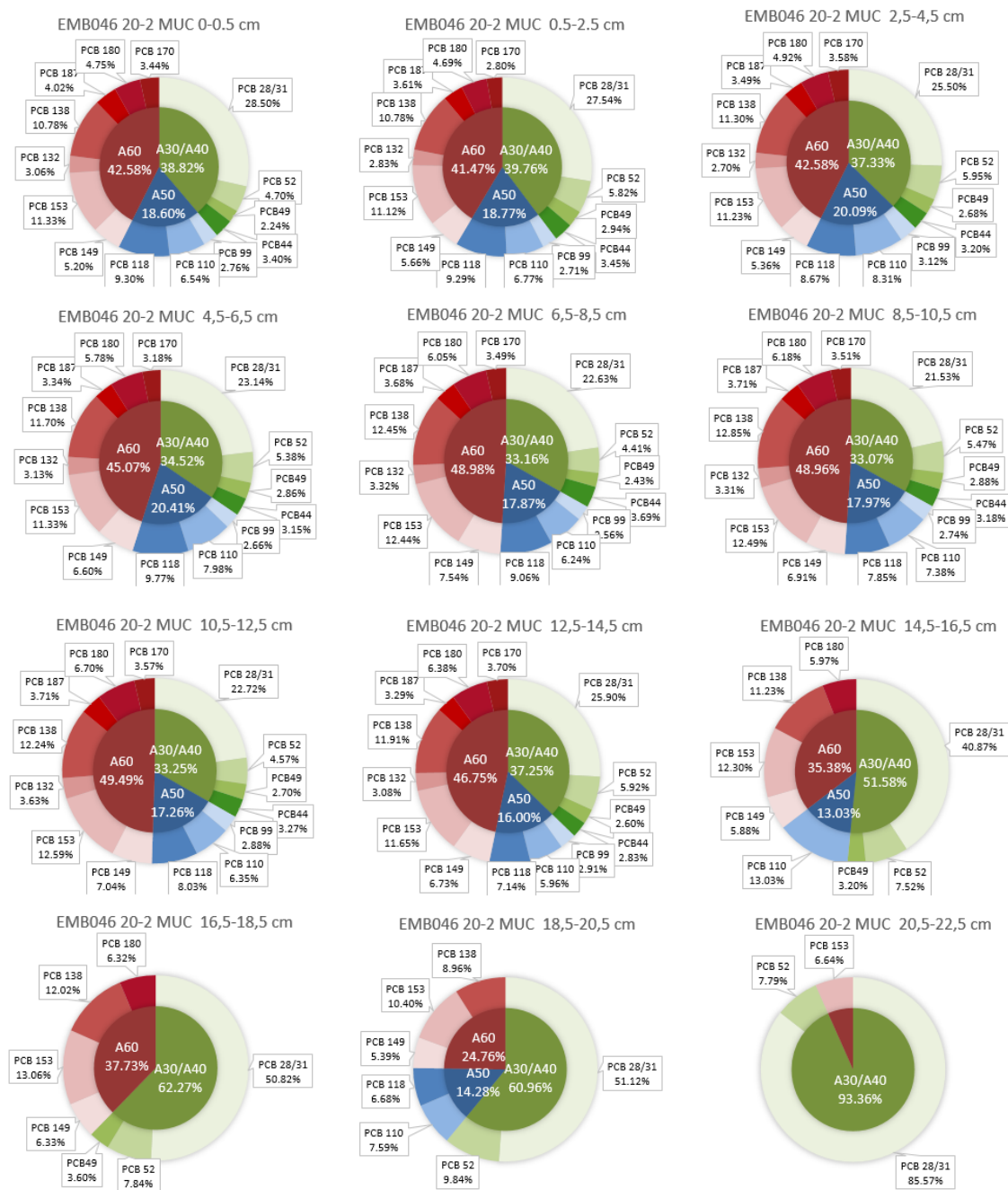


Figure S7. (continued)

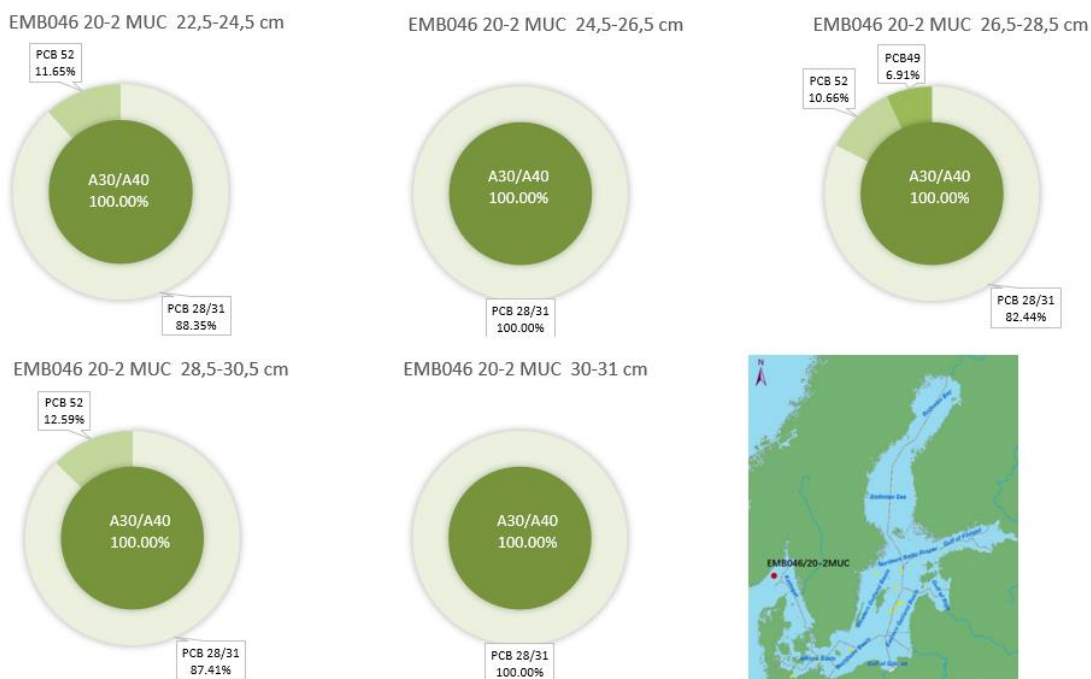


Figure S8. The distribution of the commercial products from all the slices in the sediment cores EMV046/20-2MUC (SK).

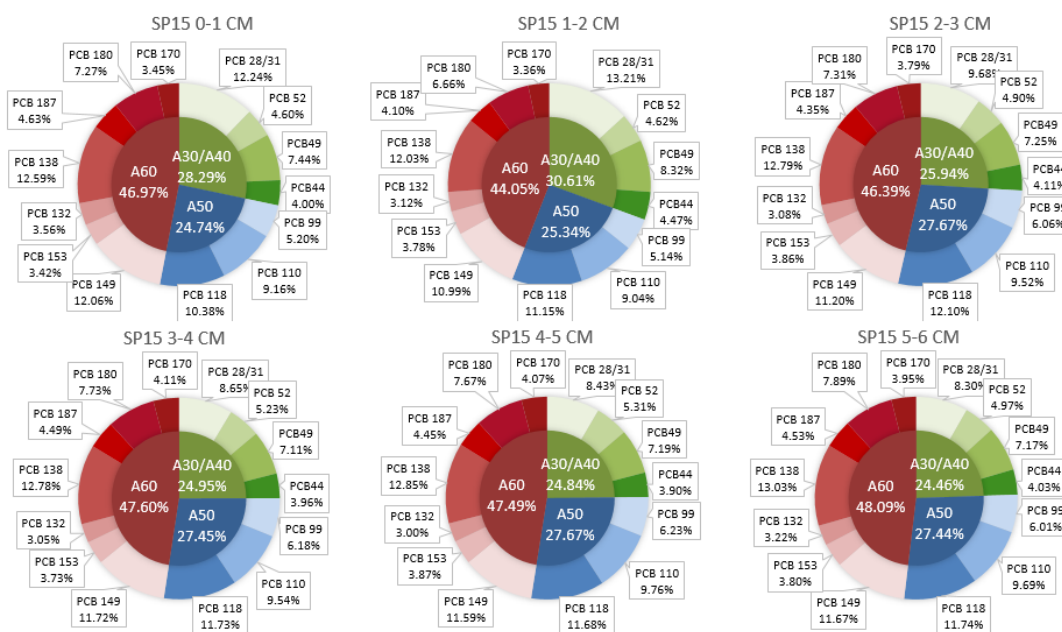


Figure S9. (continued)

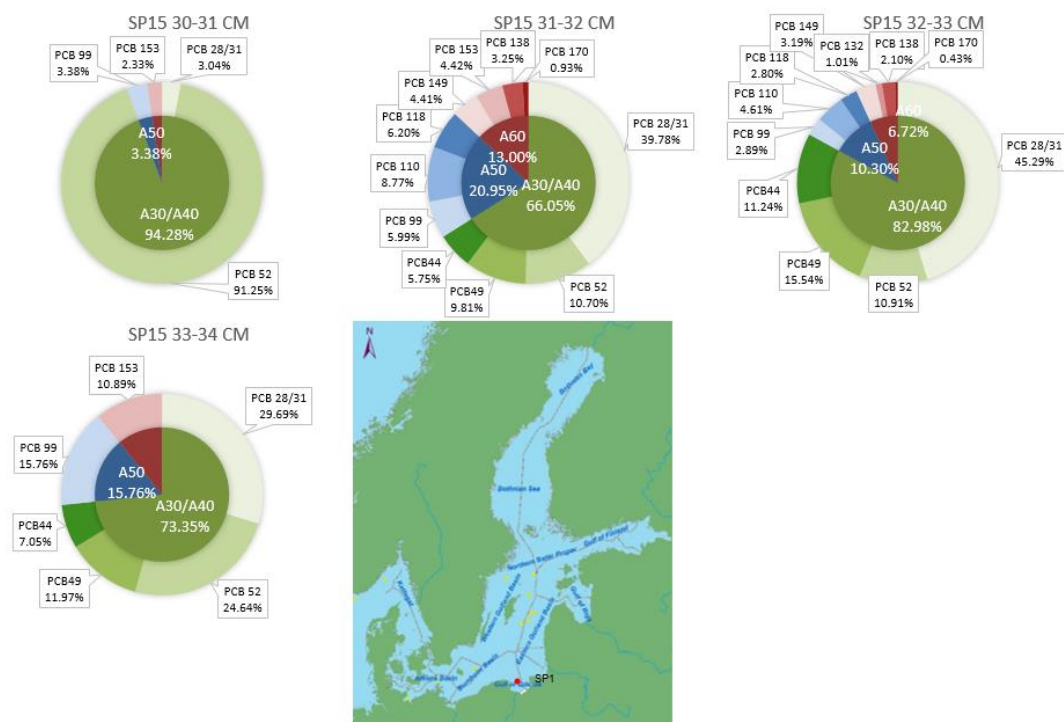


Figure S12. The distribution of the commercial products from all the slices in the sediment cores SP15 (SP) in Gdansk.

