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Metals and Organic Contaminants in Starling
(*Sturnus vulgaris*) from central and southern Sweden.

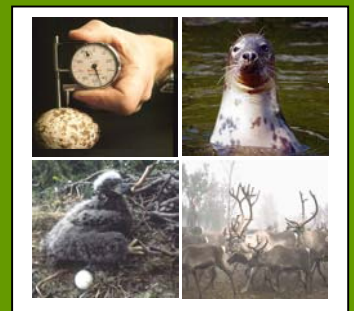
Comments Concerning the National Swedish Contaminant
Monitoring Programme in Terrestrial Biota

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Sammanfattning

Föreliggande rapport är resultatet av ett uppdrag från Naturvårdsverket (Överenskommelse 222 0744) som syftar till att ta fram en aktuell bild av förekomsten av ett antal metaller, pesticider samt några ofullständigt kända föroreningar i svensk natur där alltså osäkerhet om ämnenas spridning och ackumulation i framför allt den terrestra organismvärlden råder. Som matris i detta fall har valts ungfåglar av stare från 8 övervakningslokaler i södra delen av Sverige. Matriserna är insamlade under våren 2006. För studien har vävnad av muskel och lever analyserats. Varje lokal representeras av ett lever- och ett muskelhomogenat omfattande lika mängd vävnad från tio individer.

Valet av ämnen har vägletts bl.a. av tidigare resultat från övervakning av föroreningar i svensk natur samt av resultat från screeningundersökningar av ofullständigt kända ämnen som tagits fram i Naturvårdsverkets regi.

Listorna över prioriterade ämnen innehåller 54 pesticider där vissa ämnen har varit förbjudna i Sverige sedan lång tid. Studier av metaller och grundelement har ingått i de svenska övervakningsprogrammen sedan starten 1980 men har delvis utgått ur vissa program under senare år till förmån för analys av andra ämnen. I denna studie har 13 metaller och grundämnen analyserats för att få en dagsaktuell bild av läget.

Av frekvent använda flamskyddsmedel har polybromerade difenyletrar (PBDE) och hexabromcyclododekan (HBCD) analyserats. Fem substanser inom gruppen fenolära ämnen har analyserats. Gruppen perfluorerade ämnen (PFCs) har blivit känd för delvis höga och tilltagande halter i biota från akvatiska miljöer. Ämnesgruppen har övervakats i miljön under senare år, men halter i organismer tillhörande landfaunan är fortfarande relativt dåligt kända varför dessa ämnen har ingått i denna undersökning.

Av pesticiderna förekommer endast mätbara spår av klorpyrifos och β -HCH.

Ingen av metallerna eller grundelementen uppträder i anmärkningsvärt höga halter på någon av lokalerna. De högsta halterna av kadmium finns i Krankesjön, Ottenby and Fleringe. De högsta halterna av bly återfanns i Krankesjön och Tyresta. Den högsta kvicksilverförekomsten fanns i Ottenby och den lägsta i Svartedalen.

Av bromerade flamskyddsmedel analyserades tetra-, penta-, hexa-, octa-, nona-, deca-BDE and HBCDD. Den dominerande kongeneren på samtliga lokaler var BDE99, vilket överensstämmer med tidigare studier av terrestra arter. Den högsta halten av PBDEer fanns i Boa Berg (258 ng/kg, färskvikt), där även BDE99 hade sin högsta halt (132 ng/kg, färsk vikt). Koncentrationerna av octa-, nona- och deca- BDE liksom av HBCDD visade sig ligga under kvantifieringsnivån (LOQ) på samtliga åtta lokaler.

Inom gruppen fenolära ämnen analyserades 4-tert-oktylfenol, 4-nonylfenol, triklosan, pentaklorfenol och bisfenol A. Detekterbara halter av triklosan återfanns på samtliga lokaler. Högsta halten av triklosan uppmättes i Boa Berg (0.25 ng/g färskvikt) och den lägsta i Tiveden (0.02 ng/g, färskvikt). Höga värden på blankprover störde analyserna av oktyl- och nonylfenol. Resultaten kan därmed inte anses vara tillförlitliga. Koncentrationerna av pentaklorfenol och bisfenol A låg under LOD på samtliga lokaler 5 resp. 10 ng/g, färskvikt).

Perfluorerade ämnena (PFCs) tillverkas och används huvudsakligen som ytbehandlingsmedel för papper, läder och tyger och utnyttjas där för sina vatten- och smutsavvisande egenskaper. PFCer används även i t.ex. rengöringsmedel och skum för brandsläckare. Ämnena har ökat över tid i biota i Sverige, framförallt i den akvatiska miljön. Perfluoroktan sulfonat (PFOS) har fasats ut under 2002 men ännu har ingen nedgång kunnat spåras i miljön. Av samtliga PFCer i denna studie var PFOS den dominerande med en genomsnittlig halt på 3,5 ng/g, färskvikt. I starar från nästan samtliga lokaler fanns PFNA, PFUnA och PFTriA med en genomsnittlig halt av ca 0,6 ng/g, färskvikt, följt av PFDoA med en genomsnittlig koncentration av 0,3 ng/g, färskvikt. Detekterbara men låga halter av PFHxA och PFOSA fanns sporadiskt. Koncentrationerna av PFHpA, PFOA, PFDcA, PFTeA, PFPeDA, PFBS och PFDcS var samtliga under respektive substans detektionsnivå på samtliga lokaler.

Summary

The present study has been carried out on mandate of and in cooperation with the Swedish Environmental Protection Agency (SEPA) according to Agreement 222 0744. By use of liver and muscle of starling as a matrix representing parts of the terrestrial environment, the study will focus on accumulation, profiles and concentrations of some pesticides used in semi-agricultural areas of Sweden as well as the accumulated levels of some metals and ground elements. Flame retardants are materials added or applied to a product to increase its fire resistance. This study focuses on accumulated levels of PBDEs and HBCD. Five phenolic substances were analysed in muscle of starling; 4-tert-octylphenol (OP), nonylphenol, triclosan, bisphenol A and pentachlorophenol (PCP). Finally we screened the great group of perfluorinated compounds (PFCs).

The analyses of more than 50 pesticides show that only traces of chlorpyrifos and β -HCH were found in some localities.

None of the metals and elements occurs in notable high concentrations in any of the eight localities. The highest concentrations of cadmium occur in Krankesjön, Ottenby and Fleringe and of lead in Krankesjön and Tyresta. The highest concentration of mercury was found in Ottenby and the lowest in Svartedalen.

Brominated flame retardants (BFRs) is a generic term for several groups of organic substances that contains bromine and are used for fire suppressing purposes. Brominated flame retardants are not produced in Sweden. They enter the country to some extent in chemical substances but foremost in goods. The starlings were analysed on tetra-, penta-, hexa-, octa-, nona-, deca- BDE and HBCD. The dominant congener in all eight localities was BDE99, which seems to be in accordance with previous studies on terrestrial species. The highest overall level of PBDEs (Poly Brominated Diphenyl Ethers) was found at Boa Berg (258 pg/g, fresh weight), where also BDE99 had its peak concentration (132 pg/g, fresh weight). The concentrations of octa-, nona- and deca- BDE as well as HBCDD were found to be beneath the quantification limit (LOQ) in all eight localities.

The phenolic substances analysed in this study were 4-tert-octylphenol, 4-nonylphenol, triclosan, pentachlorophenol and bisphenol A. Detectable levels of triclosan were found at all eight localities. The highest concentration was detected at Boa Berg (0.25 ng/g,

w.w.) and the lowest at Tiveden (0.02 ng/g, w.w.). High values in blank samples were disturbing the analysis of octyl- and nonylphenol. The results can therefore not be considered as reliable. The concentration of pentachlorophenol and bisphenol A was beneath the level of detection at all eight localities (5 and 10 ng/g, w.w., respectively).

Perfluorinated compounds have been produced and used since the 1950s, mainly due to their exceptional ability to lower surface tension. Perfluorinated surfactants are amphiphilic and therefore used as emulsifiers and for water- and dirt-proofing in packing-paper, leather and textiles, as well as in cleaning products and fire fighting foams. The substances are widely spread in the environment and concentrations in Swedish biota have increased over time the latest decades. Perfluorooctane sulfonate (PFOS) was phased out by its main producer in 2002. However, so far no decreasing trend of PFOS in the Swedish marine environment could be detected as result of the phase-out. Of all PFCs analysed in this study, PFOS was the dominant in all localities, with an average concentration of 3.5 ng/g, fresh weight (fw). In almost all localities PFNA, PFUnA and PFTriA were found at average concentrations of approximately 0.6 ng/g, fw, followed by PFDoA at an average level of 0.3 ng/g, fw. Detectable but very low levels of PFHxA and PFOSA were found occasionally. The concentrations of PFHpA, PFOA, PFDcA, PFTeA, PFPeDA, PFBS and PFDcS were found to be below the respective detection limit (LOD) in all eight localities.

Aim

This report has been carried out on request of and in cooperation with the Swedish Environmental Protection Agency (SEPA) to be part of the National Swedish Contaminant Monitoring Programme in Terrestrial Biota. The aim is to reveal the state of the art of contamination in the terrestrial environment by screening a well-known matrix – young of starling – according to levels of some well-known metals and some chlorinated and brominated chemicals as well as some pesticides used in agriculture, orchards, gardens and households. The aim is also to assess and document concentrations of pesticides and other contaminants used in agric-cultivated and semi-urban areas, their spread to and accumulation in neighbouring areas and biota. Monitoring studies of contaminants in terrestrial environments have earlier been carried out by use of starling. The earlier real time and retrospective studies comprised DDT- and PCB-substances, metals and trace elements (Odsjö, 2000). The present study is a real time and a screening study based on material collected in 2006. Based on results from this study, decision may be taken to go further with long-term retrospective trend studies.

