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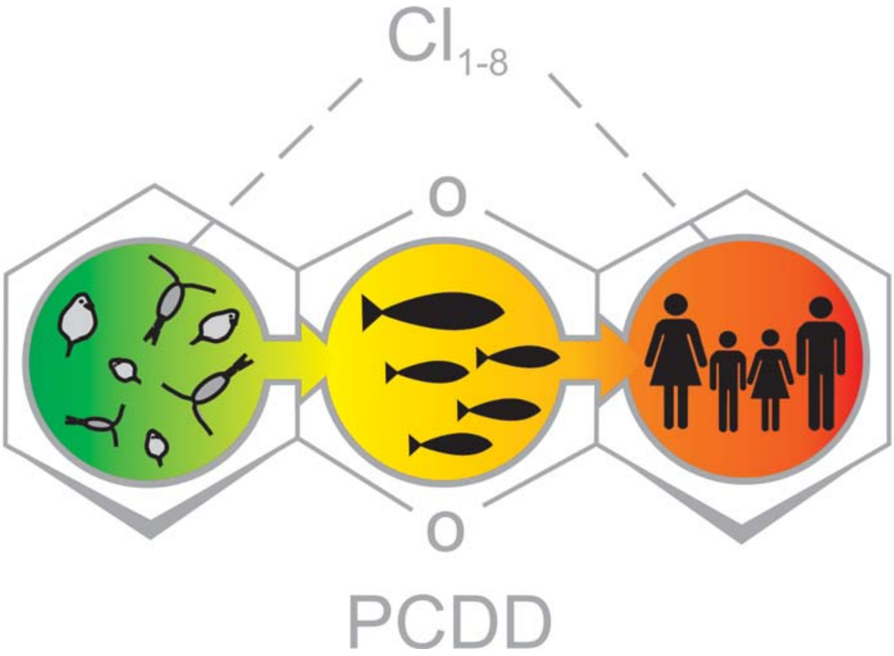
184

Mikko Kiljunen

Accumulation of Organochlorines in Baltic Sea Fishes



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UNIVERSITY OF JYVÄSKYLÄ

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Editors
Timo Marjomäki
Department of Biological and Environmental Science, University of Jyväskylä
Irene Ylönen, Marja-Leena Tynkkynen
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ABSTRACT

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Yhteenveto: Organoklooriyhdisteiden kertyminen Itämeren kaloihin
Diss.

Commercially important Baltic Sea fish species such as herring (*Clupea harengus* L.) suffer from high concentrations of toxic and highly bioaccumulative organochlorines (OCs). This thesis investigates accumulation of these compounds in the Baltic Sea from invertebrates through herring, sprat (*Sprattus sprattus* (L.)) and three-spined stickleback (*Gasterosteus aculeatus* L.) into salmon (*Salmo salar* L.) and onwards to humans. Strategies to reduce present OC concentrations in fish and therefore human intake are also tested. The thesis presents some methodological insights into application of stable isotope analysis, used in accumulation studies. Age and growth seems to explain most of the individual variation in herring OC concentrations. An accumulation model constructed for herring together with empirical data suggested that growth plays a significant role in explaining the differences in OC concentration between sea areas. Changes in herring growth during past decades are the most probable explanation for observations that herring organochlorine concentrations have levelled out. Stable isotopes combined with an accumulation model developed for salmon revealed that individual and spatial variability in salmon OC concentrations arose from the differences in the salmon diet, trophic position, as well as prey OC concentrations and lipid content. Based on the theory of density-dependence in herring growth, the accumulation model combined with age-structured simulations and a probabilistic human intake model showed that concentration in the Baltic herring could be decreased substantially by increased fishing. This would also decrease human dietary intake of OCs. However, significant reduction in concentrations would require high exploitation rates and there is a risk that this would lead to over fishing of herring. Therefore, risk management of organochlorines by regulating fishing seems to be a less effective way to decrease the human dietary intake of organochlorines than directly regulating the consumption of the most contaminated herring.

Keywords: Baltic Sea; bioaccumulation; fish; human intake; PCB; PCDD/F; stable isotopes.

Mikko Kiljunen, University of Jyväskylä, Department of Biological and Environmental Science, P.O. Box 35, FI-40014 University of Jyväskylä, Finland

Author's address
Mikko Kiljunen
Department of Biological and Environmental Science
P.O. Box 35
FI-40014 University of Jyväskylä
Finland
mikkilj@bytl.jyu.fi

Supervisors
Professor Juha Karjalainen
Department of Biological and Environmental Science
P.O. Box 35
FI-40014 University of Jyväskylä
Finland

Professor Roger I. Jones
Department of Biological and Environmental Science
P.O. Box 35
FI-40014 University of Jyväskylä
Finland

Reviewers
Professor James F. Kitchell
University of Wisconsin-Madison
680 North Park Street
Madison WI 53706
U.S.

Academy Professor Jussi Kukkonen
University of Joensuu
P.O. Box 111
80101 Joensuu
Finland

Opponent
Professor Sture Hansson
Department of Systems Ecology
Stockholm University
SE-106 91 Stockholm
Sweden

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LIST OF ORIGINAL PUBLICATIONS

LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following original papers, which will be referred to in the text by their Roman numerals I-V. I was responsible author and have planned, performed and written a significant part of the papers I-III and V. In paper IV, Heikki Peltonen was the responsible author while I was responsible for the accumulation modelling and made a significant contribution to writing and planning the paper. In paper V the expertise of Mari Vanhatalo, Samu Mäntyniemi and Sakari Kuikka was used in constructing a probabilistic model and interpreting the results. All the co-authors have contributed to planning, data collection and analysis, and writing of the papers.

I Kiljunen, M., Grey, J., Sinisalo, T., Harrod, C., Immonen, H. & Jones, R. I. 2006. A revised model for lipid normalizing $\delta^{13}C$ values from aquatic organisms, with implications for isotope mixing models. Journal of Applied Ecology 43: 1213-1222.

II Kiljunen, M., Peltonen, H., Vuorinen, P. J., Kiviranta, H., Verta, M. & Karjalainen, J. 2007. Reduced growth rate offsets expected decline in organochlorine concentrations in the Baltic Sea herring (Clupea harengus L.). Submitted manuscript.

III Kiljunen, M., Peltonen, H., Jones, R. I., Kiviranta, H., Vuorinen, P. J., Verta, M. & Karjalainen, J. 2007. Coupling stable isotopes with bioenergetics to evaluate sources of variation in organochlorine concentrations in Baltic salmon (Salmo salar L.). Submitted manuscript.

IV Peltonen, H., Kiljunen, M., Kiviranta, H., Vuorinen, P. J., Verta, M. & Karjalainen, J. 2007. Predicting effects of exploitation rate on weight-at-age, population dynamics and bioaccumulation of PCDD/Fs and PCBs in herring (Clupea harengus L.) in the northern Baltic Sea. Environmental Science & Technology 41: 1849-1855.

V Kiljunen, M., Vanhatalo, M., Mäntyniemi, S., Peltonen, H., Kuikka, S., Kiviranta, H., Parmanne, R., Tuomisto, J. T., Vuorinen, P. J., Hallikainen, A., Verta, M., Pönni, J., Jones, R. I. & Karjalainen, J. 2007. Human dietary intake of organochlorines from Baltic herring: Implications of individual fish variability and fisheries management. Ambio 36: 257-264.

1 INTRODUCTION

1.1 The “dioxin dilemma” in the Baltic Sea

The Baltic Sea is a relatively shallow and semi-enclosed brackish water system. Due to these unique characteristics, the Baltic Sea and its fauna are very sensitive to human activities. In addition to atmospheric input from other parts of Europe, millions of people (85 million at the present) in the Baltic Sea drainage basin have loaded the system for decades. This has lead to the Baltic Sea being among the most heavily polluted sea areas in the world (Schultz-Bull et al. 1995). In a relatively short time the Baltic Sea has experienced large ecological changes such as increased eutrophication due to an exponential increase in anthropogenic activity (Omstedt et al. 2004). Along with eutrophication, persistent toxic substances such as dioxins and other organochlorines (OCs) have accumulated in the ecosystem and caused a variety of problems in top predators of the Baltic Sea, such as seals and fish eating birds (e.g. Vos et al. 2000, Lundstedt-Enkel et al. 2006), and are considered a serious risk for human health. At present, eutrophication and persistent pollutants can be considered the main problems in the Baltic Sea (Skei et al. 2000).

Concentrations of OC compounds in the Baltic biota, along with human dietary exposure, have generally declined, but very high levels are still measured from commercially important fish species. These include Baltic herring (*Clupea harengus* L.), in which concentrations have not changed during the 1990s (Olsson et al. 2003, Kiviranta et al. 2003), and Baltic salmon (*Salmo salar* L.). Despite the fact that the OC concentration of Baltic salmon and large Baltic herring may exceed EU maximum level for fish and fisheries products manyfold (Kiviranta et al 2001, Parmanne 2006), Finland and Sweden are still authorized to place these fish on their domestic markets for a transitional period until 2011 (Anon. 2006a). At the national level, Finnish and Swedish health and food authorities have considered that risks of contaminants in Baltic fish are outweighed by their health benefits; therefore a total ban on consumption has not been recommended (Assmuth & Jalonen 2005). However, health and food authorities have recommended that children and persons of reproductive age should consume only once or twice per month large Baltic herring (>17 cm) or wild Baltic salmon, which can exceed the present EU maximum level for OC compounds in fish and fisheries products (Anon. 2005, Anon. 2007). Nevertheless, in the case of Baltic herring and salmon a significant amount of toxins is concentrated in one particular foodstuff. This may cause increased health risk for high-level consumers of these foodstuff. Therefore there is a continued need to find new ways of reducing contaminant concentrations in the Baltic fish and to investigate the sources of contaminants.

1.2 Organochlorines and their accumulation

Organochlorines are organic compounds that contain covalently bonded chlorine atoms. The term organochlorine covers numerous classes of compounds, but this thesis deals only with polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), commonly known as "dioxins" and with polychlorinated biphenyls (PCBs). Altogether there are 209 different PCB compound types called congeners. Similarly, the "dioxin" family consists of 70 different PCDD and 135 PCDF congeners (Kiviranta 2005). Not all these congeners are toxic, but 17 PCDD/F and 12 PCB congeners have been shown to cause toxic responses similar to those caused by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), which is considered the most potent of all congeners in these groups (Van den Berg et al. 1998). PCBs have been banned from production in most countries, but they were used for decades in electrical transformers, pesticides, cosmetics, varnishes, inks, paints etc. (Anon. 2000). PCDD/Fs, however, have not been intentionally produced, but have been by-products in pesticides, wood preservatives and chlorine bleaching products and are released in combustion processes (Wenborn et al. 1999).