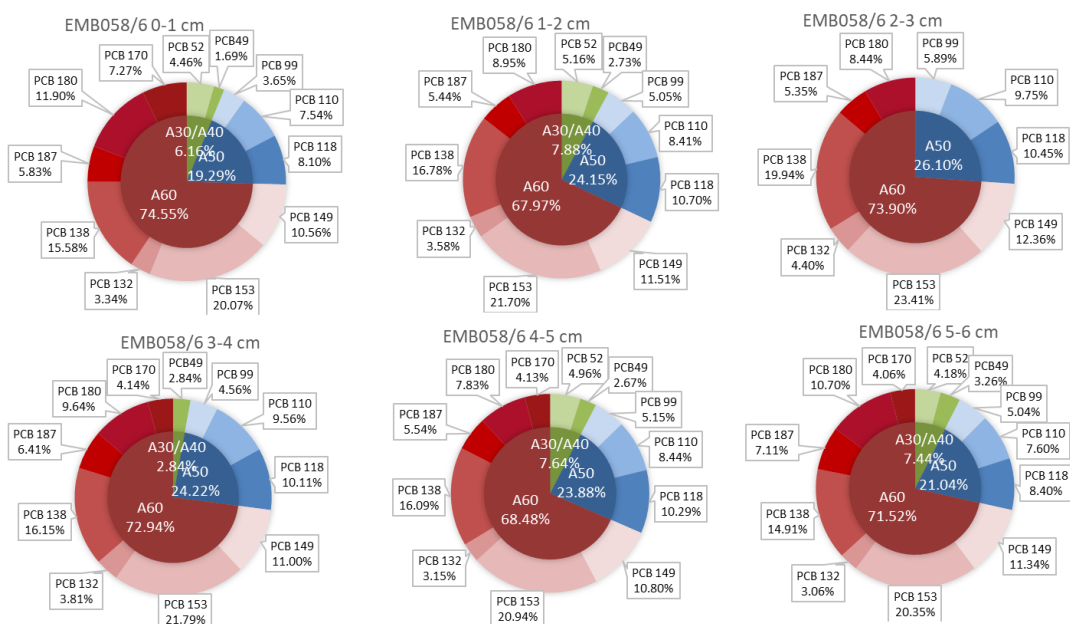


Figure S13. (continued)

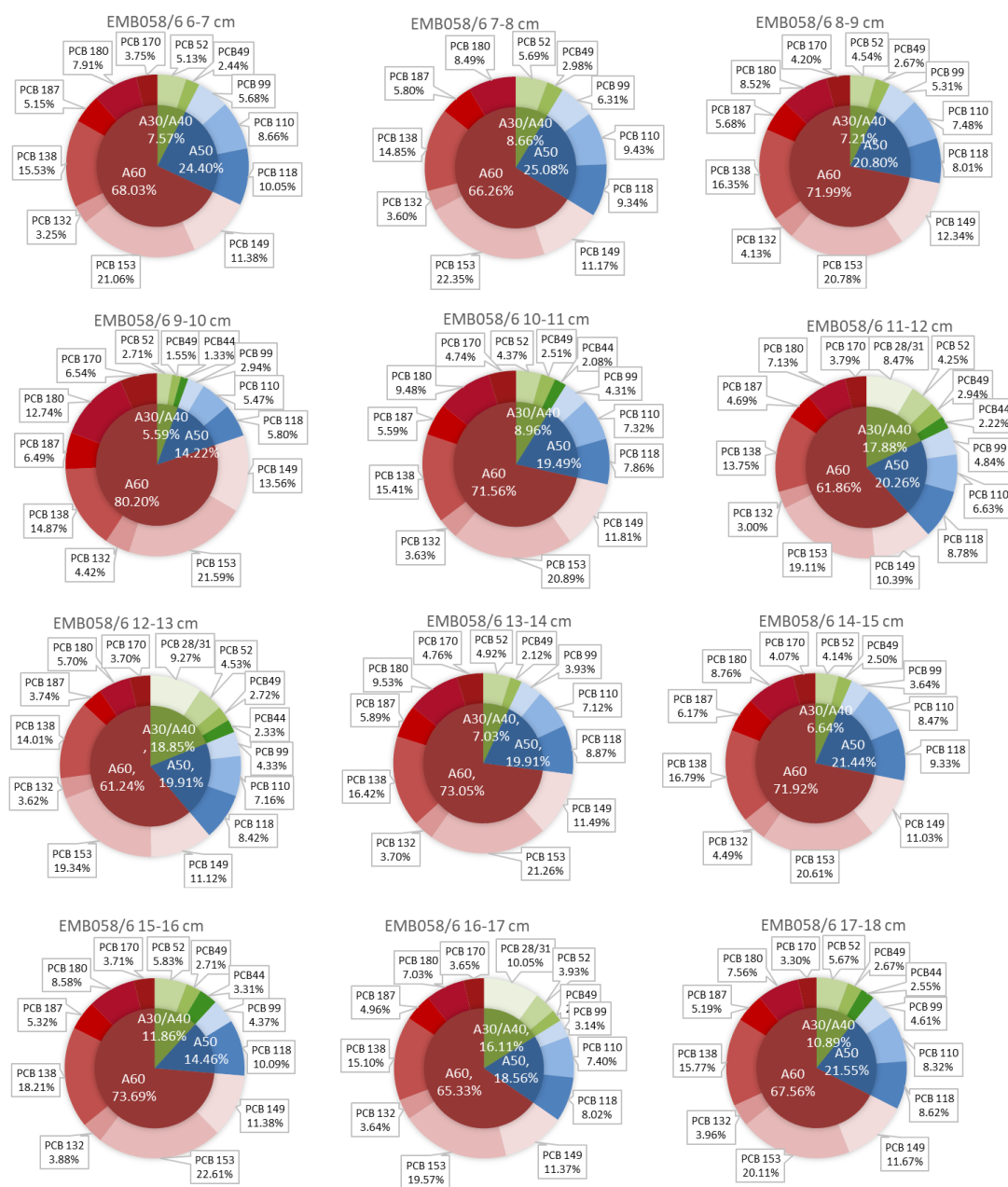


Figure S14. (continued)

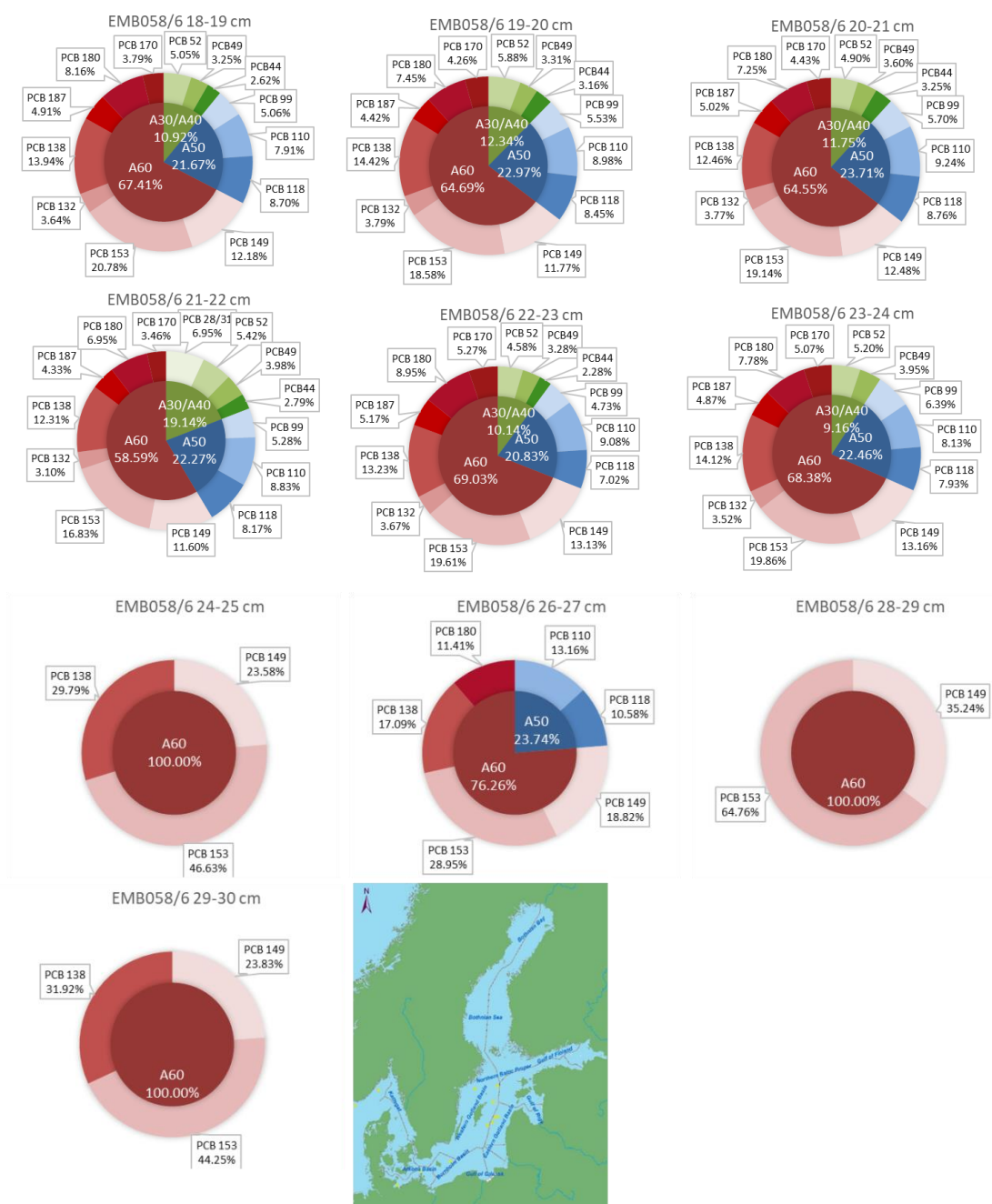


Figure S15. The distribution of the commercial products from all the slices in the sediment cores EMB058/6 (AB).