Organisation

The analysed material is collected by the Swedish Museum of Natural History, Dept of Contaminant Research (DCR) and stored in the Environmental Specimen Bank (ESB) in cooperation with the Swedish EPA as part of the National Swedish Monitoring Programmes. Chemical analyses have been carried out in cooperation with Jenny Kreuger and Märit Peterson, SLU Swedish University of Agricultural Sciences, (pesticides), Vera Galgan and Lars Petersson, Department of Chemistry, National Veterinary Institute, (metals), Lillemor Asplund, ITM Department of Applied Environmental Science, Stockholm University, (brominated flame retardants), Margaretha Adolfsson-Erici, ITM Department of Applied Environmental Science, Stockholm University, (phenolic substances) and Urs Berger, ITM Department of Applied Environmental Science, Stockholm University, (perfluorinated compounds). The laboratories have written the description of analysing methods and also taken an active part in the evaluation of the data. Elisabeth Nyberg, Tjelvar Odsjö and Anders Bignert at the DCR have analysed and evaluated the results and prepared the report, partly in cooperation with the chemists.

The study has been carried out in cooperation with Britta Hedlund, Jonas Rodhe and Axel Hullberg, SEPA, who also gave the financial support to the study.

Introduction

National and regional monitoring of pollution of contaminants in the Swedish environment comprises studies of the body burden of bio-accumulated substances in biota from terrestrial and freshwater reference areas in the Swedish mainland and from the surrounding seas and coastal areas (Odsjö and Olsson, 1979a,b). Primarily the monitoring of pollutants aims at studying long-term changes of concentrations in the environment (trend monitoring) as well as spatial variation. Trend monitoring is considered as an important instrument for studies of the general bioaccumulation due to national and international use as well as measures against use of different pollutants in order to minimise pollution of nature. By use of data from a network of localities, the transport and geographical distribution of contaminants is possible to study.

As a matrix for monitoring of bio-accumulating substances in terrestrial environments in Sweden, tissues of starling (*Sturnus vulgaris*) have been used since the mid-1960s.

Starling was chosen as a terrestrial species for monitoring of chemical residues in wildlife also in USA in the National Contaminant Biomonitoring Programme. Monitoring of starling at 110 predetermined locations started in 1967 (Jacknow *et al.*, 1986). Nestlings of starling have also been collected and analysed for contaminants in Finland since the end of the 1960s (Paasivirta *et al.*, 1985).

Beside annual studies of an established cluster of contaminants in different matrices of the programmes, special studies are regularly carried out in order to screen new and/or poorly investigated substances judged as presumptive contaminants. The present study can be regarded as a screening study to reveal new threats of contaminants in rural and semi-agricultural areas of Sweden.

Material and method

Material

The starling is a migratory species breeding in connection to agricultural areas principally all over the country of Sweden. However, the population density significantly decreases to the north and north-west. Due to the migration behaviour, young starling only has been collected from nesting boxes in the present programme. Collection has been carried out in late May-early June at an age of the young of about three weeks, *i.e.* shortly before they were fledged. Starling has been collected from eight reference areas in Sweden. In order to achieve homogeneity in the material between years, only live young have been picked up from the boxes. From a contaminant monitoring point of view, young starling are considered as representative for the area in which they were collected since they were raised by food, chiefly invertebrates, from the vicinity of the nest. Directly after capture, the starlings were frozen at a temperature of about -20 °C (some at -80 °C) and were transported frozen to the laboratory.

Localities

The localities referred to in this presentation cover the central and southern part of Sweden. Sampling localities are listed in Table 1 and indicated in Figure 1. Due to the generally sparse populations of starling in northern Sweden and a recent population decrease, it has been difficult or impossible to collect material from the northern part of Sweden. The sampling sites are all locally uncontaminated *i.e.* there are no local outlets in the vicinity of the sampling area that might constitute a major influence on the measured concentrations in the studied material.

Table 1. Sampling sites and provinces for collection of young starling.

Sampling site	Year	Tissues
Grimsö, Västmanland	2006	Liver, muscle
Tyresta, Södermanland	2006	Liver, muscle
Tiveden, Östergötland	2006	Liver, muscle
Svartedalen, Västergötland	2006	Liver, muscle
Fleringe, Gotland	2006	Liver, muscle
Boa Berg, Halland	2006	Liver, muscle
Ottenby, Öland	2006	Liver, muscle
Krankesjön, Skåne	2006	Liver, muscle



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Figure 1. The Swedish Monitoring Programme of Contaminants in Terrestrial Biota, sampling sites for starling.

Tissue samples

From each of the 8 localities listed above a homogenate was prepared consisting of aliquots of 10 individual young of starling. Depending of the cluster of substances to be analysed the homogenates were based on either breast muscle or liver. The weight of the pooled samples varied between 0.5 and 10 g.

Analysed compounds and elements

Below are all analysed compounds, metals and elements listed in Tables 2-6.

Pesticides

A number of pesticides potentially used in industry, agriculture, horticulture, forestry, and indoor in house-holds were analysed (Table 2).

Analysis of pesticides

Sample preparation was performed by mincing 7 g of muscle with a scalpel followed by adding surrogate standards before extraction. The sample was extracted three times with *i*) acetone, *ii*) dichloromethane and *iii*) a mixture of acetone and dichloromethane, using both ultrasonic bath (20-30 min) and shaking (30-40 min). Extraction clean-up was carried out using size exclusion chromatography (SEC) packed with Bio-Beads S-X3. The final extracts (3 g muscle/mL) were analysed on a gas chromatography system coupled to a mass spectrometer (GC-MS). The mass spectrometer was operated in either electron ionization (EI) or negative chemical ionization (NCI) mode using the standard procedure applied when analysing semi-polar and non-polar pesticides in water (accredited method OMK 51). Quantification was performed against an external standard curve (relative the internal standard) with results corrected for recovery efficiency.

Table 2. Pesticides analysed in muscle and level of detection, LOD (ng/g, fresh weight)

Substance	LOD	Substance	LOD	Substance	LOD
alachlor	3	beta-endosulfan	0.02	alpha-HCH	0.1
alphacypermethrin	0.03	endosulfansulfate	0.02	beta-HCH	0.1
aclonifen	3	esfenvalerate	0.03	delta-HCH	0.1
atrazine	3	ethofumesate	4	metalaxyl	3
desethylatrazine (DEA)	2	fenitrothion	3	metazachlor	10
BAM 2,6-dichlorobenzamide	3	phenmedipham	10	metribuzin	2
bitertanol	10	fenpropimorph	2	pendimethalin	5
cyanazine	6	flurtamone	3	permethrin	0.5
cyfluthrin	0.1	fuberidazole	5	pirimicarb	2
cyprodinil	2	hexazinone	3	prochloraz	20
b-cyfluthrin	0.3	iprodione	3	propiconazole	10

cypermethrin	0.3	isoproturon	3	propyzamide	2
deltamethrin	0.04	carbofuran	3	simazine	1
diflufenican	1	chlorfenvinphos	0.02	Terbutylazine	3
dichlobenil	1	chloridazon	6	Desethylterbutylazine (DETA)	1
dimetoat	6	chlorpyrifos	0.03	Tolclofosmethyl	1
diuron	2	lambda-cyhalothrin	0.02	Trifluralin	0.5
alpha-endosulfan	0.02	lindane (γ -HCH)	0.1	Vinclozolin	0.03

Metals and elements

13 metals and ground elements were analysed (Table 3)

Analysis of metals and elements

Pre-treatment of samples

Combustion of organs (5 g liver for multi-element determination using HNO₃, HClO₄ and H₂SO₄; about 3 g muscle for analysis of Hg using HNO₃ and HClO₄) was performed by automatic wet digestion according to a standard program (Frank, 1976; Frank and Petersson, 1983; Frank, 1988; Frank *et al.*, 1992). An electrically heated block of aluminium was used (Foss Tecator Digestion System, Model 40, Foss Tecator AB, Höganäs, Sweden).

Analysis

Analysis of 13 elements (Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, V and Zn) was performed using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Jobin Yvon-Horiba SA, 91165 Longjumeau, France).

The determination of Hg was performed by using cold vapour (CV)- ICP-AES. (The methods are accredited according to SS-EN-ISO/IEC 17025).

Quality control was performed using appropriate reference materials (NCS ZC 71001 Beef Liver and DORM-3).

The chemical analyses were carried out by the Department of Chemistry, National Veterinary Institute, Uppsala.

Table 3. Metals analysed in liver (mg/kg, fresh weight) and muscle (mercury) (ug/kg, fresh weight). Levels given in the intervals are below the level of quantification (LOQ) (at least 10s) but above the level of detection (LOD) (3s).

Element		LOD - LOQ
Calcium	Ca	0.44 – 2.0 (mg/kg, fresh weight)
Cadmium	Cd	0.004 – 0.03 (mg/kg, fresh weight)
Cobalt	Co	0.002 – 0.01 (mg/kg, fresh weight)
Chromium	Cr	0.005 – 0.02 (mg/kg, fresh weight)
Copper	Cu	0.15 – 1.0 (mg/kg, fresh weight)
Iron	Fe	0.44 – 2.0 (mg/kg, fresh weight)
Mercury	Hg	1.8 – 5.4 (µg/kg, fresh weight)
Magnesium	Mg	0.46 – 2.0 (mg/kg, fresh weight)
Molybdenum	Mo	0.002 – 0.01 (mg/kg, fresh weight)
Nickel	Ni	0.022 – 0.08 (mg/kg, fresh weight)
Lead	Pb	0.020 – 0.06 (mg/kg, fresh weight)
Vanadium	V	0.002 – 0.01 (mg/kg, fresh weight)
Zinc	Zn	0.62 – 2.0 (mg/kg, fresh weight)

Brominated flame retardants

The major technical polybrominated diphenyl ethers (PBDE) and Hexabromocyclododecane (HBCD) were analysed as given in Table 4.