In the environment, organochlorines usually appear as complex congener mixtures, each congener having its own level of toxicity. Therefore, the total amount of organochlorines is not the best measure of the actual toxicity. To estimate toxicity of organochlorine mixtures, toxic equivalent factors (TEF) have been developed, which are toxicity estimates of individual congeners relative to 2,3,7,8-TCDD. TEF values can be used to calculate toxic equivalent (TEq) concentrations by summing concentrations of the toxic congeners which have been multiplied by their TEF values (Van den Berg et al. 1998). In the European Union (EU), World Health Organisation toxic equivalents (WHO-TEq) are used to express organochlorine concentrations and their maximum levels in foodstuffs (Anon. 2006a). The present EU maximum level for the sum of PCDD/Fs and PCBs in fish and fisheries products has been set to 8 pg $\mathrm{WHO_{PCDD/F\text{-}PCB}}$-TEq g^{-1} (except 12 pg g^{-1} for eel (*Anguilla anguilla* (L.)) (Anon. 2006a).

Many organochlorines have accumulative properties defined by their stability in the environment, persistence through biological processes and lipophilicity (Sinkkonen & Paasivirta 2000). Therefore these compounds bioaccumulate and biomagnify in the food webs, causing an increase in concentration during the lifetime of an animal and with every trophic level (Gobas et al. 1993) — all the way to humans. In the process of bioaccumulation, chemical concentration in an organism comes to exceed that in the ambient water due to uptake of a chemical by dietary absorption, transportation through respiratory surfaces and dermal absorption (Mackay & Frazer 2000), of which dietary absorption is the dominant pathway in higher trophic levels (Gobas et al. 1993). A special case of bioaccumulation, when dietary absorption dominates the accumulation process and the flux of contaminant into the fish through dietary absorption is not compensated by fluxes out of the fish, can be regarded as biomagnification (Mackay & Frazer 2000, Burreau et al. 2006). This thesis deals with both of these processes by investigating bioaccumulation of organochlorines into particular Baltic Sea fish species and studying biomagnification in the Baltic Sea food web.

1.3 Trends in organochlorine concentrations

Due to their widespread usage and persistence through biological processes, organochlorines can be found all over the world and in all organisms. Baseline concentrations depend on latitude and compound volatility, since they are subject to condensation in the earth's athmosphere during long-range transportation (Wania & Makay 1993, Simonich & Hites 1995). Therefore, volatile compounds have higher concentrations in the Polar Regions, but non-volatile and thus immobile compounds have highest concentrations near the source (Wania & Makay 1993, Simonich & Hites 1995, Blais et al. 1998, Kallenborg 2006). It has also been shown that high altitude environments can act as a "cold condenser" for atmospheric contaminants and therefore exhibit higher concentrations than low-altitude ecosystems of the same geographical region (Blais et al. 1998, Blais et al. 2003, Kallenborg 2006).

Worldwide comparison of the OC concentrations in animals is difficult due to differences in ecosystems structures, analysed tissue and presentation of the results (Aguilar et al. 2002, Domingo & Bocio 2007). However, marine animals with similar feeding habits seem to have the highest OC levels in the temperate fringe of the northern hemisphere in Europe and North America (Aguilar et al. 2002). Hites et al. (2004) compared farmed and wild salmon OC concentrations between North and South America and Europe and found that salmon produced in Europe have generally higher contaminant levels than in other areas. Lowest concentrations can be found from the tropical and equatorial fringes as well as from Polar Regions (Aguilar et al. 2002), except for some highly volatile compounds (Wania & Makay 1993).

The first concerns about high concentrations of organochlorines (DDT) in marine wildlife were published in the mid 1960s (Koeman & Van Genderen

1966). Just three years later the first PCB analyses were made from Baltic Sea biota and concentrations were found to be alarmingly high (Jensen et al. 1969). According to sediment core analyses (Jonsson et al. 2000, Olsson et al. 2000, Isosaari et al. 2002a), organochlorine concentrations reached their highest levels in the Baltic Sea just at the time of the investigations by Jensen et al. (1969). OC concentrations in the Baltic Sea in general have since come down and the decrease in concentrations of PCBs has been about 3-5 % a year (Bignert et al. 1998, Olsson et al. 2000). However, there has been no major change in OC concentrations in Baltic herring or concentration in eggs of common guillemot (*Uria aalge* Pontoppidan) feeding on Baltic herring in the 1990s (Kiviranta et al. 2003, Olsson et al. 2003). There is a general trend for fish PCB and PCDD/F concentrations to be lower in the southern parts of the Baltic Sea than in northern parts (Bignert et al. 1998, Isosaari et al. 2006).

1.4 Towards better ecological understanding

Since organochlorine research in the Baltic Sea has been rather survey-orientated, the ecological processes in organochlorine cycling and initial bioaccumulation are poorly known. There are considerable spatial and individual variations in OC concentrations of Baltic fish (Bignert et al. 1998, Berglund et al. 2001, Parmanne et al. 2006, Isosaari et al. 2006, Bignert et al. 2007) which make risk management of these contaminants challenging. Spatial and temporal variations in food web biomagnifications, from phytoplankton through zooplankton to fish, are affected by anthrophogenic loading and environmental factors as well as by differences in community structure and function (Madenjian et al. 1994). Spatial differences could also arise through differences in baseline OC concentrations. Studies of spatial differences in sediment organochlorine concentrations from around the Baltic Sea (Isosaari et al. 2002a, Verta et al. 2007) have shown that spatial differences do indeed exist in organochlorine concentrations, but mainly due to a few major point sources. However, those congeners most abundant in Baltic herring seem to be more of atmospheric origin and hence fairly evenly distributed around the Baltic Sea (Verta et al. 2007). Therefore, it has been supposed that variation in the OC concentrations of herring is mainly due not to baseline differences but to other factors, such as herring diet composition and quality or differences in herring growth rates between different sea areas (Verta et al. 2007). There have been some attempts to assess the origin of this variation for Baltic salmon (Larsson et al. 1996, Vuorinen et al. 1997, Berglund et al. 2001, Vuorinen et al. 2002), but there are still open questions for both herring and salmon, such as why individuals from the same geographical region of similar size and age exhibit high variation in OC concentrations (Parmanne et al. 2006).

Modern tools can offer better knowledge about the ecological processes underlying accumulation of organochlorines. Techniques such as stable isotope analysis (SIA) have become increasingly available for scientists during past decades and are now commonly used in ecotoxicological studies (Broman et al. 1992, Cabana & Rasmussen 1994, Kidd et al. 1995, Kiriluk et al. 1995, Kidd et al. 1998, Berglund et al. 2001, Jardine et al. 2006, Paterson et al. 2006). Trophic transfer causes predictable fractionation of isotope ratios in consumers relative to their diets (DeNiro & Epstein 1978), which allows inference of a consumer's diet or trophic position by comparing its isotopic ratios with those of other species in its food web. The method is most powerful when several isotope ratios are studied simultaneously (Harvey et al. 2002). Many animals are highly opportunistic foragers and their diet may vary substantially over time (Pinnegar & Polunin 1999). Stable isotopes turn over in animal tissue over long periods of time and therefore link consumers to their diet and contaminant source (Cabana & Rasmussen 1994). Moreover, stable isotopes reflect assimilation, unlike conventional gut content analysis which can only reveal what has been ingested. Based on these basic principles, SIA has been used to explain variation in consumer contaminant concentrations in several applications (Jardine et al. 2006). Although SIA seems to be conceptually sound, there are several sources of uncertainty in the methods which are still partly unsolved and need further investigation, such as the role of different body constituents in isotopic fractionation (Gannes et al. 1997). In the worst case such uncertainties in the isotope data may lead to serious misinterpretation of results.

Mathematical modelling is also a widely used tool to predict and understand the accumulation processes (Mackay & Fraser 2000). Bioenergetics combined with SIA makes it possible to study energy flow and interspecific interactions (Caut et al. 2006) as well as biomagnification and bioaccumulation of harmful substances. The increased understanding of accumulation and growth dynamics in animals have resulted in bioenergetics and bioaccumulation models and combinations of these (e.g. Madenjian et al. 1993, Hanson et al. 1997, Luk 2000, DeBruyn & Gobas 2006). Bioenergetics modelling is based on analysis of the growth and metabolic rates of individuals, but due to the hierarchic structure of the energetic budgets it also describes efficiently the trophic transfer and thus, links different levels of biological organization (Kooijman 2000, DeBruyn & Gobas 2006). Therefore bioenergetics processes have a key role in the uptake of persistent pollutants, and variation in concentrations between species and individuals can be largely explained by variation in feeding habits and energy allocation (Debruyn & Gobas 2006)

Combining empirical research, accumulation models and new techniques such as stable isotope analysis, opens new opportunities to investigate bioaccumulation pathways of organochlorines in the Baltic Sea food web from zooplankton through herring, sprat (*Sprattus sprattus* (L.)) and three-spined stickleback (*Gasterosteus aculeatus* L.) into salmon and ultimately into humans.

1.5 Can concentrations be actively reduced?

Limiting input has been the main practice for reducing contaminant levels in the Baltic Sea, and the actual removal process is based on passive removal by sedimentation, volatilisation and export by currents (MacKenzie et al. 2004). Although these measures have been rather successful in the Baltic Sea (Bignert et al. 1998, Jonsson et al. 2000, Olsson et al. 2000, Isosaari et al. 2002a), concentrations in some species have levelled out and there is a need to further diminish concentrations actively. MacKenzie et al. (2004) suggested that collecting highly contaminated organs from the cod (*Gadus morhua* L.) fisheries and not throwing them overboard would have a significant impact on pollution management of the Baltic Sea. Another option would be to increase fishing of some highly abundant species in such a way as not to endanger the fish stocks. These two techniques are based on biomass removal and therefore they would decrease contaminant levels of the whole system, assuming that removed contaminants will not return. Increased fishing mortality or natural mortality could also affect the concentration through alternative pathways. For example, using more intensive fishing in order to enhance the growth rate of individual fish has been suggested as a means to reduce concentrations of OC in the Baltic Sea herring (Parmanne et al. 2006).

