Screening of new flame retardants in biota

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NATIONELL
MILJÖÖVERVAKNING
PÅ UPPDRAG AV
NATURVÅRDSVERKET

Sammanfattning

Förekomsten av nya flamskyddsmedel undersöktes i både marina (musslor, tånglake, strömming, sillgrissla, gråsäl, tumlare och havsörn) och limniska ekosystem (abborre och utter). Totalt studerades drygt 50 prover. Organofosfater (OP), dekloran plus (DP) och närbesläktade ämnen (mirex, dekloran 602 och dekloran 603) detekterades frekvent, tetrachlorobisfenol-A (TCBPA) detekterades i två prover (abborre) och pentabromtoluen och 2,3,5,6-tetrabromo-p-xylen detekterades inte i något prov.

Det är stora skillnader i förekomst av OP, dekloraner (inklusive Mirex) och bromerade difenyl etrar (BDE, referensämnen) i arter vid basen och toppen av näringsvävarna. OP är de klart dominerande föroreningarna vid basen (musslor och fiskar). De utgör också en stor andel (ca 75%) av de detekterade föreningarna i sillgrisslor och uttrar. Däremot står BDE och dekloraner för en stor andel (cirka 3/4) av föroreningarna i tumlare och gråsäl och dominerar (ca 90 %) i havsörn. Detta indikerar att OP är mindre beständiga än BFR, medan mirex och de andra dekloranerna har liknande persistens som BFR.

Föroreningsprofilerna för OP:er är likartade i de flesta arter, med undantag för gråsäl, tumlare och tånglake. Tri(1-klor-2-propyl) fosfat (TClPP) är i allmänhet den vanligaste OP:n, följt av butylfosfater och 2-etylhexyl difenylfosfat. Gråsäl och tumlare innehöll enbart klorerade OP (TClPP och tri(2-kloretyl) fosfat). Föroreningsprofilerna för OP i tånglake varierade kraftig mellan och inom provplatser. Bland dekloranerna dominerar två föreningar, mirex och dekloran 602, i marina toppkonsumenter. De förekom i lägre halter vid basen på födoväven och där påvisades även dekloran plus i liknande halt.

Totalhalten av de tre studerade grupperna (OP, dekloraner och BFR) i de mest förorenade proverna är mycket lika, runt 1 µg/g fett, men det är stora haltskillnader mellan olika arter. OP förekommer i liknande koncentrationer i arter vid basen och på toppen av födovävarna. Sålunda verkar inte OP biomagnifiera. De råder sannolikt ett jämviktstillstånd som kännetecknas av ett relativt högt upptag och en lika hög eller högre (tumlare och gråsäl) metabolisk nedbrytning. Däremot finns det mycket som tyder på att dekloran 602 och mirex biomagnifierar och gör så i liknande utsträckning som BFR. Halterna av båda föroreningsklasserna är cirka 10 gånger högre i däggdjur och sillgrissla än i musslor och fisk och minst 10 gånger högre i havsörn än i däggdjur och sillgrissla. TCBPA hittades i två av fyra prover av abborre, men inte i något av de tolv undersökta utterproverna, vilket tyder på att den inte biomagnifierar.

Proverna av sillgrissla täcker en tidsperiod på mer än 30 år, vilket möjliggör tidstrendanalys. Samtliga ämnesklasser uppvisar tidstrender och samtliga uppvisar minskande halter under senare år. Emellertid har aromatiska OP varit i stadig nedgång under hela perioden, medan koncentrationerna av klorerade OP och alkylerade OP först ökade, nådde en topp runt år 2000 och sedan minskade. Liknande haltprofiler observeras för mirex, dekloran 602 och dekloran 603, men dessa nådde en topp omkring 2005-2010. Koncentrationerna av Dechlorane Plus minskar långsamt men stadigt med tiden. Tidstrenderna för BDE skiljer sig mellan BDE:er med olika bromeringsgrad. De mindre bromerade ämnena minskar snabbt i halt med tid, medan dess att medelbromerade ämnen minskar relativt långsamt och högbromerade ökar något med tiden.

Abstract

The occurrence of new flame retardants was investigated in both marine (mussels, eelpout, herring, grey seal, harbor porpoise and white-tailed sea eagle) and limnic ecosystems (perch and otter). More than 50 samples were analysed and organophosphates (OP), Dechlorane Plus and closely related substances (Mirex, Dechloranes 602 and 603) were frequently detected, tetrachlorobisphenol-A (TCBPA) was detected in two samples and pentabromtoluene and 2,3,5,6- tetrabromo-p-xylene were not detected in any sample.

There are large differences in the occurrence of OP, dechloranes (including Mirex) and brominated diphenyl ethers (BDE, reference substances) in species at the base and top of the food webs. OP is the clearly dominant contaminant at the base (mussels and fish). They also make up a large proportion (about 75%) of the detected compounds in herring, guillemot and otter. On the other hand, BDE and dechloranes account for a large proportion (about 3/4) of the pollutants in harbor porpoise and grey seal and dominate (about 90%) in white-tailed sea eagle. This indicates that OP is less persistent than BFR, while Mirex and the other dechloranes have similar persistence as BFR.

The contaminant profiles of OPs are similar in most species, with the exception of grey seal, harbor porpoise and eelpout. Tris(1-chloro-2-propyl) phosphate (TClPP) is generally the most common OP, followed by butyl phosphates and 2-ethylhexyl diphenyl phosphate. Grey seal and harbor porpoise contain only chlorinated OPs (TClPP and tri(2-chloro-ethyl) phosphate). The contaminant profiles for OP in eelpout vary greatly between and within sampling sites. Among the dechloranes, two compounds, Mirex and Dechlorane 602, dominate in marine top consumers. They occur in lower concentrations at the base of the food web; there also Dechlorane Plus is detected in similar concentrations.

The total content of the three groups studied (OP, dechloranes and BFR) in the most contaminated samples is very similar, around 1 µg/g fat, but there are large concentration differences between species. OP occurs in similar concentrations in species at the base and at the top of the food webs. Thus, OP does not appear to biomagnify. They probably have a state of equilibrium, which is characterized by a relatively high uptake and an equally high or higher (porpoise and grey seal) metabolic degradation. However, there is much to suggest that Dechlorane 602 and Mirex biomagnify and do so to a similar extent as BFR. The levels of both classes of compounds are about 10-fold higher in mammals and guillemot than in mussels and fish and at least 10-fold higher in white-tailed sea eagle than in mammals and guillemot. TCBPA was found in two of four samples of perch, but not in any of the twelve otter samples examined, indicating that it does not biomagnify.