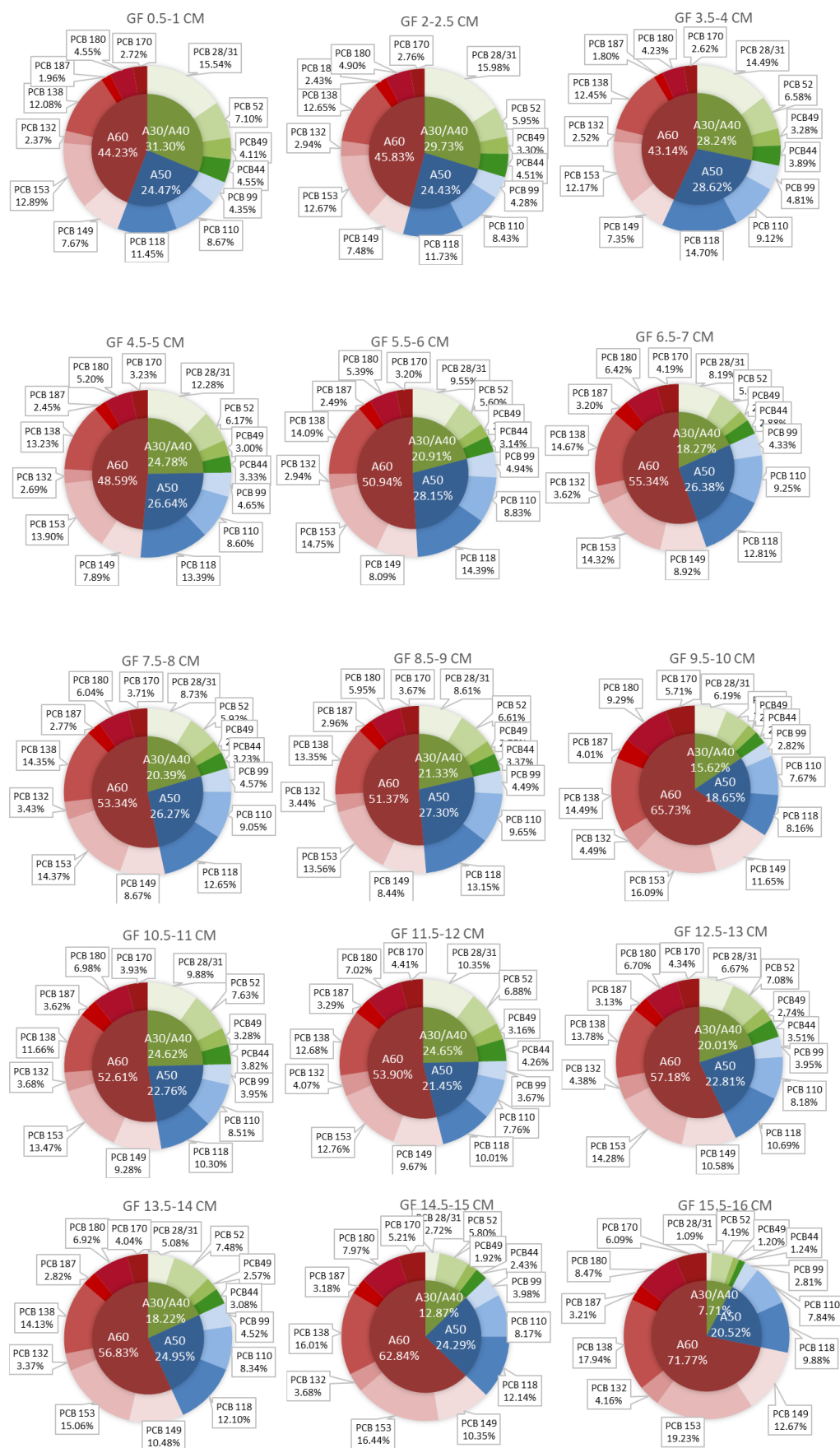


Figure S16. (continued)

Appendix

94	No.50	47°11'N 134°56'E	TF015	02	2014	0.07	Surface	9.5	156	198	160	628	413	0.0	42.2	54.1	31.8	37
53	No.51	54°16'N 134°56'E	TF014	02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
54	No.52			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
55	No.53			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
56	No.54			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
57	No.55			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
58	No.56			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
59	No.57			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
60	No.58			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
61	No.59			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
62	No.60			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
63	No.61			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
64	No.62			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
65	No.63			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
66	No.64			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
67	No.65			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
68	No.66			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
69	No.67			02	2008(F+E)	6.50	Surface	206.9	4300	6196	6163	1199.8	1199.8	5827.9	1868.1	1697.7	866.9	
70	No.68	54°15.5'N 134°56'E	TF013	02	2008(F+E)	6.40	Surface	94.2	306.0	358.2	877.0	370.7	370.7	2186.4	972.3	1718.5	483.7	
71	No.69	55°15'N 134°56'E	TF015	02	2008(F+E)	6.40	Surface	120.2	486.8	490.7	574.6	794.4	794.4	4491.2	1185.8	1361.6	483.7	
72	No.70	55°15'N 134°56'E	TF014	02	2008(F+E)	5.90	Surface	100.6	333.8	395.2	688.2	760.3	760.3	4209.0	1040.0	1654.3	561.0	
73	No.71	55°15'N 134°56'E	TF012	02	2008(F+E)	5.30	Surface	36.0	143.3	199.7	199.1	307.6	307.6	1746.3	677.7	1084.2	409.8	
74	No.72			02	2008(F+E)	5.70	Surface	103.5	283.8	365.7	313.6	423.4	423.4	3405.0	1334.9	1538.5	728.6	
75	No.73			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
76	No.74			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
77	No.75			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
78	No.76			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
79	No.77			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
80	No.78			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
81	No.79			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
82	No.80			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
83	No.81			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
84	No.82			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
85	No.83			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
86	No.84			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
87	No.85			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
88	No.86			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
89	No.87			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
90	No.88			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
91	No.89			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
92	No.90			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
93	No.91			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
94	No.92			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
95	No.93			02	2008(F+E)	5.8	Surface	74.1	245.9	322.9	334.1	423.4	423.4	3405.0	1334.9	1538.5	728.6	
96	No.94	33°01'N 182°4'E	TF029	06	2008	2.42	Surface	357.84	0.00	366.88	155.62	43.71	484.59	173.68	0.00	151.08	536.71	536.71

Number	Station	Cause No.	Year	Depth	TOC%	HCB	PCB 28/29	PCB 52	PCB 54	PCB 99	PCB 110	PCB 77	PCB 151	PCB 149	PCB 118	PCB 146	PCB 153	PCB 152	PCB 105	PCB 138	PCB 187	PCB 189	PCB 128	PCB 177	PCB 180	PCB 170	PCB	pp-DDT	pp-DDT			
No.95	5F38N 1935E	TF0280	06	Surface	9.77		1749.6	819.8	PCB44	PCB95	PCB 101	PCB 99	PCB 110	PCB 77	PCB 151	PCB 149	PCB 118	PCB 146	PCB 153	PCB 152	PCB 105	PCB 138	PCB 187	PCB 189	PCB 128	PCB 177	PCB 180	PCB 170	PCB	pp-DDT	pp-DDT	
No.96	5F43N 1949E	TF0272	06	Surface	13.19		756.6	714.0			1341.3				1145.0		1145.0		2160.4		1768.3				894.8							
No.97	5F48N 1949E	TF0272	06	Surface	13.75		802.7	859.0			1351.0				1183.1		1183.1		2339.4		2339.4				976.9							
No.98	5F48.3N 204.6E	TF0271	06	2-4 cm	9.20		746.8	453.37			1351.0				1183.1		1183.1		2339.4		2339.4				976.9							
No.100	204.6E		06	4-8 cm	9.02		403.85	334.83			1351.0				1183.1		1183.1		2339.4		2339.4				976.9							
No.101			06	8-10 cm	11.05		457.17	1071.55			1351.0				1183.1		1183.1		2339.4		2339.4				976.9							
No.102			06	Surface	12.075		800.0	759.6			1370.5				1227.2		1227.2		2279.1		1809.1				1157.6							
No.103	5F39N 1949E	TF0270	06	Surface	12.306		899.8	939.6			1391.4				1349.4		1349.4		2122.5		1809.1				1023.9							
No.104	5F39N 1949E	TF0285	07	Surface	5.77		504.10	279.81			323.19				297.31		297.31		769.30		658.71				84.71							
No.105	5F39N 1949E	TF0284	07	Surface	8.175		552.5	394.3			797.7				701.8		701.8		1434.6		1335.1				619.2							
No.106	5F39N 1949E	TF0240	06	Surface	0.1		13.8	< 10			9.8				< 10		< 10		19		26.2				8.5							
No.107			06	Surface	0.16		30.9	19.2			19.4				29.9		29.9		97.0		71.4				50.0							
No.108			06	Surface	0.14		16.1	15.8			10.5				11.0		11.0		23.0		17.3				15.2							
No.109			06	Surface	0.35		10.3	173.0			124.8				92.9		92.9		121.0		105.0				71.4							
No.110			07	Surface	0.13		39.3				29.2				27.6		27.6		29.2		27.6				69.0							
No.111	5A038N 14120E	O08	06	Surface	0.24		31.5	73.7			139.8				154.1		154.1		273.5		273.5				159.8							
No.112			03	Surface	0.27		32.2				35.9				29.3		29.3		22.2		29.3				20.4							
No.113			02	Surface	0.13																											
No.114			02	Surface	0.203		27.5	15.9			8.7				13.9		13.9		30.4		20.0				13.9							
No.115			02	Surface	0.44		37.75	24.38			39.21				25.17		25.17		11.33		56.05				nn							
No.116			02	Surface	2.50		59.0	118.0			150.7				72.8		72.8		329.4		202.9				102.1							
No.117	5F10N 1457E		02	Surface	2.50		48.0	125.8			317.6				222.9		222.9		339.3		413.4				131.6							
No.118	1457E		02	Surface	2.88		182.1	325.1			275.4				329.6		329.6		888.4		754.6				412.0							
No.119	26.52N 11927E	O0V2	06	Surface	1.46		160.7	627.2			128.1				135.6		135.6		358.6		277.9				145.4							
No.120	26.52N 11927E	O0V3	06	Surface	0.19		11.7	15.0			20.7				18.1		18.1		62.5		53.1				31.3							
No.121	26.52N 11927E	O0V4	06	Surface	4.70		210.1	347.2			56.8				486.6		486.6		2066.3		2067.8				1384.9							
No.122	26.52N 1312E	O0V5	06	Surface	6.43		322.7	711.7			809.8				648.7		648.7		1990.1		1556.1				867.5							
No.123	40.02N 1940E	O0V6	06	Surface	6.43		322.7	711.7			809.8				648.7		648.7		1990.1		1556.1				867.5							