It has been suggested that during the twentieth century the Baltic Sea has shifted from a top-down controlled, oligotrophic, seal-dominated system to a bottom-up controlled, eutrophic, clupeid-dominated system, mainly due to human activity (Hansson et al. 2007, Österblom et al. 2007). This has resulted in extremely large changes in Baltic herring growth during the last few decades (Anon. 2006b). There is evidence that in the Baltic main basin herring growth is regulated by density-dependence, as abundant planktivorous fish, especially sprat and herring, deplete zooplankton resources and induce poor growth rates in these fish species (Kornilovs et al. 2001, Möllmann et al. 2005, Casini et al. 2006). Existence of density-dependence in fish growth would mean that actively decreasing stock density by fishing or by increasing predation pressure (e.g. decreasing exploiting of cod) could lead to higher growth rates. Higher growth rate would ultimately lead to lower OC concentrations compared to individuals at same size with lower growth rate (Stow & Carpenter 1994, Trudel & Rasmussen 2006), since individuals with high growth rate have lower activity costs and therefore allocate more energy for growth and less for maintenance than fish with low growth rate (Borgmann & Whittle 1992, Trudel & Rasmussen 2006). The less fish feed to attain a certain weight, the fewer persistent organic pollutants they get from food and the lower concentrations of toxicant they have in their tissues. This growth dilution hypothesis has been used to explain OC concentrations in the Great Lakes fish populations. Modelling studies on predator-prey interactions and their effect on accumulation of OCs (Madenjian & Carpenter 1993, Stow & Carpenter 1994, Madenjian et al. 1995, Jackson 1996) have investigated the approach.

1.6 New knowledge for human risk assessment

Several causal dependencies behind the Baltic "dioxin dilemma" are highly uncertain (Assmuth & Jalonen 2005). This uncertainty in human intake of organochlorines has been largely ignored in human risk assessment, partly due to lack of basic information such as variability in fish concentrations. However, in recent years variability in organochlorine concentration in commercially important fish species such as herring, which is the origin of about one third of the total dietary intake of PCDD/Fs and PCBs in Finland and about one fifth in Sweden (Darnerud et al. 2000, Hallikainen et al. 2006), has been recognized (Parmanne et al. 2006) and techniques taking account of causal dependencies are being developed. The role of this thesis in human risk assessment of toxicants is to provide improved knowledge on the significance of different variables in the accumulation process of PCBs and PCDD/Fs. Hopefully these will improve the basis for future development of these techniques and means to diminish these toxicants in Baltic fish, thereby reducing risks for human health from Baltic fish consumption.

2 OBJECTIVES

The main objectives of this thesis were: 1) to study biomagnification of PCBs and PCDD/Fs from aquatic invertebrates through Baltic herring, sprat, and three-spined sticklebacks into salmon and human; 2) to identify reasons for the great individual and spatial variation in PCBs and PCDD/Fs concentrations in Baltic Sea fish; and 3) to evaluate the effects of alternative exploitation patterns (e.g. variable fishing efforts) on the contaminant accumulation in Baltic herring and humans. The thesis has the following specific aims.

i) To evaluate the applicability of carbon stable isotope lipid-normalisation methods in aquatic animals and use stable isotopes to study variation in organochlorine accumulation (I, III).
ii) To use bioenergetics modelling to analyse whether differences in herring growth rates observed around the Baltic Sea could explain variation in their PCDD/F and PCB concentrations (II).
iii) To couple bioenergetics accumulation models to SIA in order to quantify the contribution of each prey species to PCB and PCDD/F accumulation in Baltic salmon, and to determine the extent to which factors explain the observed variation in organochlorine concentrations of individual salmon (III).
iv) To couple bioenergetics accumulation and probabilistic human intake models in order to assess whether PCBs and PCDD/Fs concentrations in Baltic herring could be regulated by fisheries management and what would be the implications of these management actions for human dietary intake of PCB and PCDD/F (IV-V).

3 MATERIAL AND METHODS

3.1 Sampling and analytical procedures

This thesis is based for the most part (II-V) on samples collected from the Bothnian Sea, northern Baltic Proper and Gulf of Finland (Fig. 1), except for the study presented in the following chapter (I). 25 salmon individuals and their main prey species, herring, sprat and three-spined sticklebacks were obtained from commercial and experimental catches in 2003 and 2004. Age-group pools for herring (1, 2, 3, 6 and 10) and for sprat (1, 3 and 7) from each study site were created. Three-spined sticklebacks were pooled according to sampling year and location. To estimate energy loss and elimination of toxicants during spawning (IV), the somatic parts and gonads of 20 individual spawning-ready herrings from the Gulf of Finland were analysed for OCs. Specimens were divided equally between both sexes, and two age-groups. Gutted, weighted, measured and aged individual salmon, pooled prey fish carcases and gonads were further homogenised using a mincer. To generate trophic position for the analysed fish using stable isotopes of nitrogen (III), cladocerans from 17 bulk zooplankton samples, collected from the same time periods and locations as fish, were hand picked from the samples and pooled according to sampling year and location. A small part of each homogenized and freeze-dried salmon, herring and sprat sample was analyzed for energy density using an adiabatic bomb calorimeter at the Finnish Game and Fisheries Research Institute. Supplementary herring samples, analysed only for organochlorines (V), were obtained from the Finnish National Public Health Institute. These 90 individual herring were caught from the commercial trawl fishery in the eastern part of the Bothnian Sea (Fig 1.) in 2002 and analysed for OCs using procedures similar to other fish in the thesis.

FIGURE 1 The three study areas in the northern Baltic Sea: Bothnian Sea, northern Baltic Proper and Gulf of Finland.

The fish samples were analysed for lipid content and organochlorines at the Finnish National Public Health Institute Laboratory where homogenized fish samples were freeze-dried and Soxhlet-extracted for 20 h with toluene, and lipid content was measured gravimetrically from the extract. Purification of the samples and fractionation of the studied compounds as well as the analytical procedure and quality control, were similar to Isosaari et al. (2002b), Kiviranta et al. (2003) and Isosaari et al. (2006). High resolution gas chromatography-mass spectrometry was used to determine organochlorine concentrations. Concentrations of 17 PCDD/F and 12 PCB congeners were calculated as lower bound values (concentrations of non-detected congeners are set to zero) per wet weight (WW) of fish muscle tissue. The toxic equivalent concentrations (WHO-TEq) for both PCDD/Fs and PCBs were calculated according to Van den Berg et al. (1998). Results are presented as pg WHO_{total}-TEq g^{-1} (WW) which is the sum of $WHO_{PCDD/F}$-TEq and WHO_{PCB}-TEq concentrations. Although all the calculations in this thesis have been made congener-specifically, most of the results are expressed in WHO toxic equivalents in order to characterize the risks of organochlorines from a human perspective by maintaining comparability of concentrations to maximum levels set by EU authorities (8 pg $\mathrm{WHO_{total}}$-TEq g^{-1}).

Stable isotopes of carbon and nitrogen were analysed in the University of Jyväskylä, Finland (I, III) and Max Planck Institute for Limnology in Plön, Germany (I). Prior to stable isotope analysis fish and invertebrate samples were dried to constant weight and ground to fine powder. Nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) stable isotope ratios of samples were determined using an elemental analyser connected to a continuous-flow stable isotope ratio mass spectrometer. Fish $\delta^{13}C$ values were lipid normalized according to paper I. Nitrogen isotope values were used to calculate trophic positions of studied fish species (III). Trophic position (TP) was calculated using the equation of Vander Zanden et al. (1997)

$$TP_{organism} = [(\delta^{15}N_{organism} - \delta^{15}N_{primary\ consumer}) / \Delta 15N] + 2$$

where $\delta^{15}N_{organism}$ and $\delta^{15}N_{primary\ consumer}$ are measured $\delta^{15}N$ values of fish and cladocerans. $\Delta 15N$ is enrichment of $\delta^{15}N$ for one trophic level which was here assigned to be 2.9 ‰, based on Sweeting et al. (2007). These trophic position estimates were used to explain variation observed in salmon OC concentrations.

3.2 Lipid normalisation model for carbon stable isotopes (I)

All the fish $\delta^{13}C$ values in the thesis were normalized for lipids, since lipids are ^{13}C–depleted relative to other major tissue constituents and therefore can potentially complicate interpretation of dietary sources of carbon. Mathematical normalisation models have frequently been applied in order to remove this effect of lipids. However, these models have never been properly validated. In the methodological part of the thesis (I), two widely used lipid-normalisation models (McConnaughey & McRoy 1979, Alexander et al. 1996) based on C:N ratios were evaluated by comparing model $\delta^{13}C$ predictions with observed data from samples with and without chemical lipid-extraction. Data included dorsal muscle tissue from 20 fish species (n = 289) and five groups of whole invertebrates (n = 47) from three different aquatic environments (I). Dried and powdered samples were divided in two and one part was treated to extract lipids chemically (Blight & Dyer 1959). Both halves were analysed for dual isotope ($\delta^{13}C$, $\delta^{15}N$) isotope ratios.

Since neither model provided a satisfactory fit to the observed data, the McConnaughey & McRoy (1979) model was modified by iteratively fitting it to observations. The modified model, and for a comparison estimates of previous models, were validated using independent fish data. The model was then used to investigate how lipid-normalisation could influence isotope mixing model calculations of diet contributions to a Baltic Sea top predator using scenarios covering all possible combinations of lipid correction of predator and prey $\delta^{13}C$

values. Dual isotope ratios ($\delta^{13}C$, $\delta^{15}N$) were applied to determine the contribution of each prey species to the diet of the predator using the IsoSource computer program (Phillips & Gregg 2003).

3.3 Bioenergetics accumulation models (II-V)

Bioenergetics accumulation models were used to estimate accumulation of PCBs and PCDD/Fs in Baltic herring and salmon. The models were based on the well known mass balance energy budget (Winberg 1960)

$$C = R + E + G$$

in which energy consumed by a predator (C) is equal to the sum of metabolism (R), waste loses (E) and growth (G). The model structure relied on the so-called "Wisconsin model" (Hanson et al. 1997). This model has procedures for contaminant analysis, but the software (Fish Bioenergetics 3.0b) itself is not adaptable for calculation of several contaminants at once. In this thesis the aim was to calculate toxic equivalence values (TEqs) for PCDD/Fs and PCBs, which requires simultaneous calculation of 29 congeners. Therefore more adaptable bioenergetics accumulation models were designed for calculation of contaminants. The new models were constructed using VBA (Visual Basic for Applications) programming language. Extensive input data for the models were obtained from our own analyses, analyses from several collaborators and a large amount of literature reviewed.