The guillemot samples cover a period of more than 30 years, which is sufficient for time-trend analysis. All compound classes show temporal trends and all have declining levels in recent years. However, aromatic OPs have been in steady decline throughout the period, while the concentrations of chlorinated and alkylated OPs first increased, peaked around the year 2000 and then decreased. Similar concentration profiles are observed for Mirex, Dechlorane 602 and Dechlorane 603, but these peaked around 2005-2010. Dechlorane Plus decrease slowly but steadily in concentration of over time. The time trends for BDEs differ depending on the degrees of bromination. The concentrations of less brominated substances decrease rapidly in over time, while medium-brominated substances decrease slowly, and highly brominated substances increase slightly over time.

Aim
To investigate the occurrence of new flame retardants in biota.

Background
A literature study performed as part of the Swedish Environmental Protection Agency's screening program revealed a number of new flame retardants that are used as replacements for regulated flame retardants (http://urn.kb.se/resolve?urn=urn:nbn:se:naturvardsverket:diva-7144). As a continuation of the project, measurements of these substances were made in different types of water streams (http://urn.kb.se/resolve?urn=urn:nbn:se:naturvardsverket:diva-7873). Based on these two studies, the agency identified a need to investigate whether the identified new substances are also found in biota.

Implementation

Substances
The substances detected in surface water (see above) with a detection frequency above 10% have been included as far as possible. Two substances (tri (2-butoxyethyl) phosphate and tris(2-ethylhexyl) phosphate) had to be excluded, as they cannot be analysed with the selected sample processing method. Two more (resorcinol bis (diphenyl phosphate) and bisphenol A bis (diphenyl phosphate)) proved difficult to analyse as they are so thermally unstable that they degraded during GC-MS analysis (even under the gentle conditions used in BDE209 analysis). To compensate for these losses, four additional Dechloranes were included (besides *syn*-Dechlorane Plus), i,e *anti*-Dechlorane Plus, Dechlorane (Mirex), Dechlorane 602 and Dechlorane 603 and one organophosphate triester (di(2-ethylhexyl) phenyl phosphate). Eight brominated diphenyl ethers (BDE) were also included to be used reference substances.

The following substances were finally included in the project:

New halogenated flame retardants (NFRs)	Abbreviation	CAS number
Pentabromotoluene	PBT	87-83-2
2,3,5,6-Tetrabromo-p-xylene	TBX	23488-38-2
Tetrachlorobisfenol-A	TCBPA	27360-90-3
Dechloranee Plus, syn isomer	sDDC-CO	135821-03-3
Dechloranee Plus, anti isomer	aDDC-CO	135821-74-8
Dechloranee (Mirex)	Mirex	2385-85-5
Dechloranee 602	Dec602	31107-44-5
Dechloranee 603	Dec603	13560-92-4

Phosphorous flame retardants (OPs)	Abbreviation	CAS number
Tris(2-chloroethyl) phosphate	TCEP	115-96-8
Tri(1-chloro-2-propyl) phosphate	TCIPP	13674-84-5
Tris(1,3-dichloro-isopropyl) phosphate	TDCIPP	13674-87-8
Triisobutyl phosphate	TiBP	126-71-6
Tri-n-butyl phosphate	TNBP	126-73-8
2-Ethylhexyl diphenyl phosphate	EHDPP	1241-94-7
Di(2-ethylhexyl)phenyl phosphate	DEHPP	16368-97-1
Triphenyl phosphate	TPHP	115-86-6
Tricresyl phosphate	TMPP	1330-78-5

Tri(2-isopropylphenyl) phosphate	TiPPP	64532-95-2
Brominated flame retardants (BFRs)	Abbreviation	CAS number
2,4,4'-Tribromophenyl ether	BDE28	41318-75-6
2,2',4,4'-Tetrabromodiphenyl ether	BDE47	5436-43-1
2,2',4,4',5-Pentabromodiphenyl ether	BDE99	32534-81-9
2,2',4,4',6-Pentabromodiphenyl ether	BDE100	189084-64-8
2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE153	68631-49-2
2,2′,4,4′,5,6′-Hexabromodiphenyl ether	BDE154	207122-15-4
2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE183	207122-16-5
Decabromodiphenyl ether	BDE209	1163-19-5

Samples

The sample selection was made by the contractor together with the responsible administrator at the Swedish Environmental Protection Agency. It was based on availability and was adapted to provide a good overall view of the state of the environment. The samples were provided by the Swedish and German environmental specimen banks, and they include:

- Four fish samples (perch) from freshwater lakes, including a sample from Lake Fysingen, which is close to Arlanda airport.
- Twelve samples of otters that are feeding on freshwater fish.
- A selection of samples from the Baltic Sea ecosystem that cover several trophic levels, from filters to white-tailed sea eagles. The samples have been collected from relatively pristine areas and they include both coastal and offshore species. Three samples were included for each species and location, except for Guillmot eggs. The samples have been collected within the framework of the EU project "BaltHealth" and are in most cases covering a recent (ca 10-year) period.
    - Mussel flesh (Swedish and German coast)
    - Eelpout muscle (Swedish and German coast)
    - Herring muscle (Baltic Proper)
    - Grey seal blubber (Baltic Proper)
    - Harbor porpoise blubber (Baltic Proper)
    - Guillemot egg extract (Baltic Proper, 12 samples)
    - White-tailed sea eagle muscle (Swedish coast)
- The 12 samples of Guillemot eggs were collected over the period 1986-2019, which makes it possible to investigate time trends.

Most samples are pooled samples of several individuals (about 10), which reduces the biological variation. The exception is the otter samples, which are from individuals.

Analysis and quality control

The samples were extracted, processed and analysed using a generic method for non-polar and medium-polar organic substances (Rebryk et al., 2022). Briefly, the samples were extracted with organic solvent (acetone/hexane followed by hexane/ether) according to Jensen et al., 2003. They were then fractionated by polarity on a Florisil column according to Norstrom et al., 1980. Four fractions were collected, containing substances with increasing polarity, with NFRs found in fractions 1-3 and OPs in fraction 4. Chemical analysis was finally performed by gas chromatography – high-resolution mass spectrometry. As many of the samples had already been prepared for analysis within the

BaltHealth project, it was not possible to use internal standards to compensate for losses during sample preparation. Instead, quantification was done using a volumetric standard (13C-isotope of PCB188; compensates for differences in sample volumes and instrument sensitivity) and an external reference standard (Haglund and Rebryk, 2022). However, for perch and otter, new samples were provided for the study and it was, thus, possible to use internal standard quantification. The quality assurance included control of internal standard recovery (perch, otter), laboratory background (via blanks) and instrument status.