Number	Position	Couple No	Station No.	months	Year	Depth	TOC%	HCB	PCB 99	PCB 101	PCB 99	PCB 110	PCB 77	PCB 151	PCB 149	PCB 118	PCB 146	PCB 133	PCB 105	PCB 138	PCB 87	PCB 183	PCB 108	PCB 177	PCB 180	PCB 170	ΣPCB	sp-DDD	sp-DDT	sp-DDT			
No.124	402N ARK03 544E	06	BMP	06	2008	Surface	1.07	52.7		87.1						78.1		233.9		196.1				107.7		827.9		247.4					
No.125	2036N 1955E	08	BMP	06	2008	Surface	0.38	35.4		385						34.6		110.5		83.4				54.0		350.4		139.8		184.9			
No.126	5935N 1915E	03	MSW003	03	2006	Surface- 2cm	2.876	395.95	0.00	158.52	350.24	0.00	284.32	0.00	0.00	265.62	284.56	0.00	520.87	0.00	539.51	105.88	0.00	0.00	537.98	163.27	3770.2	634.80	258.10				
No.127	5937N 231E	03	MSW003	03	2006	Surface- 2cm	1.872	0.00	0.00	228.05	0.00	158.33	0.00	0.00	242.74	179.56	0.00	669.09	89.15	570.34	102.14	81.66	0.00	0.00	395.37	151.33	2865.2						
No.128	6195N 1935E	03	MSW003	03	2006	Surface- 2cm	3.217	530.88	235.66	132.37	77.38	0.00	56.62	248.44	84.27	109.34	47.84	595.46	48.78	116.14	499.24	131.21	57.62	0.00	68.83	399.01	190.79	3756.2	923.50	337.90	484.00		
No.129	6195N 1935E	03	MSW003	03	2006	Surface- 2cm	3.223	495.12	235.68	145.70	49.32	34.37	102.16	224.06	90.64	0.00	53.70	252.12	60.95	585.20	0.00	472.21	134.10	48.65	0.00	76.09	397.59	3429.4	726.90	334.00	439.40		
No.130	6015N 191E	03	MSW003	03	2006	Surface- 1cm	3.748	402.06	335.07	165.22	0.00	0.00	103.91	251.73	0.00	172.79	271.80	39.81	472.48	69.26	394.03	97.12	45.72	76.59	335.17	124.35	3058.9	490.00	481.10				
No.131	5945N 181E	03	MSW003	03	2006	Surface- 2cm	3.726	405.65	0.00	162.10	0.00	0.00	124.77	265.42	0.00	232.72	250.76	50.36	538.68	80.44	458.16	103.37	58.43	71.87	348.41	170.22	3185.0	587.10	519.80				
No.132	5945N 181E	03	MSW003	03	2006	Surface- 1cm	6.34	208.01	493.03	321.66	120.02	172.81	207.76	447.71	0.00	355.91	430.25	137.88	964.01	87.89	762.57	264.12	93.57	0.00	115.02	606.27	239.95	6520.4	2207.40	208.00			
No.133	5945N 181E	03	MSW003	03	2006	Surface- 2cm	5.02	172.39	390.76	289.67	108.20	230.40	283.19	417.28	202.48	448.53	462.29	149.43	850.92	123.48	689.40	234.27	73.97	0.00	100.59	542.28	194.88	6412.8	2032.20	234.10			
No.134	5978N 1017E	07	MSW0803	07	2008	Surface	3.17	448.90	694.39	405.97	130.93	156.09	432.12	704.88	123.74	542.14	204.45	1638.29	373.81	1182.37	284.39	161.87	189.56	169.34	719.67	0.00	10718.4	576.00	1123.20	1033.20			
No.135	5199N 1917E	06	MSW0803	06	2008	Surface	7.69	710.50	759.25	641.08	244.53	286.64	639.34	1036.92	478.83	1034.02	1000.23	293.54	1993.74	419.17	1594.96	462.77	182.79	289.39	228.18	1051.28	481.01	14842.5	4701.10	9933.70	1682.00		
No.136	4697N 2015E	07	MSW0803	07	2008	Surface	14.65	387.94	0.00	214.59	64.97	141.26	142.19	264.36	95.76	175.90	204.39	0.00	449.30	91.88	86.89	371.05	57.66	0.00	0.00	207.40	0.00	2871.2	598.00				
No.137	2615N 2015E	07	MSW0803	07	2008	Surface	4.90	270.85	368.17	98.14	240.09	0.00	0.00	276.87	319.66	0.00	719.84	104.08	136.14	554.54	110.05	62.52	98.38	70.58	419.89	202.92	4695.9	711.40	1052.70				
No.138	3827N 1958E	07	MSW0803	07	2008	Surface	3.25	407.46	191.24	123.59	34.89	0.00	69.61	195.59	88.10	133.14	52.35	614.19	0.00	41.95	538.26	124.17	65.54	0.00	65.99	390.06	197.49	3433.4	633.70	204.70	277.70		
No.139	5915N 191E	07	MSW0803	07	2008	Surface	2.42	232.72	349.36	150.48	77.04	0.00	157.35	291.48	113.37	385.62	353.46	86.75	729.42	0.00	614.19	206.01	53.79	0.00	133.60	219.67	13176	4149.6	623.30	423.70			
No.140	4924N 2013E	05	MSW0803	05	2008	Surface	8.08	332.48	222.85	415.16	220.58	0.00	366.07	637.33	375.70	682.21	711.07	228.64	1338.26	182.00	879.26	407.20	128.08	138.71	193.54	512.75	241.72	8709.9	3190.90	2675.80	403.90		

Number	Position	Cause No.	Station No.	months	Year	Depth	TOCN	HCB	PCB 2831	PCB 52	PCB 99	PCB 110	PCB 77	PCB 151	PCB 149	PCB 116	PCB 145	PCB 153	PCB 152	PCB 105	PCB 158	PCB 187	PCB 183	PCB 128	PCB 177	PCB 160	PCB 170	2PCB	p-p-OCe	p-p-ODT	p-p-DDT					
No.225						0-1 cm	2.907	180.6	<8.5	165.4	240.1	126.1	260.5	<8.5	113.3	403.6	280.1	128.4	765.7	127.7	4.85	595.4	244.1	109.5	100.2	169.0	4.983	504.3	4.823	884.7	530.2	<8.5				
No.226						1-2 cm	3.172	138.0	<8.5	132.3	69.9	48.8	112.0	<8.5	118.0	385.1	144.8	350.7	113.5	<8.5	131.0	187.0	187.0	<8.5	103.0	31.0	4.95	447.4	897.7	537.2	<8.5					
No.227						3-4 cm	2.822	174.4	<8.5	152.2	104.8	101.7	240.9	<8.5	113.2	350.7	144.8	350.7	113.5	<8.5	131.0	187.0	187.0	<8.5	103.0	31.0	4.95	447.4	897.7	537.2	<8.5					
No.228						5-6 cm	2.751	144.3	<8.5	139.9	84.6	68.5	130.1	<8.5	128.7	278.5	130.1	130.1	130.1	<8.5	130.1	130.1	130.1	<8.5	130.1	130.1	130.1	130.1	130.1	130.1	130.1	<8.5				
No.241						5-6 cm	2.969	195.1	<8.5	124.1	97.0	82.3	232.3	<8.5	122.9	416.3	278.8	135.3	464.9	112.2	<8.5	547.3	285.9	111.7	<8.5	116.0	326.3	154.7	475.9	999.9	600.0	<8.5				
No.242						6-7 cm	2.788	156.0	<8.5	156.4	74.5	68.0	198.2	<8.5	159.9	428.9	342.6	120.0	793.4	122.4	<8.5	585.3	212.6	119.3	118.3	118.3	118.3	118.3	118.3	118.3	118.3	118.3	<8.5			
No.243						8-9 cm	2.882	172.3	<8.5	152.3	104.8	101.7	240.9	<8.5	113.2	350.7	144.8	350.7	113.5	<8.5	131.0	187.0	187.0	<8.5	103.0	31.0	4.95	447.4	897.7	537.2	<8.5					
No.244						10-11 cm	2.620	149.8	<8.5	271.9	156.6	109.0	430.0	<8.5	145.6	408.8	197.1	154.4	356.7	164.5	150.4	71.3	307.1	207.1	371.7	147.5	73.1	131.3	150.3	1097.9	48.0	<8.5				
No.245						12-13 cm	2.771	188.3	<8.5	259.7	143.3	123.8	350.0	<8.5	169.2	868.2	522.6	234.2	144.4	133.9	450.1	188.2	171.5	251.5	763.8	381.7	94.0	143.8	1266.4	48.0	<8.5					
No.246						14-15 cm	2.896	196.8	<8.5	256.2	176.9	137.7	318.4	<8.5	221.1	773.6	597.2	422.1	223.4	4.85	102.2	362.3	358.3	232.1	58.4	58.4	58.4	58.4	58.4	58.4	58.4	<8.5				
No.247						16-17 cm	2.944	217.6	<8.5	354.6	207.6	184.5	584.5	<8.5	478.7	638.6	338.9	443.3	480.2	480.2	480.2	480.2	480.2	480.2	480.2	480.2	480.2	480.2	480.2	480.2	480.2	480.2	<8.5			
No.248	64					17-18 cm	3.734	200.9	<8.5	273.9	117.9	4.95	353.9	<8.5	257.9	197.1	152.1	218.9	148.3	196.2	196.2	196.2	196.2	196.2	196.2	196.2	196.2	196.2	196.2	196.2	196.2	196.2	<8.5			
No.249	47.1N	ENB2566		10.	2013	15-16 cm	3.332	258.5	<8.5	230.1	106.9	193.7	263.3	<8.5	470.0	192.8	415.0	192.8	192.8	192.8	192.8	192.8	192.8	192.8	192.8	192.8	192.8	192.8	192.8	192.8	192.8	<8.5				
No.250	15130E					16-17 cm	4.836	306.8	<8.5	307.3	176.0	96.0	480.0	<8.5	344.2	363.3	197.4	154.4	175.6	639.8	402.1	162.8	194.7	201.9	172.7	835.9	307.2	18.8	133.8	1265.9	1167.2	<8.5				
No.252						17-18 cm	4.078	267.6	<8.5	359.6	169.6	161.7	344.5	<8.5	282.4	91.1	81.6	236.5	157.2	310.9	4.85	1266.4	445.1	197.7	197.1	257.6	642.9	283.9	9756.3	1974.3	1835.5	<8.5				
No.254						18-19 cm	2.787	179.2	<8.5	327.2	206.7	166.8	424.1	<8.5	576.8	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	589.3	<8.5			
No.255						19-20 cm	2.924	231.1	<8.5	497.2	265.4	264.1	750.6	<8.5	350.0	1715.9	989.8	333.2	979.0	392.0	4.85	1489.7	500.4	15.4	287.9	842.9	487.8	1315.9	2397.3	3607.6	48.0	<8.5				
No.256	1742.1N					20-21 cm	2.958	172.3	<8.5	152.3	104.8	101.7	240.9	<8.5	113.2	350.7	144.8	350.7	113.5	<8.5	131.0	187.0	187.0	<8.5	103.0	31.0	4.95	447.4	897.7	537.2	<8.5					
No.258						21-22 cm	2.758	211.8	<8.5	242.2	242.2	242.2	242.2	<8.5	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	242.2	<8.5			
No.258						22-23 cm	2.864	180.9	<8.5	303.5	217.6	150.9	518.5	<8.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	303.5	<8.5			
No.259						23-24 cm	2.341	137.5	<8.5	197.2	149.7	<8.5	270.5	<8.5	438.6	270.7	344.6	<8.5	182.1	616.4	336.2	171.7	390.1	163.1	<8.5	14.11	399.4	269.2	5898.9	1635.7	3719.7	48.0	<8.5			
No.259						24-25 cm	2.056	107.8	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	88.1	<8.5	174.2	<8.5	111.3	<8.5	111.3	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5			
No.251						25-26 cm	1.980	106.8	<8.5	152.7	152.7	152.7	152.7	<8.5	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	152.7	<8.5			
No.252						27-28 cm	1.512	137.2	<8.5	137.2	137.2	137.2	137.2	<8.5	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	137.2	<8.5			
No.253						28-29 cm	1.832	62.3	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5			
No.264						29-30 cm	1.316	105.9	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5	<8.5		
No.265	1719.2N	ENB100		04.	2015	0-1 cm	11.37	293	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn			
No.267	2093E	SLZ71				1-2 cm	9.97	366	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn		
No.268	1742.1N	ENB120				0-1 cm	0.97	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn		
No.270	1742.1N	ENB124				0-1 cm	0.95	258	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn		
No.271	2072.1E	SLZ71				0-1 cm	12.21	220	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn		
No.272	1742.1N	ENB135				1-2 cm	10.86	449	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn		
No.273	1922N	SLZ71(FS)				1-2 cm	10.86	449	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn		
No.274	1922N	SLZ71(FS)				1-2 cm	10.86	449	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	
No.275	1922N	SLZ71(FS)				1-2 cm	10.86	449	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	
No.276	1914.4E	DM6				1-2 cm	10.86	449	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	
No.277	1914.4E	DM6				1-2 cm	10.86	449	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn	nn
No.278						5 MUC2A	1.08	765.5																												