Analysis of brominated flame retardants

The samples of 10 g muscle tissue were extracted with a mixture of acetone/*n*-hexane and *n*-hexane/diethyl ether. The organic phase was liquid/liquid partitioned with a solution of sodium chloride/phosphoric acid. The aqueous phase was reextracted with *n*-hexane and the combined organic phases were evaporated to dryness. The lipid content was determined gravimetrically. After treatment of the dissolved lipid extract with concentrated sulphuric acid (Jensen *et al.*, 1983), the samples were analysed by gas chromatograph/mass spectrometry (GC-MS) in electron capture ionization (ECNI) mode. Ammonia was used as the reaction gas. A 15 m DB-5 MS fused silica column (0.25 mm i.d., 0.25 µm film thickness) was used. The mass fragments monitored were *m/z* 79 and 81 for all brominated compounds and *m/z* 237 and 239 for dechlorane, used as internal standard (Sellström *et al.*, 2003).

Table 4. Brominated flame retardants analysed in muscle

Name	Congener number
2,2',4,4'-TeBDE	BDE-47
2,2',4,4',5-PeBDE	BDE-99
2,2',4,4',6-PeBDE	BDE-100
2,2',4,4',5,5'-HxBDE	BDE-153
2,2',4,4',5,6'-HxBDE	BDE-154
2,2',3,3',4,4',5,6'-OctaBDE	BDE-196
2,2',3,3',4,4',6,6'-OctaBDE	BDE-197
2,2'3,4,4',5,5',6-OctaBDE	BDE-203
2,2',3,3',4,4',6,6'-OctaBDE	BDE-205
2,2',3,3',4,4',5,5',6-NonaBDE	BDE-206
2,2',3,3',4,4',5,6,6'-NonaBDE	BDE-207
2,2',3,3',4,4',5,5',6,6'-DecaBDE	BDE-209
	sPBDE
Hexabromocyclododecane	HBCD

Phenolic compounds

The phenolic compounds listed in Table 5 were analysed in muscle of starling.

Analysis of phenolic compounds

The sample, 3 g of muscle tissue, was homogenized with hexane/acetone twice, and the combined organic phases were treated with sodium chloride / phosphoric acid. The aqueous phase was reextracted with hexane and the combined organic phases were evaporated to dryness. The lipid content was determined, and the residue was redissolved in hexane/MTBE. The phenols were extracted into KOH/ethanol, and neutral compounds were removed by extracting the aqueous phase with hexane. After acidification of the aqueous phase, the phenolic compounds were extracted into hexane, and converted into their pentafluorobenzoyl esters. For clean-up, the derivatives were treated with sulphuric acid monohydrate. The determination was done by GC/ECNI/MS (Allmyr *et al.*, 2006). The following surrogate standards were added to the muscle homogenate: ¹⁶d-Bisphenol A, ¹³C-6-pentachlorophenol, ¹³C-12-triclosan and n-nonylphenol.

Table 5. Phenolic compounds analysed in muscle.

Name	
4-tert-octylphenol (OP)	
4-nonylphenol	
Triclosan	
Bisphenol A	
Pentachlorophenol, PCP	

Perfluorinated compounds PFCs

This report focuses on the perfluorinated compounds listed in Table 6.

Analysis of perfluorinated compounds

Sample extraction and clean-up was based on the method by Powley *et al.* (2005) with modifications for biota samples described by Verreault *et al.* (2007). In short, 1 g of the homogenized liver was spiked with the mass-labeled internal standards. Extraction was performed twice with 5 mL acetonitrile in an ultrasonic bath. The combined extracts were concentrated to 1 mL and subjected to dispersive clean-up on graphitized carbon. The cleaned-up extract was added to aqueous ammonium acetate. Precipitation occurred and the extract was centrifuged before instrumental analysis of the clear supernatant. Aliquots of the final extracts were injected automatically on a high performance liquid chromatography system coupled to a tandem mass spectrometer. Compound separation was achieved on an C18 reversed phase column with a binary gradient of buffered (ammonium acetate) methanol and water. The mass spectrometer was operated in negative electrospray ionization mode. Quantification was performed in selected reaction monitoring chromatograms using the internal standard method.

Table 6. Perfluorinated compounds analysed in liver

Substance	Name
PFHxA	Perfluorohexanoate
PFHpA	Perfluoroheptanoate
PFOA	Perfluorooctanoate
PFNA	Perfluorononanoate
PFDCa	Perfluorodecanoate
PFUnA	Perfluoroundecanoate

PFD _o A	Perfluorododecanoate
PFTriA	Perfluorotridecanoate
PFTeA	Perfluorotetradecanoate
PFPeDA	Perfluoropentadecanoate
PFBS	Perfluorobutane sulfonate
PFH _x S	Perfluorohexane sulfonate
PFOS	Perfluorooctane sulfonate
PFDC _s	Perfluorodecane sulfonate
PFOSA	Perfluorooctane sulphonamide

Results

Pesticides

A variety of pesticides used in industry, agriculture, horticulture and forestry in Sweden are included in the analytical package for pesticides utilized in this study. The substances are used for different kinds of protection and preservation. In agriculture and horticulture substances are mainly for plant protection as *e.g.* herbicides, insecticides, fungicides and rodenticides. The greatest amount of pesticide substances is used in industry for industrial pressure and vacuum treatment to preserve wood by penetration of the sapwood that gives a prolonged protection against fungi and/or insects. Impregnation of other material as leather, heavy textiles and plastics also uses substances belonging to this group of chemicals.

Since 1979, data have been published annually on quantities of pesticides (active substances) sold in Sweden. Data on sold quantities are based on information from holders of pesticide approvals. In 2006, a total of 9,685 metric tonnes of pesticides (active substances) was sold in Sweden, which is an increase of 395 tonnes compared to the previous year. The main part (76 percent) was sold to industry, primarily for wood treatment using pressure and vacuum technology. The industrial use of pesticides (biocidal products) increased by 306 tonnes during 2006 compared to the previous year. This rise is partly due to an increase of 423 tonnes in the use of industrial pressure and vacuum impregnating agents. The use of slimicides in the paper and pulp industry has decreased this year by 128 tonnes, from 467 tonnes to slightly more than 338 tonnes. The use of antifouling products has gone up by about 7 tonnes compared to the previous year, 4 tonnes of which were for recreational boats. Even insecticides have risen by nearly 7 tonnes compared to the previous year. (KEMI, 2007)

Some of the analysed pesticides are nowadays prohibited for use in Sweden and some of them are not considered as interesting for monitoring either from a national or from a regional or local point of view since concentrations in biota in different parts of Sweden have been found to be low (Naturvårdsverket, 2008). There were only two substances analysed in the present study that were found in detectable amounts; chlorpyrifos and beta-HCH.

Chlorpyrifos was found in muscle of starling from Krankesjön, Boa Berg, Svartedalen and Grimsö. Chlorpyrifos is a substance used mainly as a broad-spectrum insecticide, rodenticide and for preservation of wood used all over the world. It has been in use in Sweden since 1973 as a substitute to DDT-substances (Esbjörnsson, 2002). Chlorpyrifos is fat-soluble and is easily accumulated via inhalation or via skin contact. The substance has a high acute toxicity and is considered as persistent in nature (Esbjörnsson, 2002). The concentrations in starling were just above the LOD, 0.03 ng/g. The use in Sweden is restricted. The SEPA states that chlorpyrifos in different studies mainly is found in concentrations below LOQ, why no regular monitoring of the substance is justified (Naturvårdsverket, 2008). The present study confirms this statement.

Technical grade hexachlorocyclohexanes (HCH) consists of 65-70% α -HCH, 7-10% β -HCH, 14-15% γ -HCH and approximately 10% of other isomers and diverse compounds. Technical lindane contains more than 90% of γ -HCH, the substance with insecticidal effect (Izmerorov 1983). β -HCH is probably spread by earlier use of technical HCH or technical lindane (γ -HCH) where β -HCH is considered as an unwanted byproduct. β -HCH was found in muscle of starling from Ottenby in a concentration just above the LOD, 0.1 ng/g.

Metals and elements

Calcium, Ca

In nature calcium occurs in calcium carbonate (CaCO_3) or calcium fluoride (CaF_2) and calcium sulphate (CaSO_4). It is used mainly in alloys with other metals and in cement and for manufacturing of concrete.

Most Ca in living organisms is stored in skeleton bones and teeth. A certain amount is circulating in the body fluids or bound to proteins. Ca is important for the function of muscles and the nervous system. Deficiency of body calcium may lead to diseases of various kinds. The mean concentration in liver of starling was 54.3 mg/kg, fresh weight. No notable difference between localities was found.