Results

Occurrence

The occurrence of OPs, NFRs and BDEs are summarized in the form of detection frequencies (**Tables 1-3**). The butyl-OPs were frequently detected in samples of mussels, fish, otter, and eagle, but not in porpoise and grey seal (**Table 1**). The chlorinated OPs exhibited a similar profile, with the exception that TClPP was frequently detected in porpoise and grey seal, while TCEP was not detected in otter and TDClPP was not detected in eagle. There was a substantial variability in the occurrence of aryl-OPs, with TPHP detected in most samples, EHDPP and TiPPP in more than half of the samples, and DEHPP and TMPP in less than half the samples (primarily in low trophy level samples).

The two NFRs TBX and PBT was not detected in any of the samples (**Table 2**). TCBPA was rarely detected and only found in two perch samples. In contrast, Mirex, Dechlorane 602 (D602), Dechlorane 603 (D603), dechloranes were detected in almost all samples, although only the most abundant compounds (Mirex and Dechlorane 602) were detected in grey seal. Dechlorane 601 (D601), Dechlorane 604 (D604), Dechlorane 604 component B (604CB) and Chlordene Plus (CP) were screened for but not found.

The BDE reference compounds were found in almost all samples (**Table 3**). The detection frequency was lower for the perch samples, mainly due to low levels. In addition, BDE 28 and BDE 209 were missing in about half the otter samples and all guillemot and porpoise samples, respectively.

Relative abundance of compound classes

There are big differences in the relative concentrations between the different compound classes in species at the base and top of the food webs. **Figure 1** show the relative abundances (based on geometric mean values) of organophosphate esters (Sum-OP), Mirex, other dechloranes (Sum-Dec), and brominated diphenyl ethers (Sum-BDEs) in marine samples from Baltic Proper and limnic samples (perch and otter). OPs clearly dominates in the lower trophy level filter feeder (mussels) and fish species They also make up a big share (ca 75%) of the detected compounds in guillemot and otter samples. In contrast, BDEs and dechloranes (including Mirex) account for large share (around 3/4) of the contaminants in porpoise and grey seal and dominates (ca 90%) in white-tailed sea eagle samples. This indicates that the OPs are less persistent than the BFRs, while Mirex and the other dechloranes have similar persistence to the BFRs. However, Mirex account for a low percentage of the contaminants in otter, which may be due to differences in exposure between the marine and limnic species or differences in metabolic specificity between otter and the marine mammals and birds.

Table 1. *Detection frequency of organophospates (OPs).*

Species	Environ-ment	TiBP	TNBP	TCEP	TICPP	TDCIPP	TPHP	EHDPP	DEHPP	TMPP	TiPPP
All		83%	87%	65%	98%	81%	94%	62%	46%	40%	73%
Mussels	Marine	100%	100%	100%	100%	100%	100%	100%	50%	100%	100%
Eelpout	Marine	100%	100%	100%	100%	100%	100%	80%	40%	80%	60%
Herring	Marine	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Guillemot	Marine	100%	100%	100%	100%	100%	100%	100%	100%	67%	83%
Porpoise	Marine	0%	0%	33%	100%	0%	33%	0%	0%	0%	0%
Grey seal	Marine	0%	0%	0%	100%	0%	100%	0%	0%	0%	0%
Eagle	Marine	100%	100%	100%	100%	0%	100%	100%	0%	0%	0%
Perch	Limnic	50%	75%	75%	75%	75%	75%	75%	75%	0%	75%
Otter	Limnic	100%	100%	0%	100%	100%	100%	0%	0%	0%	100%

Table 2. *Detection frequency of new halogenated flame retardants (NFRs).*

Species	Environ-ment	TBX	PeBT	Mirex	D602	D603	Syn-DP	anti-DP	TCBPA	D601/CP	D604/604CB
All		0%	0%	69%	100%	88%	87%	94%	4%	0%	0%
Mussels	Marine	0%	0%	100%	100%	100%	100%	100%	0%	0%	0%
Eelpout	Marine	0%	0%	100%	100%	67%	100%	100%	0%	0%	0%
Herring	Marine	0%	0%	100%	100%	100%	100%	100%	0%	0%	0%
Guillemot	Marine	0%	0%	100%	100%	100%	100%	100%	0%	0%	0%
Porpoise	Marine	0%	0%	100%	100%	100%	100%	100%	0%	0%	0%
Grey seal	Marine	0%	0%	100%	100%	0%	0%	0%	0%	0%	0%
Eagle	Marine	0%	0%	100%	100%	100%	100%	100%	0%	0%	0%
Perch	Limnic	0%	0%	0%	75%	50%	75%	75%	50%	0%	0%
Otter	Limnic	0%	0%	0%	100%	100%	75%	100%	0%	0%	0%

Table 3. *Detection frequency of brominated diphenyl ethers (BDEs).*

Species	Environ-ment	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
All		81%	100%	100%	100%	100%	98%	94%	71%
Mussels	Marine	100%	100%	100%	100%	100%	100%	100%	100%
Eelpout	Marine	100%	100%	100%	100%	100%	100%	100%	100%
Herring	Marine	100%	100%	100%	100%	100%	100%	100%	100%
Guillemot	Marine	100%	100%	100%	100%	100%	100%	100%	0%
Porpoise	Marine	100%	100%	100%	100%	100%	100%	100%	0%
Grey seal	Marine	100%	100%	100%	100%	100%	100%	100%	100%
Eagle	Marine	100%	100%	100%	100%	100%	100%	100%	100%
Perch	Limnic	0%	75%	75%	75%	75%	75%	25%	75%
Otter	Limnic	50%	100%	100%	100%	100%	92%	100%	100%