Number	Position	Cruise No.	Station No.	months	Year	Depth	TOC%	HCB	PCB 28/31	PCB 52	PCB 49	PCB 44	PCB 95	PCB 101	PCB 99	PCB 110	PCB 77	PCB 151	PCB 149	PCB 116	PCB 146	PCB 133	PCB 132	PCB 105	PCB 138	PCB 187	PCB 193	PCB 138	PCB 177	PCB 180	PCB 170	PCB	pp-DDT	pp-DDT	pp-DDD	pp-DDT		
No.332	18°14'N	EM8461	2016-02 N	05	2013	20-3.5CZ	2.097	< BG	414.4	61.8	< BG	< BG	56.0	< BG	< BG	< BG	< BG	< BG	42.8	< BG	< BG	55.1	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	630.1	84.6	< BG	< BG	< BG			
No.332	18°14'N	EM8461	2016-02 N	05	2013	20-3.5CZ	2.136	< BG	431.9	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	44.7	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG		
No.332	18°14'N	EM8461	2016-02 N	05	2013	20-3.5CZ	2.136	< BG	419.5	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	45.0	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG		
No.332	18°14'N	EM8461	2016-02 N	05	2013	20-3.5CZ	2.136	< BG	419.5	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	45.0	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	
No.332	18°14'N	EM8461	2016-02 N	05	2013	20-3.5CZ	2.136	< BG	419.5	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	45.0	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	< BG	
No.338	19°21'N	EM8171	11	2017	0-1.5 cm	0.137	383.3	395.8	374.8	467.3	290.1	815.8	922.3	515.2	609.9	0.0	0.0	782.2	675.0	193.0	193.0	nn	330.2	1171.7	877.7	0.0	116.5	0.0	116.5	0.0	277.1	198.8	506.3	967.8	4663.0	4275.0	198.4	497.8
No.338	19°21'N	EM8171	11	2017	0.5-1 cm	0.147	222.1	335.5	244.8	418.3	299.5	707.2	580.8	275.5	327.6	0.0	0.0	432.1	582.9	135.1	135.1	nn	193.8	861.2	732.7	0.0	160.8	0.0	247.4	209.7	339.4	7245.9	3402.8	584.8	211.2	300.0		
No.340	19°21'N	EM8171	11	2017	1-1.5 cm	0.167	173.0	251.3	371.2	561.6	374.8	955.2	851.5	439.3	509.9	237.6	39.1	582.2	884.2	227.1	227.1	nn	355.4	1266.3	945.2	238.3	160.8	165.2	354.4	271.9	504.0	10854.4	4397.9	7593.5	140.9	248.1		
No.341	19°21'N	EM8171	11	2017	1.5-2 cm	0.227	196.0	275.5	419.0	594.9	419.0	1200.3	1045.2	570.8	707.6	295.8	51.9	854.6	1113.4	303.0	303.0	nn	373.6	1684.1	1427.7	318.1	209.8	180.5	485.5	428.3	725.8	14256.6	5712.2	3892.4	149.9	248.1		
No.342	19°21'N	EM8171	11	2017	2-2.5 cm	0.288	333.6	454.2	675.2	975.0	654.8	1595.1	1178.5	624.2	750.0	304.2	53.0	1130.8	1319.8	351.9	351.9	nn	430.3	1979.8	1809.9	450.0	354.2	313.0	630.3	537.5	833.2	16368.8	6526.2	4327.1	137.7	510.4		
No.343	19°21'N	EM8171	11	2017	2.5-3 cm	0.388	333.6	454.2	675.2	975.0	654.8	1595.1	1178.5	624.2	750.0	304.2	53.0	1130.8	1319.8	351.9	351.9	nn	430.3	1979.8	1809.9	450.0	354.2	313.0	630.3	537.5	833.2	16368.8	6526.2	4327.1	137.7	510.4		
No.344	20°3'E	EM8171	11	2017	3-4 cm	0.155	380.7	447.3	655.6	210.8	1102.1	1439.0	2109.4	1086.3	1820.6	439.9	242.9	2280.3	1831.0	548.0	548.0	nn	352.8	1309.2	2106.3	2106.3	339.2	268.9	744.0	718.7	1333.1	2807.6	11273.2	11144.5	219.7	549.0		
No.345	20°3'E	EM8171	11	2017	4-5 cm	0.215	628.5	979.7	1525.9	3336.7	1938.8	2548.5	3417.0	1712.3	2302.2	743.9	358.3	3238.4	2784.2	803.3	803.3	nn	1027.1	4773.1	3163.9	683.9	539.9	431.4	1151.2	1272.5	2184.6	43571.7	16907.0	39146.8	336.4	1070.0		
No.346	20°3'E	EM8171	11	2017	5-6 cm	0.278	737.2	1095.9	2245.5	3035.9	1985.7	2623.5	3448.9	1744.1	2448.1	1014.3	285.7	3238.4	2857.1	851.9	851.9	nn	1272.4	5414.0	3528.3	837.3	714.0	521.1	1495.1	1431.8	3624.0	46441.9	24201.3	65403.2	573.7	1589.3		
No.347	20°3'E	EM8171	11	2017	6-7 cm	0.271	519.7	851.9	933.2	1316.2	640.9	1475.2	2001.6	932.4	1589.9	550.0	107.6	1635.6	1967.7	607.8	607.8	nn	740.8	3056.5	1927.3	485.9	416.8	289.2	863.6	863.0	131.8	24153.8	15202.3	4274.2	505.6	1307.8		
No.348	20°3'E	EM8171	11	2017	7-8 cm	1.04	332.3	269.2	495.9	715.5	390.0	802.8	1032.6	421.0	840.3	31.1	75.5	825.1	1102.9	342.9	342.9	nn	407.2	1884.7	1277.7	214.8	246.8	182.2	425.6	567.3	965.1	13855.0	9133.5	29665.1	339.3	951.4		
No.349	20°3'E	EM8171	11	2017	8-9 cm	2.650	102.3	37.6	111.2	37.6	284.7	384.4	192.2	219.3	115.2	22.7	104.0	442.0	184.6	184.6	nn	131.8	326.4	127.9	104.3	33.1	134.7	365.1	365.2	485.6	1614.4	3972.3	859.3	135.7	155.7			
No.350	20°3'E	EM8171	11	2017	9-10 cm	1.884	35.8	15.0	42.3	35.8	84.4	32.9	35.2	49.2	35.2	44.8	35.2	44.8	35.2	35.2	35.2	nn	39.0	284.3	189.5	46.2	44.2	28.8	37.3	147.3	184.1	197.8	1342.8	nn	nn	nn	nn	nn

Table S2. Dry Bulk Density (DBD) calculation for the inventory study.