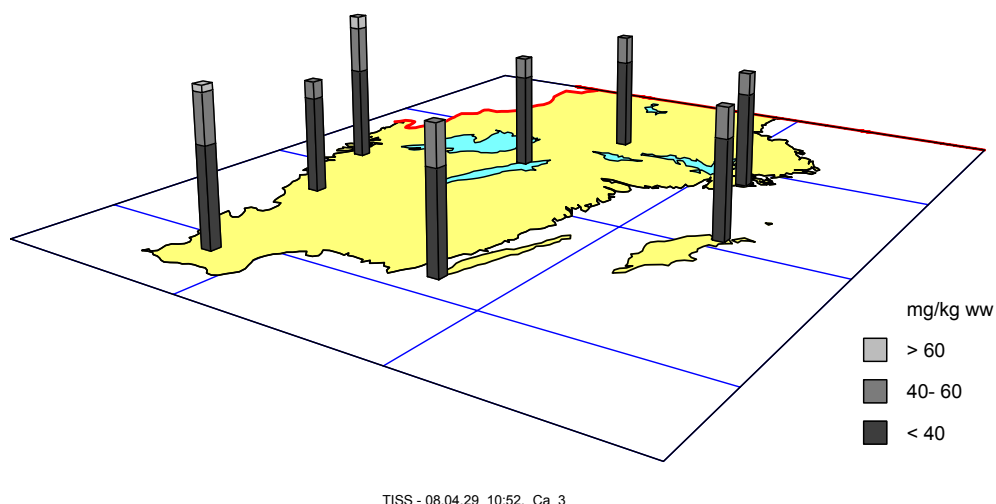


Figure 2. Spatial variation in concentration (w.w.) of calcium in starling liver.

Cadmium, Cd

Cadmium has been used for a variety of purposes as *e.g.* color pigments, for surface treatment of metals, as stabilizers in plastic, in Ni-Cd batteries. Mines and metal smelting plants are other sources to cadmium pollution. Cadmium has been spread to farming lands by artificial phosphate fertilizers based on natural phosphorous minerals containing cadmium. For many of the earlier purposes, Cd is prohibited in Sweden today, why also pollution of Cd has decreased successively.

Cd is a toxic element mainly accumulated via ingested food. The excretion of Cd from the body via urine is relatively slow why a corresponding increase occurs during life span. Most cadmium is accumulated in the cortex of the kidneys and in the liver. High concentration may lead to injuries of the kidneys and, as a consequence, to deformation of the skeleton.

In the present study Cd was detected in starling from four out of eight localities. The mean concentration in liver of starling from those four sites was 0.023 mg/kg, fresh weight. The highest levels were found in Krankesjön, Ottenby and Fleringe. In an earlier trend study (1983-1998) of Cd in young starling the mean concentration of Cd in Fleringe was found to be 0.422 mg/kg, fresh weight, which is far higher than in 2006; 0.020 mg/kg, fresh weight in kidney (Odsjö, 2000).

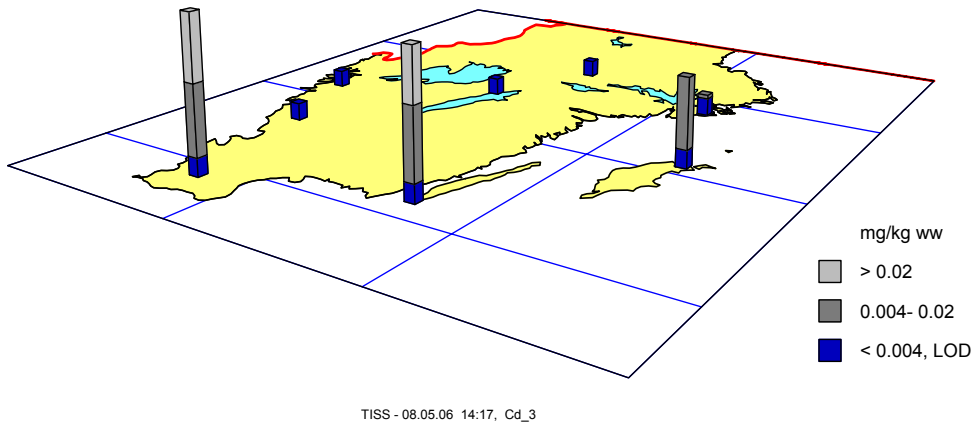


Figure 3. Spatial variation in concentration (w.w.) of cadmium in starling liver.

Cobalt, Co

Cobalt is an essential trace element and the concentration of Co varies in the earth crust. Co is spread around industries treating or using cobalt in different forms. Co is an important ingredient in alloys of hard steel in which the main part of cobalt is used. It is also used in manufacturing of pigments, in catalysts and ceramic materials. Burning of fossil fuels is also a source of spread.

In the present study cobalt was present in detectable amounts in liver of starling from all localities. The mean concentration was 0.038 mg/kg, fresh weight. The highest levels were found in the two southernmost localities and that might indicate an influence from Central Europe, 0,057 mg/kg in Krankesjön and 0,058 mg/kg in Ottenby. Notable is also the level found in starling from Fleringe (0.047 mg/kg).

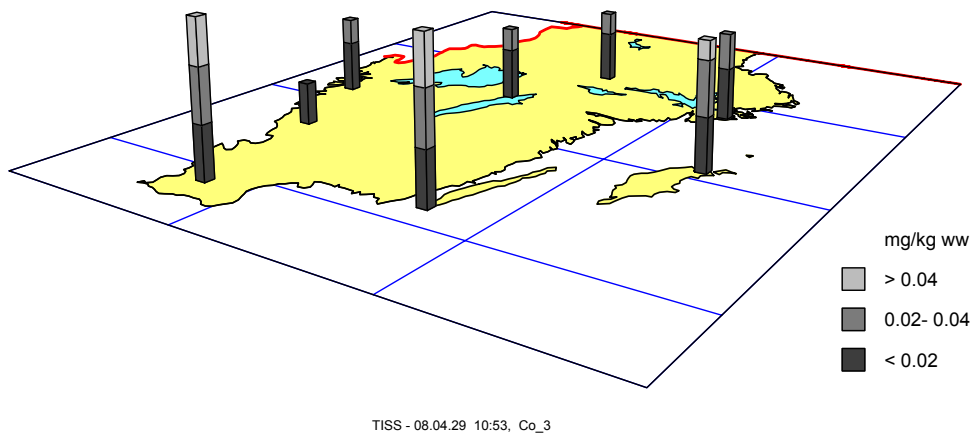


Figure 4. Spatial variation in concentration (w.w.) of cobalt in starling liver.

Chromium, Cr

Chromium is an element that is used as ingredient in alloys, mostly in stainless steel. It is also used for surface treatment of metals, as catalyst and for tanning leather. Cr is probably essential for living organisms but excess levels may be toxic.

In the present study chromium was present in detectable amounts in liver of starling from all eight localities. The mean concentration was 0.021 mg/kg, fresh weight. The highest level (0.035 mg/kg, fresh weight) was found in Grimsö, which might indicate an influence from old metallurgic industries in that area of the country.

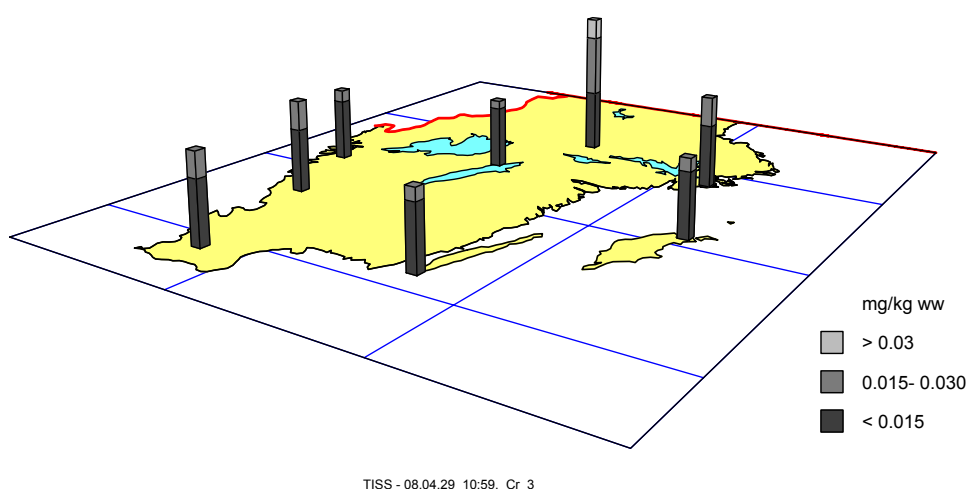


Figure 5. Spatial variation in concentration (w.w.) of chromium in starling liver.

Copper, Cu

Copper is a metal that is used either as pure or in combination with some other metals as an ingredient in alloys. Cu is mostly used in electric equipments, buildings, and industrial machines.

Copper is an essential element for living organisms although excess concentrations may cause negative effects of different kind, especially for aquatic organisms. Copper is not bio-accumulated in tissues but regulated and excreted by a lot of organisms. The present study shows a mean copper concentration of 5.0 mg/kg, fresh weight, in liver of starling from the eight localities. The highest concentration (7.0 mg/kg, fresh weight) was found in the sample from Boa Berg in the southwestern part of the country. Otherwise the concentration in starling is fairly on the same level.

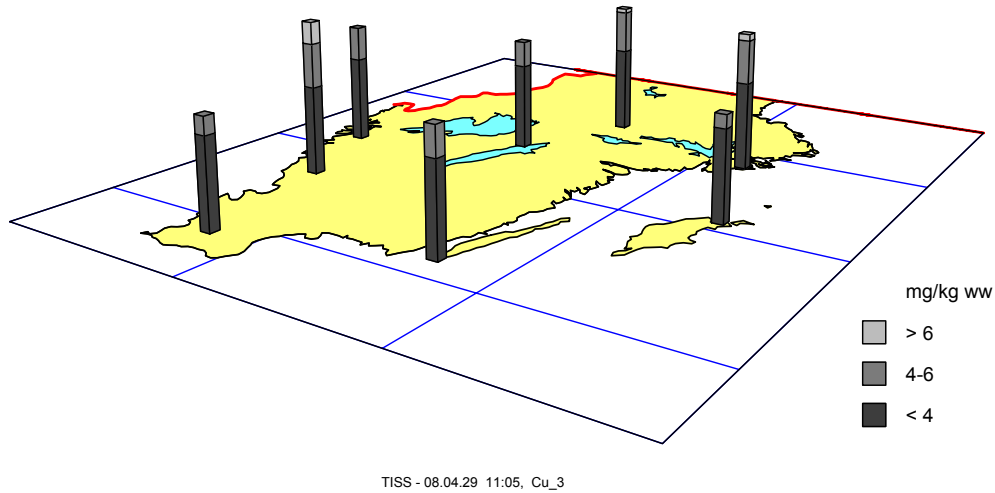


Figure 6. Spatial variation in concentration (w.w.) of copper in starling liver.