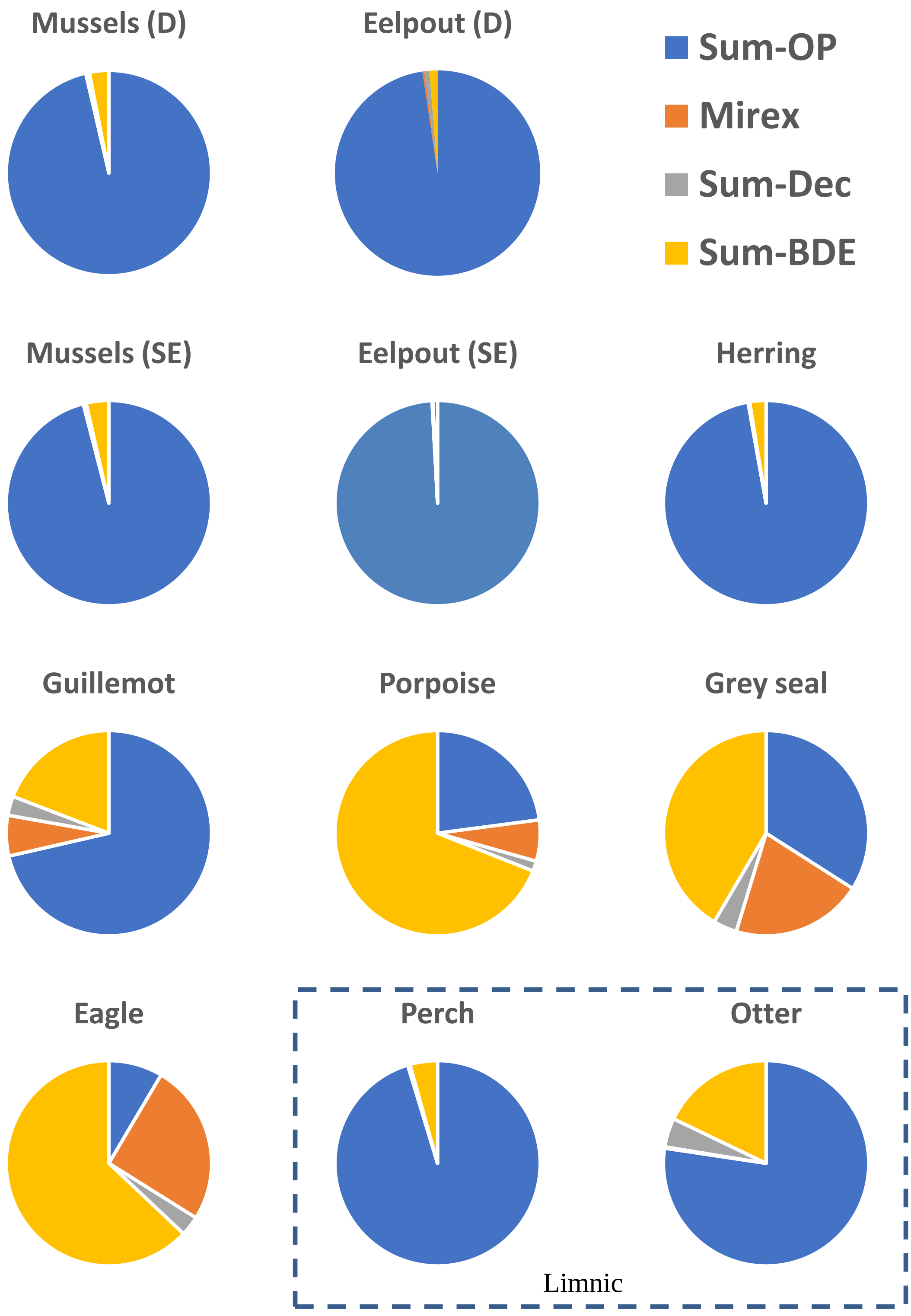

Figure 1. Relative abundances (based on geometric mean values) of organophosphate esters (Sum-OP), Mirex, dechloranes (Sum-Dec) and brominated diphenyl ethers (Sum-BDEs) in marine samples from Baltic Proper and limnic samples (perch and otter).

Relative abundance of individual new flame retardants in biota

The contaminant profiles of OPs are similar in most species, with the exception for eelpout, porpoise and grey seal. TClPP is generally the most abundant OP, followed by butyl phosphates (TiBP and TNBP) and EHDPP (**Figure 2**).

The eelpout samples deviates from the other fish and mussels samples, deviates between Swedish and German samples, and even between the two Swedish samples analyzed. One Swedish sample contained elevated concentrations of TDCPP, EHDPP and DEHPP as compared to the other fish samples (**Appendix 1**). This sample was therefore excluded from the geometric mean calculations and the data set used to construct the figures.

The variability in contaminant profiles observed for eelpout may reflect differences in food availability or feeding habits, which can lead to temporal variations in concentrations of compounds with limited metabolic resistance (such as the OPs). Metabolism may also explain the deviating contaminant profiles of the harbor porpoise, grey seal and to some extend otter samples. Samples of these species all have low concentrations of aryl-OPs, which are likely to readily undergoing phase-1 metabolism.

Among the other new halogenated FRs, two compounds, Mirex and Dechlorane 602 (Dec 602), dominate in marine top consumer species. At lower trophy levels, the two occur at similar concentrations to Dechlorane Plus (DP) (all concentrations quite low).

A similar dechlorane profile was found for freshwater perch. However, half of the perch samples (2 of 4) also contained TCBPA, at similar concentrations. Otters deviated from the marine mammals in that they contained relatively high Dechlorane 602 levels and relatively low Mirex concentrations.

Concentrations and biomagnification of new flame retardants

The maximum concentration of each of the three groups (OPs, other NFRs, and BFRs) are very similar, all around 1 µg/g lipids (**Figure 2**). However, there is a big difference in the relative concentrations (i.e. contaminant profile) in the different species for the OPs as comparted to the other two groups.

The OPs occur at similar concentrations in species at high and low trophy level and range from 170 to 720 ng/g in all species except harbor porpoise and grey seal (ca 20 ng/g). Thus, the OPs do not appear to biomagnify. They are likely in a steady-state condition, characterized by a relatively high uptake and an equally high or higher (harbor porpoise and grey seal) metabolic transformation.

In contrast, there is much to suggest that Dechlorane 602 and Mirex biomagnify to a similar extend to the BFRs. The total concentration profile of the dechloranes across the various species (**Figure 2, middle panel**) are almost identical to that of the BFRs (**Figure 2, lower panel**). The total concentrations are about 10-fold higher in the guillemot and mammal samples than in the mussels and fish samples. Similarly, the concentrations are at least 10-fold higher in white-tailed sea eagle than in the guillemot and mammal samples.