Station No.	Cruise No	Year	Depth cm	TOC %	DBD g/cm ³	Area
TF0012	BMP	1993/1994	1	4	0.2609315	Mecklenburg Bight
TF0010	BMP	1993/1994	1	1.3	1.4947609	Mecklenburg Bight
TF0012	BMP	2004 (10.06)	1	4	0.2609315	Mecklenburg Bight
TF0012	BMP	2007	1	4.03	0.2579212	Mecklenburg Bight
LB1	BMP	2007	1	6.17	0.1331107	Mecklenburg Bight
IOW3	BMP	2008	1	1.46	1.2482046	Mecklenburg Bight
IOW2	BMP	2008	1	2.89	0.4322663	Mecklenburg Bight
TF0010	BMP	2008	1	1.45	1.2615987	Mecklenburg Bight
TF0010	BMP	2009	1	1.2	1.6926115	Mecklenburg Bight
TF0010	BMP	2011	1	1.55	1.1374718	Mecklenburg Bight
TF0012	BMP	2017	1	4.0470193	0.2562387	Mecklenburg Bight
TF0109	BMP	1993/1994	1	5.8	0.1465285	Arkona Basin
TF0069	BMP	1993/1994	1	6.1	0.1354904	Arkona Basin
145/2	BMP	2004	1	2.3	0.6162578	Arkona Basin
TF0109	BMP	2004	1	5.6	0.1547354	Arkona Basin
TF0102	BMP	2004(F+E)	1	3.5	0.3210614	Arkona Basin
TF0104	BMP	2004(F+E)	1	5.9	0.1426897	Arkona Basin
TF0105	BMP	2004(F+E)	1	6.4	0.1257559	Arkona Basin
TF0113	BMP	2004(F+E)	1	5.4	0.1637262	Arkona Basin
TF0114	BMP	2004(F+E)	1	6.2	0.1321118	Arkona Basin
TF0109	BMP	2006	1	5.44	0.1618604	Arkona Basin
TF0069	BMP	2006	1	5.21	0.1730919	Arkona Basin
TF0110	BMP	2007	1	6.5	0.1227641	Arkona Basin
TF0069	BMP	2008	1	5.76	0.1481118	Arkona Basin
IOW5	BMP	2008	1	4.7	0.2031224	Arkona Basin
ARK03	BMP	2008	1	1.07	2.0225196	Arkona Basin
IOW6	BMP	2008	1	6.43	0.1248459	Arkona Basin
TF0110	BMP	2011	1	6.09	0.1358361	Arkona Basin
TF0109	BMP	2017	1	5.5081982	0.1587588	Arkona Basin
St. 27	MSM001	2006	1	1.8717693	0.848629	Bothnian Bay
BB03	MSM0803	2008	1	8.08	0.087562	Bothnian Bay
St. 24	MSM001	2006	1	2.8762075	0.4354898	Bothnian sea
St. 34	MSM001	2006	1	3.2174086	0.3659052	Bothnian sea
St. 35	MSM001	2006	1	3.7482008	0.2886549	Bothnian sea
EMB262/12-2	EMB262	2022	1	7.404	0.1002869	Gulf of Finland
302	MSM0803	2008	1	12.63	0.0437569	Gulf of Finland
TF0285	BMP	2003	1	12.306	0.045559	northern Gotland Basin
St. 36/TF0284	MSM001	2006	1	6.3355464	0.1277483	northern Gotland Basin
305	MSM0803	2008	1	4.8996	0.1904173	northern Gotland Basin
P435-17-5-2W	Geokern	2012-2013	1	19.9685	0.0214827	northern Gotland Basin
TF0240	BMP	2003	1	8.175	0.0859869	Western Gotland Basin
TF0270	BMP	2003	1	12.075	0.0469197	Eastern Gotland Basin
TF0271/St.271	BMP	2003	1	12.755	0.0430927	Eastern Gotland Basin
TF0272	BMP	2003	1	13.19	0.0409059	Eastern Gotland Basin

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TF0260	BMP	2003	1	9.977	0.0631072	Eastern Gotland Basin
TF0259	MSM0803	2008	1	2.4196	0.5696026	Eastern Gotland Basin
P435-3-2-2	Geokern 2012-13	2012-2013	1	18.6785	0.0276371	Eastern Gotland Basin
P435-1-4-1-A	Geokern 2012-13	2012-2013	1	15.218	0.032169	Eastern Gotland Basin
EMB100 St.271	Annox 2016 EMB100	2015	1	9.9734426	0.0631421	Eastern Gotland Basin
TF0271/St.271	A0ox 2016 EMB135	2016	1	10.240345	0.0606048	Eastern Gotland Basin
EMB1215/7-3 MUC3A	OP-2016-02 NAR	2016	1	17.041	0.0274798	Eastern Gotland Basin
SP15	EMB242	2021	1	8.5325454	0.0804564	Gulf of Gdansk
233	MSM0803	2008	1	7.6932	0.0944934	Gulf of Gdansk
TF0213	BMP	2008	1	4.4813	0.2187234	Bornholm Basin
355	MSM0803	2008	1	2.42	0.5694564	Kattegat
358	MSM0803	2008	1	3.1705	0.374347	Kattegat
EMB046/10-2 MUC	OP-2016-02 NAR	2016	1	2.366	0.5897675	Kattegat
EMB046/20-2 MUC	OP-2016-02 NAR	2016	1	2.516	0.5360708	Kattegat

Table S3. The toxicity Equivalency Factor (TEF) method calculation.

Station No.	Cruise No	Year	PCB 77	PCB 118	PCB 105	TEF-PCB 77	TEF-PCB 118	TEF-PCB 105
			pg/g d.w.	pg/g d.w.	pg/g d.w.	pg/g d.w.	pg/g d.w.	pg/g d.w.
ODER	BMP	1993	0.00	0.00	0.00	0.00000	0.00000	0.00000
TF0109	BMP	1993	0.00	123.4	0.00	0.00000	0.00370	0.00000
TF0069	BMP	1993	0.00	436.9	0.00	0.00000	0.01311	0.00000
TF0030	BMP	1993	0.00	18.1	0.00	0.00000	0.00054	0.00000
TF0012	BMP	1993	0.00	564.6	0.00	0.00000	0.01694	0.00000
TF0010	BMP	1993	0.00	636.3	0.00	0.00000	0.01909	0.00000
St. 27	MSM001	2006	0.00	179.56	0.00	0.00000	0.00539	0.00000
BB03	MSM0803	2008	0.00	711.07	182.00	0.00000	0.02133	0.00546
St. 24	MSM001	2006	0.00	284.66	0.00	0.00000	0.00854	0.00000
St. 34	MSM001	2006	0.00	329.26	116.14	0.00000	0.00988	0.00348
St. 35	MSM001	2006	0.00	211.80	0.00	0.00000	0.00635	0.00000
St. 35	MSM001		0.00	230.76	0.00	0.00000	0.00692	0.00000
EMB262/12-2 MUC3		2022	23.34	241.98	89.85	0.00233	0.00726	0.00270
302	MSM0803	2008	0.00	204.39	86.89	0.00000	0.00613	0.00261
305	MSM0803	2008	0.00	319.66	136.14	0.00000	0.00959	0.00408
St. 36/TF0284	MSM001	2006	0.00	430.25	89.72	0.00000	0.01291	0.00269
TF0285	BMP	2003	0.00	1,249.4	0.00	0.00000	0.03748	0.00000
TF0240	BMP	2003	0.00	701.8	0.00	0.00000	0.02105	0.00000
TF0270	BMP	2003	0.00	1,227.2	0.00	0.00000	0.03682	0.00000
TF0271/St.271	BMP	2003	0.00	1,402.2	0.00	0.00000	0.04207	0.00000
TF0272	BMP	2003	0.00	1,183.1	0.00	0.00000	0.03549	0.00000

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TF0260	BMP	2003	0.00	1,145.0	0.00	0.00000	0.03435	0.00000
TF0259	MSM0803	2008	0.00	454.08	0.00	0.00000	0.01362	0.00000
SP15	BALTPOLL	2021	117.29	929.27	306.12	0.01173	0.02788	0.00918
233	MSM0803	2008	0.00	1000.23	424.85	0.00000	0.03001	0.01275
TF0213	BMP	2008	0.00	514.39	0.00	0.00000	0.01543	0.00000
ODER	BMP	2009	0.00	11.0	0.00	0.00000	0.00033	0.00000
145	BMP	2004	0.00	72.8	0.00	0.00000	0.00219	0.00000
145	BMP	2004	0.00	232.9	0.00	0.00000	0.00699	0.00000
TF0102	BMP	2004(F +E)	0.00	193.1	0.00	0.00000	0.00579	0.00000
TF0109	BMP	2004	0.00	446.0	0.00	0.00000	0.01338	0.00000
TF0109	BMP	2006	0.00	575.3	0.00	0.00000	0.01726	0.00000
TF0110	BMP	2007	0.00	551.1	0.00	0.00000	0.01653	0.00000
TF0110		2008	0.00	546.8	0.00	0.00000	0.01640	0.00000
TF0104	BMP	2004(F +E)	0.00	688.2	0.00	0.00000	0.02065	0.00000
TF0105	BMP	2004(F +E)	0.00	574.6	0.00	0.00000	0.01724	0.00000
TF0113	BMP	2004(F +E)	0.00	385.2	0.00	0.00000	0.01156	0.00000
TF0114	BMP	2004(F +E)	0.00	616.3	0.00	0.00000	0.01849	0.00000
TF0069		2006	0.00	975.9	0.00	0.00000	0.02928	0.00000
TF0069	BMP	2008	0.00	784.1	0.00	0.00000	0.02352	0.00000
ARKO3	BMP	NO	0.00	78.1	0.00	0.00000	0.00234	0.00000
IOW6	BMP	NO	0.00	648.7	0.00	0.00000	0.01946	0.00000
IOW8	BMP	NO	0.00	34.6	0.00	0.00000	0.00104	0.00000
IOW5	BMP	2008	0.00	485.6	0.00	0.00000	0.01457	0.00000
TF0030	BMP	2004	0.00	10.3	0.00	0.00000	0.00031	0.00000
IOW4	BMP	2008	0.00	18.1	0.00	0.00000	0.00054	0.00000
IOW3	BMP	2008	0.00	135.6	0.00	0.00000	0.00407	0.00000
IOW2	BMP	2008	0.00	329.6	0.00	0.00000	0.00989	0.00000
TF0012	BMP	2007	0.00	379.4	0.00	0.00000	0.01138	0.00000
TF0010	BMP	2008	0.00	187.7	0.00	0.00000	0.00563	0.00000
TF0010	BMP	2009	0.00	134.4	0.00	0.00000	0.00403	0.00000
TF0360	BPM	2008	0.00	37.0	0.00	0.00000	0.00111	0.00000
TF0360		2009	0.00	51.7	0.00	0.00000	0.00155	0.00000
LB1	BMP	2007	0.00	1076.3	0.00	0.00000	0.03229	0.00000
355	MSM0803	2008	0.00	353.46	0.00	0.00000	0.01060	0.00000
358	MSM0803	2008	0.00	542.14	0.00	0.00000	0.01626	0.00000
TF0213	BMP	2003	0.00	400.8	0.00	0.00000	0.01202	0.00000
TF0213		2008	0.00	262.13	0.00	0.00000	0.00786	0.00000
ODER	BMP	2008	0.00	29.9	0.00	0.00000	0.00090	0.00000
TF0030		2007	0.00	6.7	0.00	0.00000	0.00020	0.00000
TF0030	BMP	2008	0.00	7.4	0.00	0.00000	0.00022	0.00000
TF0012	BMP	2004	0.00	901.9	0.00	0.00000	0.02706	0.00000
TF0012		2004	0.00	487.0	0.00	0.00000	0.01461	0.00000
P435-17-5-2W	Geokern 2012- 13	2012- 2013	0.00	995	0.00	0.00000	0.02984	0.00000