Iron, Fe

Iron is one of the most common basic elements in the earth crust, mostly combined with oxygen in different minerals. The Swedish bedrock is rich in iron and for hundreds of years metallurgic industries have spread iron to the surrounding environment from mines and smelters. Iron is an important trace element in living organisms especially in blood (red blood capsules), red muscles and enzymes. A lot of iron is stored in different organs as liver, spleen and bone marrow. Inhalation of iron in form of dust and smoke may lead to illness in man.

The mean concentration of iron in liver of starling in the present investigation was 1040 mg/kg, fresh weight. The highest amounts in starling were found in Grimsö and Tyresta; 1504 mg/kg and 1482 mg/kg, fresh weight, respectively.

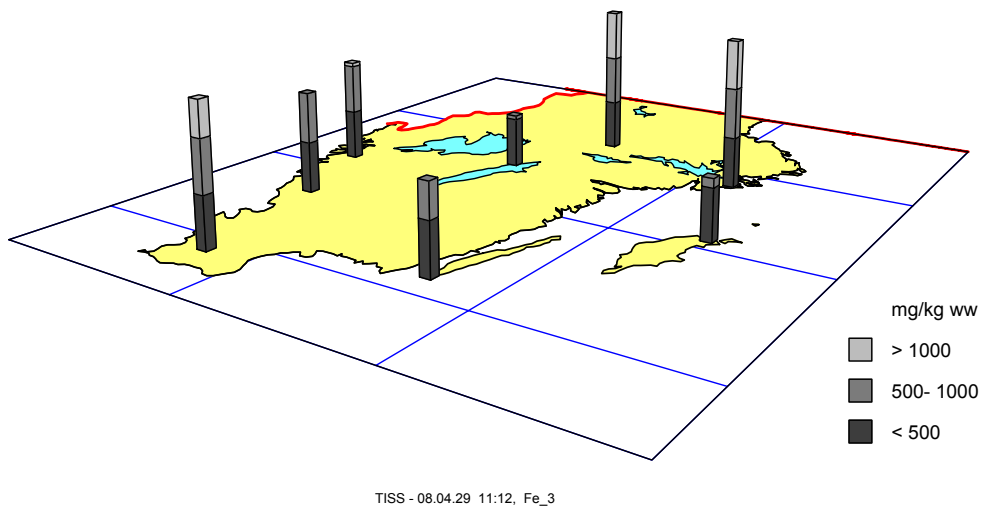


Figure 7. Spatial variation in concentration (w.w.) of iron in starling liver.

Mercury. Hg

Mercury is a metal that appears in floating form at normal temperature, why it is volatile and easily spread in air over long distances. Hg will occur in nature in inorganic and organic compounds. It has since long been a known fact that mercury in some forms is very toxic to living organisms. This is also why it has been used in certain compounds as a fungicide and as a bactericide. Mercury will easily amalgamate with other metals. That has been utilized in e.g. in dentistry and in extraction of gold and silver in metallurgy.

Measures have since long been taken to decrease the use of mercury in the society. Still the pollution and deposition of mercury is judged to be too heavy. Swedish authorities work on widening of measures against use and pollution of mercury, both national and international. The most extensive sources of mercury today are believed to be burning of coal, pollution from smelting plants and destruction of garbage. Mercury is also spread from industries and via sludge from sewage treatment works and leach from waste deposits.

Mercury, mainly the organic forms are known to cause serious effects in living organisms. It is known to be able to pass the blood-brain barrier, the placenta barrier and thus cause foetal damage. Methyl-Hg is fat-soluble and may penetrate the cell kernel and cause damage to chromosomes. It is also known to be carcinogenic. The mean concentration of mercury in muscle of starling in the present investigation was 5.7 µg/kg, fresh weight. The highest amount was found in Ottenby; 12.6 µg/kg, fresh weight. The lowest concentration (2.6 µg/kg, fresh weight) was found in Svartedalen. The reason for the divergent value for mercury in starling from Ottenby is not possible to establish on the present basis.

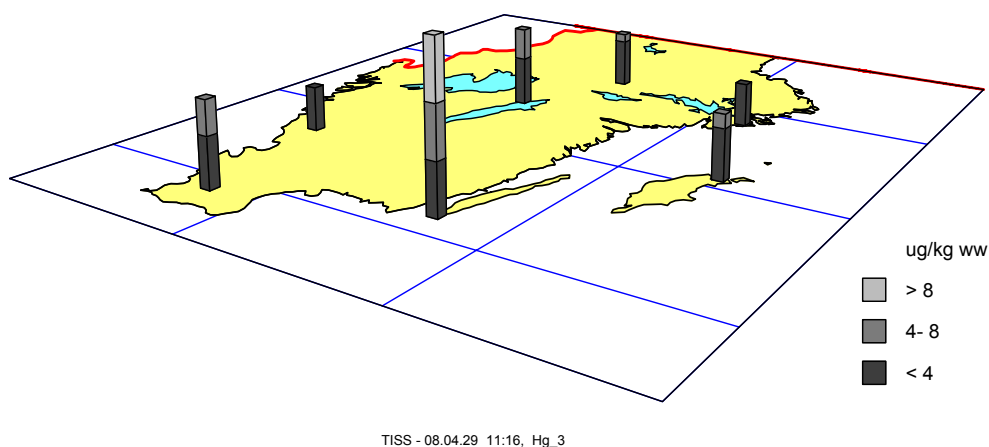


Figure 8. Spatial variation in concentration (w.w.) of mercury in starling muscle.

Magnesium, Mg

Magnesium occurs frequently in the earth crust and seawater. Mg is used in constructions e.g. building, in alloys together with aluminium and zinc (light metals). Magnesium compounds are also ingredients in different medicines. Magnesium is essential for living organisms and is important for regulation of blood pressure and function of muscles.

The mean concentration of magnesium in liver of starling in the present investigation was 201 mg/kg, fresh weight. The concentrations are all on the same level.

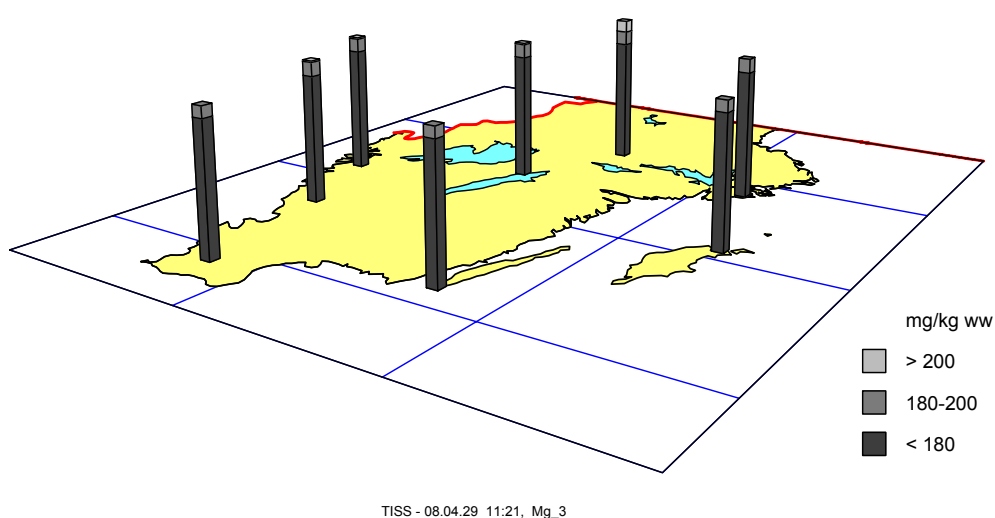


Figure 9. Spatial variation in concentration (w.w.) of magnesium in starling liver.

Molybdenum, Mo

The properties of molybdenum make it valuable as an ingredient in different steel alloys to increase strength and thermo durability. The metal and compounds containing Mo is also used in electrical equipments, in catalysts, as lubricant at high temperatures. Mo is an essential trace element for plants.

The mean concentration of molybdenum in liver of starling in the present investigation was 1.038 mg/kg, fresh weight. The highest concentrations of molybdenum were found in starling from Grimsö and Tyresta; 1.530 mg/kg and 1.380 mg/kg, fresh weight, respectively.

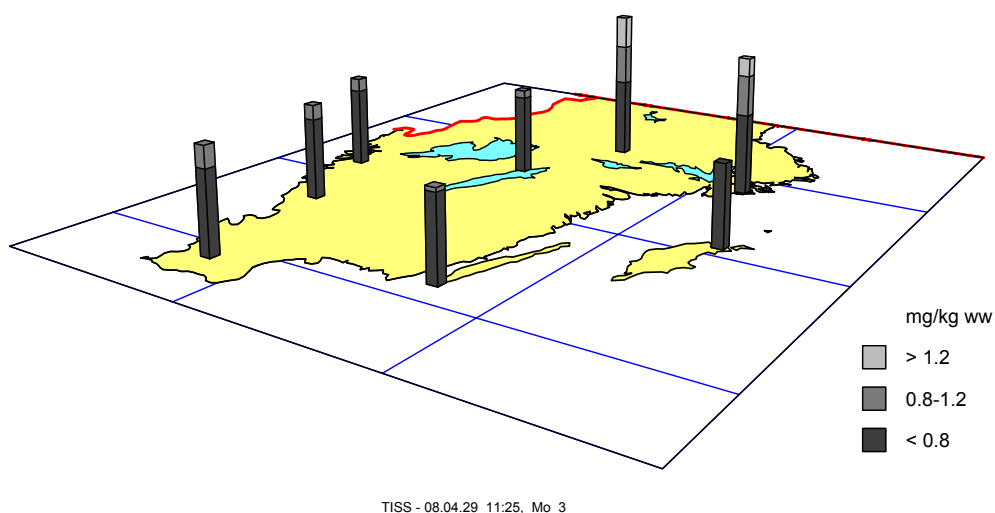


Figure 10. Spatial variation in concentration (w.w.) of molybdenum in starling liver.