3.3.1 Accumulation model for Baltic herring (II, IV and V)

The herring bioenergetics model parameters were set according to Rudstam (1988). Based on Winters and Wheeler (1994) one of the model parameters was iteratively re-estimated to prevent too high seasonal variations in the body weight and excessive weight loss during winter at temperatures below 1°C. The average monthly water temperatures from the Bothnian Sea obtained from the Finnish Environmental Institute Water Quality Register were used. Herring diet consisted of zooplankton, mysids and amphipods, with seasonal and length-dependent variations in proportions (Arrhenius & Hansson 1993). Energy densities of diet items were set according to literature (Cummins & Wuychuck 1971, Hakala 1979, Downing & Rigler 1984, Wiktor & Szaniawska 1988). Herring energy density was calculated according to Arrhenius & Hansson (1996). It was assumed that herring mature at an age of three years and thereafter spawn annually in mid June.

The Proportion of each OC congener eliminated during spawning was estimated from the somatic parts and gonads of spawning-ready herrings, analysed for OCs. The same constant congener-specific OC concentrations were used for both mysids and amphipods (Näf et al. 1997). Zooplankton OC concentrations were obtained from the Finnish Environmental Institute (Chief Scientist M. Verta, personal communication, 2005). Calculated daily consumption estimates were used to predict the daily uptake of 29 OC congeners into salmon tissue from the food consumed (Hanson et al. 1997)

$$X_c = C_c \, AE_c$$

where assimilation of a congener into fish tissue (X_c) equals total amount of a congener consumed in food (C_c) multiplied by the assimilation efficiency of the congener (AE_c). Most congener-specific assimilation efficiencies were derived from Isosaari et al. (2005). If these were not available, mean values of all other congeners were used. It was assumed that herring assimilates each OC congener at a congener-specific rate which was in each case constant, except for one congener (2,3,4,7,8-PeCDF). The total uptake of each individual congener was calculated as a cumulative sum of the daily uptakes and the final concentration estimates (pg g^{-1}) were calculated by dividing the total uptake by fish mass. The predicted concentrations from the bioenergetics accumulation model were compared to the observed herring OC concentrations from the Bothnian Sea (IV). The model predicted the observed concentrations well, except for 2,3,4,7,8-PeCDF (IV). Therefore, the accumulation efficiency for this congener was calibrated with the observed concentrations and a weight-dependence model was fitted for assimilation (IV). After calibration, the accumulation model produced congener profiles that closely resembled those from the independent data from Bothnian Sea herring (IV).

In paper II the results from the herring bioenergetics accumulation model developed for Bothnian Sea (IV) were set as a baseline for OC concentration. In order to investigate whether growth could explain concentration differences between sea areas, this baseline model was modified for weight-at-age (WAA) data (Anon. 2006b) and water temperature from the Gulf of Finland and Northern Baltic Proper. Fixing all factors other than growth and water temperature would reveal the extent to which growth affects observed OC differences in herring between study areas. This was investigated by comparing predicted weight-to-OC-concentration relationships to the similar observed relationships from the same locations, and calculating the proportional shift in the predicted exponential regression slope between baseline and observed values. Site-specific WAA data (Anon. 2006b) were further used to estimate temporal changes in herring OC concentrations in the Bothnian Sea and northern Baltic Proper. For the Bothnian Sea we used the same baseline model described earlier. For the northern Baltic Proper the same model was calibrated for the diet concentration by iteratively changing diet OC concentration until it equalled observed concentrations for the northern Baltic Proper. These two models were used to predict the temporal change in herring OC concentration from the beginning of the 1980s to the present. Since there is no reliable information on temporal change of the diet concentrations of herring, predictions were not corrected for this. Predictions were further compared to the herring average weights from the same time period.

In paper IV a simulation model was applied to predict the stock dynamics and weight-at-age of the Bothnian Sea herring assuming different exploitation alternatives: a) herring mortality rates unchanged, b) 50 % increase in herring fishing mortality (F), c) 100 % increase in herring F, d) 50 % increase in herring natural mortality (M) e) 50 % decrease in herring F and f) herring fishery completely closed. A stochastic recruitment model with the deterministic population model and the weight-at-age model were integrated. The resultant average weight-at-age values from the models were used as input data to the subsequent bioenergetics model and contaminant accumulation estimations. The accumulation rates of PCBs and PCDD/Fs in different herring age-groups were estimated with a bioenergetics accumulation model for each exploitation alternative to investigate how fishing and natural mortality of the Bothnian Sea herring would affect their OC concentrations.

The simulation model constructed in paper IV was coupled with probabilistic human consumption model. This combined model was used in an attempt to account for the variation in human intake of organochlorines originating from the variation among herring individuals (V). Population and bioenergetics models were used to evaluate the effect of fisheries on organochlorine concentrations in the herring catch through density-dependent growth and herring physiology. The data were further used for probabilistic estimation of human organochlorine intake. Estimates were compared to present precautionary limits and recommendations for herring consumption.

3.3.2 Accumulation model for Baltic salmon (III)

A similar bioenergetics accumulation model to that described in the previous section was applied to Baltic salmon to study sources of variation in salmon OC concentrations (III). The bioenergetics model, parameterized according to Beauchamp et al. (1989), was applied to evaluate the contributions of different prey fish species to salmon PCB and PCDD/Fs (Fig. 2). Salmon diet was assumed to consist only of herring, sprat and three-spined stickleback. The original "Wisconsin model" was reformulated by incorporating stochastic prey selectivity functions (Prof. S. Hansson, Stockholm University, personal communication, 2004) in order to create "predation windows" for individual salmon (Fig. 2). Diet proportions were obtained from Hansson et al. (2001). These dietary proportions were supported by the stable isotope results (chapter 4.2.3, III). Based on bomb calorimeter analyses, mean herring and sprat energy densities for each site were used in the model. An average energy density obtained from the literature was used for three-spined stickleback (Meakins 1976, Smith & Wootton 1995) at all study areas. Salmon energy density input values were set according to the original parameters, which were congruent with analysed energy density data. The water temperatures used in calculations were obtained from the Finnish Environmental Institute Water Quality Register.

Daily uptake calculations and assimilation efficiencies of 29 OC congeners into salmon tissue were similar to the herring model. Congener-specific exponential models for herring and sprat lengths (means of the pools analysed for OCs) in relation to congener concentration were generated in order to estimate concentrations in particular sizes of salmon prey. Three-spined stickleback concentrations were set to a constant. We assumed that salmon assimilates each congener at a congener-specific constant rate. The model was validated for the consumption (*C*) by comparing published experimental consumption estimates by Koskela et al. (1997a,b) to those estimated by the bioenergetics model. The whole model, including contaminant calculations, was further validated by comparing the predicted concentration estimates from the bioenergetics accumulation model to the observed OC concentrations.

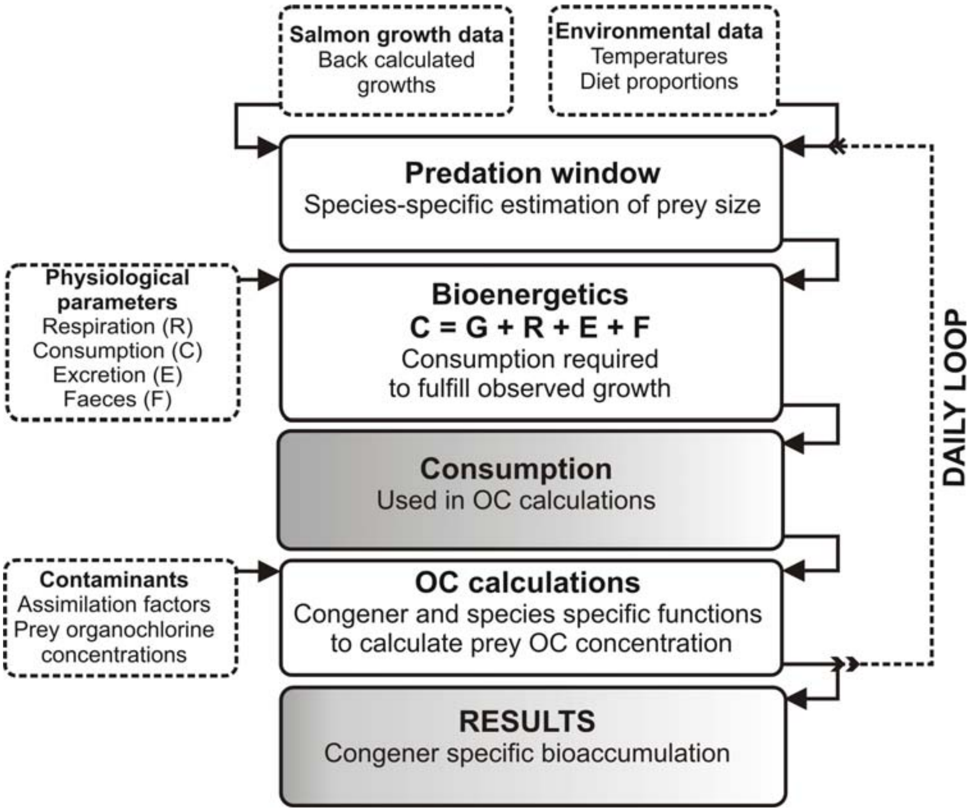

FIGURE 2 The salmon bioenergetics accumulation model used in simulation of organochlorine concentrations in paper III. White dashed boxes represent input data, white solid boxes represent calculation units and grey boxes results.

4 RESULTS AND DISCUSSION

4.1 Concentrations of organochlorines in Baltic Sea fish

WHO_{total}-TEq concentrations of all measured salmon, herring and sprat increased with their age due to bioaccumulation (Fig. 3). Baltic salmon mean WHO_{total}-TEq concentrations markedly exceed EU limits (8 pg WHO_{total}-TEq g^{-1}) for fish and fishery products in all sea-winter groups (Fig. 3). Herring in Bothnian Sea and Gulf of Finland seems exceed this limit at six years old, whereas only sprat in Gulf of Finland exceeded the limit at seven-year-old (Fig. 3).