TCBPA was found in two of the four samples of perch, but not in any of the twelve otter samples (**Appendix 1**), which suggests that it do not biomagnify.

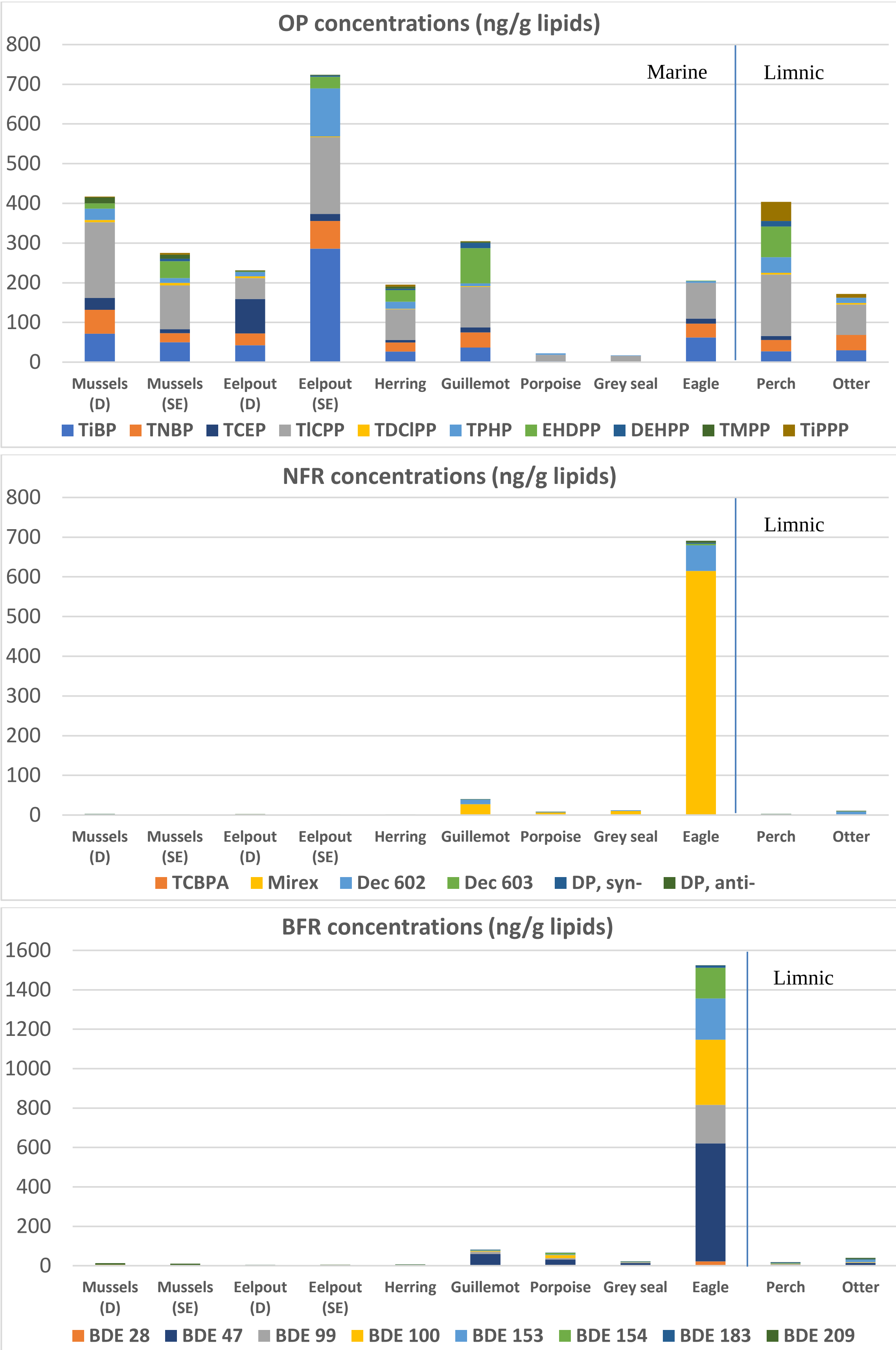

Figure 2. Total concentrations and relative abundances (based on geometric mean values) of organophosphate esters (OPs), other new halogenated flame retardants (NFRs) and brominated diphenyl ethes (BDEs) in marine and limnic (perch, otter) samples. Swedish eelpout (n=1).

Temporal trends of contaminant concentrations in guillemot eggs

The guillemot egg samples covers a time-span of more than 30 years, which allow for temporal trend analysis and comparisons. There appears to be temporal trends in the concentrations of all three groups of contaminants (**Table 4** and **Table 5**), but the trends differ between the groups and sub-groups.

The OPs all appears to have a decreasing temporal trend in recent times. However, the aryl-OPs have been in steady decline over the entire period, while the Cl- and alkyl-OP concentrations first increased, peaked around year 2000, and then decreased.

While the concentrations of Cl-OPs and aryl-OPs in recent years samples are much lower (ca 10-fold) than in the earliest samples, the concentrations of alkyl-OPs are almost exactly the same in the earliest (1986) and latest (2019) sample.

Tabell 4*. Relative concentrations (percent) of organophosphate esters (OPs) in guillemot egg collected between 1986 and 2019.*

Year	Alkyl-OP		Cl-OP			Aryl-OP				
	TiBP	TNBP	TCEP	TlCPP	TDClPP	TPHP	EHDPP	DEHPP	TMPP	TiPPP
1986	26%	49%	44%	3%	72%	61%	43%	36%	100%	100%
1989	38%	71%	54%	4%	60%	100%	100%	100%	51%	46%
1992	41%	49%	36%	4%	16%	60%	32%	31%	30%	41%
1995	100%	100%	25%	100%	28%	30%	26%	83%	42%	7%
1998	33%	47%	18%	19%	94%	32%	46%	40%	23%	17%
2001	98%	88%	10%	6%	100%	20%	24%	20%	8%	11%
2004	44%	61%	26%	12%	91%	27%	41%	38%	6%	0%
2007	50%	80%	100%	13%	41%	11%	14%	18%	0%	6%
2010	45%	70%	33%	5%	25%	22%	33%	36%	8%	12%
2013	56%	69%	29%	4%	40%	13%	28%	32%	0%	9%
2018	29%	42%	10%	2%	12%	7%	1%	3%	0%	7%
2019	25%	48%	4%	2%	9%	7%	1%	2%	0%	0%