Nickel, Ni

Nickel is a metal, produced and used in large quantities for its special properties. It is mostly used in industrial and consumer products, including stainless steel, magnets, rechargeable batteries, coins, and special alloys. It is also used for plating and as a green tint in glass. Exposure to nickel metal and soluble compounds of Ni should be avoided since some of them are carcinogenic and may lead to allergies. Ni is essential for some plants and probably important for liver function of birds and mammals.

The concentrations of nickel in the liver samples of starling in the present investigation were all below the LOD (0.022 mg/kg, fresh weight).

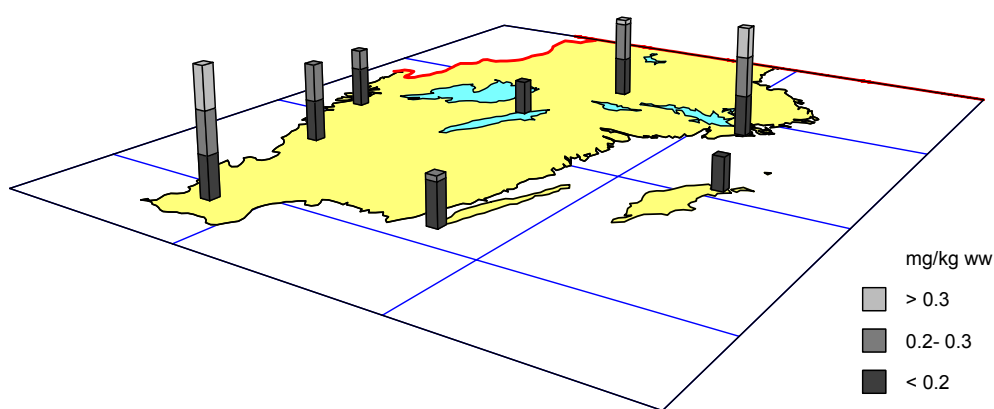
Lead, Pb

Lead is an easily extracted metal that has been used by man since way back. From a national point of view, Swedish authorities have lately suggested total bans and measures against the former wide use of lead in the society for a great variety of purposes. It has mostly been used in accumulators, as anti-knocking agents in fuels (tetra-ethyl and tetra-methyl lead), pigments, cable coating, ammunition, pipes and plates, in fishing-net and fishing tackle, in alloys, *etc.* The emission of lead to biota is highly bound to use of lead containing products. As a consequence of the ban on the former use in *e.g.* car fuels, lead concentration in biota has decreased.

Lead and lead compounds tends to bio-accumulate in living organisms and may cause *e.g.* foetal damage and permanent injuries on the kidney and on the central nervous system.

A recent compilation of results from monitoring studies of lead in biota from terrestrial, freshwater and marine environments in Sweden shows decreasing levels in general, probably mostly depending on a deliberate reduction in use of lead in various fields (Lind *et al.*, 2006).

The mean concentration of lead in liver of starling in the present investigation was 0.187 mg/kg, fresh weight. The highest concentrations of lead were found in starling from Kranskesjön and Tyresta; 0.382 mg/kg and 0.276 mg/kg, fresh weight, respectively.



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Figure 11. Spatial variation in concentration (w.w.) of lead in starling liver.

Vanadium, V

Vanadium is a metal mostly used for production of steel and hard steel alloys. Spread of V to the surrounding mostly occurs from metallurgic processing and from burning fossil fuels. Vanadium generally occurs in plants. The metal also may accumulate in subcutaneous fat and skeleton bones. Hyper-exposure to V may lead to chronic health effects.

The concentration of vanadium was below the LOD (0.002 mg/kg, fresh weight) in three sites out of eight investigated in this study. In the remaining five sites the mean concentration was 0.015 mg/kg, fresh weight. The highest concentrations of vanadium were found in starling from Ottenby, Svartedalen and Tyresta (0.013-0.026 mg/kg, fresh weight).

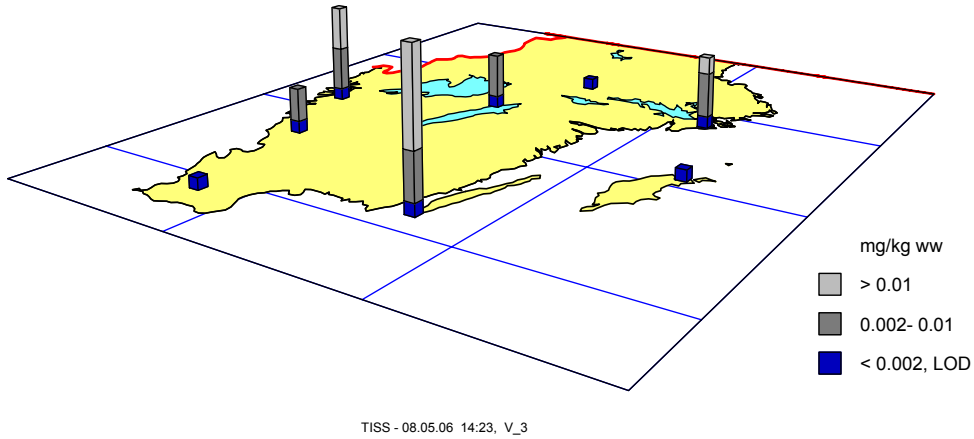


Figure 12. Spatial variation in concentration (w.w.) of vanadium in starling liver.

Zinc, Zn

Zinc is a metal that has an important role as an anti corrosion agent and for metal surface coatings (galvanization). It is also used as alloy metal and as a pigment (Zn-oxide) in paint. The spread of zinc to the environment mostly occurs from mine industries and smelters and other metallurgic factories. Smaller amounts are spread from burning of fossil fuels and coal.

Zinc is essential for animals and plants. Effects of deficiency of Zn are known for both animals and plants.

The mean concentration of zinc in liver of starling in the present investigation was 25.6 mg/kg, fresh weight. The concentrations of zinc in starling were fairly the same in all localities.

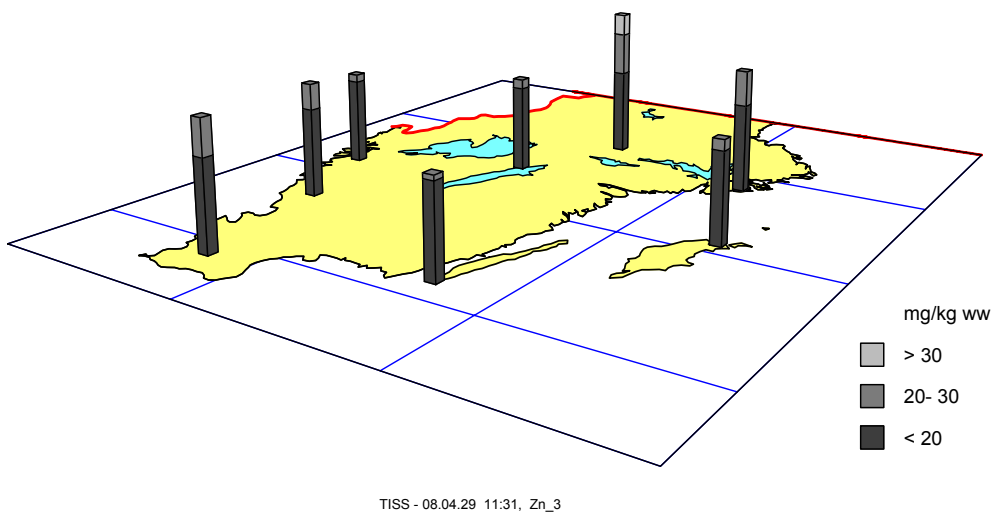


Figure 13. Spatial variation in concentration (w.w.) of zink in starling liver.

Summary metals

Figure 14 illustrates the relative magnitude of values and patterns of the metals at the various sites. The height of a bar is proportional to the maximum value at all sites for that specific metal.

The highest overall level of metals is found at Grimsö, the most northern starring locality. Cr, Fe, Mg, Mo and Zn all have top notifications at this site. Even the Cu level is relatively high. The reason for this may be that the site is in the center of a former mine and metallurgic region. The lowest overall level of metals is seen at Tiveden close to lake Vättern in Östergötland. This result is due to very low levels of iron in the area.