Herring mean WHO_{total}-TEq concentrations of all measured samples was highest in the Bothnian Sea but those of sprat were highest in the Gulf of Finland (Fig. 3). However, OC concentration in herring and sprat at a certain length was clearly higher in the Gulf of Finland than in the northern Baltic Proper and the Bothnian Sea (III). Similarly, observed WHO_{total}-TEq concentration at a certain weight was also highest in the Gulf of Finland and lowest in the Northern Baltic Proper. Due to the exponential increase in concentration, differences in concentrations between areas increased dramatically with increasing weight (II). Present EU limits for foodstuff (8 pg WHO_{total}-TEq g^{-1}) were estimated to be exceeded in the Gulf of Finland, Bothnian Sea and northern Baltic Proper in herring of weight 22, 33 and 46 grams, respectively (III). Equivalent length values in the Gulf of Finland, Bothnian Sea and northern Baltic Proper were 16.6, 17.6 and 19.0 centimetres (II). These values are in line with recommendations by Finnish and Swedish health and food authorities, that pregnant women, children and people of fertile age should consume only moderate amounts of fatty Baltic fish and mainly small herring (<17 cm), which do not exceed the 8 pg WHO_{total}-TEq g^{-1} limit (Anon. 2005, Anon. 2007). Although 17 cm herring in the Gulf of Finland exceeds the EU- limit, the present herring fishery in the Gulf of Finland is practically non-existent. There were only small differences in WHO_{total}-TEq concentration of three-spined sticklebacks. Mean concentration varied from 2.5 pg g^{-1} in the Gulf of Finland to 3.2 pg g^{-1} in the northern Baltic Proper (Fig. 3).

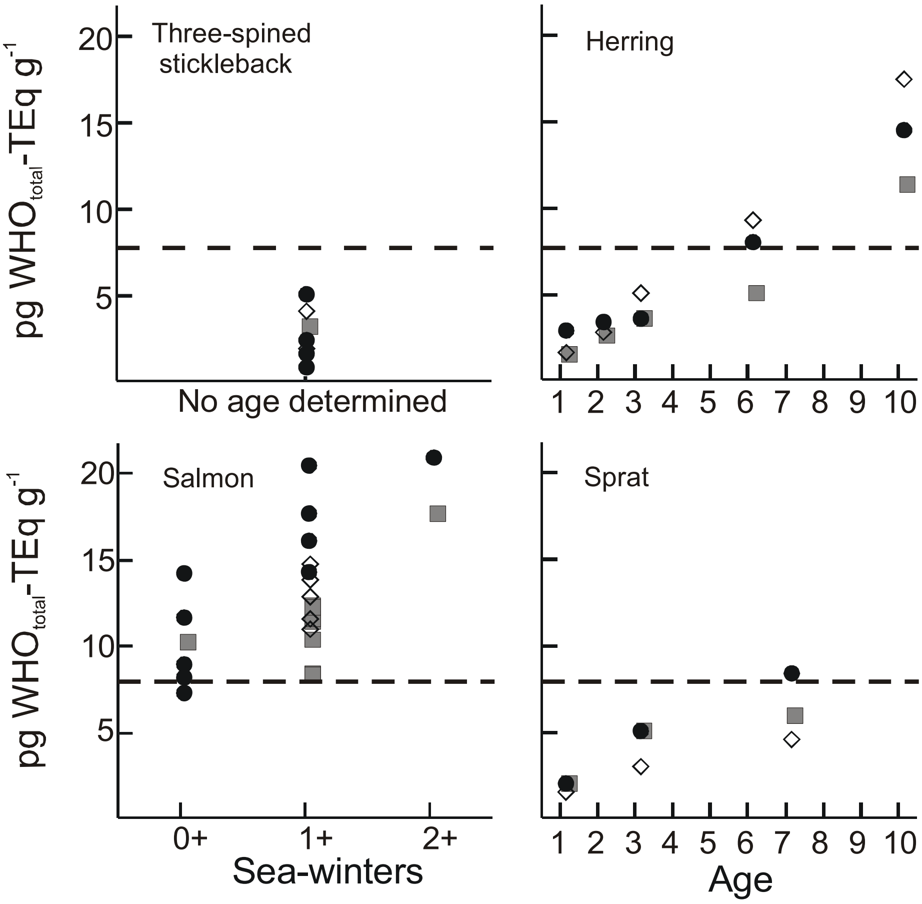

FIGURE 3 Scatterplots of Baltic Sea fish WHO_{total}-TEq concentrations (pg g^{-1} WW^{-1}) in fish at different age, collected from three locations around the northern Baltic Sea: ◇, Bothnian Sea; ■, northern Baltic Proper; ●, Gulf of Finland. Dashed horizontal line represents present EU-limit for PCBs and PCDD/Fs in foodstuff.

The mean salmon concentrations were significantly higher in the Gulf of Finland than in the northern Baltic Proper or Bothnian Sea (Fig. 3), but no difference in concentrations was observed between these latter two sites (III). The difference was not due to age or weight differences between sites, since the same pattern was seen in comparison of one-seawinter individuals and no inter-site difference in weight was observed (III). Mean concentrations of one-seawinter salmon in the Gulf of Finland were on average 5.6 pg g^{-1} (33 %) higher than the mean concentrations in other sea areas (II). These results differ from earlier observations (Isosaari et al. 2006) that muscle concentrations of two year old Bothnian Sea salmon were almost 9 pg g^{-1} higher than concentrations in muscle of the Gulf of Finland salmon. This difference is probably because those analysed salmon were collected during the spring spawning migration which will lead to mixing of feeding populations (Kallio-Nyberg & Ikonen 1992, Salminen et al. 1994, Salminen et al. 2001), whereas samples in this thesis were all collected during the sea feeding phase. Moreover, our analyses were made from whole fish homogenates, which can give different results compared to individual tissues such as muscle (Amrhein et al. 1999). Since WHO_{total}-TEq concentrations are associated with lipids and there was significant inter-site difference in the lipid content of one-seawinter individuals, WHO_{total}-TEq concentrations were ANCOVA lipid normalized. Normalization did not change the interpretation of the results, but the mean difference became even more prominent. The average difference between the Gulf of Finland and other sea areas increased to 8.5 pg g^{-1} (48 %) after lipid normalisation (II). This was due to lower salmon lipid content in the Gulf of Finland than in the other areas.

4.2 Sources of variation in accumulation of organochlorines

4.2.1 Dietary differences and trophic position

The role of dietary differences in observed variation in accumulation of organochlorines in Baltic fish was intended to be investigated using dual stable isotope ratios ($\delta^{15}N$, $\delta^{13}C$). Since it was known that tissues of the studied fish species contain different amounts of lipids, which are ^{13}C–depleted relative to other major tissue constituents (DeNiro & Epstein 1978, Focken & Becker 1998, Thompson et al. 2000), the effect of lipids was to be removed by lipid normalisation models (McConnaughey & McRoy 1979, Alexander et al. 1996). However, the methodological part of the thesis (I) showed that these models are biased and therefore the new modified model was developed. The new model was demonstrated to be applicable to fish samples (I) and was used in the thesis to normalise fish $\delta^{13}C$ values for lipids (III). Unfortunately $\delta^{13}C$ values were eventually too similar between studied fish species and therefore could not be used in the stable isotope mixing models (similar to that in paper I) to estimate proportions of food sources in individual salmon (III) or herring diet. Nevertheless, stable isotopes of nitrogen proved their applicability in accumulation studies (Fig. 4, III).

Correlation between trophic position calculated from $\delta^{15}N$ values for all studied fish species and organochlorine concentrations was highly significant in the Baltic Sea and most of the variation (61 %) in the WHO_{total}-TEq concentration of food web leading to salmon seems to be explained by biomagnification (Fig. 4). Similar results for different fishes have been observed in previous contaminant studies (Broman et al. 1992, Kidd et al. 1995, Kiriluk et al. 1995, Kidd et al. 1998, Berglund et al. 2001, Fisk et al. 2001, Burreau et al. 2006, Paterson et al. 2006). However, there was large species-specific variation, especially with herring. Some of this variation can be explained by age, especially with herring. Older individuals have higher concentrations due to bioaccumulation overtime, although they may have the same diet and therefore occupy the same trophic level as younger individuals.

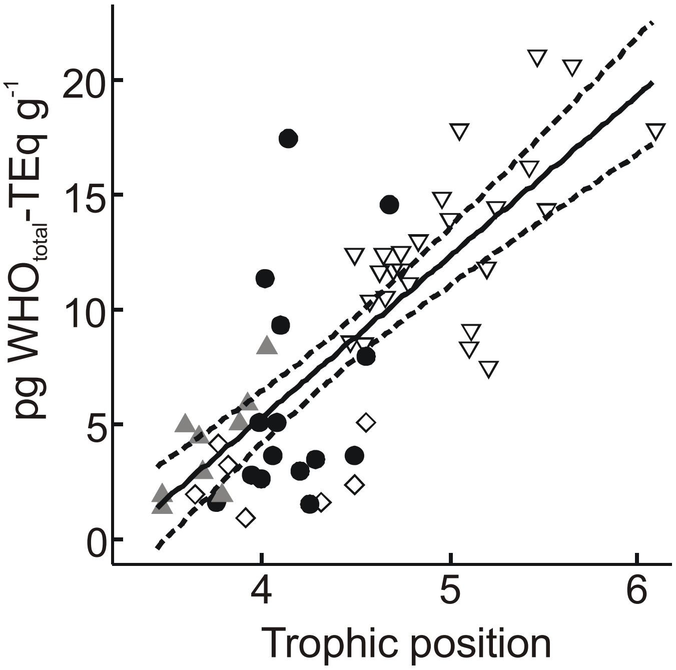

FIGURE 4 Trophic position of all the measured Baltic Sea fish samples (calculated from $\delta^{15}N$ values using cladocerans as baseline values) in relation to WHO_{total}-TEq concentrations (pg g^{-1} WW^{-1}). The solid line indicates the fitted linear relationship and the dashed lines 95 % confidence limits (n = 56, r^2 = 0.612, p < 0.001). ▽, salmon; ●, herring; ▲, sprat; ◇, three-spined stickleback.