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EMB1215/7-3 MUC3A	OP-2016-02 NAR	NO	0.00	494.5	203.4	0.00	0.01484	0.00610
EMB100 St.271	EMB100 St.271		0.00	754	0	0.00	0.02263	0.00
EMB100 St.271	Annox 2016 EMB100	2015	0.00	1583	0	0.00	0.04750	0.00
P435-3-2-2	Geokern	2012	0.00	727	0	0.00000	0.02181	0.00000
P435-3-2-2	Geokern	2012- 2013	0.00	819	0	0.00000	0.02456	0.00000
P435-1-4-1-A	Geokern	2012- 2013	0.00	1487	699	0.00000	0.04461	0.02096
TF0109	BMP	2017	267.8	437.3	121.1	0.02678	0.01312	0.00363
TF0110	BMP	2011	0.00	656.7	0.00	0.00000	0.01970	0.00000
TF0110	BMP	2014	0.00	660.8	0.00	0.00000	0.01982	0.00000
TF0069	BMP	2014	0.00	830.3	0.00	0.00000	0.02491	0.00000
TF0069	BMP	2018	238.59	904.22	1470.20	0.02386	0.02713	0.04411
TF0030	BMP	2010	0.00	0.00	0.00	0.00000	0.00000	0.00000
TF0012	BMP	2013	0.00	569.3	0.00	0.00000	0.01708	0.00000
TF0012	BMP	2014	0.00	604	0.00	0.00000	0.01812	0.00000
TF0012	BMP	2017	53.2	313.3	100.9	0.00532	0.00940	0.00303
TF0010	BMP	2011	0.00	207.6	0.00	0.00000	0.00623	0.00000
TF0010	BMP	2014	0.00	130.2	0.00	0.00000	0.00391	0.00000
TF0010	BMP	2018	0.00	149.06	212.07	0.00	0.00447	0.00636
TF0360	BPM	2014	0.00	58.7	0.00	0.00000	0.00176	0.00000
EMB046/10-2 MUC	OP-2016-02 NAR	NO	0.00	326.2	0.00	0.00	0.00979	0.00
EMB046/20-2 MUC	OP-2016-02 NAR	NO	0.00	274.1	155.5	0.00	0.00822	0.00467
TF0271/St.271	Annox 2016 EMB135	2016	0.00	556	0.00	0.00	0.01667	0.00
TF0272/St.272	Annox 2016 EMB120	2016	0.00	124	0.00	0.00	0.00372	0.00
TF0272/St.272	Annox 2016 EMB120	2016	0.00	0.00	0.00	0.00	0.00	0.00

Table S4. The calculation of the Hazard Quotient (HQ).

Station No.	Cruise No	Year	TOC %	ΣPCB pg/g d.w.	ΣPCB mg/g	Cfish pg/g	risk male mg/g/d	female kg	HQ male	HQ female
							76.46 kg	66.57 kg		
ODER	BMP	1993	0.1	63.50	6.35E-08	654.05	1.171E- 14	9.53883E -16	5.85502E -10	4.76942E -11
TF0109	BMP	1993	5.8	1661.50	1.6615E-06	295.06	3.06397E -13	2.49587E -14	1.53199E -08	1.24793E -09
TF0069	BMP	1993	6.1	6201.30	6.2013E-06	1047.10	1.14358E -12	9.31546E -14	5.71791E -08	4.65773E -09
TF0030	BMP	1993	0.1	197.50	1.975E-07	2034.25	3.6421E- 14	2.9668E- 15	1.82105E -09	1.4834E- 10
TF0012	BMP	1993	4	7646.00	0.00000764 6	1968.85	1.41E-12	1.14857E -13	7.05E-08	5.74283E -09
TF0010	BMP	1993	1.3	5545.20	5.5452E-06	4393.50	1.02259E -12	8.32988E -14	5.11296E -08	4.16494E -09
St. 27	MSM001	2006	1.872	2866.16	2.86616E- 06	1577.19	5.28549E -13	4.30548E -14	2.64274E -08	2.15274E -09

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BB03	MSM0803	2008	8.08	8709.92	8.70992E-06	1110.30	1.6062E-12	1.30838E-13	8.03098E-08	6.54192E-09
St. 24	MSM001	2006	2.876	3270.23	3.27023E-06	1171.10	6.03064E-13	4.91247E-14	3.01532E-08	2.45624E-09
St. 34	MSM001	2006	3.217	3756.19	3.75619E-06	1202.48	6.92679E-13	5.64247E-14	3.4634E-08	2.82123E-09
St. 35	MSM001	2006	3.748	3058.89	3.05889E-06	840.58	5.6409E-13	4.59499E-14	2.82045E-08	2.2975E-09
St. 35	MSM001		3.726	3184.95	3.18495E-06	880.48	5.87337E-13	4.78436E-14	2.93669E-08	2.39218E-09
EMB262/12-2 MUC3		2022	7.40	2693.41	2.69341E-06	374.69	4.96693E-13	4.04599E-14	2.48346E-08	2.02299E-09
302	MSM0803	2008	12.63	2811.21	2.81121E-06	229.26	5.18416E-13	4.22294E-14	2.59208E-08	2.11147E-09
305	MSM0803	2008	4.90	4695.89	4.69589E-06	987.18	8.65969E-13	7.05406E-14	4.32985E-08	3.52703E-09
St. 36/TF0284	MSM001	2006	6.34	6520.43	6.52043E-06	1060.06	1.20243E-12	9.79484E-14	6.01216E-08	4.89742E-09
TF0285	BMP	2003	12.306	7660.55	7.66055E-06	641.18	1.41268E-12	1.15075E-13	7.06342E-08	5.75376E-09
TF0240	BMP	2003	8.175	5835.22	5.83522E-06	735.20	1.07607E-12	8.76554E-14	5.38037E-08	4.38277E-09
TF0270	BMP	2003	12.075	9503.10	9.5031E-06	810.62	1.75247E-12	1.42753E-13	8.76234E-08	7.13767E-09
TF0271/St.271	BMP	2003	12.755	11846.21	1.18462E-05	956.61	2.18456E-12	1.77951E-13	1.09228E-07	8.89756E-09
TF0272	BMP	2003	13.19	9141.08	9.14108E-06	713.82	1.68571E-12	1.37315E-13	8.42854E-08	6.86577E-09
TF0260	BMP	2003	9.977	9908.46	9.90846E-06	1022.92	1.82722E-12	1.48843E-13	9.1361E-08	7.44214E-09
TF0259	MSM0803	2008	2.42	5463.08	5.46308E-06	2325.58	1.00745E-12	8.20652E-14	5.03724E-08	4.10326E-09
SP15	BALTPOLL	2021	8.53	12427.80	1.24278E-05	1500.21	2.29181E-12	1.86688E-13	1.14591E-07	9.33438E-09
233	MSM0803	2008	7.69	14642.51	1.46425E-05	1960.41	2.70023E-12	2.19957E-13	1.35011E-07	1.09978E-08
TF0213	BMP	2008	6.11	9322.55	9.32255E-06	1571.87	1.71917E-12	1.40041E-13	8.59586E-08	7.00206E-09
ODER	BMP	2009	0.14	98.80	9.87965E-08	726.86	1.82191E-14	1.4841E-15	9.10953E-10	7.42049E-11
145	BMP	2004	2.30	1102.33	1.10233E-06	493.65	2.0328E-13	1.65589E-14	1.0164E-08	8.27946E-10
145	BMP	2004	2.30	1920.78	1.92078E-06	860.18	3.54211E-13	2.88535E-14	1.77106E-08	1.44268E-09
TF0102	BMP	2004(F+E)	3.50	1746.29	1.74629E-06	513.91	3.22034E-13	2.62324E-14	1.61017E-08	1.31162E-09
TF0109	BMP	2004	5.60	6484.08	6.48408E-06	1192.61	1.19573E-12	9.74025E-14	5.97865E-08	4.87012E-09
TF0109	BMP	2006	5.44	5816.96	5.81696E-06	1101.37	1.07271E-12	8.7381E-14	5.36353E-08	4.36905E-09
TF0110	BMP	2007	6.50	5743.41	5.74341E-06	910.11	1.05914E-12	8.62763E-14	5.29572E-08	4.31382E-09
TF0110		2008	5.72	5494.99	5.49499E-06	989.48	1.01333E-12	8.25446E-14	5.06666E-08	4.12723E-09
TF0104	BMP	2004(F+E)	5.90	4209.04	4.20904E-06	734.80	7.7619E-13	6.32273E-14	3.88095E-08	3.16137E-09
TF0105	BMP	2004(F+E)	6.40	4491.17	4.49117E-06	722.80	8.28217E-13	6.74654E-14	4.14109E-08	3.37327E-09
TF0113	BMP	2004(F+E)	5.40	3136.42	3.13642E-06	598.24	5.78388E-13	4.71146E-14	2.89194E-08	2.35573E-09
TF0114	BMP	2004(F+E)	6.20	5827.87	5.82787E-06	968.18	1.07472E-12	8.7545E-14	5.37359E-08	4.37725E-09
TF0069		2006	5.21	7976.83	7.97683E-06	1576.99	1.47101E-12	1.19826E-13	7.35504E-08	5.99131E-09
TF0069	BMP	2008	5.76	7462.61	7.46261E-06	1334.46	1.37618E-12	1.12102E-13	6.8809E-08	5.60508E-09