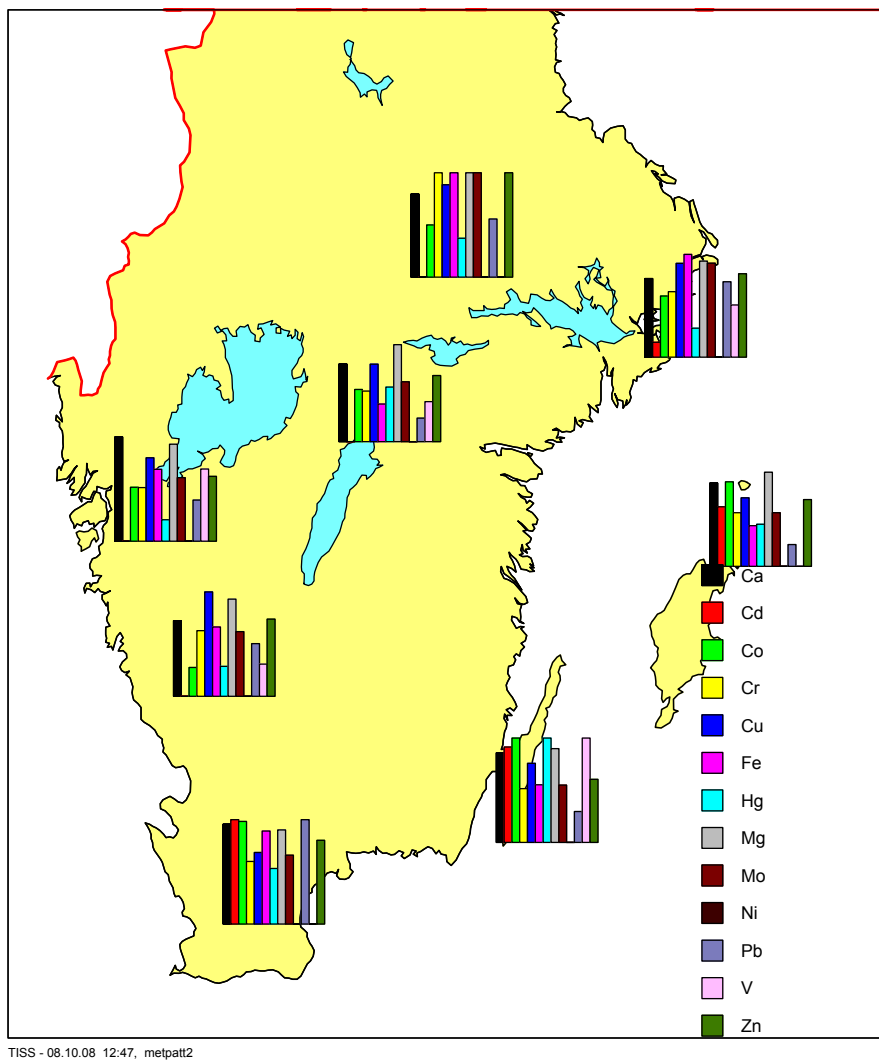


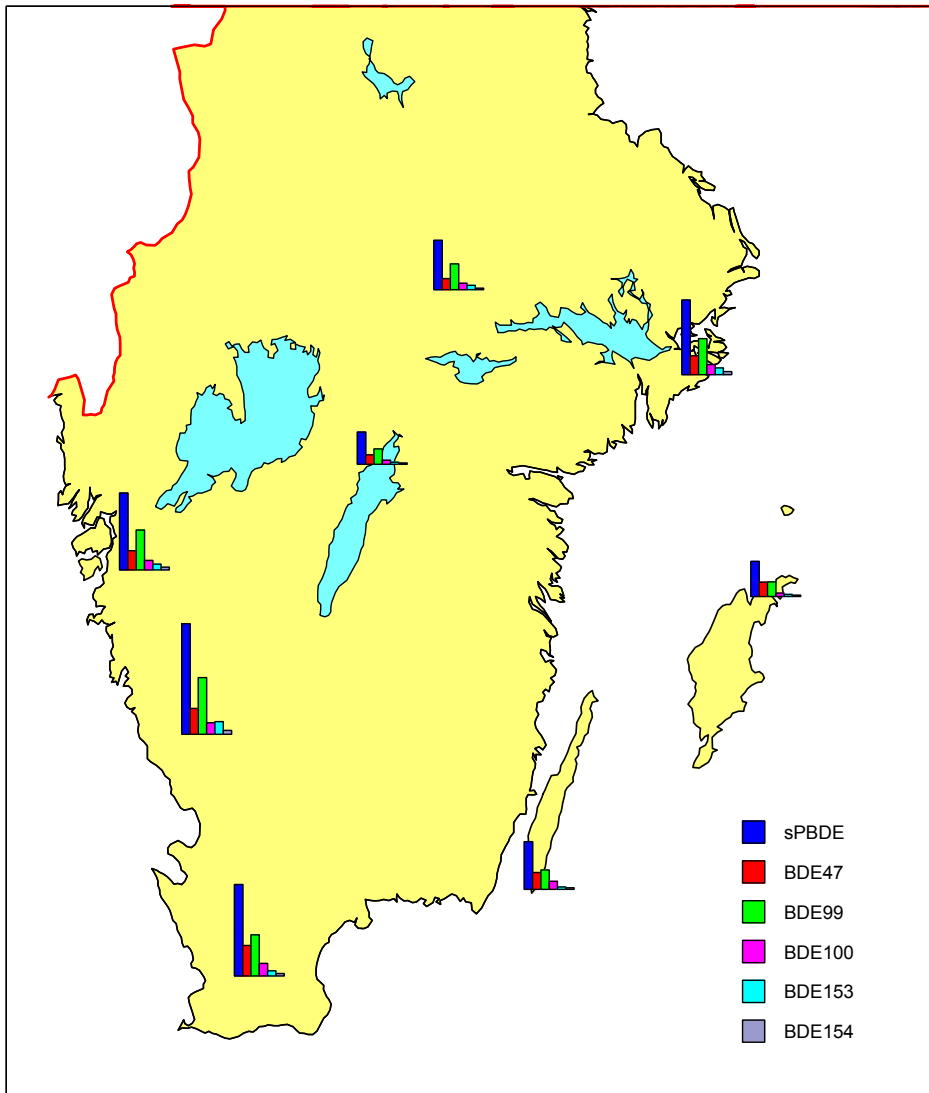
Figure 14. The figure illustrates the relative magnitude of values and patterns at the various sites of (from left to right) Ca, Cd, Co, Cr, Co, Cu, Fe, Hg, Mg, Mo, Ni, Pb, V and Zn. The height of a bar is proportional to the maximum value at all sites for that variable.

Brominated flame retardants

Flame retardants are materials added or applied to a product to increase its fire resistance. Brominated flame retardants (BFRs) is a generic term for several groups of organic substances that contains bromine and are used for fire suppressing purposes. Brominated flame retardants are not produced in Sweden. They enter the country to some extent in chemical substances but foremost in goods. (KEMI, 2003)

Around 70 different BFRs are produced around the world and the most common are penta-, octa- and deca-brominated diphenylether (BDE), TBBP-A and HBCD. Deca-, penta and octa indicate the number of bromine atoms in the molecule. (KEMI, 2003). All three are very persistent but differs in toxicity and ability to bioaccumulate. Penta-BDE is classified as harmful to the environment and injurious to health, but also as very toxic for organisms living in water. Penta-BDE is nominated as a substance for the LRTAP-convention. Octa-BDE is classified as disturbing for reproduction (KEMI, 2008c) and also assessed as bioaccumulating and toxic. The risk evaluation on deca-BDE is not yet finished within EU:s existing substance program. (KEMI, 2008b).

Recent studies suggest that birds feeding in the terrestrial environment may be more exposed to higher brominated BDE congeners than birds feeding in the aquatic environment (Law *et al.*, 2003; Lindberg *et al.*, 2004). Jaspers *et al.* (2006) suggests that there are higher levels of BDE47 (tetra) in heron and grebes (feeds on fresh water fish) than in terrestrial species studied where the dominating congeners were BDE99 (penta) and BDE153 (hexa) (Figure 15). The starlings in this study were analysed on tetra-, penta-, hexa-, octa-, nona-, deca- BDE and HBCD. The dominant congener in all eight localities was BDE99, which seems to be in accordance with previous studies on terrestrial species. The highest overall level of sPBDEs (Poly Brominated Diphenyl Ethers) was found at Boa Berg (258 pg/g, fresh weight), where also BDE99 had its peak concentration (132 pg/g, fresh weight). The concentrations of octa-, nona- and deca- BDE as well as HBCDD were found to be beneath the quantification limit (LOQ) in all eight localities.



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Figure

15. The figure illustrate the relative magnitude of values as well as the relative patterns at the various sites of (from left to right) sPBDE, BDE47, BDE99, BDE100, BDE153 and BDE 154. The height of a bar is proportional to the maximum value for all variables. The dominant congener at all sites was BDE99 and the highest concentration of BDE99 was found at Boa Berg (132 pg/g w.w.).

Phenolic compounds

4-tert-octylphenol (OP)

OP is an alkylphenol etoxylate used for production of detergents, emulsifiers and solubilizers *etc.* (Talmage, 1994). OPs have been reported to disrupt endocrine functions in for example fish (Gronen *et al.*, 1999), frogs (Kloas *et al.*, 1999) and rats (Majdic *et al.*, 1997).

Nonylphenol

The greater part of all nonylphenol produced is used for manufacturing of surface active substances, foremost nonylphenol etoxylate (KEMI, 1994). The use in Sweden varies a lot between years (Enviro planning, 2005).

Triclosan

Triclosan is an antibacterial substance foremost used in hygienic and cleaning products. The use of triclosan increased over the last decade but seems to have decreased during 2005-2006. (KEMI, 2008a) It is classified as irritating and dangerous for the environment, very toxic for water living organisms and it might cause long term effects in the aquatic environment (KEMI, 2005). In the present study triclosan was detected in starling from all eight localities. The mean concentration in muscle of starling sites was 0.11 ng/g, fresh weight. The highest amount was found in Boa Berg; 0.25 ng/g, fresh weight. The lowest concentration, 0.02 ng/g, fresh weight, was found in Tiveden. (Figure 16).