4.2.2 Source of variation in herring and sprat

OC concentrations of herring and sprat seem to be largely explained by their growth rate (II, Fig. 5). Growth rate has been shown to be an important factor in the accumulation of toxicants (Jensen et al. 1982, Thomann & Connolly 1984, Borgmann & Whittle 1992, Connolly 1991, Hammar et al. 1993, Madenjian et al. 1993, Blais et al. 2003, Trudel & Rasmussen 2006, Demers et al. 2007). A negative relationship between growth rate and OC concentration in both species demonstrated that fast growing individuals accumulate less OCs than those with lower growth rate (Hammar et al. 1993). This growth dilution or biodilution effect (e.g. Hammar et al. 1993, Blais et al. 2003, Trudel & Rasmussen 2006) seems to decrease the OC concentration in both species. However, fish growth rate decreases with age (II). Therefore these relationships could include hidden dependencies on energy allocation and hence might just present the accumulation process during fish life history without necessarily describing growth dilution.

Intercepts of the relationships were markedly different and herring exhibited a higher concentration than sprat with the same growth rate (Fig. 5). These differences are most likely due to differences in diet composition. Sprat feed almost exclusively on zooplankton whereas herring may also utilize nektobenthos and zoobenthos (Peltonen et al. 2004), which also exhibit higher concentrations of organochlorines (Näf et al. 1997, IV). Physiological dissimilarities between the species might also explain part of the observed difference. Trudel & Rasmussen (2006) demonstrated how different activity rates affected biomagnification of contaminants. These two species might indeed exhibit different activity levels and allocate their energy differently due to differences in their life history traits. Sprat spawn younger (Arrhenius & Hansson 1993) and therefore their metabolic costs associated with increased reproductive activity (Trudel & Rasmussen 2006) and increased energy allocation to reproductive products are larger compared to same age herring. This might lead to differences in bioaccumulation between these two species.

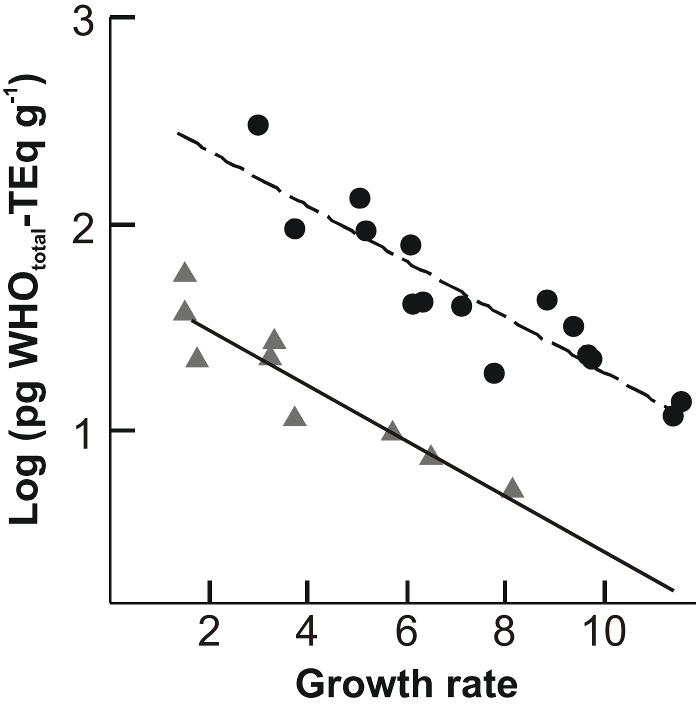

FIGURE 5 Organochlorine concentration (lipid weight) in relation to growth rate (g yr^{-1}) in Baltic Sea, herring (●, $n = 15$, $r^2 = 0.84$, $p < 0.001$) and sprat (▲, $n = 9$, $r^2 = 0.86$, $p < 0.001$).

Simulations using the herring bioenergetics accumulation model suggested that spatial variation in herring OC concentrations in the Baltic Sea is largely a consequence of differences in the herring growth rates (II). The predicted relationship between weight and WHO_{total}-TEq concentration for the Bothnian Sea herring used as a baseline fitted well to the observed herring concentrations from the same area. Applying the northern Baltic Proper growth and temperature in the model changed the slope of the exponential regression line towards the slope of the observed weight – WHO_{total}-TEq relationships in the northern Baltic Proper, suggesting that about 63 % of the concentration differences between the Bothnian Sea and northern Baltic Proper herring were due to differences in growth. The remaining difference (37 %) was presumably related to the diet concentration. Similar analysis using growth and temperature data from the Gulf of Finland revealed that the slope of the baseline was almost equal to that of observed weight – $\mathrm{WHO}_{\mathrm{total}}$-TEq relationships in the Gulf of Finland. Therefore, 95 % of the concentration differences between Bothnian Sea and Gulf of Finland herring were apparently due to the differences in growth and only 5 % was attributable to diet concentrations. Changing growth and temperature data for a particular area in the baseline model shifted OC concentrations towards observed concentrations, suggesting that growth is the major factor in accumulation of persistent OCs in Baltic herring. However, the effect of growth seemed to be less important to the difference in OC concentrations between the Bothnian Sea and the northern Baltic Proper than to that between the Bothnian Sea and the Gulf of Finland. It should be noted, that the analysis ignored potential differences in diet composition between areas.

Simulation also suggests that temporal variation in growth rates has had a marked influence on herring OC concentrations during the past 25 years especially in the northern Baltic Proper. There are numerous factors affecting herring growth in the Baltic Sea. Rönkkönen et al. (2004) have shown that herring growth correlates with salinity. Other factors, such as temperature, food availability and food quality, also affect fish growth (Hanson et al. 1997, Neer et al. 2007) and generate temporal and spatial differences in herring growth. Thus, the growth of clupeids is regulated by complex biotic and abiotic processes which have undergone large changes during the past 20 years in the Baltic Sea (Hansson et al. 2007, Österblom et al. 2007). The ultimate controls over these processes are still not well known, with herring growth having been suggested to be regulated on the one hand by density-independent and on the other hand by food resource mediated density-dependent processes (Österblom et al. 2007). Nevertheless, our analyses suggest that spatial variation in concentration induced by growth is a significant factor in the accumulation process in Baltic herring and therefore should be taken into account when improving the basis for future development of means to diminish human intake of organochlorine from the Baltic Sea herring.

4.2.3 Sources of variation in salmon

Diet proportions had a major effect on accumulation of OC in individual salmon. Concentrations in the herring size class preferred by salmon were 2 to 4 times higher than in sprat or three-spined stickleback (III). Highest herring concentrations were observed in the Gulf of Finland (II, III) where herring is the main salmon prey. Higher concentrations in prey have resulted from extremely retarded growth during recent decades (Rönkkönen et al. 2004), which has lead to increased OC concentrations as shown in the previous section (II). The contribution of each prey species in the salmon $\mathrm{WHO}_{\mathrm{total}}$-TEq accumulation calculated by the bioenergetics model reflected these differences in the diet proportions and prey concentrations (III). Lower lipid content in prey fish in general might also have contributed to the spatial variation in OC concentrations. According to energy content analyses, the main prey species in the Gulf of Finland had up to 22 % lower energy content per unit weight and had almost 40 % lower weight than herring of the same age at other sites (III). Energetically, a low-energy diet (i.e. prey with lower lipid content) necessitates higher consumption to fulfil the growth requirements and hence increases the intake of toxins by fish (Trudel & Rasmussen 2006).

Stable isotopes of nitrogen ($\delta^{15}N$) supported the idea that individual variation of WHO_{total}-TEqs in Baltic salmon is of dietary origin (III). There was a strong linear relationship between WHO_{total}-TEqs and trophic position in the food web calculated from the $\delta^{15}N$ values of individual salmon, which suggests that salmon WHO_{total}-TEq accumulation is related to the diet composition. Some individuals clearly feed more on herring which have a generally high trophic position and therefore higher OC concentration, whereas some individuals feed more on sprat or three-spined stickleback obtaining generally lower trophic positions and OC concentration (Fig. 4). The higher salmon trophic position in the Gulf of Finland may have two explanations. Firstly, in the Gulf of Finland salmon seems to feed mainly on prey items (herring) with a higher trophic position. But secondly, stable isotope data suggest that prey species of salmon in general seems to occupy a slightly higher trophic position in the Gulf of Finland compared to other areas (III). High numbers of the non-indigenous predatory cladoceran, *Cercopagis pengoi* (Ostroumov), have been observed in the herring diet since the 1990s in the Gulf of Finland (Peltonen et al. 2004). *C. pengoi* is truly zooplanktivorous and obtains a higher trophic position than other zooplankters in the Gulf of Finland. Gorokhova et al. (2005) found that invasion of *C. pengoi* elevated the trophic level of herring at the Swedish coast. Hence high abundance of *C. pengoi* might partly explain the elevated trophic positions and increased OC concentrations in the salmon and its fish prey species in the Gulf of Finland. Previous studies applying nitrogen stable isotopes have found other factor such as age, growth and size to be better predictors of OC accumulation in fish (Berglund et al. 2001, Paterson et al. 2006). However, instead of using $\delta^{15}N$ values directly to study OC biomagnifications, this study (III) investigated differences in WHO_{total}-TEq accumulation of single species between different sea-areas using estimates of trophic level calculated from $\delta^{15}N$. This could partly explain the very strong relationship found between salmon trophic position and OC concentration.

The diet of Baltic salmon varies around the Baltic Sea (Andersson 1980, Hansson et al. 2001, Salminen et al. 2001, Ikonen 2006) and reflects the abundance of its prey species in the feeding areas (Hansson et al. 2001) Abundance of prey species varies markedly between Baltic Sea sub basins (Anon. 2006b). This study shows that these differences in prey abundance between Baltic Sea areas, along with differences in prey fish OC concentrations, energy content and trophic position, are factors inducing variable OC concentrations in Baltic Sea salmon.