Tabell 5*. Relative concentrations (percent) of new halogenated flame retardants (NFRs) and brominated diphenyl ethers (BDEs) in guillemot eggs collected 1986 to 2019.*

Year	NFRs				BDEs						
	Mirex	Dec 602	Dec 603	Sum-DP	BDE28	BDE47	BDE99	BDE100	BDE153	BDE154	BDE183
1986	8%	9%	2%	62%	86%	69%	98%	100%	100%	100%	17%
1989	18%	16%	17%	100%	100%	100%	100%	84%	69%	40%	25%
1992	25%	10%	3%	80%	63%	28%	13%	21%	13%	33%	19%
1995	36%	21%	5%	84%	27%	14%	14%	31%	32%	41%	45%
1998	55%	68%	14%	97%	17%	6%	8%	12%	23%	31%	37%
2001	25%	8%	3%	66%	26%	9%	12%	9%	38%	30%	51%
2004	100%	22%	100%	49%	13%	4%	5%	7%	20%	38%	75%
2007	30%	16%	26%	42%	7%	1%	3%	3%	16%	25%	69%
2010	18%	100%	14%	32%	6%	1%	3%	4%	18%	36%	74%
2013	55%	50%	46%	30%	4%	1%	3%	4%	12%	32%	82%
2018	16%	12%	28%	32%	4%	1%	2%	3%	6%	21%	100%
2019	12%	30%	22%	38%	5%	1%	2%	2%	7%	21%	89%

Mirex, Dechlorane 602 and Dechlorane 603 show increasing concentrations from 1986 to around 2005-2010, after which the concentrations decrease with time. In contrast, the concentrations of Dechlorane Plus seems to decrease slowly but steadily with time.

The BDE profiles differs between compounds with different degree of bromination. The less brominated BDEs, with three to five bromines, all had high concentrations in early year's samples, from the late 1980's, and rapidly declining levels over time. BDEs 153 and 154, with six bromines, also had high levels in the early samples but considerably slower decreasing concentrations over time. However, BDE183, with seven bromines, seems to increase steadily with time (at least until the last years). This may be due to higher metabolic stability of BDE183 as compared to the lower brominated compounds in guillemot. It is also possible that it is an effect of differences in regulation. PentaBDE and OctaBDE flame retardants were regulated in parallel (listed on the Stockholm Convention on POPs in 2009) whilst DecaBDE was regulated later (listed 2017). It is known that BDE183 is one of the main photodegradation products of DecaBDE (Zeng et al., 2008). And that the lower brominated BDEs were gradually replaced by DecaBDE during the decade preceding their regulation.

Recommendations

Dechlorane Plus (DP) is currently under review for listing under the Stockholm Convention on POPs. However, Dechlorane 602 occur at similar levels or higher levels in the investigated samples. In addition, both Dechlorane 602 and Dechlorane 603 biomagnify strongly and reach concentrations in white-tailed sea eagle much higher and similar to DP, respectively. Further, a recent paper of Haglund and Rebryk, 2022, presents data for dechlorane transformation products (TPs) for the marine samples included in the current study. It reports that some dechlorane TPs occur at higher concentrations than the parent compound (e.g., Dechlorane 603 TPs were >10-fold more abundant than their parent). Thus, the results obtained in the current and the cited study suggest that additional dechloranes and dechlorane-TPs should be considered in the review process. Furthermore, it may be of interest to complement the current study with analysis of dechlorane-TPs in limnic samples.

The OPs occur at much higher concentrations than the BFRs in low trophic level species and at similar or lower levels in top consumers. This observation be explained by the fact that OP-triesters are readily metabolized to di- and mono-esters. Thus, it may be advisable to focus potential follow up studies on biological/ecological effects of OP on lower trophic level species and on metabolite screening in top consumer species.

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Appendix 1. *Concentrations (ng/g lipid weight) of organophosphate esters (OPs), polybrominated diphenyl ethers (BDEs), tetrachlorobisphenol A (TCBPA), Mirex, dechloranes 602 and 603 and Dechlorane Plus (DP) in marine (Baltic Proper) and limnic (perch, otter) biota samples.*