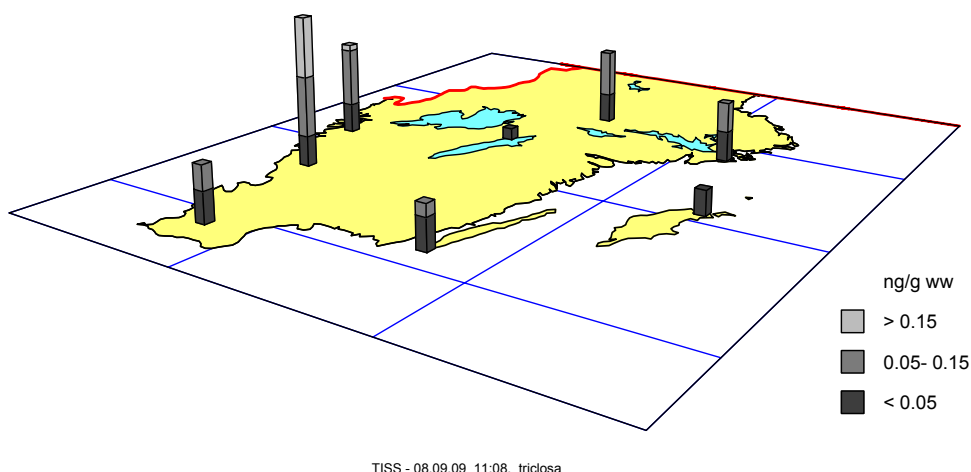


Figure 16. Spatial variation in concentration (w.w.) of triclosan in starling muscle.

Bisphenol A

Bisphenol A is produced by a reaction between phenol and acetone. Together with epichlorohydrine it is used for synthesis of bisphenol-A-diglycidyl ether (DGEBA), which is the most common starting substance for epoxy resin. Resins are for example used in adhesive, flooring material, paint and furnish. (KEMI, 1994) The concentrations of bisphenol A in the muscle samples of starling in the present investigation were all below the LOD (10 ng/g, fresh weight).

Pentachlorophenol, PCP

PCPs have previously been used for surface treatment and impregnation of wood to protect it from rot and surface growth. The latest approval of use was in 1978 (KEMI 2007). The concentrations of PCP in the muscle samples of starling in the present investigation were all below the LOD (5 ng/g, fresh weight).

Perfluorinated compounds PFCs

Perfluorinated compounds (PFCs) form a group of organic substances characterized by carbon chains in which all hydrogen atoms have been replaced by fluorine atoms. PFCs have been produced and used since the 1950s, mainly due to their exceptional ability to lower surface tension (Kissa, 2001). Perfluorinated surfactants, possessing an ionic group additionally to the perfluorinated carbon chain, are amphiphilic and therefore used as emulsifiers and for water- and dirt-proofing in packing-paper, leather and textiles, as well as in cleaning products and fire fighting foams (Kissa, 2001; Hekster *et al.*, 2003; Lehmler, 2005; Schultz *et al.*, 2003). The substances are widely spread in the environment and concentrations in Swedish biota have increased over time the latest decades (Holmström *et al.*, 2005; Berger *et al.*, 2008). Due to its detection in human blood of the general population and negative health effects on living organisms, PFOS has been phased out in 2002 by its main producer. However, so far no decreasing trend of PFOS in the Swedish marine environment could be detected as result of the phase-out (Berger *et al.*, 2008).

Of all PFCs analysed in this study, perfluorooctane sulfonate (PFOS) was the dominant in all localities, with an average concentration of 3.5 ng/g, fresh weight (fw). In almost all localities PFNA, PFUnA and PFTriA were found at average concentrations of approximately 0.6 ng/g, fw, followed by PFDoA at an average level of 0.3 ng/g, fw. This perfluorocarboxylate pattern with dominance of odd numbered long-chain compounds is well known for biota samples (Holmström and Berger, 2008). It may partly be the result of atmospheric transport and degradation of precursor compounds (Martin *et al.*, 2004) and partly reflect the industrial emission pattern (Prevedouros *et al.*, 2006) in combination with a chain-length dependant bioaccumulation potential. Detectable but very low levels of PFHxA and PFOSA were found occasionally. The concentrations of PFHpA, PFOA, PFDcA, PFTeA, PFPeDA, PFBS and PFDcS were found to be below the respective detection limit (LOD) in all eight localities. The levels of the detected PFCs are given in Table 7. In general, the levels found in starling are much lower than

concentrations in livers of marine birds (e.g. Verreault *et al.*, 2005), reflecting the preference of surfactant PFCs to stay in water (Prevedouros *et al.*, 2006) and the subsequent higher contamination of the marine compared to the terrestrial environment.

Table 7. PFCs in liver of starling (ng/g, fresh weight). < means that the concentration is lower than the given typical method detection limit (LOD).

Locality	PFHxA	PFNA	PFUnA	PFDoA	PFTriA	PFOS	PFOSA
Fleringe	<0.15	0.33	0.53	0.19	0.51	1.89	<0.03
Tyresta	0.18	0.45	0.46	0.26	0.54	2.14	<0.03
Skärverud	<0.15	<0.30	0.58	0.32	0.46	3.54	<0.03
Ottenby	<0.15	0.69	0.84	0.35	0.53	4.74	0.08
Grimsö	<0.15	0.78	0.96	0.25	0.56	2.06	0.03
Svartedalen	0.25	0.54	0.51	0.08	<0.15	2.65	<0.03
Boa Berg	<0.15	0.35	0.44	0.20	0.50	4.14	0.05
Krankesjön	0.23	0.84	1.03	0.60	0.73	6.73	0.08

The PFCs in this study are known to have a high chemical and biological stability (apart from PFOSA, which can be degraded to PFOS) and will thus to a high degree resist abiotic and biotic degradation. This also means that this group of substances will bioaccumulate in humans and wildlife species from urban as well rural districts around the world. No distinct geographical trend or concentration difference was observed in this study as would be expected if a current point source was dominant. This suggests that the concentrations found derive from long-term releases from multiple diffuse sources. No quickly decreasing trend of PFC contamination can therefore be expected for the future, despite industrial efforts to restrict emissions.

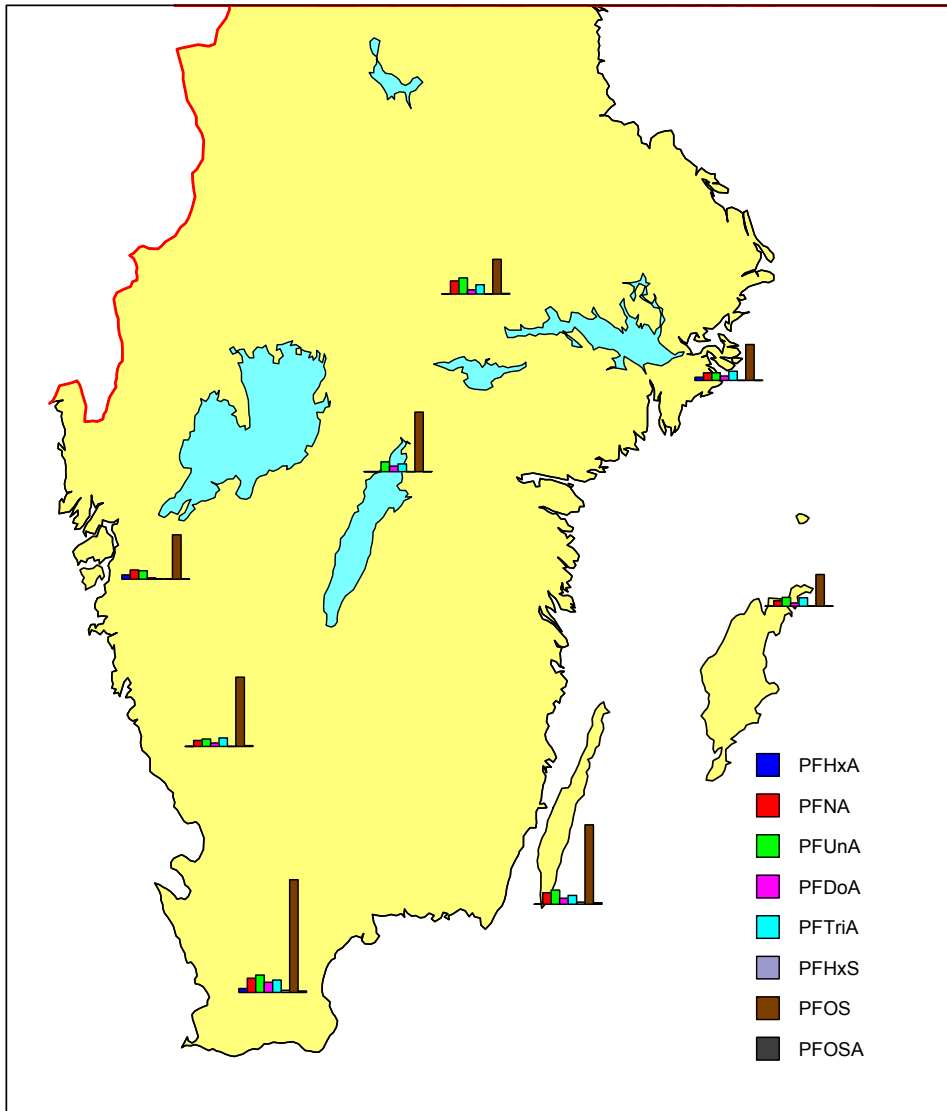


Figure 17. The figure illustrates the relative magnitude of values and patterns at the various sites of (from left to right) PFHxA, PFNA, PFUnA, PFDoA, PFTrIA, PFHxS, PFOS and PFOSA. The height of a bar is proportional to the maximum value for all variables. PFOS was dominant at all eight localities and the highest concentration of PFOS was found at lake Krankesjön in Skåne (6.73 ng/g, fw)

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