4.3 Managing accumulation of organochlorines

The herring simulation model predicted substantial changes in growth rates if fishing mortality or natural mortality rates change (IV). Thus, the growth of herring seems to be density-dependent in the Bothnian Sea. Further bioenergetics simulations suggest that sustaining present fishing mortality rates would have no major effect on the sum of WHO_{total}-TEq in herring in the coming 20 years (IV). In contrast the changes in exploitation rate would influence the WHO_{total}-TEq concentrations-at-weight but only slightly the concentrations-at-age. Increasing fishing would produce only a slight decrease in the concentration in small herring size-categories. However, the influence on the largest size-category would be bigger and concentrations could be expected to decline from 25 to 15 pg g^{-1} if catches doubled. Complete closure of the herring fishery would have an opposite effect and would clearly lead to an increase in WHO_{total}-TEq concentrations of Baltic herring (IV).

However, one must take into account that size-dependent changes in food composition may to some extent counteract any decrease and that there might be environmental changes in the future such as increasing water temperature. Nevertheless, if growth accelerates, fish in a certain weight category would have lower OC concentrations (II, IV). It is likely that somewhat more intensive fishing could produce lower concentrations of toxicants in herring. However, according to the simulations, there is a high risk that increasing fishing by more than 50 % during the coming two decades would lead to a substantial decrease in the herring spawning stock biomass; in other words, there would be a high probability to over fish herring stocks (IV).

Increasing fishing mortality by 50 % would decrease the mean PCDD/F and PCB TEq-concentration of the catch used for human consumption by about 20 %. However, the total exposure in humans would increase, if the additional catches were used for human food. The recommendation by Finnish and Swedish health and food authorities for herring size (Anon. 2005, Anon. 2007) would only increase from 17 cm to 18 cm if fishing increased by 50 %. Therefore, the average concentrations in catches would still exceed the maximum limit set by the EU (Anon. 2006a) for the next two decades. It seems inevitable that fishing alone cannot solve this problem; restrictions of current sources of PCDD/Fs and PCBs will be needed as well.

4.4 Human dietary intake of organochlorines from Baltic fish

The ultimate aim of the manipulation of herring OC concentration described in the previous chapter (IV) would be to reduce the health risk of organochlorines in humans. Therefore, it is necessary to investigate whether such manipulation would actually have any affect on human intake of organochlorines. The simulation model for human dietary intake suggested some differences in WHO_{total}-TEqs of herring in the Finnish fish market under different fishing scenarios (V). At present there is high variation in the herring OC concentration in the Bothnian Sea and there is a 57 % probability that randomly-picked herring in the fish market would exceed the EU limits of 8 pg g^{-1}. Under the future fishing scenarios, corresponding randomly-picked herring in the fish market would have a 50 % probability of exceeding this limit if present fishing mortality is maintained for next 20 years. Under the other fishing scenarios of 50 % increase in fishing, 100 % increase in fishing and 50 % decrease in fishing, the probabilities would be 43 %, 38 % and 52 %, respectively. Thus, further increases in exploitation rate and subsequent changes in growth rates of herring only slightly influenced WHO_{total}-TEqs in herring. On the other hand, complete closure of the herring fishery would clearly increase WHO_{total}-TEq concentrations in the Bothnian Sea herring.

The mean human intake rate of OCs obtained in this study equalled earlier estimates (Kiviranta et al. 2001, Kiviranta et al. 2004, Hallikainen et al. 2006). These mean intake rates were clearly under the recommended maximum daily intake of OCs from herring. Our results, however, showed clearly that even those consumers who use herring only once a month could have remarkably high weekly loads of OCs due to the high variation in the organochlorine concentration among herring individuals. The mean human dietary intake of WHO_{total}-TEqs would decrease relative to present day intake according to all fishing scenarios. The relative decrease in mean intake varied between 14 % and 30 % depending on the fishing scenario used. However, the probability of exceeding the recommended maximum limit of human intake from herring is high under all fishing scenarios, if the consumption rate is higher than one portion per month. These results clearly demonstrate that regulating the fisheries is not really an effective way of reducing risks for human intake of organochlorines. Present OC concentrations in the Bothnian Sea are way too high to be reduced below the EU-limits by increased fishing alone.

On the other hand, the results demonstrate that the randomness arising from the large differences in toxin concentrations among herring individuals is an underestimated issue. It is likely that the randomness in other sources of uncertainty of organochlorines may also be high, and therefore all these uncertainties should be taken into account when considering risk management in future.

5 CONCLUSIONS

The general aims of this thesis were to study the origins of observed variation in Baltic fish organochlorine concentrations, the consequences of this variation from the human point of view and whether human dietary intake of organochlorines could be reduced. These rather practical questions were investigated using a variety of applications. Although this thesis demonstrates the potential power of these applications, they have become increasingly complicated. Therefore, more care needs to be paid to procedures such as stable isotope analysis used to study sources in contaminant accumulation. In this thesis the combination of carbon and nitrogen stable isotopes could not provide such specific information as originally hoped, but isotopes of nitrogen alone provided new insight into accumulation of contaminants at the individual level.

The ecological processes underlying the spatial and temporal variation have been poorly known. This thesis demonstrates that differences in herring organochlorine concentrations between sea areas can be largely explained by differences in growth rates, and that change in herring growth during past decades is the most probable explanation for observations that herring organochlorine concentrations have levelled out since the end of the 1980s. In contrast, by combining stable isotopes and bioaccumulation models, variation in salmon organochlorine concentrations were concluded to differ at a spatial level due to differences in proportions of the prey species in the diet and differences in prey OC concentrations. However, there was some indication that differences in the food web structures might also partly explain spatial differences in organochlorines in Baltic salmon. Time spent in the sea, dietary differences and trophic position explain most of the variation in organochlorine concentrations in salmon within sea areas. The thesis clearly demonstrates that background concentrations in the environment are not the only factors contributing to the final concentrations in the aquatic biota, but biological factors such as growth have major impacts on the accumulation processes. In the Baltic Sea, growth of the clupeids (sprat, herring) might be one of the key factors regulating the concentrations in higher trophic levels, including predatory fish, fish-eating birds, seals and human. The thesis provides important new information about how foodweb dynamics influence organochlorine concentrations in Baltic fish. Such information is essential to improve the basis for future development of means to diminish human dietary intake of organochlorines.

The thesis investigated one active technique to reduce organochlorine concentration in Baltic herring and further human intake of organochlorines. It seems that increased fishing would increase herring growth rate which would lower organochlorine concentrations in herring. However, to achieve a large reduction of concentrations would require a very high exploitation rate, which would potentially lead to over fishing of herring. Therefore, managers would face a difficult trade-off between over fishing the herring stock and organochlorine health risks. The results also demonstrate that the randomness arising from the big differences in organochlorine concentrations among herring individuals is an underestimated issue in risk assessment of human dietary intake of these compounds. It is likely that the randomness in other sources of uncertainty of organochlorines may also be high, and therefore all these uncertainties should be taken into account when considering risk management in future.

Management of organochlorines by regulating the fishing seems to be a far less effective way to decrease the risk than directly regulating the consumption of herring. At the moment most of the herring on the market are fairly large and rather toxic individuals. Ironically, the smallest and least toxic herring are used as feed in the fur farming industry. Also sprat consumption should be increased at the expense of herring consumption for two particular reasons. Firstly, OC concentrations in most sprat are under EU maximum limit. And, secondly, the present sprat stock in Baltic Proper is in better condition than the herring stock. Therefore using these two fractions of the clupeid catch, sprat and small herring, for human consumption would probably be the easiest way to reduce human OC intake from Baltic fish. This might also assure future clupeid fisheries in the Baltic Sea. But, would consumers change their feeding habits, would there be new requirements for fish processing, would fishing and processing of such fish even be profitable? These are open questions, which should be considered and evaluated in the near future.

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YHTEENVETO (RÉSUMÉ IN FINNISH)

Organoklooriyhdisteiden kertyminen Itämeren kaloihin

Itämeri on kokenut suuria muutoksia viimeisen sadan vuoden aikana. Ihmisen aiheuttamaa rehevöitymistä ja pysyviä ympäristömyrkkyjä, kuten organoklooriyhdisteitä, pidetään vakavimpina uhkina Itämeren eliöstölle ja koko ekosysteemille. Tällä hetkellä Itämeri onkin yksi pahiten organoklooriyhdisteiden saastuttamia merialueita. Useilla organoklooriyhdisteillä, kuten tässä väitöskirjassa käsiteltävillä polykloorratuilla dipenzo-*p*-dioksiineilla ja furaaneilla (PCDD/F) sekä polykloorratuilla bifenyyleillä (PCB), on myrkkyvaikutuksia, ja niiden on havaittu kertyvän eliöihin sekä rikastuvan ravintoketjuissa. Organoklooriyhdisteet ovatkin aiheuttaneet vakavia ongelmia Itämeren ravintoverkkojen huippupedoille, kuten hylkeille ja kalaa syöville petolinnuille. Lisäksi niitä pidetään vakavana uhkana ihmisten terveydelle.

Vaikka organoklooriyhdisteitä kulkeutuu edelleen luontoon mm. palamisprosesseista, metalliteollisuudesta, saastuneista sedimenteistä ja maa-aineksista, ovat tuntuvat päästörajoitukset ja useiden yhdisteiden käytön kieltäminen johtaneet tasaiseen kuormituksen laskuun Itämeressä aina 1970-luvun huippupitoisuuksista lähtien. 1980-luvun puolivälin jälkeen selvää laskua Itämeren taloudellisesti merkittävien kalalajien, kuten silakan ja lohen, pitoisuuksissa ei ole kuitenkaan enää havaittu. Lohen ja suuren silakan PCDD/F- ja PCB -pitoisuudet ylittävätkin Euroopan Unionin (EU) näille yhdisteille asettaman nykyisen raja-arvon kaloille ja kalatuotteille (8 pg $\text{WHO}_{\text{total}}$-TEq g^{-1}). Suomella ja Ruotsilla on kuitenkin poikkeuslupa pitää kaupan Itämerestä pyydettyä lohta tai silakkaa omilla alueillaan aina vuoteen 2011 asti. Kansalliset terveysviranomaiset ovat katsoneet kalojen terveysvaikutusten olevan myrkkyjen haittavaikutuksia suurempia, ja siksi silakan ja lohen kauppaa ei ole haluttu kieltää. Terveysviranomaiset kuitenkin suosittelevat, että lapset, nuoret ja hedelmällisessä iässä olevat rajoittaisivat Itämeren lohen ja suuren silakan (>17 cm) käyttöä 1-2 kertaan kuukaudessa.