Species	Tissue	Sampling site	Year	TiBP*	TNBP*	TCEP	TlCPP	TDClPP	TPHP	EHDPP	DEHPP	TMPP	TiPPP	TCBPA	TBX	PeBT	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209	Mirex	Dec 602	Dec 603	DP, syn-	DP, anti
Mussels (D)	Flesh	S. Baltic Proper	2012	88	102	57	455	6.8	35	26	<1	27	5.2	<1	<0.5	<1	0.36	2.4	1.4	0.95	0.37	0.46	0.11	11	2.0	0.81	0.03	0.28	0.67
Mussels (D)	Flesh	S. Baltic Proper	2015	52	33	23	99	2.6	22	10	<1	16	0.77	<1	<0.5	<1	0.17	2.6	1.7	0.90	0.17	0.24	0.07	3.7	0.65	0.29	0.02	0.12	0.33
Mussels (D)	Flesh	S. Baltic Proper	2017	82	64	21	155	9.2	32	8.8	<1	7.5	1.6	<1	<0.5	<1	0.16	2.0	1.2	0.51	0.28	0.28	0.09	12	1.4	0.73	0.03	0.21	0.53
Mussels	Flesh	Kvädöfjärden	2012	123	73	19	200	12	18	42	8.1	14	5.0	<0.3	<0.2	<0.5	0.16	0.81	0.46	0.35	0.14	0.10	0.03	2.2	0.42	0.48	0.01	0.14	0.28
Mussels	Flesh	Kvädöfjärden	2014	21	4.9	5.2	50	3.7	9.2	22	2.5	7.8	5.4	<0.3	<0.2	<0.5	0.13	0.60	0.36	0.11	0.04	0.23	0.02	13	0.28	0.40	0.004	0.18	0.27
Mussels	Flesh	Kvädöfjärden	2017	49	34	12	134	5.7	10	85	10	10	3.6	<0.3	<0.2	<0.5	0.11	0.91	1.49	0.24	0.25	0.26	0.02	19	0.42	0.31	0.19	0.42	0.61
Eelpout (D)	Muscle	S. Baltic Proper	2012	24	28	13	44	2.1	5.8	1.8	<0.5	0.9	0.3	<0.3	<0.2	<0.5	0.11	1.4	0.60	0.74	0.12	0.20	0.02	1.8	1.3	1.2	0.03	0.43	1.5
Eelpout (D)	Muscle	S. Baltic Proper	2015	65	29	176	62	8.3	15	<0.5	<0.5	5.3	1.1	<0.3	<0.2	<0.5	0.13	1.4	0.33	0.50	0.12	0.37	0.03	1.3	0.45	0.25	0.005	0.15	0.83
Eelpout (D)	Muscle	S. Baltic Proper	2017	50	33	283	53	5.3	14	1.4	<0.5	<0.8	<0.3	<0.3	<0.2	<0.5	0.11	0.6	0.18	0.23	0.08	0.19	0.02	0.15	0.65	0.35	0.01	0.27	1.1
Eelpout	Muscle	Kvädöfjärden	2012	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<0.3	<0.2	<0.5	0.31	1.2	0.30	0.52	0.15	0.41	0.04	4.6	0.40	0.15	0.003	0.16	0.34
Eelpout	Muscle	Kvädöfjärden	2014	173	362	19	193	127	116	8 628	203	4.8	0.3	<0.3	<0.2	<0.5	0.21	0.84	0.18	0.49	0.13	0.26	0.05	3.1	0.32	0.16	<0.003	0.12	0.19
Eelpout	Muscle	Kvädöfjärden	2017	286	70	18	193	1.7	121	29	3.0	2.2	<0.3	<0.3	<0.2	<0.5	0.41	1.8	0.33	0.68	0.14	0.51	0.03	1.4	0.51	0.31	<0.003	0.12	0.36
Herring	Muscle	Landsort	2014	43	32	4.9	38	1.1	13	36	3.9	3.7	5.7	<0.3	<0.2	<0.5	0.34	2.0	1.1	0.86	0.12	0.71	0.01	0.26	0.29	0.06	0.005	0.04	0.05
Herring	Muscle	Landsort	2017	21	22	6.1	200	1.1	5.3	9.5	1.8	1.0	1.8	<0.3	<0.2	<0.5	0.31	1.7	0.88	1.1	0.10	0.54	0.02	0.20	0.26	0.10	0.010	0.03	0.08
Herring	Muscle	Landsort	2018	21	17	7.7	60	3.1	85	72	6.4	33	17	<0.3	<0.2	<0.5	0.25	2.4	0.87	1.01	0.10	0.63	0.01	0.12	0.32	0.11	0.006	0.08	0.15
Grey seal	Blubber	Baltic Propper	2012	<4	<4	<1	18	<0.5	1.9	<0.5	<0.5	<0.8	<0.3	<0.3	<0.5	<0.5	1.0	13	2.0	2.6	2.2	1.5	0.23	0.08	13	3.2	<0.03	<0.03	<0.03
Grey seal	Blubber	Baltic Propper	2016	<4	<4	<1	16	<0.5	3.3	<0.5	<0.5	<0.8	<0.3	<0.3	<0.5	<0.5	1.3	11	1.5	1.8	1.2	1.3	0.15	0.06	8.3	1.3	<0.03	<0.03	<0.03
Grey seal	Blubber	Baltic Propper	2018	<4	<4	<1	14	<0.5	0.9	<0.5	<0.5	<0.8	<0.3	<0.3	<0.5	<0.5	1.6	12	1.6	3.1	2.0	1.9	0.19	0.13	11	1.6	<0.03	<0.03	<0.03
Harbor porpoise	Blubber	Baltic Proper	2012	<4	<4	<1	11	<0.5	<0.5	<0.5	<0.5	<0.8	<0.3	<0.3	<0.5	<0.5	5.1	40	13	21	5.0	12	0.61	<0.1	7.3	1.8	0.05	0.02	0.05
Harbor porpoise	Blubber	Baltic Proper	2016	<4	<4	<1	15	<0.5	<0.5	<0.5	<0.5	<0.8	<0.3	<0.3	<0.5	<0.5	3.3	23	5.8	13	3.1	10	0.50	<0.1	9.0	2.0	0.07	0.01	0.03
Harbor porpoise	Blubber	Baltic Proper	2018	<4	<4	19	24	<0.5	3.7	<0.5	<0.5	<0.8	<0.3	<0.3	<0.5	<0.5	3.8	22	6.4	11	2.1	6.3	0.39	<0.1	3.7	0.85	0.01	0.02	0.04
Guillemot	Egg	St Karlsö	1986	53	41	23	52	3.7	17	206	19	15	6.6	<0.3	<0.2	<0.5	10	780	129	46	13	4.8	1.0	<0.1	52	23	0.25	0.26	0.57
Guillemot	Egg	St Karlsö	1989	44	111	29	69	3.1	28	477	55	7.8	3.1	<0.3	<0.2	<0.5	12	1 123	131	38	9.3	1.9	1.4	<0.1	46	30	0.56	0.43	0.91
Guillemot	Egg	St Karlsö	1992	72	154	19	67	0.82	17	154	17	4.7	2.7	<0.3	<0.2	<0.5	7.5	318	17	9.6	1.8	1.6	1.1	<0.1	29	23	0.38	0.25	0.82