Appendix

					06		-12	-13	08	-09
ARKO3	BMP	NO	1.07	827.90	8.279E-07	796.95	1.52673E-13	1.24365E-14	7.63366E-09	6.21826E-10
IOW6	BMP	NO	6.43	7360.16	7.36016E-06	1179.00	1.35729E-12	1.10563E-13	6.78644E-08	5.52814E-09
IOW8	BMP	NO	0.38	350.41	3.50414E-07	949.81	6.46198E-14	5.26384E-15	3.23099E-09	2.63192E-10
IOW5	BMP	2008	4.70	7264.01	7.26401E-06	1591.90	1.33956E-12	1.09118E-13	6.69778E-08	5.45591E-09
TF0030	BMP	2004	0.10	174.92	1.74921E-07	1801.69	3.22573E-14	2.62763E-15	1.61286E-09	1.31381E-10
IOW4	BMP	2008	0.19	200.70	2.00702E-07	1088.02	3.70115E-14	3.0149E-15	1.85058E-09	1.50745E-10
IOW3	BMP	2008	1.46	1878.05	1.87805E-06	1324.92	3.46331E-13	2.82116E-14	1.73166E-08	1.41058E-09
IOW2	BMP	2008	2.89	3246.05	3.24605E-06	1156.90	5.98604E-13	4.87614E-14	2.99302E-08	2.43807E-09
TF0012	BMP	2007	4.03	3637.34	3.63734E-06	929.64	6.70762E-13	5.46393E-14	3.35381E-08	2.73196E-09
TF0010	BMP	2008	1.45	2068.15	2.06815E-06	1469.10	3.81389E-13	3.10674E-14	1.90694E-08	1.55337E-09
TF0010	BMP	2009	1.20	1802.66	1.80266E-06	1547.28	3.32428E-13	2.70791E-14	1.66214E-08	1.35396E-09
TF0360	BPM	2008	0.41	513.94	5.1394E-07	1291.12	9.47758E-14	7.7203E-15	4.73879E-09	3.86015E-10
TF0360	BPM	2009	0.48	680.30	6.80304E-07	1459.82	1.25455E-13	1.02194E-14	6.27275E-09	5.10969E-10
LB1	BMP	2007	6.17	11699.21	1.16992E-05	1953.03	2.15745E-12	1.75743E-13	1.07873E-07	8.78715E-09
355	MSM0803	2008	2.42	4149.63	4.14963E-06	1766.17	7.65234E-13	6.23349E-14	3.82617E-08	3.11674E-09
358	MSM0803	2008	3.17	10123.43	1.01234E-05	3288.80	1.86686E-12	1.52072E-13	9.33431E-08	7.6036E-09
TF0213	BMP	2003	6.468	4026.14	4.02614E-06	641.14	7.42461E-13	6.04798E-14	3.71231E-08	3.02399E-09
TF0213	BPM	2008	4.48	6161.93	6.16193E-06	1416.28	1.13632E-12	9.25632E-14	5.68162E-08	4.62816E-09
ODER	BMP	2008	0.16	308.23	3.08233E-07	1984.25	5.68414E-14	4.63022E-15	2.84207E-09	2.31511E-10
TF0030	BPM	2007	0.11	82.44	8.24376E-08	771.92	1.52023E-14	1.23836E-15	7.60116E-10	6.1918E-11
TF0030	BMP	2008	0.05	85.17	8.51674E-08	1754.45	1.57057E-14	1.27937E-15	7.85287E-10	6.39683E-11
TF0012	BMP	2004	4.00	5532.88	5.53288E-06	1424.72	1.02032E-12	8.31137E-14	5.1016E-08	4.15569E-09
TF0012	BPM	2004(25.07)	4.40	5104.95	5.10495E-06	1195.02	9.41405E-13	7.66855E-14	4.70702E-08	3.83427E-09
P435-17-5-2W	Geokern 2012-13	2012-2013	19.9685	10073.97	1.0074E-05	519.63	1.85774E-12	1.51329E-13	9.28871E-08	7.56645E-09
EMB1215/7-3 MUC3A	OP-2016-02 NAR	2016	17.041	5834.59	5.83459E-06	352.66	1.07596E-12	8.7646E-14	5.37979E-08	4.3823E-09
EMB100 St.271	EMB100 St.271		11.37	6130.81	6.13081E-06	555.37	1.13058E-12	9.20956E-14	5.65291E-08	4.60478E-09
EMB100 St.271	Annox 2016 EMB100	2015	9.97	14734.06	1.47341E-05	1521.65	2.71711E-12	2.21332E-13	1.35855E-07	1.10666E-08
P435-3-2-2	Geokern 2012-13	2012-2013	18.679	6677.44	6.67744E-06	368.22	1.23139E-12	1.00307E-13	6.15694E-08	5.01535E-09
P435-3-2-2	Geokern 2012-13	2012-2013	16.9785	8194.76	8.19476E-06	497.13	1.5112E-12	1.231E-13	7.55598E-08	6.15499E-09
P435-1-4-1-A	Geokern 2012-13	2012-2013	15.397	5057.78	5.05778E-06	338.35	9.32706E-13	7.59769E-14	4.66353E-08	3.79884E-09
P435-1-4-1-A	Geokern 2012-13	2012-2013	15.218	16379.26	1.63793E-05	1108.60	3.0205E-12	2.46046E-13	1.51025E-07	1.23023E-08
ODER	BMP	2011	0.13	56.88	5.68801E-08	450.67	1.04893E-14	8.54441E-16	5.24464E-10	4.2722E-11

Appendix

ODER	BMP	2014	0.13	22.20	2.22E-08	175.89	4.09391E-15	3.33484E-16	2.04695E-10	1.66742E-11
TF0109	BMP	2017	5.508	7868.37	7.86837E-06	1471.34	1.45101E-12	1.18197E-13	7.25503E-08	5.90984E-09
TF0110	BMP	2011	6.09	4760.31	4.76031E-06	805.11	8.77849E-13	7.15083E-14	4.38925E-08	3.57542E-09
TF0110	BMP	2014	5.93	4639.20	4.6392E-06	805.80	8.55516E-13	6.9689E-14	4.27758E-08	3.48445E-09
TF0069	BMP	2014	5.69	6035.50	6.0355E-06	1092.54	1.11301E-12	9.0664E-14	5.56504E-08	4.5332E-09
TF0069	BMP	2018	5.25	12031.11	1.20311E-05	2360.39	2.21866E-12	1.80729E-13	1.10933E-07	9.03643E-09
TF0030	BMP	2010	0.08	51.07	5.10675E-08	657.49	9.41736E-15	7.67124E-16	4.70868E-10	3.83562E-11
TF0012	BMP	2013	4.34	4181.80	4.1818E-06	992.45	7.71166E-13	6.28181E-14	3.85583E-08	3.1409E-09
TF0012	BMP	2014	4.01	4414.90	4.4149E-06	1134.00	8.14152E-13	6.63197E-14	4.07076E-08	3.31598E-09
TF0012	BMP	2017	4.047	8155.12	8.15512E-06	2075.54	1.50389E-12	1.22504E-13	7.51943E-08	6.12522E-09
TF0010	BMP	2011	1.55	1331.60	1.3316E-06	884.87	2.45561E-13	2.0003E-14	1.2278E-08	1.00015E-09
TF0010	BMP	2014	1.66	973.60	9.736E-07	604.10	1.79542E-13	1.46252E-14	8.97709E-09	7.3126E-10
TF0010	BMP	2018	0.96	1144.52	1.14452E-06	1227.98	2.11061E-13	1.71927E-14	1.05531E-08	8.59637E-10
TF0360	BPM	2014	0.42	464.60	4.646E-07	1139.38	8.5677E-14	6.97912E-15	4.28385E-09	3.48956E-10
EMB046/10-2 MUC	OP-2016-02 NAR	NO	2.366	2672.34	2.67234E-06	1163.36	4.92806E-13	4.01433E-14	2.46403E-08	2.00716E-09
EMB046/20-2 MUC	OP-2016-02 NAR	NO	2.516	3465.69	3.46569E-06	1418.78	6.39108E-13	5.20608E-14	3.19554E-08	2.60304E-09
TF0271/St.27 1	Annox 2016 EMB135	2016	10.24	4462.36	4.46236E-06	448.84	8.22904E-13	6.70326E-14	4.11452E-08	3.35163E-09
TF0272/St.27 2	Annox 2016 EMB120	2016	0.87	1361.80	1.3618E-06	1604.87	2.5113E-13	2.04567E-14	1.25565E-08	1.02284E-09

Table S5. Mass balance sum 6PCB, DDT, and HCB in seawater. (a) Concentrations (pg/dm³). (b) mass balance, calculation with total Baltic Sea water volume (21. 630 km³) and concentration range.

(a)

Year	Western Baltic Sea		Central Baltic Sea	
	2001			
pg/dm ³	dissolved	particulate	dissolved	particulate
6PCB	10,6	7,7	6,7	1,5
DDTs	19,4	7,5	17,1	2,0
HCB	6,1	0,8	5,7	0,4

Year 2018	Western Baltic Sea		Central Baltic Sea	
	pg/dm ³	dissolved	particulate	dissolved
6PCB	4,0	3,1	2,3	0,3
DDTs	4,1	3,2	3,8	0,5
HCB	8,0	0,5	5,8	0,1

(b)

	Total Baltic Sea	
Year 2001	dissolved (kg)	particulate (kg)
6PCB	145 - 229	32 - 166
DDTs	369 - 419	43 - 162
HCB	123 - 132	8 - 16
	Total Baltic Sea	
Year 2018	dissolved (kg)	particulate (kg)
6PCB	50 - 86	7 - 67
DDTs	82 - 88	11 - 80
HCB	125 - 173	2 - 11

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