Tämän väitöskirjan tavoitteina oli tutkia edellä mainittujen yhdisteiden kertymisprosesseja Itämeren selkärangattomista silakkaan, kilohailiin ja kolmipiikkiin ja näiden kautta loheen sekä selvittää pitoisuuksien suureen kalayksilöiden väliseen vaihteluun vaikuttavia tekijöitä. Tavoitteena oli lisäksi tutkia, kuinka kalastuksen säätelyllä voidaan vaikuttaa silakan organoklooripitoisuuksiin ja kuinka säätelytoimenpiteet vaikuttaisivat organoklooriyhdisteiden kertymiseen ihmiseen. Näitä kysymyksiä tutkittiin keräämällä näytteitä kolmelta Itämeren alueelta: pääaltaalta, Selkämereltä ja Suomenlahdelta. Kala- ja selkärangatonnäytteistä analysoitiin organoklooriyhdisteet, hiilen ja typen vakaiden isotooppien suhteet ($\delta^{13}C$, $\delta^{15}N$), energiasisällöt ja rasvapitoisuudet. Aineistoa käytettiin bioenergeettisissä kertymämalleissa, joilla simuloitiin ja arvioitiin organoklooriyhdisteiden kertymistä silakkaan ja loheen. Lisäksi kertymisreittejä pyrittiin tutkimaan luonnossa esiintyvillä vakailla isotoopeilla, jotka toimivat erinomaisina aine- ja energiavirtojen kuvaajina ekosysteemeissä.

Vaikka tämä väitöskirja osoitti uusien menetelmien, kuten vakaiden isotooppien, olevan tehokkaita haitallisten aineiden kertymän kuvaamisessa, menetelmät ovat usein monimutkaisia ja sisältävät useita virhelähteitä. Väitöskirjan menetelmällisessä osassa (I) testattiin kahta matemaattista mallia, joilla normalisoidaan rasvapitoisuuserojen aiheuttamaa vaihtelua kudosten hiilen vakaiden isotooppien suhteissa eli $\delta^{13}C$ -arvoissa. Koska mallien havaittiin tuottavan harhaisia arvioita, toista malleista paranneltiin ja malli testattiin riippumattomalla havaintoaineistolla. Uusi malli tuotti harhattomia arvioita rasvapitoisuuden vaikutuksesta $\delta^{13}C$ -arvoihin ja sillä korjattiin kaikki myöhemmin tässä väitöskirjassa esitetyt $\delta^{13}C$ -arvot. Väitöskirjassa hiilen isotooppien käyttö jäi lopulta vähäiseksi johtuen niiden puutteellisesta erottelukyvystä. Typen isotooppisuhteiden ($\delta^{15}N$) avulla lasketut trofiatasot eli arviot eliöiden paikoista ravintoverkossa osoittautuivat tehokkaiksi työkaluksi kertymän kuvaamisessa. Noin 60 % eliöiden organoklooripitoisuuksien vaihteluista loheen päätyvässä ravintoketjussa voitiin selittää $\delta^{15}N$ arvoista lasketuilla trofiatasoilla.

Silakan organoklooriyhdistepitoisuudet vaihtelevat merialueittain niin, että eteläisellä Itämerellä pitoisuudet ovat huomattavasti pienempiä verrattuna pohjoiseen Itämereen, missä pitoisuudet ylittävät usein EU:n asettaman enimmäispitoisuuden. Syitä alueelliseen vaihteluun ei kuitenkaan tunneta. Yhtenä syynä alueelliseen vaihteluun on esitetty kalan kasvueroja. Nopeasti kasvava yksilö saavuttaa tietyn saaliskoon nopeammin suhteessa hitaasti kasvavaan yksilöön. Saaliiksi joutuessa hitaasti kasvava yksilö on elänyt pidempään ja kerännyt itseensä enemmän organoklooriyhdisteitä verrattuna nopeasti kasvavaan yksilöön. Väitöskirjassa havaittiin, että silakan organoklooripitoisuudet ovat negatiivisesti riippuvaisia kalan kasvunopeudesta (II). Silakan bioenergeettisellä kertymämallilla voitiin osoittaa vaihtelun silakan alueiden välisissä organoklooripitoisuuksissa olevan pääasiassa kasvusta johtuvaa. Silakan kasvu on hidastunut kaikilla merialueilla 1980-luvun alusta lähtien. Mallinnukset silakan historiallisella kasvuaineistolla viittaavatkin siihen, että 1980-luvun puolivälin jälkeen tapahtunut silakan pitoisuuksien tasaantumisen johtuu juuri kasvun heikkenemisestä.

Myös lohen organoklooripitoisuuksissa on havaittu suuria alueiden ja yksilöiden välisiä eroja, joiden taustaa ei juuri tunneta. Vaihtelun on oletettu syntyvän alueiden ja yksilöiden välisistä eroista lohen ravinnonkäytössä ja eroista ravintokohteiden organoklooripitoisuuksissa. Vaikka lähes kaikki mitatut lohet ylittivät EU:n asettaman enimmäispitoisuuden, kaikkein korkeimmat pitoisuudet mitattiin Suomenlahden lohista (III). Pitoisuuseroja ei voitu selittää lohen kokoeroilla tai eroilla rasvapitoisuuksissa, vaan Suomenlahden korkeampien pitoisuuksien todettiin olevan seurausta ravintokohteiden korkeista pitoisuuksista Suomenlahdella sekä niiden erilaisista suhteista lohen ravinnossa. Suomenlahdella pääasiallisten ravintokohteiden, silakan ja kilohailin, pitoisuudet olivat korkeammat muihin alueisiin verrattuna. Lisäksi Suomenlahdella lohen on havaittu syövän enemmän silakkaa, jolla havaittiin korkeampia pitoisuuksia kilohailiin verrattuna. Lisäksi Suomenlahden lohen ravintokohteiden energiasisällöt ja rasvapitoisuudet olivat muita alueita matalammat. Suomenlahdella lohen on siis syötävä enemmän saavuttaakseen tietyn painon, jolloin se kerää kudoksiinsa myös enemmän myrkkyjä. Lohelle rakennettu bioenergeettinen kertymämalli osoitti silakan olevan pääasiallinen organoklooriyhdisteiden lähde Suomenlahden ja Selkämeren lohelle. Pääaltaalla lohet saavat suurimman osan organoklooriyhdisteistä sen sijaan kilohailista. Lohien typen vakaiden isotooppien suhteista ($\delta^{15}N$) arvioidut lohiyksilöiden trofiatasot selittivät lähes 80 % yksilöiden välisistä eroista organoklooripitoisuuksissa, mikä osaltaan vahvistaa käsitystä siitä, että lohen ravinto on meressä vietettyjen vuosien määrän ohella tärkein organoklooriyhdisteiden kertymiseen vaikuttava tekijä. Suomenlahden lohet ruokailivat keskimäärin korkeammalla trofiatasolla muihin alueisiin verrattuna, mikä saattaa selittyä viimeaikaisilla muutoksilla Suomenlahden ravintoverkossa.

Väitöskirjassa tutkittiin myös keinoja, joiden avulla Itämeren kaloista ihmiseen tulevaa kuormaa voitaisiin vähentää. Eräs ehdotettu keino on kalastuksen avulla säätää silakan populaatiotiheyttä riittävän alhaiseksi, jolloin kalat kasvavat nopeammin haluttuun saaliskokoon ja siten keräävät vähemmän myrkkyjä. Säätely perustuu siis havaintoihin siitä, että silakan kasvu on riippuvainen sen populaatiotiheydestä. Tämän menetelmän tutkimista varten kehitettiin simulaatiomalli, jonka avulla arvioitiin organoklooriyhdisteiden kertymistä silakkaan eri kasvunopeuksilla ja kannan runsauksilla (IV). Tulokset osoittavat, että nykyisiin kalastuskuolevuuksiin suhteutettuna 50 % lisäys kalastuskuolevuudessa johtaisi noin 20 % vähenemään ihmisille kaupattavan silakan organoklooripitoisuuksissa. Kalastuksen vähentäminen tai sen lopettaminen taas kasvattaisi silakan pitoisuuksia (IV). Vaikka pitoisuuksien vähenemä kalastusta lisäämällä on merkittävä, kalastuksen säätelyllä ei kuitenkaan voida pudottaa kaikkien silakoiden pitoisuuksia alle EU:n asettaman raja-arvon. Todennäköisyyksiin perustuvalla mallilla arvioitiin tällä hetkellä olevan noin 60 % todennäköisyys, että silakkasaaliista satunnaisesti poimitun yksilön pitoisuus ylittää EU:n raja-arvon (V). Todennäköisyys putoaisi noin 40 %:iin, jos kalastusta lisättäisiin 50 %. Tällä ei kuitenkaan olisi juurikaan merkitystä nykyisiin käyttösuosituksiin.

Yhteenvetona voidaan todeta Itämeren kalojen organoklooriyhdisteiden pitoisuuksien olevan vahvasti riippuvaisia biologisista tekijöistä, kuten kasvusta, paikasta ravintoverkossa, ravintokohteiden suhteista ja niiden laadusta, eikä pelkästään alueellisista eroista kemikaalien taustapitoisuuksissa. Näiden tekijöiden aiheuttama vaihtelu yksittäisten kalojen pitoisuuksissa heijastuu Itämeren huippupetojen pitoisuuksiin ja lisäksi sillä on tärkeä rooli organoklooriyhdisteiden kertymisessä ihmiseen. Tämä vaihtelu tulisi ottaa huomioon organoklooriyhdisteiden aiheuttaman terveysriskin arviointia tehtäessä. Näiden yhdisteiden aiheuttamaa riskiä ihmiselle voidaan pienentää kalastusta lisäämällä, mutta lisäkalastuksen tuoma hyöty ei yksin riitä pudottamaan pitoisuuksia alle raja-arvojen. Kalastuksen lisääminen kasvattaa myös riskiä kantojen liikakalastukseen. Parempana keinona voidaan pitää ihmisten ohjaamista käyttämään ravintona pienempää, raja-arvot alittavaa silakkaa, joka tällä hetkellä käytetään pääasiassa turkiseläinten rehuksi. Myös kilohailin käyttöä tulisi lisätä silakan kustannuksella, koska kilohailikannat kestävät paremmin kalastusta tämän hetkisiin silakkakantoihin verrattuna ja pääosa saaliista alittaa EU:n organoklooriyhdisteille asettaman raja-arvon kaloissa ja kalatuotteissa.

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