Guillemot	Egg	St Karlsö	1995	39	61	13	1 552	1.5	8.4	125	45	6.5	0.5	<0.3	<0.2	<0.5	3.2	159	19	14	4.2	1.9	2.6	<0.1	60	20	0.25	0.27	0.85
Guillemot	Egg	St Karlsö	1998	75	40	9.3	288	4.9	9.1	219	22	3.5	1.1	<0.3	<0.2	<0.5	2.0	64	11	5.4	3.0	1.5	2.1	<0.1	63	20	0.22	0.40	0.90
Guillemot	Egg	St Karlsö	2001	22	107	5.2	91	5.2	5.5	115	11	1.2	0.7	<0.3	<0.2	<0.5	3.1	98	16	4.3	5.0	1.4	2.9	<0.1	48	17	0.32	0.31	0.57
Guillemot	Egg	St Karlsö	2004	210	29	14	186	4.7	7.5	195	21	0.9	<0.3	<0.3	<0.2	<0.5	1.5	43	6.4	3.2	2.7	1.8	4.3	<0.1	28	13	0.08	0.14	0.51
Guillemot	Egg	St Karlsö	2007	41	35	52	208	2.1	3.1	67	10	<0.8	0.4	<0.3	<0.2	<0.5	0.84	14	3.9	1.6	2.1	1.2	4.0	<0.1	17	9.2	0.09	0.12	0.44
Guillemot	Egg	St Karlsö	2010	23	16	17	74	1.3	6.1	157	20	1.2	0.8	<0.3	<0.2	<0.5	0.74	13	4.3	1.9	2.4	1.7	4.2	<0.1	13	6.9	0.11	0.16	0.27
Guillemot	Egg	St Karlsö	2013	34	57	15	68	2.1	3.7	132	17	<0.8	0.6	<0.3	<0.2	<0.5	0.51	8.6	3.6	1.6	1.6	1.5	4.7	<0.1	10	4.4	0.07	0.12	0.28
Guillemot	Egg	St Karlsö	2018	11	5.4	5.2	28	0.61	2.0	5.4	1.5	<0.8	0.4	<0.3	<0.2	<0.5	0.49	6.9	2.5	1.2	0.79	1.0	5.7	<0.1	15	4.9	0.04	0.05	0.38
Guillemot	Egg	St Karlsö	2019	7.8	11	2.3	24	0.48	1.9	3.6	1.1	<0.8	<0.3	<0.3	<0.2	<0.5	0.60	9.5	2.9	1.1	0.96	0.99	5.1	<0.1	14	4.8	0.01	0.12	0.39
Sea eagle	Muscle	Baltic coast	2006	51	28	28	61	<0.5	4.1	2.5	<0.5	<0.8	<0.3	<0.3	<0.2	<0.5	33	1 155	253	488	240	165	10	1.1	822	98	4.5	2.7	6.5
Sea eagle	Muscle	Baltic coast	2011	74	51	12	90	<0.5	3.2	0.9	<0.5	<0.8	<0.3	<0.3	<0.2	<0.5	25	572	177	315	181	146	10	0.18	677	60	3.0	2.2	3.2
Sea eagle	Muscle	Baltic coast	2017	63	30	6.2	132	<0.5	6.4	1.3	<0.5	<0.8	<0.3	<0.3	<0.2	<0.5	12	327	165	236	209	159	14	0.47	418	46	3.9	2.7	5.9
Perch	Muscle	Brännträsket	2020	27	31	32	269	6.3	53	94	14	<3	44	1.3	<0.5	<1	<0.3	3.5	4.9	3.9	2.0	2.6	<0.1	2.3	0.49	0.18	<0.02	0.10	0.57
Perch	Muscle	Lilla Öresjön	2020	<10	45	9.2	91	5.2	19	34	6.1	<3	18	1.0	<0.5	<1	<0.3	5.1	6.1	3.2	2.5	7.6	3.7	2.2	0.55	0.44	0.04	0.22	0.48
Perch	Muscle	Fysingen	2020	28	44	10	271	5.9	42	69	15	<3	75	<1	<0.5	<1	<0.3	5.7	3.2	1.4	0.8	2.7	<0.1	1.7	0.41	0.30	0.08	0.24	1.4
Perch	Muscle	Sännen	2020	<10	11	3.3	86	1.4	59	156	32	<3	94	<1	<0.5	<1	<0.3	1.6	2.4	0.5	0.3	1.2	<0.1	0.67	0.29	0.52	0.03	<0.1	0.37
Otter	Muscle	Dalarna	2021	18	30	<2	61	4.3	11	<1	<1	<2	12	<0.5	<0.3	<0.6	<0.2	1.5	0.3	0.14	1.0	0.07	0.69	1.5	0.20	1.2	0.18	<0.1	0.94
Otter	Muscle	Gästrikland	2021	26	44	<2	58	2.4	9.5	<1	<1	<2	7.1	<0.5	<0.3	<0.6	1.0	28	2.0	4.3	20	0.51	5.4	3.6	0.35	10	3.0	0.95	2.0
Otter	Muscle	Norrbotten	2021	28	30	<2	57	3.8	18	<1	<1	<2	16	<0.5	<0.3	<0.6	<0.2	2.7	0.27	0.31	2.0	<0.05	0.54	4.9	0.23	1.9	0.22	0.18	1.2
Otter	Muscle	Värmland	2021	68	62	<2	108	3.6	12	<1	<1	<2	5.6	<0.5	<0.3	<0.6	4.8	26	4.5	7.1	18	2.1	2.1	7.1	0.47	3.3	0.12	0.30	0.73
Otter	Muscle	Jämtland	2021	22	29	<2	62	2.4	18	<1	<1	<2	12	<0.5	<0.3	<0.6	9.1	26	2.8	4.2	27	0.91	14	11	1.5	8.2	0.66	<0.1	0.30
Otter	Muscle	Dalarna	2021	66	54	<2	86	5.3	14	<1	<1	<2	10	<0.5	<0.3	<0.6	1.8	5.1	0.96	1.1	5.4	0.13	1.7	4.9	0.17	1.7	0.12	0.13	0.64
Otter	Muscle	Närke	2021	30	37	<2	117	8.9	39	<1	<1	<2	15	<0.5	<0.3	<0.6	<0.2	27	1.6	6.1	74	1.6	55	20	0.49	60	3.5	1.8	2.6
Otter	Muscle	Uppland	2021	34	49	<2	93	4.8	13	<1	<1	<2	10	<0.5	<0.3	<0.6	2.1	8.4	0.91	1.3	4.9	0.18	1.1	5.9	0.35	15	0.25	1.6	4.0
Otter	Muscle	Skåne	2021	30	43	<2	92	3.4	8.4	<1	<1	<2	7.2	<0.5	<0.3	<0.6	<0.2	10	4.1	9.5	23	4.4	9.5	3.5	2.2	8.5	4.7	0.7	2.1
Otter	Muscle	Västmanland	2021	38	43	<2	115	3.8	22	<1	<1	<2	24	<0.5	<0.3	<0.6	3.5	90	2.9	12	69	2.4	29	11.0	1.1	27	2.0	1.1	2.1
Otter	Muscle	Småland	2021	20	26	<2	64	1.1	9.0	<1	<1	<2	3.8	<0.5	<0.3	<0.6	<0.2	6.7	0.64	0.66	9.5	0.22	2.0	3.2	0.27	17	1.3	0.9	1.7
Otter	Muscle	Lappland	2021	17	29	<2	52	4.5	6.1	<1	<1	<2	4.3	<0.5	<0.3	<0.6	<0.2	13	2.4	2.8	8.5	0.9	10	2.3	0.65	13	0.2	<0.1	0.16

* Blank corrected values (with higher measurement uncertainty).